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COMPRESSIVE STRESS RELAXATION OF
WOOD PULPS WITH PARTICULAR REFERENCE
TO PULP CHEMISTRY

By

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ABSTRACT

Stress relaxation responses in compression following steeping either in distilled water or 18.6% NaOH were examined on wood pulp mats with the objective to relate quantitative, physical, as well as structural features of pulp polymers to mat rheology. The study included 32 commercial and laboratory prepared pulps (groundwood, holocellulose, paper grade, viscose, acetate and alpha-cellulose pulps) which provided wide variation in chemical characteristics.

Rate of stress relaxation was found to differ considerably between individual pulps, indicating that each pulp possesses a different ability to dissipate stress. The stress relaxation traces, following quasi steploading (1.0 - 1.5 sec), suggest that pulp mat relaxation is governed by two mechanisms (M_1 and M_2). M_1 , dominating between 0.0 to 1.0 min, is believed to involve primarily inter-fibre processes, while M_2 , controlling the response thereafter, comprises intra-fibre, essentially molecular processes.

Swelling media were found to influence pulp mat rheology. Considerably higher rates of stress dissipation were observed with caustic (18.6% NaOH) than with water swollen mats. This indicates that intra-crystalline swelling, in addition to inter-crystalline, enhances time dependent responses. The effect of any swelling medium on pulp mat rheology appears to be highly dependent on length of swelling treatment, since it was observed that the capacity of pulps to dissipate stress changes inversely with length of steeping time. This phenomenon suggests interchangeability of chemical and physical stress systems.

Evidence presented in the study shows that pulp chemistry controls time dependent behavior of pulp mats. Quantitative and structural characteristics of hemicelluloses appeared to be most important for rheological processes. In the caustic swollen state, decrease in hemicellulose caused proportional changes in stress relaxation. The same observation was made for water swollen groundwood, holocellulose and paper pulps. In water saturated low yield pulps, however, the viscoelastic

effect of hemicelluloses was reversed, due to degradation and redeposition phenomena. Here, residual hemicelluloses were found to retard stress dissipation. From these observations, it was deduced that this group of wood polymers functions as an important linkage in stress distribution and dissipation systems of the undegraded or only slightly degraded lignin-carbohydrate system. Low DP and high degree of branching make hemicelluloses highly suited to dissipate stress in the wood of living trees, as well as ground-woods and holocellulose pulps and to a lesser extent in other pulp types.

Cellulose was found to account for most of the dissipated stress in pulp polymeric systems. Its quantitative contribution to pulp rheology appeared to vary little between pulps of no or limited cellulose degradation. Severe degradation, e.g. in low yield pulping, however, enhanced the time dependent response. This was demonstrated further by relaxation tests on viscose pulps degraded by radiation. Lignin appeared to be of only subordinate importance for pulp mat stress relaxation in compression, primarily attributable to orientation or layer effects and to the dominant role of hemicelluloses.

Relaxation measurements on wood pulp products are suggested as useful tools for predicting and estimating pulp and paper properties, such as pressing behavior and alkali solubility of viscose pulps, pulp beating response, runnability and printability of paper.

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1.0 INTRODUCTION

When mechanical and chemical excitation systems are applied to wood or wood derived cellulosic materials the ligno-cellulosic polymer systems undergo elastic, viscoelastic and viscose deformation. These rheological processes are known or can be expected to depend on the molecular structure and compositional characteristics of wood polymers, as well as on other factors such as magnitude and nature of the external force, stress or strain history, temperature and degree of swelling.

Stress relaxation studies in tension on wood tissues using infrared polarisation techniques provided evidence that wood rheological behavior is a combined response of the three structural polymers: cellulose, hemicellulose and lignin (48). It was shown that the original response is disturbed by removing wood constituents. Thereby viscoelastic behavior of the remaining complex was drastically changed.

Based on this observation and other studies (95,273,283) showing dependence of mechanical properties on compositional characteristics a postulate was put forward. In this, rheological properties of wood derived materials, such as mechanical and chemical pulps, must be related to quantitative and structural features of residual wood polymers.

Since compression treatments are frequently involved in pulp processing, it appeared appropriate to examine water and caustic swollen pulp mats subjected to constant compressive strain. It is thought that experimental evidence on relationships between mechanical-rheological properties and chemical-physical features of fibres may be of practical, as well as theoretical value.

The study was designed around five main objectives.

First, to extend rheological techniques to wood based cellulosic materials prepared mechanically or by removal and/or reportioning of wood constituents in industrial and laboratory processes.

Second, to determine to what extent such manipulations affect or change wood and pulp rheological properties. The study included materials

representing the whole pulp spectrum (groundwoods, holocelluloses, bleached sulphite, unbleached and bleached sulphate, viscose, acetate, and alpha-cellulose pulps).

Third, to examine rheological effects following treatments, such as inter-crystalline (steeping in distilled water) and intra-crystalline swelling (steeping in 18.6% NaOH) and purposeful degradation by gamma-irradiation.

Fourth, to elucidate the effect of stress history on rheological properties by subjecting pulp samples to various periods of swelling stresses.

Fifth, to examine stress relaxation as a physical-mechanical procedure for characterising pulps, i.e., development of rheological indices for predicting chemical and mechanical properties of pulps.

2.0 BACKGROUND TO THE STUDY

2.1 Morphology and Composition of Wood Cell Walls

Woody cells of Coniferales (gymnosperms) and some Dicotyledons (angiosperms) are the principal sources of commercial pulps. Numerous studies over the last century have centered on morphological and chemical structures of various cell types from these sources. Often the purpose has been to increase utilisation of wood as a fibre source, or to improve the properties of fibrous products already being manufactured. In spite of intense research activities, which have lead to an ever increasing accumulation of information on the subject, many questions on wood cell walls remain unanswered.

2.1.1 Major wood cell types

Tree cambiums produce four distinct types of xylary elements: (i) parenchyma cells; (ii) tracheids; (iii) fibres; and (iv) vessel elements. Parenchyma cells are present in all woody species, whereas any of the other structural elements may be wanting. In conifers longitudinal tracheids are dominant, with few if any fibres and no vessels present, but in angiosperms tracheids are scarce, while fibres and vessels are often dominant cell types (103,121,128,182,226,251,301).

Longitudinal tracheids in stem woods of Scotch pine (Pinus sylvestris L.) and European spruce (Picea abies Karst.) have been found to amount to 95% and 93% of the wood volume and 99% and 98% of the wood weight. In comparison, libriform fibres in European birch (Betula verrucosa L.) occupy 65% of the wood volume and account for 86% of the wood weight (232,251).

For a more complete description of the various wood elements, the reader is referred to a number of excellent reviews published within recent years (103,226,251).

2.1.2 Cell wall organisation

Characteristic to all types of wood cell walls is the fact that they are composed of three groups of substances. Wardrop (316) has classified

these as: (i) framework substances; (ii) matrix substances; and (iii) encrusting substances. Considering the predominant role of tracheids and fibres in wood structure, the following review of cell wall composition is limited to these two cell types. Since they show very similar cell wall ultrastructure, they may be considered together.

The framework substance is cellulose which is aggregated in the form of microfibrils. Hemicelluloses and other non-cellulosic carbohydrates are constituents of the matrix substances, whereas lignins are considered to be the main encrusting materials (19,82,316). Distribution and orientation of these materials within the cell wall and between adjacent cells produces one external and three to five internal layers. These are known as middle lamella (M); primary wall (P); outer (S_1), main (S_2) and inner (S_3) secondary wall layers; and sometimes an inner warty layer (187,301,316). Figure 1 presents three schematic pictures for accepted theories on cell wall architecture. Since there are a great number of detailed reviews on woody cell wall layers (12,41,64,79,82,157,158,167,188,314), only a few points pertinent to this study will be discussed.

The middle lamella (M) functions as an intercellular adhesive layer between adjoining cells and is characterised by its high lignin content (approximately 70%) and non-cellulosic carbohydrates (14,156); whereas cellulose microfibrils are possibly absent (12). It (M) is closely associated with the thin outermost (P) layer found in fibres or tracheids. It (P) also consists mainly of so-called amorphous materials, lignin and non-cellulosic carbohydrates; but contains only a loose aggregation of cellulosic microfibrils having no definite orientation on the outer surface, but a more or less transverse alignment to the fibre axis on the inner surface (148,316). According to Bucher (41), the high lignin content, as well as the woven fibrillar texture, gives the primary wall a very limited swelling capacity, which causes it to burst when treated with swelling agents.

It is generally accepted that the adjoining three layers which comprise the secondary wall (S_1 , S_2 and S_3), and also lamellae within the S_1 and S_3 , are arranged in cross-layered constructions (72,101,148,311,316). It has been found in experiments using a polarizing microscope that microfibril

orientation in S_1 lies between 50° to 70° from the cell axis; in S_2 between 10° to 35° depending on species and position in the growth zone; and it ranges in S_3 between 60° to 90° (148). As indicated in Fig. 1, the microfibrils form lamellae in the various layers. Dunning (60) observed with the electron microscope that the thin S_1 layer of longleaf pine (Pinus palustris Mill.) latewood fibres is comprised of at least three lamellae, which exhibit alternating orientations. When subjected to high swelling stresses this thin lamellar system can be readily torn from the bulky S_2 (251).

According to Kollmann and Côté (148), the number of non-alternating lamellae in the main secondary wall may vary from 30 to 40 for earlywood and to 150 and more for latewood, thus contributing most to the cell wall bulk, as well as dominating cell wall mechanical and physical properties. The role of the S_2 layer is also revealed by relative thickness measurements, for example those by Jayme and Fengel (131) on European spruce earlywood tracheids. These showed that the S_2 layer occupied 74 to 84% of the cell wall; whereas, the primary wall contributed only 7 to 14%; the S_1 5 to 11%; and the S_3 only 3 to 4% to the cell wall volume.

It has been observed (101,102) that microfibrils in most S_2 lamellae are oriented nearly parallel to the fibre axis. Microfibrils in outer lamellae towards S_1 and S_3 exhibit a gradual change from S_1 and S_3 orientations to that of the main S_2 body.

The S_3 , when present, is a thin layer of flat helical pattern similar to the S_1 , probably not exceeding five to six lamellae in thickness with alternating orientations (148,316). Liese (166) reported that the S_3 is somewhat thicker in conifers than in pored woods and that it is poorly developed or wanting in some genera and in compression wood tracheids.

The thin layer (W) containing warty structures may cover the S_3 or lumen lining when the S_3 is wanting. It is generally accepted that W originates from deposits of tonoplast residues (167,316). Functionally, it may improve the S_3 chemical resistance.

It is apparent from the above descriptions that tracheid or fibre cell walls are a multi-ply laminate of cellulose microfibrils which differ

considerably in orientation between and within respective plies. As Mark (182) suggests, such variations in microfibril organisation can be expected to influence the physical and mechanical and also the rheological properties of fibrous cellulosic materials. There are several published works which have investigated microfibril orientation-mechanical property relationships in wood and in individual fibres (83,115,136).

2.1.3 Characteristics of wood chemical constituents

Composition studies on many coniferous woods have shown that on average cellulose amounts to 43%, hemicelluloses 28% and lignin 29% of the extractive- and moisture-free cell wall substance (45). Respective values for pored woods are 43%, 35% and 22% (45). From this it is apparent that cell walls in coniferous woods contain considerably less matrix hemicelluloses and more encrusting lignin substances than those in pored woods. Chemical compositions for a few North American commercially important woods are given in Table 1 (294).

2.1.3.1 Cellulose

Cellulose is comprised of β -D-glucopyranose residues which are bonded together as linear chains by (1 \rightarrow 4)-glycosidic linkages (119,218). The glucose residues are present in 1C_4 chair conformation with identical bond angles of about 110° and with hydroxyl groups all equatorial (119,294). Light scattering measurements on nitrated cellulose carried out by Goring and Timell (90) indicated that at least 8,000 to 10,000 glucose units participate in formation of a wood cellulose strand.

According to Mutton (203) and Rydholm (251), cellulose is capable of undergoing reactions at its hydroxyl (addition, substitution and oxidation reactions) and acetal (acidic and alkaline hydrolysis) groups. Furthermore, the aldehyde end groups can be oxidized, reduced or rearranged. It is well known that aldehyde end groups are responsible for degradation reactions in alkaline pulping (251).

2.1.3.1.1 Supermolecular arrangement

Supermolecular arrangement of the cellulose chain molecules within fibrillar and sub-fibrillar cell wall structures has been the subject of many theories. Various chemical and physical methods, in particular electron microscopy and X-ray and electron diffraction measurements, have revealed that cellulose - the sole constituent of microfibrils - is at least partially packed into crystalline regions, known as crystallites. Much controversy exists in the literature on whether or not all cellulose lies within crystalline regions (109,110,113,141,198,199,238,240,246,249,270). Thus, several systems of fine lattice structures, which are assumed to form the microfibrils, have been proposed as models, such as: (i) perfect crystal; (ii) paracrystalline; (iii) crystal defect; (iv) fringed micelle; (v) fringed-fibril; and (vi) lamellar. The last three models are presently the most widely discussed and adopted.

The fringed micellar hypothesis, as first introduced by Hermann et al. (112), states that cellulose chain molecules pass through crystalline regions and then in the amorphous zone the chains separate. Thereafter they realign to form another crystallite. According to Frey-Wyssling (80), there exists a gradual transition between crystallites which are at least 600 Å long, 100 Å wide and 30 Å thick (238,312), and amorphous regions. The crystallites are arranged at regular intervals but randomly in the chain direction. Marchessault (177) supported this hypothesis and proposed that the crystallites are segregated as fibrils which are embedded in oriented hemicelluloses.

More recently, Hearle (108-110) developed a concept, known as the fringed-fibril model, which considers the almost infinite length of microfibrils and the phenomenon of polymolecular growth by spherulitic arrangement. In this model microfibrils are described as long, imperfectly crystalline, and arranged in spiral-form within the fibril structure and separated by amorphous zones. The cellulose molecules may run alternately through several crystalline zones, as well as through amorphous regions. This hypothesis has been found to explain sufficiently the behavior of cotton cellulose (52), but it fails, as shown by Mark (182) and Cowdrey and Preston (52), to

describe satisfactorily the mechanical behavior of coniferous tracheids.

Lamellar or folded chain theories advocate that cellulose chain molecules are folded in-plane to form a flat ribbon, which is wound as a helix (58,59,185,297). By using electron diffraction techniques, Manley (176) was able to show that cellulose derivatives exhibit this type of structural arrangement. Investigations carried out by Sullivan (284) on cellulose from several coniferous and deciduous species also lend support to the chain folding theory. However, as Mark (182) pointed out, this model is not capable of satisfactorily explaining observed physical and mechanical properties of the cell wall.

From the above, it is apparent that none of the proposed theories seems to represent all cases of cellulose molecular arrangement in microfibrils. Possibly some new or improved physical methods of examination could help to elucidate microfibrillar structure of cellulose.

2.1.3.1.2 The crystal structure

The detailed structure of cellulose crystalline zones has been deduced from X-ray diffraction measurements. Hartshorne and Stuart (107) and Preston (237) described the smallest grouping of subunits in the cellulose crystallites, the unit cell, as parallelepiped and of the monoclinic system. The crystallographic unit cell was first proposed by Meyer and Mark (196) and later modified by Meyer and Misch (197). As indicated in Fig. 2, the unit cell consists of four cellobiose units arranged in the corners of the parallelepiped and a fifth cellobiose unit turned 180° and passed through the intersection of the diagonals with a difference of $\frac{1}{2}$ -unit spacing.

A characteristic feature of cellulose unit cells is the angle between the axes a and c which has been found to be 84° for native cellulose. As indicated in Fig. 2, the arrangement of the chains in the crystal results in the formation of three planes, known as the 101, $10\bar{1}$ and 002 planes. It is assumed that the 101 planes are parallel to the larger surface of the crystallite, and consequently lie parallel to the cell wall surface (237,315). According to Frey-Wyssling (77,78), the 101 plane, which is particularly

rich in hydroxyl groups, is the plane of lamination; that is, the plane in which the fibrils tend to aggregate laterally within cell wall lamellae (81,315).

Forces which keep the glucose residues in position are, according to Honeyman and Parsons (120): (i) covalent bonds in the b-c plane; (ii) fairly strong hydrogen bonds in the a-b plane; and (iii) much weaker van der Waal's forces in the a-c plane. All of these forces are now considered to be important in determining cellulose properties (212,300).

The intermolecular forces in the unit cell are sufficiently strong to resist the penetration of water molecules into crystalline zones, in other words, limit the swelling caused by adding water to amorphous regions (206,251). Aqueous polar compounds, such as strongly alkaline or acid solutions, however, are known to attack and alter the cellulose lattice. According to Rydholm (251) this process involves first the breaking of hydrogen bonds between two cellulose hydroxyls and thereafter the formation of new hydrogen bonds between reagent and hydroxyl groups. This leads to dimensional changes of the unit cell in transverse direction, chiefly because of an increase in the 101 interplanar distance, whereas 10 $\bar{1}$ and 002 spacings exhibit only minor changes (251).

2.1.3.2 Hemicelluloses

Chemical and physical properties of the non-cellulosic wood carbohydrates, or hemicelluloses, have been critically reviewed (2,99,116, 148,169,251,258,293,295). Although related, the hemicelluloses in the cell walls of coniferous and pored woods differ to some extent. In pored woods, the O - acetyl - 4 - O-methylglucurono-xylan appears to be the dominant hemicellulose. According to Meier (190), this xylan consists of β -D-xylopyranose residues, linked together by (1 \rightarrow 4)-glycosidic bonds. It is partially substituted by 4-O-methyl- α -D-glucuronic acid and acetyl groups. Bouveng et al. (27) studying glucurono-xylan from birch showed that 1 in 10 xylan residues has a 4-O-methyl- α -D-glucuronic acid at the xylan C₂ position and about 7 of 10 carry an acetyl group at C₂ or C₃. The second hemicellulose, a glucomannan, occurs in only limited amounts (294,295). It is claimed to be linear and has been found to contain (1 \rightarrow 4) - linked β -D-glucopyranose and β -D-mannopyranose residues mostly in a ratio of 1:2 (295).

In most coniferous woods, according to Abdurahman et al. (1) and Meier (190), two types of hemicelluloses - glucuronoarabinoxylan and galactoglucomannan - appear to be dominant. The former type consists of β -D-xylopyranose residues, linked together by (1 \rightarrow 4)-glycosidic bonds. Some of the xylose residues carry 4-O-methyl- α -D-glucuronic acid groups at C₂, and some are substituted by L-arabinofuranose units at C₃. The glucomannan is composed of (1 \rightarrow 4) - linked β -D-glucopyranose and β -D-mannopyranose residues (1:3.5 ratio) with two or three branches per molecule. Meier (190) and others have reported that acetyl and galactose residues are attached to mannose units of the backbone.

A characteristic feature of non-cellulosic carbohydrates in wood is the rather low degree of polymerisation. Timell (294,295) reported that the isolated hemicelluloses mentioned above seldom have more than 150 to 200 sugar residues. This may partly explain the higher extractability of hemicelluloses in comparison with cellulose (251).

Berlyn (19) considers hemicelluloses to be the main constituents of the cell wall matrix. Marchessault (178) and Wardrop (316) reported that, for instance, native xylan surrounds cellulose fibrils by forming a somewhat amorphous matrix, and there is evidence that it may be oriented in wood (70,165). Due to a highly branched structure, however, it is doubtful that native xylan occurs in crystalline form (205). X-ray studies carried out by Nelson (205) present evidence that glucomannans may be closely associated with cellulose microfibrils and probably are even positioned between cellulose chains. It appears from studies of Lindberg and Meier (170) on European spruce holocellulose preparations that glucomannans may be un-ordered or only slightly ordered.

2.1.3.3 Lignin

Lignin is considered as the major encrusting substance between and within wood cell walls. The knowledge of its structure is still far from complete due to the fact that it is a complex, three-dimensional polymer which is difficult to isolate from the framework and matrix substances (19). Hypothetical models of its chemical structure, in particular linkages between the main structural units, phenylpropane groups, have been proposed by

Freudenberg (74,75) and Adler (3) among others.

Due to the aromatic nature and functional groups on the aliphatic side-chain and ring of the phenylpropane unit, the lignin macromolecule, according to Rydholm (251), can undergo several reactions. These include sulphonation, hydrolysis and condensation in acidic and alkaline medium, as well as mercaptation, halogenation, degradative and non-degradative oxidation. These reactions are most important in many delignification processes, such as pulping and bleaching. Excellent reviews on the subject have been published recently (47,57,230,251,309).

The physical nature of the lignin polymer system, positioning in the cell wall and its association with carbohydrates have been subject of much argument. It is often assumed that lignin in wood, due to its highly branched nature, is present in an amorphous state. Frey (76) presented evidence that wood lignin does not exhibit a crystalline structure. Its hydrophobic character, particularly its preventing effect on excessive swelling of hemicelluloses has been mentioned earlier.

Goring (89) reviewed the literature on lignin polymer properties and summarized four proposed hypotheses on the physical state of lignin polymeric systems in wood. These include network theory, small-molecule theory, lignin-carbohydrate bonds and possible "snake cage" theory, and theory on aggregation by secondary bonds.

According to the network theory, the lignin structure is treated as consisting of short linear chains cross-linked by various types of covalent bonds thus forming a three-dimensional structure. Schuerch (257) supported this hypothesis by suggesting that native lignin must be kept in position by strong bonds. The small-molecule theory considers native lignin as consisting of small, reactive molecules which tend to polymerize during isolation processes. This theory appears to be questionable, however, since Yean and Goring (324), studying the effect of sulphonation on lignin molecular weight during extraction, observed only insignificant changes.

The lignin-carbohydrate bond and possible "snake cage" effect theory tries to explain the universal protolignin insolubility of low-

molecular weight. Such bonds might attach the lignin slightly to carbohydrate compounds. However, the number of bonds is probably small and limited to "occasional spot welds" (254). Another alternative concept was proposed by Pew and Weyna (234), who stated that linear carbohydrate molecules may be surrounded by the three-dimensional lignin network. In other words, they may be held in the gel-like lignin substance by molecular entanglement or "snake cage" structures.

Various investigations (310,314,317) provide evidence that lignin must infiltrate the carbohydrate complex. Based on X-ray measurements, Wardrop (310,314) and Wardrop and Preston (317) calculated the size of wood and holocellulose crystallites and found for holocellulose an increase of 18.8% in crystallinity, which is in agreement with values determined from hydrolysed cellulose crystals. Furthermore, Wardrop (313,314) observed that hydrolysis during delignification treatments and subsequent hydrolysis of holocellulose caused microfibrils to aggregate in clumps visible under the microscope. Wardrop (314) attributed this phenomenon to crystallisation of less ordered regions surrounding the microfibrils, formerly prevented from crystallisation by infiltrated lignin.

Aggregation by secondary bonds appears to be an important mechanism for keeping lignin molecules in position within the cell wall. Benko (17) reported a considerable increase in molecular weight of soluble kraft lignins by decreasing the pH from 11.5 to 7.0. Based on these observations Benko suggested that associations of lignin molecules through weak chemical bonds, probably through solvent dependent hydrogen and hydrophobic bonds, influence markedly the actual molecular size of lignosulphonates and other lignin materials. Other studies (34,93) on kraft lignin also support the aggregation hypothesis.

2.2 Characterisation of Various Pulp Types

Pulping and subsequent bleaching or purification treatments are known to change drastically the chemical and consequently the physical nature of lignin, hemicelluloses and cellulose and their relative composition in most pulp types. Such changes undoubtedly must exert a profound influence on the mechanical properties of pulp mats. For understanding pulp mat

responses to mechanical excitations it seems useful to elucidate the chemical, physical and compositional modifications which carbohydrate and lignin fractions undergo in pulping. In the following section the present knowledge and understanding of these modifications will be reviewed in a somewhat summary way, with particular reference to pulp types examined in the present study.

2.2.1 Mechanical pulps

Fibrous materials produced in conventional groundwood processes are obtained by applying mechanical energy to wet wood. The absence of chemical treatments before and during manufacture maintains an almost quantitative yield from wood (95 to 98%). Rydholm (251) suggested that high temperatures developed during the grinding process may have three distinct effects on the lignin-carbohydrate complex: (i) softening of the lignin polymer; (ii) weakening of hydrogen bonds; and (iii) probably hydrolysis of carbohydrates. The last effect probably accounts for most of the 2 to 5% yield loss. Brecht and Klemm (30) considered alteration of chemical nature of wood during the grinding process to be below the degree needed to significantly affect physical and chemical responses of cell walls.

Brightening treatments with oxidative reagents, such as sodium dithionite or hydrogen peroxide, are considered as having only a minor influence on groundwood mechanical properties, in spite of some structural changes imparted to lignin and, under certain circumstances, also to carbohydrates. The oxidative transformation of lignin chromophores to colourless compounds (251) in peroxide brightening may be accompanied by condensation reactions. This is evidenced by the work of Katuscak et al. (142), who observed that peroxide oxidation of methanol lignins caused an increase in cross-linkage without changing lignin molecular weight; in other words, increased intramolecular covalent bonding. Because these reactions do not seem to lead to enlargements of the lignin network, their effect on the mechanical behavior may be subordinate. The carbohydrates, according to Stobo and Russel (280), are apparently not affected in cold peroxide treatments, but hot treatments cause definite degradation as indicated by decreased viscosity and increased carboxyl content (168).

2.2.2 Holocellulose pulps

Two widely used procedures for holocellulose preparation are the peracetic acid method as modified by Leopold (164); and the acid chlorite method originally proposed by Jayme (129), but developed as the present recipe by Wise et al. (323).

No proposed method produces holocelluloses without some loss of non-cellulosic carbohydrates at complete lignin removal. Recently, Ahlgren and Goring (4) carried out a study on this subject and observed that chlorite delignification of black spruce (Picea mariana (Mill.) BSP.) wood produced holocellulose in 70% yield containing 40% cellulose, 13% glucomannan and galactan, 12% xylan and other carbohydrates and 5% lignin. Further delignification was found to cause considerable carbohydrate loss, mainly mannose and galactose. Ahlgren and Goring's observations are in reasonable agreement with earlier findings (38,39,44,189,290). Timell (292) reported that acid chlorite delignification attacks the carbohydrate portion, as indicated by decrease in DP with progressive delignification. This may well explain the loss of polyoses in later stages of delignification.

Poljak (236), who first introduced peracetic acid for wood delignification (235), reported that this method completely removes the lignin without hydrolysing the carbohydrates to simple sugar units. In later comprehensive studies on the subject, which lead to a modification of Poljak's method, Leopold (164) was able to show that peracid delignification does not leave the wood carbohydrate portion entirely intact. Some loss of the glucomannan, arabinogalactan and xylan polyoses, and decrease in cellulose DP (164), indicated carbohydrate chain degradation. Furthermore, the holocellulose preparations were found to still contain between 2 and 3% lignin. Evidence regarding the degrading effect of peracetic acid on carbohydrates is also given by work of Shimada and Kondo (264), who observed that increase in chip size lowered yield in peracid cooking.

2.2.3 Sulphite pulps

Dependent on cooking variables employed, such as temperature, cooking time and liquor characteristics, sulphite pulping may be used to

produce a whole series of pulps. These range from typical hemicellulose-rich greaseproof paper pulps at 52% yield (86) through various types of ordinary paper making pulps to high alpha-type dissolving grade pulp at 35% yield (86).

Jorgensen (139) analysed the carbohydrate composition of various pulp types and reported that glucose accounted for 90.2%, mannose 5.4% and xylose 4.4% of the carbohydrate portion in an ordinary coniferous sulphite raw pulp of 47.2% yield with Roe No. of 1.6 (1.3% lignin). Other wood carbohydrates were removed during the cooking process. These observations are in reasonable agreement with data published by Thompson et al. (291) for black spruce sulphite pulps cooked at pH values below 7.

In dissolving grade pulps, the hemicellulose portion is even more reduced through additional purification steps and residues amount to only a few per cent of all pulp carbohydrates. For instance, a sulphite spruce pulp was found by Croon et al. (55) to be comprised of 95% glucose, 1.7% xylose, 3.3% mannose and 0.1% arabinose.

During sulphite pulping, lignin undergoes three reactions which are significant to both its removal and the physical nature of residues remaining with pulp fibres. These are sulphonation, hydrolysis and sometimes condensation (321). Dependent on how far these reactions are allowed to proceed, the lignin content in unbleached pulps lies between 1 and 4% (86). The various factors and mechanisms responsible for lignin reactions in sulphite cooking are discussed in several reviews (86,88,251,321).

As in other technical pulping processes, delignification in sulphite cooking is very closely interrelated with degradation of both cellulose and hemicelluloses and at least with a partial dissolution of the latter. Degree of polymerisation (DP) determinations on various tracheid wall layers carried out by Luce (171) showed that cellulose undergoes serious degradation due to acid hydrolysis, in particular in the outer wall layers where DP reaches values as low as 300. This confirms earlier proposals made by Jayme and von Koppen (134). According to Rydholm (251), cooking below 48% yield causes such serious degradation that part of the cellulose goes

into solution and even fibre fragmentation may occur.

Hamilton (97) suggested that under acidic pulping conditions less ordered zones in microfibrils are more susceptible to attack and thereby cellulose chains are cleaved preferentially in amorphous regions. The cellulose degradation by acidic hydrolysis seems to be enhanced by mechanical damage of the fibre wall during chip preparation, as indicated by lower strength properties of pulps prepared from damaged fibres (106). This may be explained by the fact that the protective action of lignin in early cooking stages is partially lost.

The hemicelluloses undergo profound structural changes during sulphite cooking, mainly caused by acidic hydrolysis of bonds between units of the main chain and between backbone and side-branches. It is well known that hydrolytic chain degradation leads to considerable hemicellulose loss, especially in low yield pulping which leaves only a few per cent of residual polyoses in pulp fibres (160).

Studying hemicelluloses in birch pulps, ["]Ohrn and coworkers (174, 217) observed that degradation effects on polyoses, as indicated by DP values, are considerably higher for sulphite than for kraft pulps. DP values for the former were found to be about 70 and for the latter 130 to 160. Acid sulphite experiments carried out by Hamilton (97), with red alder (Alnus rubra Bong.), and western hemlock (Tsuga heterophylla (Raf.) Sarg.) showed that xylans are somewhat more susceptible to hydrolytic cleavage in acidic medium than the mannan family of carbohydrates. This has been confirmed by Petterson and Rydholm (233) on European birch sulphite pulps.

Characteristic for residual xylans in sulphite pulps is a relative abundance of glucuronic acid groups which appear to be fairly stable to acid hydrolysis (251). Similarly, some of the acetyl groups tend to remain attached to the xylan backbone. This presence of acetyl groups has been proven by ["]Ohrn and Croon (216) on isolated birch sulphite xylans.

However, other linkages with side-branches seem to be acid-labile. As proven by Hamilton (97), arabinofuranose is readily split from the xylan backbone and therefore sulphite xylans contain only traces of arabinose (55).

Likewise, the galactose branches are entirely removed in acidic pulping and the former galactoglucomannan polymer is reduced to glucomannan. This is supported by Eriksson and Samuelson (66), who reported considerable amounts of galactose in spent sulphite liquor.

By adding cotton linters to a sulphite cook, Annergren and Rydholm (10) demonstrated that probably a deacetylated glucomannan was absorbed to a certain degree on to the fibre surface. This indicates that some glucomannan is dissolved in the early stage of cooking and later adsorbed. They concluded that this rearrangement of glucomannan on the surface and within the fibre possibly causes crystallisation of linear molecular fragments on to cellulose microfibrils, or at least a better ordered structure on the microfibril surface. Timell and Tyminski (296) postulated that some glucomannan adsorption may even occur inside the microfibrils. Rydholm (251) pointed out that glucomannan is preferentially adsorbed, since linear xylan chains are liberated later in the cook and therefore can not compete for the limited microfibrillar surface. This may at least partly explain the relatively low xylan content in sulphite pulps.

2.2.4 Sulphate pulps

Depending on cooking variables employed, the kraft pulping process provides yields of 40 to 55% based on oven-dry wood (251). Nolan (215) reported that highly delignified bleachable paper grade pulps contain 3 to 4% lignin, whereas high-lignin kraft pulps may contain as much as 10% lignin. That kraft pulps contain considerably more residual lignin than acid sulphite pulps of similar yield has been confirmed by Jorgenson (139). He also analysed the carbohydrate composition of sulphate pulps, i.e., a pulp of 47.6% yield was comprised of 85% glucose, 6% mannose, 8.2% xylose and 0.8% arabinose. Thompson *et al.* (291) reported that pored wood kraft pulps of similar yield also contained about 0.35% galactose. The hemicellulose portion has been found to be markedly reduced when the kraft cook is preceded by a prehydrolysis stage. For instance, Croon *et al.* (55) found that in a prehydrolysed kraft pulp made from southern pine (*Pinus* spp.), glucose accounted for 95.2% of all carbohydrates present, while xylose (2.6%), mannose (2.1%), and arabinose (0.1%) totaled only 4.8%.

As in sulphite pulping, delignification in alkaline processes is also accompanied by condensation reactions (251). These seem to be more serious in alkaline media. As Giertz (86) suggested, the impossibility of delignifying kraft pulps to the level achievable in sulphite pulping has to be entirely attributed to extensive lignin condensation. The distribution of residual lignin within the fibre wall has been studied by von Koppen (149), who found that lignin was almost evenly distributed over the entire wall of kraft pulp fibres. In contrast, it appeared to form a considerable accumulation in the outer layers of sulphite pulp fibres.

According to Hamilton (97), alkaline pulping considerably reduces cellulose DP by two major reactions: (i) stepwise end-group degradation; and (ii) hydrolytic chain cleavage. Based on viscosity measurements, Hartler (104) and Thompson et al. (291) demonstrated that these degradation reactions reduce cellulose DP more than corresponding reactions in acid sulphite pulping. But disadvantages of comparatively higher degradation are at least offset by better uniformity of chain length of alkali degraded celluloses as proved by Luce (171). This phenomenon may be attributed to faster and more uniform penetration of alkaline pulping liquors. This is due to inter- and intra-crystalline alkaline swelling which, according to Stone (281), enlarges the fibre wall capillary system.

Alkaline pulping affects hemicelluloses principally in the same way as other commercial chemical pulping processes: (i) change of molecular structures by hydrolysis; and (ii) repositioning by partial reprecipitation of dissolved compounds. Residual sulphate pulp hemicelluloses are characterised by high DP, which has been found to be twice that of sulphite hemicelluloses (174,233). This can be attributed to the tendency of low molecular carbohydrates to dissolve rather easily in alkaline cooking liquors as has been observed by Axelsson et al. (13).

It appears from several studies on carbohydrate composition of various pulp types (97,139,174,291) that glucomannans are more seriously degraded and dissolved in alkaline pulping than are xylans. This can be at least partly explained by the greater susceptibility of glucomannans to alkaline peeling reactions as shown by Richtzenhain and Abrahamson (247).

Residual glucomannans in kraft pulps occur in two forms as: (i) glucomannan; and (ii) a system of galacto-glucomannans (54,97). The former originate from native glucomannan, but have considerably reduced DP. The latter arise from O-acetyl-galacto-glucomannan which undergoes deacetylation and partial chain degradation during pulping. In prehydrolysed pulp fibres, only linear glucomannans remain due to removal of the galactopyranose units in the prehydrolysis stage (97,160,269).

The most characteristic feature of residual xylans in sulphate pulps is the absence (97,291) or infrequency (53,54,191) of 4-O-methyl- α -D-glucuronic acid residues. This is due to high alkalilability of the (1 \rightarrow 2)-glycosidic linkage. Since ester bonds between the xylan backbone and acetyl groups are likewise easily cleaved (216), residual xylan in pored wood kraft pulps consists only of xylose units. In coniferous pulps the original xylan polymer has been found to be reduced to an arabinoxylan (98). Croon and Enstrom (54) have shown that only 10% of the original arabinofuranose units are split off during the cooking process. But in prehydrolysed kraft pulps all xylan molecules are degraded to linear xylan fragments with an eventual DP of only 22 to 60 (98).

Of special importance to chemical and physical characteristics of hemicelluloses is the fact that a part of the xylan dissolved in sulphate liquors is readsorbed irreversibly by the cellulose (326). Giertz (86) attributed this phenomenon to cleavage of side-chains after the branched xylan dissolved in the pulping liquor. Thereafter, the unbranched or essentially side-chain free xylan molecule is held no longer in solution, but instead is adsorbed by or crystallized on to cellulose surfaces. Meller (193) proposed that xylan may be redeposited in three different forms: (i) loosely precipitated or adsorbed on to the surface; (ii) precipitated in crystalline form on cellulose; or (iii) chemically combined with the cellulose by transglucosidation.

Clayton and Stone (51) have shown that this redeposition can account for as much as 3% of pulp weight, regardless of the amount of hemicelluloses already in the fibres. Recent studies carried out by Simonson (266) provide evidence that even xylan-lignin compounds found in pulping liquors (265) are redeposited on to cellulose. It appears from studies of Meller (193)

that prehydrolysed xylan from birch and straw shows much less tendency toward redeposition on to cotton cellulose when heated in alkaline medium.

2.2.5 Bleached pulps

An excellent survey on the subject of wood pulp bleaching has been given by Rydholm (251) and for this reason only a limited number of publications related to the present study will be reviewed here.

Depending on final use, most raw chemical pulps are subjected to further delignification or lignin modification by bleaching treatments. In addition, dissolving grade pulps are subjected to additional carbohydrate-removing processes to further reduce hemicellulose portions. Rydholm (251) and Springer *et al.* (274) determined overall yield loss in pulp bleaching and reported that approximately 1 to 5% of the fibre cell wall components, mainly lignin and hemicelluloses are removed in bleaching of sulphite and kraft pulps cooked to 38 to 51% yield.

In multi-stage bleaching, which is generally employed in bleaching of chemical pulps, residual lignin is drastically reduced to trace amounts. Sjöström and Enström (268), for instance, reported that a seven stage bleaching sequence involving chlorination, alkaline extraction, hypochlorite and chlorine dioxide reduced lignin content of a coniferous sulphate pulp from 2.42% to less than 0.05%. In a three stage process consisting of chlorination, alkaline extraction and sodium hypochlorite treatment, Kayama and Higgins (143) observed that lignin content of two coniferous kraft pulps decreased from 2.13 to 0.51% and from 4.59 to 1.11%.

Most lignin abstracting stages in bleaching have been found to affect also the carbohydrate components. According to Meller (194), both cellulose and hemicelluloses undergo hydrolysis and subsequent oxidation reactions in the chlorination stage causing some loss in carbohydrates (143). Subsequent alkali extraction has been found to reduce the yield (143), probably due to introduced carboxylic groups (194) which render part of the low molecular carbohydrate portion soluble in alkaline extraction treatments.

Similarly, hypochlorite treatments and subsequent alkaline

extraction lead also to a yield loss due to oxidation and hydrolytic cleavage of glycosidic bonds (143,159,194). Viscosity measurements on hypochlorite bleached pulps have indicated that severe chain degradation can occur during this bleaching stage (243,245). At low to medium pH chlorine dioxide does not react with aldehydes or ketones (244) and, consequently, no degradation or noticeable losses of carbohydrates occur in this bleaching stage (251).

The work of Springer et al. (274) indicates that the extraction of lignin in bleaching without alkali purification appears to be the major factor responsible for differences in physical and mechanical properties between bleached and unbleached pulps. In such practice the removal of carbohydrates is comparatively low and these slight losses seem to be insignificant for the development of bleached pulp properties. In the case of cold or hot alkali purification, however, the low molecular carbohydrate portions, mainly as hemicelluloses and to some extent short chain cellulose, are drastically reduced (251).

According to Meller et al. (195), cold alkali extractions have considerably higher selective dissolving action on non-alpha cellulose components than do extractions with dilute, hot alkali solutions. The former method produces pulps with up to 98% alpha-cellulose content (195), while the latter gives maximum alpha-cellulose contents at 96 to 97% (251). Croon et al. (55) reported that a prehydrolysed kraft pulp purified in cold alkali still contained 0.3% mannose, 1.1% xylose and 0.1% arabinose. They attributed the high content of resistant xylan to stabilization during the sulphate cook. The presence of considerable residual mannan and xylan fractions in pulps extracted with hot alkali has been observed. For instance, a bleached standard sulphite pulp with 2.5% xylan and 2.4% mannan was found to still contain 0.5% xylan and 0.4% mannan after hot alkaline extraction (55).

2.2.6 Alpha-cellulose pulps

Alpha-cellulose is generally regarded as pure cellulose, but several analytical investigations of alpha-cellulose preparations have shown that even exhaustive and repeated alkaline extractions leave non-cellulosic

carbohydrate fractions in the pulp. Uprichard (304) published analytical data on alpha-cellulose obtained from Monterey pine (Pinus radiata D. Don) chlorite holocellulose by treating the pulp with 17.5% NaOH according to the usual alpha-cellulose procedure. Surprisingly high amounts of hemicelluloses remained in the pulp; such as 8.8% mannose, 2.3% galactose, 1.3% xylose and 0.3% arabinose. Similar observations have been made by Gillham and Timell (87), who report that an alpha-cellulose pulp prepared from white birch holocellulose by exhaustive alkaline extraction with aqueous KOH still contained considerable amounts of mannose and xylose and traces of galactose, arabinose and rhamnose. The work of Croon et al. (55) indicated that alpha-cellulose preparations from viscose pulps likewise contain mannan and xylan residues, but to a much lower extent.

2.3 Time Dependent Mechanical Properties of High Polymers, such as Wood and Cellulosics

Rheology has an ultimate objective of discovering generalized descriptions for materials and their behavior which permit prediction of time dependent mechanical behavior under specified excitation patterns. There are, basically, two main approaches in studies of materials viscoelastic behavior. One, the phenomenological approach, is based on studies linking time with stress and strain (load and deformation), usually with macro-samples. An attempt is made to discover general equations covering variations of these parameters, so that behavioral patterns, such as loading rate or rate of elongation, can be deduced. This approach, as employed in the majority of rheological studies, is essentially superficial. Such studies deal only with the whole body, or with the body in its macro form irrespective of the behavioral interrelations of structural components. In other words, gross and complex changes caused by application of external forces are reported as averaged values.

Another approach, known as molecular rheology, attempts to use rheology as a tool for elucidating the fundamental structure of a material and participation of its components in rheological phenomena.

Considering the complex molecular and sometimes also complex anatomical structure of many natural polymers, such as cellulosics and ligno-

cellulosics, it is not surprising that the majority of studies on these materials have been phenomenological. Presently, the subject of polymer viscoelasticity is still at the stage of development. The phenomenological theory of linear viscoelasticity is now essentially complete. Much attention has also been given to establishing new or improving existing theories of non-linear viscoelasticity. Many excellent surveys are now available (5,18,22,24,42,49,71,92,117).

Difficulties are experienced within development of a complete molecular theory for cellulosics. Even with simple polymers, the molecular origin of some aspects of viscoelastic behavior is complicated greatly by molecular weight, temperature, concentration (e.g., moisture content) and other factors. This becomes even more complicated for wood and wood derived materials due to the complex and incompletely understood chemical structure of the lignin-carbohydrate-polymer mixture. Indications are, however, that a molecular approach to polymer rheology, cellulosics in particular, may be feasible eventually.

2.3.1 Molecular approach to viscoelasticity

Viscoelastic behavior of cellulosic materials, such as wood and cellulose fibre networks, is the product of many factors interacting in a complicated and only partly understood way. This causes great difficulty in deriving quantitative and useful expressions for describing macroscopic effects in terms of molecular parameters.

According to Nissan and Sternstein (214,279), the following factors are expected to be important in determining mechanical properties of cellulosics: (i) inter-chain covalent bonds; (ii) ionic bonds between groups which were formed in oxidation and other degradation processes; (iii) hydrogen bonds between and within cellulose and hemicellulose chains; (iv) inter-chain van der Waal's bonds; (v) DP; (vi) degree of order and disorder; (vii) orientation of molecular chains; (viii) size of paracrystalline or crystalline regions; (ix) morphological structure; and (x) chemical composition and presence of polar liquids. The representation of these factors is by no means exhaustive but it shows well the complexity facing attempts aimed at development of formulations which describe accurately the

mechanical character and behavior of cellulosic materials.

During the last two decades some attempt has been made to give molecular interpretations to cellulosic viscoelastic behavior and to develop a first set of molecular theories based on known properties of hydrogen bonded materials (48,207-214,220,278,279).

It is presently accepted that cellulose subjected to macroscopic deformation will show the following submicroscopic deformations (202,214, 298-300): (i) valence bond length and angle deformation (intra-molecular); (ii) secondary bond deformation; and (iii) reorientation of macro-molecules in amorphous regions (inter-molecular). It can be said, therefore, that while ultrastructure is of significance to ultimate fibre property levels, the inter-molecular and intra-molecular bonds are responsible for viscoelastic properties (259).

Particularly important in cellulosic viscoelastic processes are inter-molecular forces which arise from the separation of macromolecules that are joined by covalent links, ionic bonds and van der Waal' forces. It is now advanced by one group that the hydrogen bond system dominates viscoelastic processes in cellulosic materials (210,214,220,278). Since each anhydroglucose unit can form three hydrogen bonds, and, as shown by Marrinan and Mann (183), oven-dry cellulose possesses no free hydroxyl groups, the postulation has been made that viscoelastic phenomena are accompanied by breakdown, rearrangement, bending and stretching of these hydrogen bonds (214).

The primary importance of the hydrogen bond on mechanical properties is underlined by a number of investigations undertaken by Nissan and Sternstein (214). They observed that dry regenerated cellulose (with high amorphous ratio) and strong papers show more significant hydrogen bond effects than weak papers. In the latter, van der Waal's forces dominate. while in crystalline or oriented celluloses, such as cotton, flax and ramie, valence bonds appear to be more important.

Based on postulated hydrogen bond behavior under stress or strain, Nissan and coworkers (208-211,213,278) developed several quantitative

theories to explain the rheological behavior of cellulosic materials at the molecular level. They were able to demonstrate that stress relaxation as a feature of viscoelastic behavior can be studied by following processes of hydrogen bond adjustment. According to this theory, stress dissipation in a cellulosic material under constant strain results from an independent change in the effective number of hydrogen bonds. This occurs by rupture and formation of new bonds in a state of lessened stress. In spite of the fact that their experimental observations agree with their postulation, Nissan and Sternstein (214) consider this theory to be only a first approximation to the true time dependent behavior of cellulose.

In contemplation of the viscoelastic behavior of cellulosic materials other significant facts have to be considered, such as structure of the material. Page (220) pointed out that rheological properties of fibrous networks, such as paper, are also controlled by structure at the super-molecular level. He stated that from knowledge of the exceedingly complex structure of paper it would seem unlikely that its rheological behavior can be explained directly in terms of molecular data. This, of course, partly refutes Nissan's theory which treats cellulosic networks only as a molecular assemblage. Page (220) agrees, however, that hydrogen bonds are of considerable and perhaps primary importance in governing paper sheet properties.

More recently, Chow (48) reported that rheological processes in coniferous wood tissues involve a two stage molecular motion of all three major wood components; cellulose, hemicellulose and lignin. Using infrared polarisation techniques he showed that carbohydrates and lignin move in opposite directions on receiving external excitation, whereby the wood macro-molecular structure maintains an internal equilibrium. In this way, the stress might be transmitted uniformly through the whole lignin-carbohydrate matrix.

It may be theorized that cellulosic rheological processes involve important conformational changes in addition to stretching, breaking and re-formation of hydrogen bonds, stretching of covalent bonds and bond angle deformation (145), provided that the degree of swelling is sufficiently high.

In dry cellulosic materials hydrogen bonds are abundant and probably prevent glucose units from rotating about glucosidic links as required to change conformation. However, with increasing moisture content the glucose units should be capable of such rotations and thereby undergo conformational changes in response to excitation. It is known that inter-molecular hydrogen bonds within amorphous regions are widely destroyed by absorption of water (251).

According to Lambert (154), six-member ring compounds prefer the more stable chair conformation. Therefore, hydroxyl groups on C₂, C₃ and the CH₂OH group on C₅ can be expected to lie in the equatorial position. The arrangement is known as ¹C₄ conformation. External energy applied in form of stress could cause these groups to switch to axial positions which changes the ring shape and thereby other conformational isomers are obtained (145). These conformers are characterized by higher energy levels and, consequently, lower stability (154). Under suitable conditions removal of external forces or rebalance of stresses internally may result in reversion to the lower energy level ¹C₄ conformation. In addition to providing an instant response mechanism, the process could well explain the viscoelastic memory behavior of cellulosic materials (145).

2.3.2 Phenomenological study of viscoelasticity

In general, phenomenological treatments of viscoelasticity are characterized by two factors: (i) methods employed for describing observed responses; and (ii) phenomena of viscoelastic behavior. Since both factors are to some extent related to this study they are briefly discussed in the following section.

According to Scott-Blair (260) there are two approaches for dealing with phenomenological data: (i) integrative; and (ii) analytical. The first is the purer phenomenological method, for it takes the totality of experimental data as applied to one simple generalized equation with the objective of describing a material behavior under all conditions of deformation. An equation employed in the integrative approach is the Nutting equation (242) as:

$$\psi = f^{\beta} e^{-1} t^k \dots \dots \dots [1]$$

where: f = stress,
 e = strain,
 t = time, and

ψ , β and k are constants.

The constants merely serve to describe behavior of the material as a whole. In other words, constants do not have any structural or theoretical significance.

The analytical method also attempts to represent phenomenological data by equations, but it employs an assemblage of certain ideal elements based on the very fundamental assumption that the material is structurally comparable to these elements (5,135,147,162,163,231,263,325). The two elements commonly used are ideal springs which behave according to Hookean elastic theory (161) and dashpots containing ideal viscous liquids. It has been found that more or less complex combinations of these simple models can be used to produce equations which approximately describe time dependent behavior of many polymeric materials, including dry cellulose (255). Any material, which can be characterized by suitable combinations of Hookean springs and Newtonian liquids, is said to display linear viscoelastic behavior (18,24,49). This implies that such materials obey the superposition principle (263).

More comprehensive studies on various types of polymers have shown that numerous polymeric materials display non-linear behavior, and for this reason non-linear elements have been used also to describe polymer rheological behavior (96,228,239,325).

The use of models has been widely discussed in the general field of rheology. It is obvious that they have considerable educational value. Whether or not they provide any other advantages is much debated, since descriptive equations obtained by integrative methods are more simply derived and are just as effective in use. Furthermore, as Rance (241,242) pointed out, the use of models does not account for all mechanisms responsible for the viscoelastic behavior of cellulose. Rance maintains that irreversible flow, which leads to permanent set, is not "viscous" in nature, but is the effect of a continuous series of internal ruptures which ultimately leads to final break. He also maintains that such models do not deal with this most important aspect of break nor are they linked with the structure of cellulose fibre mats. Rance (242) developed a simplified structural theory which described with sufficient accuracy time dependent behavior as the result of

progressive disruption of an elastic network.

For the reason of studying and understanding the nature of viscoelastic behavior, polymeric materials are subjected to different types of strain and stress patterns. In general, three types of excitation histories may be employed to study rheological responses to mechanical excitations: (i) "creep", which is time dependent strain ($\Delta L(t):L$) at constant stress ($P:A$). The constant stress level can be reached in a step, a ramp or after other excitation programs.

(ii) "stress relaxation", which is time dependent stress decay at constant level of strain ($\Delta L:L$). The constant strain level can be reached in a step, a ramp or after other excitation programs.

(iii) "dynamic damping", which is normally observation of the mechanical response to sinusoidal excitation in stress or strain. The frequencies can be varied but during each test it is normally kept constant.

Stress relaxation phenomena occur when a constant deformation is imposed on a viscoelastic material and the force required to maintain this continuing deformation is measured as a function of time (62,263). This can be expressed by the relationship:

$$\begin{array}{ll} \sigma(t) &= G(t) \epsilon_0 \dots\dots\dots [2] \\ \text{where: } \sigma(t) &= \text{stress at time } t, \\ G(t) &= \text{relaxation modulus, and} \\ \epsilon_0 &= \text{instantaneous strain.} \end{array}$$

Figure 3 represents diagrammatically the curve $G(t)\epsilon_0$ plotted against time, indicating a time dependent decrease of stress in viscoelastic materials.

The relaxation modulus ($G(t)$) as a monotonically decreasing function of time can be expressed also as:

$$\begin{array}{ll} G(t) &= G_e + G_d(t) \dots\dots\dots [3] \\ \text{where: } G_e &= \text{equilibrium modulus, and} \\ G_d(t) &= \text{relaxation function having initial} \\ &\quad \text{and final values of } d(0) = 1 \text{ and } d(\infty) = 0. \end{array}$$

at time $t = 0$ the equation reduces to

$$G(t) = (G_e + 1) = G_o \dots \dots \dots [4]$$

where: G_o = glass modulus.

The best way to describe stress relaxation behavior, as exhibited by high polymers, is by a diagram relating relaxation modulus $G(t)$ to the logarithm of time, t . As in the case of creep, polymers under constant strain behave like ideal elastic substances at very short times. Thereafter, they can be described by an operator equation that relates stress, strain and time. For linear solids the various methods of representation are equivalent to each other and one can be obtained from the other (263).

2.3.3 Viscoelastic behavior of cellulose fibre mats

Most published studies on cellulose fibre mat viscoelastic properties have been based on analysis of creep and stress relaxation curves obtained from moisture conditioned papers under constant tensile load or deformation. Unfortunately, little is known about the viscoelastic behavior of fibre networks in compression and even less is known about wet systems under any conditions.

Various types of cellulose networks such as paper and pulp mats have several features in common, important of which is the fact that all are made from filtered suspensions of cellulosic fibres in water, subsequently pressed and usually dried which gives coherent sheets. Due to these identical preparation procedures, fibre networks may also present certain common rheological features. For this reason the following discussion of fibre network viscoelastic behavior will include both papers and pulp mats. Again, only studies relevant to this work will be reviewed.

2.3.3.1 Rheology of paper

The first comprehensive studies on time dependent stress-strain behavior of cellulose sheets (papers) were carried out by Steenberg and coworkers (125,276,277) as early as 1947. They showed that the load-deformation properties of paper depend on numerous factors, such as manner of sheet preparation, external test conditions, rate of testing, and the previous mechanical history of the specimen.

Subsequent investigations have centered partly on mechanisms of paper rheology, particularly under tensile excitation (33,145,186,219,224,225,

227,259,260,307,308). It is now generally agreed that both inter- and intra-fibre mechanisms determine the time dependent behavior of papers.

Other studies have attempted to describe the time dependent response of paper mathematically. Thus, Andersson and Sjöberg (7) studied short time relaxation after rapid stretching at constant rates between 1% in 0.01 sec and 1% in 5 sec. They found that rate of stress decay is highly dependent on the initial strain rate, i.e., high straining rate is followed by high stress decay rate, and vice versa . By plotting fractional stress relaxation $\epsilon(t)/\epsilon(o)$ against the logarithm of time sigmoid shaped curves were obtained, which indicated a Maxwellian delayed elastic type of relaxation.

In his earlier publications on paper relaxation, Kubat (151,152) presented results of stress relaxation measurements following tensile straining at low rates (1% in 100 sec). He was able to demonstrate a linear relationship between residual stress and $\log t$. Nevertheless, he pointed out that this relationship must be regarded only as a temporary approximation. Such curves must, according to this theory, ultimately conform to an ideal Maxwellian trend at long periods of stress dissipation. In other words, the plot of ϵ against $\log t$ becomes asymptotic to a line parallel to the time axis.

In paper stress relaxation following constant rates of elongation (1% in 23 sec to 1% in 10 sec), a straight line relationship was also found between stress (ϵ) and $\log t$ for the test period of 4 hr (242). The relationship was expressed by the following equation:

$$\epsilon = x - y \log t \dots\dots\dots [5]$$

where: x and y are constants which depend on preloading history.

In a recent study on tensile stress relaxation of paper, Johanson and Kubat (137) determined the effect of strain rate, initial stress, moisture content and beating on the viscoelastic behavior of paper under constant strain. They found that the following equation related inflexion slope of stress - $\log t$ curves and total dissipated stress ($\Delta\epsilon = \epsilon(t_o) - \epsilon(t_{\infty})$) applied also to paper:

$$F = 0.1 \Delta\epsilon \dots\dots\dots [6]$$

Furthermore, results of their study indicated that activation energy for the stress relaxation process is stress dependent.

The viscoelastic response of air-dry newsprint subjected to constant load and deformation in compression was investigated by Gavelin (85). He observed increased viscoelasticity at higher moisture content and he also found very good correlation between stock freeness and the irreversible compressibility. This showed that beating makes paper less compressible. He also indicated that recovery response (which is the instantaneous and time dependent "spring back" following removal of compressive deformation) is related to the quality of the wood used in making the pulp.

Other studies on behavior of air-dry paper under compression were carried out by Brecht and Schädler (31,32). They observed that increased basis weight reduced relative compression and increased relative expansion. Furthermore, addition of a small percentage of groundwood to a basic Scotch pine sulphite stock caused a substantial increase in relative compression. Creep was found to be unimportant at low loads (20 kp/cm^2), but occurred at higher loads (200 kp/cm^2).

In a more recent study, Jackson and Ekström (127) investigated compressibility characteristics of air-dry sheets prepared from various pulp types. They reported that the recovery response following compression treatments was higher for unbleached than bleached pine sulphate pulp. Experiments with unbleached sulphate and bleached sulphite European birch pulps indicated higher recovery response for the first pulp type. In general, it appeared that sulphate pulps show a higher degree of recovery response than sulphite pulps and unbleached pulps exhibit higher recovery than bleached pulps. Jackson and Ekström observed also a "species effect". Coniferous pulps were found to compress better than hardwood pulps, but the latter group showed higher relaxation responses than the first.

Mardon et al. (180,181) observed in their investigations on the dynamic and static compressibility of papers made from various pulp types that compressibility is greatly influenced by moisture content (below the fibre saturation point), caliper, bulk, void volume and previous stress

treatments. Degree of deformation was found to increase with increasing values of the first four variables and to decrease towards a constant value with increasing previous peak pressure. Their observation with respect to bulk effects, however, is not in agreement with the findings of Brecht and Schädler (31,32), who found that mat response is indirectly proportional to bulk.

Similar studies were carried out recently by Bliesner (25), who observed the viscoelastic behavior of two air-dry coniferous kraft pulps and one groundwood pulp under dynamic excitation in compression. It was found that the effect of sheet bulk (cm^3/g) on compressibility differed widely between these two pulp types. The permanent set (non-recoverable deformation) increased with increase in bulk for kraft pulps but remained constant for the groundwood pulp. Both pulp types showed an increase in relative compression, but responded differently in relative recovery. Increase in bulk improved relative recovery in groundwood, but resulted in lower recovery in kraft pulps. Repeated stressing up to three cycles was found to change the compressive response of pulps, but thereafter no significant changes were noted.

2.3.3.2 Rheology of wet fibre mats in compression

According to Brecht and Erfurt (29) and Lyne and Gallay (172), a wet cellulose fibre network consists of fibres arranged in a manner similar to that in dry networks. But considerable differences arise from: (i) distance between the fibres; (ii) the degrees of fibre plasticity and elasticity; and (iii) degree of fibre association. Interfibre bonding, a controlling factor for mechanical properties in dry and partly dry fibre webs, does not play a significant role in the mechanical behavior of wet cellulose networks, i.e., below 20% solids. Therefore, rheological behavior of wet pulps is considered only as a function of wood fibre viscoelastic properties and characteristics of the network structure formed as result of fibre-to-fibre contacts.

The rheology of wet fibre mats was first studied by Seborg et al. (262). They compressed cylindrical small pulp sheets in wet condition at a maximum pressure of 8.5 kg/cm^2 . After no further deformation was noted they

removed the load and observed recovery. It was found that recovery figures were affected by mat caliper, where thicker mats gave less recovery for a given load. Experimental data indicated also a difference in recovery response between unbeaten and beaten pulps, with recovery higher for pulps without beating treatments. In a later publication on the same subject Seborg et al. (261), presented data which indicated that sulphate pulps show higher recovery than comparable sulphite pulps and that groundwood exhibited less recovery than the chemical pulps.

A comprehensive study on the effect of moisture content, degree of beating and caliper of pulp mats on their recovery response as derived from compressive deformation was carried out by Ivarsson (124). He observed that absolute compression and permanent set increased with increasing moisture content up to the fibre saturation point, whereas the recovery response decreased with moisture. Further, increasing moisture contents changed insignificantly the mechanical behavior of pulp mats under compression. Ivarsson's observations on effects of beating and caliper are in general agreement with those made by Seborg et al. (262). The relative permanent set was found to decrease slowly with increasing caliper. In addition, Ivarsson examined the effect of caliper on relative compression. His data showed that more relative compression is obtained for thinner sheets. Other studies (122,138) reported that beating over wide ranges did not change the nature of wet pulp compressibility for bleached pulps, but they did observe some change for unbleached pulps.

Several workers have developed mathematical expressions describing the behavior of wet fibre networks under compressive stress. Campbell (43) was the first to use a mathematical expression which he derived empirically, to describe the relationship between mat consistency (C) and stress (p):

$$C = M p^N \dots\dots\dots [7]$$

where: N and M are constants which depend on nature of the pulp. Ingmanson and Whitney (123), studied the filtration resistance of pulp slurries and pointed out the need to include a small but finite constant (C_0) in the equation to satisfy conditions required for establishing finite consistency

at zero pressure:

$$C = C_0 + M p^N \dots\dots\dots [8]$$

Both equations, however, have to be considered as first approximations for describing the stress-pad concentration relationship, since time, known as a highly important variable in mat deformation processes, has been ignored.

Wilder (322) studied wet fibre mat creep and creep recovery over long periods and for successive cycles and modified Ingmanson and Whitney's equation by replacing M with the new term ($M = A + B \log t$) which includes time dependent effects. Thereby, the stress - mat consistency relationship became:

$$C = C_0 + (A + B \log t) p^N \dots\dots\dots [9]$$

where: A, B = constants, and
t = time.

However, as Wilder (322) pointed out, the equation does not apply to extremely short time intervals during which filtration resistance controls the mat response. His experimental data also indicated that the equation constants change for each compression and relaxation phase during the first 5 to 6 cycles. Thereafter, the mat becomes conditioned and the constants remain unchanged, one set for compression and another for recovery.

As mentioned earlier, Wilder found his equation insufficient to describe the early phase of mat compression (up to 5 sec). He attributed this deviation to mat permeability and fractional drag of the water being pressed out. Jones (138) carried out compressibility studies on various types of wet fibre mats, and examined effects of fibre length and diameter and elastic modulus on compression recovery response. The purpose of this investigation was to obtain more information on fibre interaction mechanisms, such as fibre bending, fibre slippage and compression of fibres in overall mat deformation during rheological processes. The compression-recovery was found to be highly dependent on fibre length-to-diameter ratio and modulus of elasticity. Fibre diameter alone, however, did not affect significantly the recovery response. Furthermore, fibre repositioning appeared to be very

important in early compression cycles, but fibre bending was the controlling factor in compression of mechanically conditioned mats.

In a comprehensive study on specific permeability and compressibility of mats prepared with synthetic and natural pulp fibres, Higgins and De Yong (114) investigated the relationship between mat solids concentration and applied stress. Their experimental data were obtained from two series of coniferous sulphate and pored wood NSSC pulps, with each series covering a wide range of lignin contents. They found that compressibility and consolidation of wet mats was highly influenced by flexibility and lateral conformation of the wet fibres. These two factors might not only contribute to capacity for elastic deformation but also to the extent to which irreversible processes may occur.

Similar investigations were carried out by Kayama and Higgins (143), who examined the effect of bleaching on wet web compressibility of coniferous kraft pulps. They observed that pulp sedimentation volume decreased as lignin was removed, and as bleaching proceeded the compressibility decreased. This behavior has been attributed also to changes in flexibility and lateral conformability with lignin removal.

2.4 Compressibility of Cellulosic Fibre Mats

The behavior of cellulosic fibre mats under compressive deformation can be considered as the combined response of rheological and non-rheological mechanisms. They are probably highly interrelated, particularly in early stages of mat deforming processes. It is the purpose of this section to review information on fibre mat compressibility as related to this work.

The behavior of cellulosic networks under compressive stress or strain is a function of numerous factors interacting in complex and not fully understood ways. In spite of several investigations (100,138) on the subject during the last 15 years, much research is still required for more complete elucidation of mechanisms and factors determining response of wet cellulosic mats subjected to compressive excitations. It is rather surprising that so little emphasis has been placed on the subject, since industrial manufacturing processes frequently involve compression treatments of wet and dry fibre mats.

Fortunately, the knowledge and theories of air-dry paper response to tensile excitations in particular are rather advanced and, therefore, can offer some help for interpreting observations made on wet fibre mats. The following discussion also includes observations and theories of paper rheology so far as they are relevant to this study.

For a comprehensive review it is convenient to subdivide the discussion into two sections; one dealing with the mechanisms which are involved in processes of compressive deformation, and the other with factors determining the magnitude of instantaneous and time-dependent deformation of cellulosic networks.

2.4.1 Mechanisms in compression of wet cellulosic fibre mats

A wet cellulose fibre mat can be defined as a fibre network comprised of elements mostly lying loosely over each other and forming many sites of contact and potential contact. The fibres are limited to an approximately planar orientation, where within plane their position and orientation have a degree of randomness arising from the essentially disordered state of suspension from which mats are formed. In the majority of cases, however, the fibres lie in-plane and consequently the regions of contact also lie in the plane of the mat. Complete randomness may be adjusted somewhat by formation of mats on production wires.

When a wet mat is subjected to compressive deformation three compressibility mechanisms can be expected to occur during deformation processes (100,138): (i) fibre bending; (ii) fibre slippage; and (iii) fibre compression at regions of fibre-to-fibre contact. In the following these potential mechanisms are discussed separately in spite of the fact that they probably interact during compaction.

2.4.1.1 Fibre bending

According to Han (100), application of external stresses to a mat will be followed by stress transmittance through fibre-to-fibre contacts and stress distribution along fibres. This is accompanied by bending of fibre segments between two points of support which causes formation of additional contact areas between neighboring fibres and thus increases mat

density. If cellulosic fibres were entirely elastic, deformation within the fibre would be expected to be entirely recoverable. Due to the visco-elastic nature of cellulosic fibres, however, both recoverable and non-recoverable bending deformations, as well as time dependent bending deformations, take place (138). Since all three mechanisms cause permanent deformation in a very complex interaction, no exact information has been obtained as to what extent fibre bending contributes to the total mat response.

Elias (63) studied the compression response of mats prepared from various fibre types and was able to show for glass fibres that bending is the dominant mechanism during compaction. Increasing load was found to increase the glass fibre inflection points. A comparison between glass and synthetic fibres indicated that more flexible fibres, such as dacron filaments, give more contacts during bending. Elias (63) also observed that the number of contacts per unit length increased with fibre length for a given load.

Behavior of cellulose fibres as found in wet pulp mats will differ somewhat from Elias' (63) observation on mats formed by non-cellulosic fibres. Bending of pulp fibres in a wet mat is expected to be accompanied by stretching and shearing processes (140), which may be particularly intensive for swollen fibres.

2.4.1.2 Fibre repositioning

It is well known that the majority of fibres in a fibre bed obtained from suspensions lie flat in the horizontal plane. There are always a number of fibres, however, which are oriented at appreciable angles with the z-axis (perpendicular to mat direction). Elias (63) observed on non-cellulosic networks that a mat consisting of short fibres contains a higher number of individual fibres out of plane than a mat formed by long-fibre material.

During compaction fibres out of plane were found to become nearly horizontal, which implies that those fibres change position relative to their neighbours. This phenomenon is known as slippage or fibre repositioning (63). It might contribute considerably to the non-recoverable deformation of wet cellulose fibre mats, since the forces needed to restore a wet pulp fibre

to its original position are rather low. Resident restoring forces in the fibre might provide at least partial recovery upon relief of the deformation stress, thereby contributing a component of recoverable fibre slippage.

2.4.1.3 Compression at points of contact

Compressive excitations applied to cellulose networks are known to cause stress concentrations at contact areas which induce contacting fibres to conform. The conformation process is essentially characterized by changes in fibre cross-sectional shape, enlargement of contact areas, and increased fibre flattening (100). These phenomena, of course, are accompanied by deswelling processes when the fibre material is saturated with a swelling fluid such as water (100).

2.4.2 Factors determining compression characteristics of cellulose fibre mats

The behavior of cellulose fibre mats under compressive stress or strain has to be regarded as the result of numerous factors, most closely interrelated and, therefore, difficult to estimate. It seems reasonable, however, to distinguish between three categories of factors: (i) fibre morphology; (ii) fibre properties; and (iii) structure of fibre mats.

2.4.2.1 Fibre morphology

There are three fibre characteristics which have been found, or are expected, to influence the response of cellulose fibre mats to compressive excitations; (i) fibre length; (ii) fibre length/diameter ratio; and (iii) cell wall thickness.

The average dimensions of typical pored and coniferous wood fibres differ widely, wherein the latter show the greater dimensions (91). It is also known that latewood fibres are somewhat longer than those of associated earlywood (40,320). Other differences in fibre dimensions arise from machining processes in pulping. In particular, mechanical pulping produces fibre materials characterised by considerable dimensional variations between fibre fragments. Groundwood pulps are known to contain components as: (i) fibre bundles; (ii) separate fibrillated fibres; (iii) broken fibres; and

(iv) fine wood flour (16). In contrast, chemical pulps consist almost entirely of single fibre skeletons often mechanically damaged in varying amounts during processing.

Due to the absence of interfibre hydrogen bonding in wet cellulose fibre mats, fibre length has to be considered important to mat response under compressive stress and strain. It is well known that long fibres cause a high degree of mechanical entanglement (56), which strengthens both air-dry and wet cellulosic networks. Brecht and Erfurt (29) investigated the wet-web strength of mechanical and chemical pulps and pointed out that fibre length, in addition to consideration of flexibility and surface area, has to be considered as the dominant factor in determining wet-web mechanical properties. This concept has been confirmed by experiments of Forgacs et al. (73) with mats formed at low fibre consistencies, such as 0.8%. Further evidence for this can be derived from several studies on paper, which have shown, for instance, that tearing strength is highly influenced by fibre length (28,50).

Fibre length can also influence the general fibre mat structure. Watson et al. (319) were able to demonstrate this effect on sulphate pulps prepared from Monterey pine fibres of 1.7 mm and 3.0 mm length, but similar in morphological and chemical properties. It was found that the longer fibres gave sheets with much more open structure; in other words, longer fibres produced sheets of higher bulk.

Fibre length/diameter ratio was found to have at least some bearing on mat response to mechanical excitation. Hentschel (111), working with synthetic fibres, showed that this ratio influences the strength properties of fibrous networks. Jones (138) also reported a "ratio effect". By studying this effect on synthetic fibre and pulp mats under compression excitation he observed that an increase in length/diameter ratio up to a certain value enhanced the compression recovery response of fibre mats. On the other hand, Dadswell and Watson (56) provide evidence that this ratio has very little or no influence on mechanical properties of air-dry fibre networks (papers).

The importance of cell wall thickness and degree of fibre collapse to paper properties has been recognised for many years (65,118,132,150,225, 250,286,318). Most differences with coniferous pulps arise from variations in cell wall thickness between earlywood and latewood tracheids. Thin cell walls, as those in earlywood, collapse more readily and produce a dense and highly packed network; whereas thick-walled cells, such as those in latewood, collapse less and give open and bulky networks. The effect of fibre collapse appears to be two-fold: (i) increased fibre flattening provides larger contact areas between fibres; and (ii) fibre collapse entails greater fibre flexibility or conformability (248).

2.4.2.2 Fibre properties

Variations in chemical and physical characteristics of pulps arising during pulping, bleaching and subsequent treatments are expected to influence pulp mat response to compressive excitation. These variations are manifested in fibre collapsibility (influenced by residual lignin), fibre flexibility (affected by structural characteristics of residual hemicelluloses) and fibre strength (related to cellulose DP).

Due to the hydrophobic nature of lignin, as well as its probable linkage with hemicelluloses (23,35), the whole lignin-hemicellulose complex is made partly hydrophobic and is restrained from excessive swelling (86). Moreover, the three-dimensional lignin structure is known to limit the degree of fibre collapse and flexibility. For instance, high lignin content influences fibre properties in two ways as: (i) preventing hemicelluloses from excessive swelling and plasticisation; and (ii) giving fibres a high degree of stiffness which impedes collapsibility (40,86,105,133,184,221,306).

Other comprehensive investigations on fibre properties and compressibility of fibre mats have been published recently (105,221,223). Page and coworkers (221,223) studied paper structure and collapse behavior of pulp fibres, and observed that the percentage of collapsed fibres after drying increased inversely to the pulp yield and that sulphite fibres collapsed to a greater extent than sulphate fibres. Similar observations were made later by Hartler and Nyren (105), who investigated the transverse

compressibility of pulp fibres. The lower collapsibility of kraft fibres was attributed to more frequent crosslinking in those fibre parts having high lignin and hemicellulose contents. As a consequence of the hydrophobic and rigid character of lignin, fibres possessing high lignin contents exhibited low conformability and therefore produced bulky fibre mats (248). This effect has been thoroughly investigated by Kayma and Higgins (143), who were able to show that progressive delignification of sulphate pulps produces lower sedimentation volume and reduces mat compressibility.

The numerous short side chains, characteristic of many hemicelluloses, are responsible for the amorphous state of native hemicellulosic materials. Therefore, water penetrates more easily between hemicellulose chains and after delignification causes considerable swelling. This leads to formation of gels inside fibre walls, such as in inter-fibrillar spaces and on fibril surfaces (45). In addition, DP and branching are considerably reduced in chemical pulping and bleaching treatments (174,217,233). These changes are known to have a pronounced effect on mechanical properties of papers made from chemical pulps (95,201,233,282). In wet fibres the hemicelluloses enhance greatly fibre lateral swelling by inter-fibrillar swelling processes and under stress conditions they are thought to act as a kind of "internal lubricant" improving fibre flexibility. Similarly, hemicelluloses positioned on fibre surfaces are considered to function as an external lubricant promoting fibre slippage and repositioning within mats (86).

The effect of fibre strength on sheet mechanical properties is particularly important for pulps produced by chemical treatments. In chemical pulping, as well as subsequent delignification and carbohydrate removal processes, all cellulose molecules are degraded to some extent. This entails weakening of the fibre ultra-structure and thereby reduction in whole fibre strength. Many studies on paper have shown that sulphate and sulphite pulping produces fibre materials which differ widely in strength properties (11,84,104,144,233), whereby sulphate pulp fibres usually are of superior strength. It has been suggested by Jayme and von Koppen (134), for instance, that the cause for lower strength observed with sulphite pulp compared with sulphate pulp lies in weaker interfibre bonding in the sulphite sheet. This results in turn from lower carbohydrate DP, in particular of the cellulose,

at the fibre surface. Differences in carbohydrate degradation at the outer parts of fibres may also explain in part the observation made by Seborg and Simmonds (261) in compression of wet pulp mats, wherein sulphate pulps showed higher recovery figures than sulphite pulps. Another investigation giving some indication that cellulose degradation and consequently weaker fibres effect fibre mat compressibility was carried out by Petterson and Rydholm (233). They found that overcooked and overbleached pulps form denser papers than would be expected from opacity measurements.

2.4.2.3 Structure of fibre mats

The structure of fibre mats is determined by distribution and orientation of fibres, which in turn depends on processes of mat formation (8,175). According to fibre arrangement the mat structure can be characterized by: (i) the degree of separation of the fibres across the mat thickness; (ii) orientation of fibres in the three-dimensional network; (iii) degree of flocculation; (iv) extent of coiling or wrinkling of individual fibres; and (v) distribution of fine material (84,175,306). Evidence exists, in particular from studies on paper, that these mat characteristics can have an important bearing on mechanical properties of fibre networks (8,15,84). In fibre mat compression factors (i) and (ii) are expected to play major roles, as they probably determine the extent to which the three mechanisms are involved during the compaction process. This agrees with Han's statement (100) that resistance of wet fibre mats to compression increases with increasing initial solid fraction. This results in a lower final solid fraction at a given compression.

3.0 MATERIALS AND METHODS

3.1 Pulp Samples

Pulps were chosen to broadly represent the wood pulp spectrum, thus providing a wide quantitative range for residual carbohydrates and lignins and hopefully large difference in physical and rheological responses. Consequently, 24 commercial and eight laboratory pulps were used in the study. The sample collection included four groundwood pulps, four "holocellulose" pulps, four kraft pulps, one sulphite pulp, fifteen dissolving grade pulps and four alpha-cellulose preparations. Other sources of variation were introduced to the study by including both bleached and unbleached pulps and by choosing pulps prepared from both coniferous and pored woods. The various pulps employed and some of their characteristics are listed in Table 2.

The eight laboratory pulps included in the study were holocellulose and alpha-cellulose preparations of wood fibre skeletons as obtained by standard methods.

3.1.1 Holocellulose pulps

The wood materials used for preparing holocellulose pulps were taken from one mature stem each of western hemlock (Tsuga heterophylla (Raf.) Sarg.) and western cottonwood (Populus trichocarpa Torr & Gray). Special care was exercised in dissecting wood blocks into small size pieces of approximately 0.3 x 1.0 x 4.0 cm in order to minimize mechanical damage to fibres. After air-drying for three days the chips were exhaustively extracted with 2:1 ethanol-benzene. The air-dry extracted chips were divided into two parts, one part was used for pulping in peracetic acid and the other in acidified sodium chlorite solution.

Peracetic acid cooking accompanied by alternate sodium borohydride reduction stages, was carried out according to the method proposed by Leopold (164). Due to rather large chip dimensions, a total of six cycles was required for complete defiberisation. Chemical analyses of these pulp preparations indicated a higher loss in non-cellulosic carbohydrates (Table

3g) than reported in the literature (295). This discrepancy can be attributed to overcooking of the outer portion of the chips which obviously caused serious degradation and subsequent dissolution of hemicelluloses. Evidence for this occurred also in work of Shimada and Kondo (264), who observed a decrease in pulp yield with increasing chip thickness.

Chlorite holocellulose pulps were obtained by delignifying wood chips in a solution of sodium chlorite and acetic acid at 70° C. Details of the method are reported elsewhere (323). Approximately eight hours chloriting time was required to produce a completely defibrised material. Similar to peracetic acid pulps, the chlorite holocellulose pulps contained less hemicelluloses than expected based on values published in the literature. This can be explained by overcooking effects in outer portions of the relatively large chips. An investigation by Eriksson (67) on several factors influencing quality and quantity of chlorite holocelluloses supports this assumption. He observed also that increasing wood particle size and treatment time lowered holocellulose yields. In the present study, both factors exceeded considerably the values proposed by Wise et al. (323).

The freshly prepared holocelluloses were air-dried as small flakes for two days at room temperature in order to eliminate or minimize differences in mechanical properties between commercial and laboratory pulps due to moisture history, which has been found to affect pulp mat properties (29). This procedure was necessary as commercial pulps were supplied in air-dry condition following unknown drying histories.

3.1.2 Alpha-celluloses

One alpha-cellulose pulp was prepared from each of a commercial viscose and acetate pulp and the two chlorite holocellulose preparations as obtained from western hemlock and western cottonwood. The alkaline extraction with 17.5% NaOH at 20°C was carried out in accordance with TAPPI T203 os-61 (289). Alpha-cellulose residues were teased into small flakes and air-dried before further processing for sample sheets preparation.

Since part of a preliminary study on viscose pulps is included in this work and specimens used in the earlier investigation were cut from

commercial pulp sheets, it was decided to prepare other fibre mats as close as possible in basis weight and thickness to those supplied commercially.

Mats were prepared essentially according to TAPPI Standard T205m-58 (287). Following weighing, disintegration, and sheet formation in the standard sheet machine, 10 wet handsheets of each pulp type were prepared. Prior to pressing these 10 standard wet sheets (each weighing 1.2 ± 0.1 g oven-dry basis) were carefully laid over each other. In this way a wet pulp mat was obtained which, after wet-pressing and air-drying, yielded a sample sheet of desired basis weight and thickness. Both pressing stages were performed at 80 psi for time periods according to TAPPI Standard T205m-58. Conditioning of sample sheets was done between drying rings at controlled temperature - humidity conditions (22°C and 50 to 52% R.H.) for at least three days before further processing.

The preparation of sample mats by means of assembling handsheets was found by preliminary experiments to produce more uniform structures than when thicker sheets were prepared from higher consistency stock, which gave high flocculation. Thus, serious density variations across mats were avoided with the intention of minimizing variability due to this cause.

Test specimens of viscose pulps (1-1 to 4-2) were prepared from commercial sheets, while specimens representing other pulp types were obtained from laboratory made mats as described. Actual test specimens were punched randomly from sample mats by using a carefully honed mechanical cork borer of 1.45 cm diameter.

Specimens were either steeped in distilled water or aqueous sodium hydroxide for varying times, or were subjected to gamma-radiation before further treatment. Thereafter, the stress relaxation was performed by methods to be described.

The specimens used for studying stress decay on pulps in wet condition were steeped approximately one minute in distilled water. This was found to be the minimum time required for assuring complete swelling.

Those specimens exposed to caustic steeping were kept for 25 ± 2 sec in 18.6% NaOH, a concentration used in commercial steeping. Both steeping treatments were performed at a temperature of 22°C . Immediately after steeping, the pulp specimens were examined in stress relaxation. The specimens were kept in corresponding solutions during testing. In one experiment, which dealt with the effect of steeping time on stress relaxation, the caustic steeping period was varied from 0.1 to 14400 minutes (more than five time cycles of 10).

Sample irradiation treatments were done in a Gamma-Cell 220 at ambient radiation chamber temperature of 34°C . Air-dry pulp samples were exposed in an air atmosphere from 0.5 to 6 Mrad dosages at a dose rate of 0.829 Mrad/hr.

3.2 Physical Testing

All stress relaxation measurements were performed with a Floor Model TT Type C Instron testing machine. The specimens were placed between a 1.0 mm thick microslide glass and a 5.0 mm thick glass plate in order to protect the Instron load heads from corrosion in tests involving caustic steeped specimens. The glass assembly was found not to relax in any measurable way under conditions used in this experiment. A typical test assembly is shown in Fig. 4.

Five replications were done for each pulp treatment combination. Since it is not possible to determine ultimate strength values in pulp compression due to the collapsed state of the fibrous material in the mat, an arbitrary load of $3.5 \text{ kg}/2.1 \text{ cm}^2$ was applied in all tests. It can be assumed that a stress of this magnitude does not cause complete compression of the mat, although initial caliper was reduced 60 to 80%. Strain ($\Delta L:L$) was not used, since each pulp showed characteristic swelling.

The desired stress was applied in all tests at the rapid loading speed of 2 cm/min for water treated and 5 cm/min for alkali steeped specimens. These were the highest speeds possible for accurate setting of stress levels with the test engine used. Consequently, the loading process was completed in approximately 1 to 1.5 sec, which is the limit of approximation to step-function excitation of the present study.

Stress relaxation was observed over a time range of 35 min, except for experiments dealing with the effect of steeping time where relaxation tests were stopped after 100 min. Two recorders were employed for observing stress decay; an X-Y-recorder (Mosely Autograph Model 7000-A) set at chart speed of 2 in/sec was used for recording early stages of stress decay (0 to 15 sec), and the Instron recorder was run at a chart speed of 1 in/min for tracing stress decay from 15 sec onward. Both recorders were fed the same Instron signal.

Data obtained from chart traces were transformed into fractional stress relaxation values according to:

$$\zeta(t)/\zeta(t_0),$$

where: $\zeta(t_0)$ is the initial stress at time t_0 , i.e., when the loading process was completed, such as 1.0 to 1.5 sec after excitation was commenced. This differs from much of the earlier literature where, for mathematical convenience, t_0 has been taken as 1 min following completion of loading, and this often following extensive but seldom described ramp-loading times.

3.3 Determination of Pulp Constituents

In order to obtain information on the contribution of various wood and pulp constituents to pulp viscoelasticity, several analytical methods were employed including: (i) determination of the carbohydrate components; (ii) estimation of residual lignin; and (iii) other measurements.

3.3.1 Carbohydrates

Several quantitative gas chromatographic methods for analysis of wood and pulp carbohydrate compositions have been developed recently. These have proven to be less time consuming and easier to operate than earlier traditional paper chromatographic procedures. According to these methods, monosaccharides in neutralised hydrolysates originating from cellulosic materials can be analysed after conversion to trimethylsilyl derivatives (21,302), acetylated aldonitriles (61) or alditol acetates (26,94,267,269).

Trimethylsilyl derivatives are quickly prepared but, due to the

multiplicity of peaks arising from each aldose by anomeric and different ring-forms, peak interpretations are difficult to make. For this reason, the alditol acetate methods which gives only a single peak for each monosaccharide seems to be more accurate for quantitative determination of wood and pulp polysaccharide mixtures. It was decided to apply the method developed by Borchardt and Piper (26), which, compared with other alditol acetate procedures, is less time consuming and is known to separate all known wood sugars.

A 300 mg sample (oven-dry basis) was taken from each of the 32 pulp mats used for rheological testing. Thus, each pulp type investigated in the study was represented by one composite sample. After shredding and weighing, the pulps were hydrolysed following the method of Saeman *et al.* (253). Exactly 0.100 g of myo-inositol as internal standard was added to the aqueous hydrolysate before it was neutralised and further processed according to the procedure outlined by Borchardt and Piper (26). In the final step of this procedure the alditol and myo-inositol acetates were dissolved in methylene chloride and stored in tightly sealed vials, before injection into the gas chromatograph. Three injections of 0.7 μ l each were done for analysis of each sample.

Separations were carried out with aid of a MicroTek 150 gas chromatograph equipped with a flame ionisation detector and a Moseley 7100 B stripchart recorder. A 6 ft x 1/8-in glass (analytical) column packed with 3% ECNSS - M on Gas Chrom Q 80-100 mesh was installed for on column injection.

Helium was used as carrier gas with a flow rate of 33 ml/min. All operations were isothermal with the column oven at 195°C, the injection port at 210°C, and the detector at 240°C. The alditol and myo-inositol acetates were eluted in approximately 40 min with satisfactory resolution of each component as can be seen in Figs. 5 to 13.

The relative amounts of individual components were calculated according to (26):

$$\% \text{ Polysaccharide} = \frac{C \times I \times F \times 100}{R \times S \times H \times k} \dots\dots\dots [10]$$

where: C = chromatographic area of the component peak,
 R = chromatographic area of the myo-inositol peak,
 I = myo-inositol weight,
 S = oven-dry sample weight,
 F = factor converting monosaccharide weight to polysaccharide (0.88 pentose; 0.90 hexose),
 H = hydrolysis survival factor, and
 k = calibration factor for the individual component.

Peak area measurements were done manually by cutting and weighing chromatograms, since the Disc Chart Integrator was not in working order and the counter did not work satisfactorily for carbohydrate peaks. The hydrolysis survival factors of individual sugars used for this equation were determined by Saeman et al. (253) and k-values were based on slopes of calibration curves which were obtained by plotting chromatographic peak area ratios (monosaccharide area/myo-inositol area) vs. weight ratios (monosaccharide weight/myo-inositol weight) for known samples.

Uronic acid residues were determined commercially by Schwarzkoff Microanalytical Laboratory, Woodside, N.J., following the method of Anderson et al. (6). The quantitative analysis of acetyl groups was carried out by the same company using a modified method developed by Schoniger et al. (256). Data on acetyl and uronic acid groups are presented in Table 3.

Hydrolysis of wood hemicelluloses according to the procedure of Saeman et al. (253) is not without shortcomings. Meier and Wilkie (192) and Zinbo and Timell (327) observed that aldobiouronic acids formed during hydrolysis were rather stable to further hydrolytic degradation. Only one-third of 4-O-methyl-D-glucopyranuronide linkages were found to undergo further hydrolysis under conditions provided by the method of Saeman (192, 327). Since the xylose fraction which is present in non-hydrolysed aldobiouronic acid residues does not appear in the gas chromatographic analysis, some correction regarding xylose content was undertaken. This was done by multiplying the relative amount of glucuronic acid residues with a factor

of 0.66 (which relates to non-hydrolysed aldobiouronic acid). The value obtained was added to xylose as determined by the gas chromatographic procedure (Table 3).

Since the chromatographic analysis gave only information on the total amount of glucose present in pulp, it was useful to estimate those portions of glucose originating from cellulose and glucomannans. This was done according to known ratios between glucose and mannose residues in isolates from coniferous (1:3) and pored (1:2) wood glucomannans (293). The corresponding values are presented in Table 3.

3.3.2 Lignin

Lignin determinations were carried out according to the Klason lignin method as described by Browning (37) on groundwoods (10-1 to 10-4), holocelluloses (9-1 to 9-4) and paper grade pulps (6-1 to 8-2). Data are presented as Klason lignin in Table 3. Only groundwood pulps were subjected to ethanol-benzene extraction treatments prior to acidification, since chemical pulps are known to contain no or only traces of extraneous compounds.

No lignin determinations were undertaken on viscose, acetate and alpha-cellulose pulps, due to their extremely low lignin contents which are not measurable by the Klason lignin method. Their lignin contents were estimated to be $\leq 0.1\%$.

3.3.3 Other measurements

Viscosity measurements were done for characterising pulps and for determining degree of cellulose degradation by irradiation treatments. They were carried out in a modified FeTNa (EWNN, alkaline iron tartaric acid sodium complex) solution prepared according to Valtasaari (305), but with an additional 10 g/l sodium tartrate used as stabilizer. Oven-dry sample weights of 0.015 to 0.25 g pulp per 100 ml solution were used according to the method of Paszner (229), with amount adjusted to the degradation level. First, specific viscosity (η_{sp}) was determined with an Ubbelohde viscosimeter No. 1a at $20 \pm 0.02^\circ \text{C}$. Intrinsic viscosity ($[\eta]$) was then calculated by the equation (305):

$$[\eta] = \frac{\eta_{sp}}{C (140.339 \eta_{sp})} \dots\dots\dots [11]$$

where: C = amount of moisture-free pulp, g/100 ml.

TAPPI Standard method T293 os-61 (289) was followed in determining alpha-cellulose contents. This particular method was scaled to accommodate micro-amounts of material.

The solubility determinations were performed according to TAPPI Standard T 235 m - 60 (288) with 10% NaOH solution at a constant temperature of 20°C. Special care was exercised to keep the temperature at 20 ± 0.02°C for all tests, since it has been found that even slight changes in temperature influence results of alkali solubility measurements (126).

4.0 RESULTS AND DISCUSSION

4.1 Fractional Stress Relaxation Tests

As described earlier, five replicates were used in all pulp treatment combinations. Table 4 presents fractional stress relaxation data ($1.000 - \frac{\sigma(35 \text{ min})}{\sigma(0)}$) as obtained from individual measurements after 35 min relaxation time, $\sigma(0)$ mean values and standard deviations for each of the pulps tested for both water and caustic steeped conditions.

Standard deviations show relatively little variation between measurements at 35 min relaxation time as taken from individual pulps given the same steeping treatment. This means that the results are consistent, which is a strong point of the experiments. Degree of variation was approximately the same for all pulp types with comparable steeping treatments, but differed considerably between water and caustic steeped specimens of the same pulp. On average, caustic treated samples exhibited less variability in rate of stress decay, as compared with water saturated specimens, after 35 min relaxation. As will be shown later, the reproducibility of stress relaxation data, particularly when obtained from caustic treated samples, appears to be sufficiently high to employ relaxation measurements for characterising pulps.

Characteristic of all viscoelastic materials is their ability to dissipate stress when subjected to deformation. It is well known that stress relaxation of viscoelastic solids occurs at the highest rate immediately after a constant deformation is applied, and thereafter decreases gradually with time. A similar type of response can be expected also from pulp mats placed under constant compressive strain.

Two-dimensional $\sigma(t)/\sigma(0)$ vs. log time plots of typical fractional stress relaxation curves, as obtained from pulps steeped either in distilled water or 18.6% NaOH prior to relaxation tests, are shown in Figs. 14 to 18. The curves represent average values of five measurements. It appears from each set of plots that rate of stress dissipation in pulp compression follows patterns similar to those observed in woods or other cellulose examined under constant compressive or tensile strains (137,145,146). Wet or caustic

steeped pulp mats exhibited the highest rate of stress decay immediately after strain application, which is characteristic for relaxation processes of ligno-cellulosic materials and often expressed as log time relationships. A more detailed analysis of the $\epsilon(t)/\epsilon(0)$ vs. log time plots reveals that stress relaxation processes take place as two distinct phases. These are indicated as two slopes within each fractional stress relaxation trace.

The writer emphasizes that responses have been observed only over the short time range of 35 min following almost instantaneous strain application. In particular, rate of strain has been found to exert a profound influence on the magnitude of initial stress decay. Kirbach (145) studied the stress decay in wood microspecimens and observed that a high straining rate was followed by a high initial stress decay, but that this did not affect significantly the later process of stress dissipation. Similar observations were reported also by Anderson and Sjöberg (7) who explain this phenomenon as an immediate consequence of the Boltzmann superposition principle or as dependent on previous history. Such observation show that special care is needed for interpreting initial stress relaxation responses.

The first and non-linear period of the $\epsilon(t)/\epsilon(0)$ vs. log t plot will be called Phase I relaxation. It varies in duration (Figs. 14-18) and has been found to involve rather short times for viscose and high alpha-pulps (0.00 to 0.03 min); often intermediate times for holocellulose and chemical paper pulps (0.00 to approximately 0.10 min); and comparatively longer times for groundwoods, particularly when steeped in caustic (to approximately 1.00 min). The common characteristics in Phase I for all pulp-water or pulp-caustic treatments is the sigmoid type relationship between $\epsilon(t)/\epsilon(0)$ vs. log t. Such relationships have been found also by Anderson and Sjöberg (7), and to some extent by Johanson and Kubat (137), for paper tensile stress relaxation. They also used extremely short periods for load or strain application. Anderson and Sjöberg (7) strained their 100 mm long specimens at constant rates between 1% in 0.01 sec and 1% in 5 sec and Johanson and Kubat (137) employed a strain rate of 1.25×10^{-3} sec⁻¹ in the majority of experiments on 10 mm long strips. As mentioned earlier, 1.0 to 1.5 sec was the elapsed time for completion of loading in this study.

The "linear" period, which will be termed Phase II relaxation, characterises the remaining part of the 35 min response of pulp mats steeped in either water or 18.6% NaOH. A straight line relationship between $\epsilon(t)/\epsilon(o)$ vs. $\log t$ has been reported also for other cellulosic materials, such as wood at micro- and macro-levels (145,146) and papers (137,242), while several equations have been developed to describe this linear inflection region. For instance, Johanson and Kubat (137) used the following equation to describe rate of stress decay (Phase II) mathematically as:

$$\epsilon = \epsilon_o - F \log t \dots\dots\dots [13]$$

where: F = slope of the main inflection of $\epsilon(\log t)$.

A similar equation was derived empirically by Kitazawa (146) earlier and was used to describe wood stress relaxation:

$$\epsilon(t)/\epsilon(o) = 1 - m \log t \dots\dots\dots [14]$$

where: m = constant relaxation coefficient which takes into account factors such as species variations.

Kitazawa reported that his equation covered the total stress relaxation process as observed after 1 min. In contrast to other studies in stress relaxation (7,137,145), Kitazawa's work ignored stress relaxation in the 1 min period and therefore does not report existence of a non-linear Phase I relationship.

Since the constants F and m in the two equations above may be replaced by any number representing a certain slope, both equations can be employed to describe pulp mat stress relaxation following water or caustic steeping. Such application, of course, is limited to the linear (Phase II) inflection region.

The steep slopes observed in Phase I, compared with Phase II, for other cellulose suggests profound differences in mechanisms responsible for initial stress decay, especially in the water and caustic swollen state of pulp mats and other cellulosic materials. This includes observations by Johanson and Kubat (137) for paper stress relaxation in tension and Kirbach

(145) for wood microspecimens in compression and tension. The possibility that rate of straining effects may have induced these differences can be excluded, since for all experiments investigating short term or initial stress dissipation (Phase I) strain was applied at high rates.

Dissimilarities in initial stress dissipation (Phase I) between various cellulosecs are attributed mainly to factors which determine inter-relations between individual structural units in wood and fibrous cellulosecs, such as type and intensity of fibre association and order. In water and caustic saturated pulp mats the randomly arranged fibres can exert only rather limited interaction. Hydrogen bonds, characteristic for interfibre bonding of air-dry fibrous materials, are lacking and the only interacting forces in saturated pulp mats are due to mechanical entanglement or friction at fibre surfaces. Consequently, external mechanical excitations are expected to reposition easily individual fibres. In woods, where the strong middle lamella holds various structural elements in spacial arrangement and in dry papers which obtain strength from inter-fibre hydrogen bonding along contact areas, mechanical excitations encounter considerably higher resistance before structural units are separated from each other or repositioned.

During, and immediately following load application, saturated pulp mat response is expected to include both initial fibre rearrangements and, of course, intra-fibre processes causing molecular rearrangements. Consequently, the early stages of stress decay (Phase I) would seem to be controlled by two fundamentally different mechanisms. One of these, which may be called M_1 , can be attributed to inter-fibre processes. These processes might largely control rate of Phase I stress decay.

The other mechanism, which may be called M_2 , is associated with intra-fibre processes taking place at the molecular level. As will be discussed below, these may be of inter- and intramolecular nature. Based on slopes of curves in Figs. 14 to 18, it can be concluded that M_2 is the less important mechanism in Phase I, but seems to control almost entirely Phase II, i.e., after interfibre processes are at a minimum.

The interfibre processes which are thought to play the major role in Phase I stress decay involve essentially fibre movements, such as bending

slippage, deswelling effects at points of contact and, to a lesser extent, movement of fluids in the saturated mat. Certainly, most fibre slippage occurs during the loading process, but some fibre repositioning can be expected in early stages of the stress relaxation process. This might contribute significantly to Phase I stress decay. The rather long periods of Phase I observed for groundwood pulps support this assumption. The low length/diameter ratio of groundwood fibres, together with presence of a considerable amount of fines, provides a mat of low coherence. Therefore, some fibre movement in particular toward the sample edge can be expected. The consequence is decreasing stress.

Changes in fibre bending, which according to Jones (138) are time dependent, may be also of great importance to stress relaxation in Phase I.

Deswelling processes at points of contact are, according to Han (100), a significant feature of water saturated mat compression. Removal of internal fluids from areas under compression requires time, therefore, these processes will continue beyond conclusion of strain application (t_0), adding to the high rate of Phase I stress dissipation.

It is not believed that filtration resistance plays more than a subordinate role in initial stress relaxation processes. Slopes of the loading curves indicate that only low stresses (less than 5% of σ at t_0) develop during early periods of the straining process. This holds even when a high degree of straining (approximately 90% of total mat deformation) is employed. It appears from this that almost all free liquid is removed from the mat before the desired initial stress level is attained.

The conclusion can be drawn that initial stress relaxation (Phase I) in saturated pulp mats involves mechanisms at least partly different from those responsible for stress decay in dry fibrous webs or in dry or saturated woods. This is due mainly to the fact that associations between structural units of saturated fibre mats are profoundly different from those existing in wood and papers.

4.2 Effect of Steeping Media (Water vs. Caustic)

It is known from studies on wood and other cellulosic materials

that steeping treatments with strong alkaline solutions cause both inter- and intra-crystalline swelling, whereas steeping in water entails only extension of inter-crystalline regions (251,275). Former investigations on caustic steeping for adjustment of cellulose fibre mechanical properties (46) and creep behavior of wood (204) provide evidence that differences in swelling exert profound influences on the response of cellulose to mechanical excitations.

Based on this information, and because a major objective of the present study was to elucidate the role of residual wood pulp polymers in rheological processes, it appeared useful to undertake relaxation studies on both caustic and water steeped samples.

Fractional stress relaxation traces as averages of five trials obtained in 35 min tests of various pulp types steeped in water, and in 18.6% NaOH, are presented in Figs. 14 to 18; whereas Table 4 contains individual stress relaxation data for all pulps as observed at 35 min. Each plot and the Table 4 data show considerably higher rates of stress dissipation in pulp mats treated with caustic solutions than in water saturated mats. In other words, caustic steeping in comparison with steeping in water resulted in reduction of the elastic and enhancement of the plastic behavior of the lignin-carbohydrate or carbohydrate complex. As can be seen, rate of stress dissipation increased between 10 and 54% at 35 min after conclusion of loading.

Slopes of the quickly descending portion (Phase I) of relaxation curves in Figs. 14 to 18 indicate clearly that differences in relative amount of stress decay between water or caustic treated pulps are set essentially during the first 0.01 to 0.1 min of relaxation. It appears from this observation that effects of caustic swelling within the pulp fibre structural polymer complex is only active during early stages of the stress dissipation processes. It can be concluded that caustic swelling must activate some mechanisms which, after dissipating considerable amounts of stress, exhaust quickly. The contribution to rheological response is quantitatively large but limited in duration.

As noted above, differences in stress decay over 35 min, as caused by various steeping treatments, ranged between 10 and 54%. It can be seen in Figs. 14 to 18 and Table 4 that the "steeping" effect is essentially independent of pulp type tested, in spite of wide variations in lignin and hemicellulose contents (see Table 3). This proves that the higher rate of stress decay observed following caustic steeping is mainly caused by (M_2) processes at inter- and intra-molecular levels of cellulose organisation, in particular within highly oriented regions.

It is generally accepted that strong alkaline solutions, of at least 8 to 9% NaOH, penetrate cellulose crystalline regions by first breaking H-bonds and thereafter forming new H-bonds between the reagent and cellulose hydroxyl groups (173,251,275). This causes dimensional changes in the unit cell, in particular an increase in the 101 inter-planar distance (179). The former strong inter-molecular bonds in crystallites, H-bonds in the a-b plane and van der Waal's forces in the a-c plane (120, see Fig. 3), are replaced by weak H-bonds which have been found to be associated with decreased crystallinity (153).

The higher stress decay in intra-crystalline swollen pulps under compressive strain may involve any of several processes. These may include: (i) conformational changes of cellulose; (ii) sliding effects within the cellulose crystallites; (iii) enhanced molecular motion of cellulose chains on the cellulose crystallite surface, and (iv), in the case of chemical pulps, possibly enhanced mobility of formerly crystalline hemicelluloses.

Since the swelling power of water is limited to amorphous zones of the lignin-carbohydrate complex, no short term viscoelastic processes probably take place within crystalline portions of cellulose or redeposited crystalline xylan and glucomannan in water treated samples. These components may undergo elastic deformation when subjected to stresses, which would mean storage but not dissipation of energy. That elastic deformations of the cellulose lattice can occur has been shown by X-ray measurements on Hinoki (Cupressus obtusa, Koch) wood specimens subjected to tensile strains (285).

It has been proposed (145) that the 1C_4 conformation in unstressed

cellulosic material can be expected to switch by mechanical excitations to the less stable (higher energy level) 4C_1 conformation, thus providing an abrupt means for energy storage. The reduction of inter- and intra-crystalline forces by caustic solutions, which converts the cellulose from a three-dimensional body to a more or less two-dimensional form, may allow glucose units to switch conformations more easily by mechanical excitation. The fact that capacity of glucose units to absorb energy is limited, and that glucose units in alkaline swollen celluloses are rather flexible, can be used to explain the high but limited rate of stress decay observed immediately after application of straining.

At the same time, converting transition zones between crystalline and amorphous regions, and part of cellulose crystallites (153) into amorphous zones, may also contribute to initial stress relaxation. Such changes can be expected to increase molecular movement around the crystalline cores. The changes in cellulose crystalline lattice, particularly increase in 101 interplanar distance (179) provides a further system for redistributing or dissipating stress through less tight bonding. In addition, the deposition of water and hydroxyl ions with counter ions between 101 planes (153) can be expected to act as lubricants promoting sliding along 101 planes when the lattice system is stressed above a critical value. This, of course, is accompanied by breaking and reforming the rather weak H-bonds between reagents and cellulose hydroxyl groups.

That sliding phenomena are involved only in initial stress relaxation can be explained by a critical stress level below which no further intra-crystalline sliding occurs. At beginning of the stress relaxation process, the strain level used in this work may have exceeded such a critical level. With progressive relaxation, however, the residual stress would soon fall below that level. Thereby, intra-crystalline processes would be excluded from further involvement in the rheological behavior of pulp mats maintained at constant strain.

Stress relaxation differences between caustic and water steeped chemical pulp samples (with the exception of holocellulose preparations) can be attributed also to some extent to crystalline (redeposited) hemi-

celluloses. Observations on wood glucomannans in sulphite pulping (10), and xylans in sulphate pulping (51,326), show that these hemicelluloses can be redeposited or adsorbed during later cooking stages. The redeposition process occurs preferentially on the fibre surface or, more accurately, on the surface of microfibrils on the outer part of the fibres. The result is formation of crystalline layers.

The abundant H-bonds between individual xylan or glucomannan chains in these layers are sufficiently strong to resist the penetration of water, but yield to attack by strong alkaline solutions. Consequently, the short chain and inter- and intra-crystalline swollen hemicelluloses may provide a lubricant layer between fibrils of the same fibre or adjacent fibres. This might promote repositioning of fibres within the mat which, as described earlier, is thought to be partly responsible for high rate of initial (Phase I) stress relaxation. Such lubricant effects may be expected also to enhance slippage of microfibrils within fibres.

Figure 19, which shows correlation between $1 - \zeta(35 \text{ min}) / \zeta(0)$ and hemicellulose content for 14 viscose pulps steeped either in water or 18.6% NaOH, lends evidence to this assumption. The inverse relationship for water and caustic treatments indicates that an increase in essentially crystalline hemicelluloses reduces the viscoelastic response of water swollen pulp mats, but enhances the time dependent response in caustic swollen pulps. That this effect is rather short, i.e., limited to Phase I, is evidenced by Fig. 18 which shows typical stress relaxation traces of three viscose pulps.

The hemicellulose content of viscose pulps examined in the study ranged from 2.2 to 6.1%. As the work of Clayton and Stone (51) showed, xylan adsorption in raw paper pulps can reach values up to 3% of the pulp weight and 10.2% of this redeposited xylan was found to resist a 90 min extraction with 10% NaOH at room temperature. Therefore, it can be expected that, in spite of severe purification treatments, a certain portion of the adsorbed hemicelluloses are retained.

Further, Fig. 19 also indicates that the hemicelluloses, after removal of side branches and redeposition, have lost most of their original stress dissipation function in the lignin-carbohydrate complex of wet pulps.

This function seems to be partly regained, however, when caustic solutions "soften" the layer of highly oriented hemicellulose on the fibril surface. A more detailed discussion on this particular subject appears in a following paragraph.

4.3 Effect of Residual Chemical Constituents

Stress relaxation data obtained from all water and caustic steeped pulps at 35 min relaxation time (Table 4) indicate wide variations in stress decay between various pulps given the same steeping treatment. These variations, however, were less pronounced between pulps of the same type (for instance within groundwood pulps, holocellulose preparations, bleached sulphate and viscose pulps) than between different pulp types. It is also apparent that stress decay variations seem to be somewhat higher for pulps steeped in caustic.

It is further evident from Table 4 that the highest rates in stress relaxation following caustic steeping occurred in groundwoods, wherein the cottonwood pulps exhibited slightly higher rates. In this respect, groundwood pulps were followed in order by holocellulose preparations, sulphite, bleached sulphate, unbleached sulphate, acetate and viscose pulps and, finally, by alpha-cellulose preparations (with the exception of O-1 and O-2).

In water saturated pulp mats differences were less distinct and the sequence for stress dissipation is not identical with results from caustic treated samples. It appears that water saturated groundwood pulps and holocellulose preparations exhibited approximately the same rate of stress decay, followed by unbleached sulphate pulp, bleached sulphate pulps, sulphite pulp; then viscose, acetate and alpha-cellulose pulps which showed the lowest rates of stress relaxation.

Experimental variables such as sample preparation and testing conditions were carefully controlled throughout the experiments. Therefore, the above differences must be attributed to inherent variations in chemistry of the pulp samples. The analytical data presented in Table 3 exhibit large differences in chemical composition for the various materials. Lignin contents were estimated to vary between ≤ 0.1 and 30.5%, total hemicelluloses

between 0.8 to 31.9%, while the cellulose portion ranged from 42.2 to 99.3%. Some evidence that such broad variations can be expected to influence pulp mat rheological properties appears in several works showing that quantitative changes of lignin and hemicelluloses result in profound variations of mechanical-rheological properties of ligno-cellulosics (200,201,283).

The following discussion relates these variations in pulp chemistry with rheological responses observed in relaxation tests on water and caustic swollen samples. For convenience, individual effects of the three components, lignin, hemicelluloses and cellulose, on time dependent behavior of various pulp types, will be discussed separately.

4.3.1 Lignin

The most characteristic features of lignin are its three-dimensional supposedly amorphous structure, formed by phenylpropanoid units, and its hydrophobic nature which restrains associated carbohydrates from excessive swelling (3,74-76,86). In the native state lignin is thought to be deposited between cells and within amorphous parts of cell walls as encrusting substances (316). It is apparent from the lignin structure, physical nature and position, as well as association with hemicelluloses, that it may play an outstanding role in governing the response of wood and wood derived materials, especially in the water saturated state, to mechanical excitation.

Lignin can be expected to resist mechanical excitation both directly and indirectly. The work of Murakami and Yamada (200) showed that lignin restricts absorption of water in plant cell walls. This proves lignin to be a controlling factor in swelling processes and leads to the conclusion that lignin must exert also an indirect influence on mechanical properties. Eriksson (68,69) studied the effect of delignification on wood creep and explained his data according to indirect effects of lignin on the rheological response.

It is unquestioned that the aromatic character and three dimensional structure of the lignin polymeric system (3) influences directly mechanical and rheological behavior. This has been evidenced for strength properties, for instance by an investigation carried out by Stone and Kallmes (283).

They showed that progressive delignification of wood reduced drastically its shear strength. The ability of aromatic systems to store energy, and the high rigidity provided by the three-dimensional polymeric structure, is expected to exert a similar distinct effect on rheological properties of ligno-cellulosics. It can be assumed that the lignin component will retard viscoelastic processes in wood. As shown in Figs. 20 and 21, such an effect was not observed for water and NaOH steeped pulp mats subjected to compressive stress relaxation testing. Both figures indicate, independent of steeping treatment, that pulps with the highest lignin content (groundwoods) exhibited higher rates of stress relaxation than most materials of low lignin content. There were surprisingly large differences between groundwoods and highly delignified pulps such as alpha-celluloses, acetate and viscose pulps. Altogether, only two of the holocellulose preparations dissipated stress at slightly higher rate than the groundwoods when steeped in distilled water.

Two alternative explanations may account for this unexpected observation. Firstly, perhaps no retarding effect of lignin occurs in compressive stress relaxation of pulp. Secondly, the more likely case that lignin exhibits only a modest retarding effect which is much subordinate to a more dominant role of hemicelluloses. Thereby, the lignin effect is not recognized in the complex total response. Unfortunately, the pulps used in this experiment varied in both hemicellulose and lignin contents so that no direct information on contribution of lignin to compressive pulp mat relaxation was obtained. However, it can be concluded that participation of native or residual lignins in fibre mat rheological properties does not reach a controlling level.

These unexpected results may be related also to other factors. Thus, the resistant behavior of lignin in the case of groundwood could be partly lost due to the high mechanical damage imparted during the grinding process. Mechanical damage could cause a loosening of the inter-fibrillar structure in such ways that partial weakening of the close lignin-carbohydrate association may occur. This, in turn, may reduce the retarding effect of lignin on swelling and consequently on the time dependent response of carbohydrates to straining. Support to this assumption is lent by the

observation that unbeaten wet pulps exhibit a higher degree of recovery from compressive creep, in other words, showed less viscoelasticity, than beaten wet pulps (261). Beating is known to cause fibrillation and delamination of the fibre wall (222), which has been found to facilitate swelling of fibres and inhibition of liquids (251). These effects are expected to be similar to those occurring in grinding of wood.

Another factor possibly responsible for the subordinate role of lignin in compressive pulp mat relaxation might be an orientation and/or lamellation effect. There exists evidence from several studies (130,155, 200,252) investigating the status of lignin in the fibre wall that lignin is at least partly oriented and layered. An orientation might be related to the function of lignin which is to resist in particular high stresses in the living tree along the fibre axis, and less to counteract stresses perpendicular to this axis. In this experiment the fibres were loaded preferentially perpendicular to the fibre axis. The excitation, therefore, was applied to a kind of layered system at two levels.

One of the layered systems occurs at the microlevel. It is formed by a lignin-rich (20) layer (M and P) and the S_2 layer predominately occupied by carbohydrates. The other layer type of structure which is found at the ultra-structural level, is caused by the deposition of lignin and hemicelluloses between microfibrils. In such layered systems the carbohydrates are forced to carry the same loads as the lignin complex when compressed in transverse direction. This seems to be different for compressive stresses applied parallel to the grain where the resistance to deformation will be predominantly controlled by the more rigid lignin structure. Consequently, it can be believed that compressive straining of fibres perpendicular to their axis lessens the influence of lignin on rate of stress decay, but enhances viscoelastic response of the carbohydrates.

The only indication that lignin may exert some indirect influence on rate of stress decay of chemical paper pulps can be deduced from the fact that the unbleached sulphate pulp (7-1), when steeped in water, dissipated stress at a somewhat higher rate than the bleached sulphate paper pulps (7-2,8-1,8-2) (Fig.20). When the same pulps were steeped in caustic, however,

the response level was reversed (Fig. 21). Since hemicellulose content did not vary greatly between these pulps (Table 3) the observation has to be attributed to increased cellulose crystallinity by removal of lignin through purification treatments. That cellulose crystallinity increases as delignification progresses has been proven by Wardrop (310,314), Wardrop and Preston (317) and Murakami and Yamada (200) with holocellulose preparations. In water steeping, the relatively larger crystalline portion in bleached pulp cellulose caused a somewhat lower degree of swelling and, consequently, less viscoelasticity than in unbleached pulps. However, by steeping in 18.6% NaOH this crystallinity effect seemed to be lost or of subordinate importance in rheological processes, due to intra-crystalline swelling phenomena in strong alkaline media.

4.3.2 Hemicelluloses

It is well known that hemicelluloses contribute to mechanical properties of cellulose, such as strength of individual fibres and papers and pulp beating behavior (95,173,201,272,273). In pulping, most chemical treatments have been found to cause profound changes, in particular in the molecular structure of non-cellulosic carbohydrates. Such changes certainly must affect pulp mat viscoelasticity.

In this study an attempt was made to relate pulp viscoelastic behavior, under constant compressive strain, to residual hemicelluloses in the pulp material. Emphasis is placed on establishing an interrelationship between quantitative features and rheological response. The discussion is also concerned with structural characteristics of residual hemicelluloses as they may relate to viscoelastic behavior.

Experimental data obtained from stress relaxation measurements at 35 min relaxation time (Table 4), and from carbohydrate analyses (Table 3), are presented in Fig. 22 as plots showing $1 - \sigma(35 \text{ min})/\sigma(0)$ as a function of hemicellulose content. The points show average values of five relaxation measurements.

It is apparent from the two regression lines, and evidenced by statistical calculations, that rate of stress decay in pulp mats under

constant strain is highly correlated with the amount of hemicelluloses present in the pulp materials. As indicated by slope changes, the relationships are characterized by two distinct stages. In the case of water steeped pulps, the slope descends from 0 to approximately 6% hemicelluloses, which shows that pulp viscoelasticity was lowered by increasing contents up to the 6% level. Further increases in hemicelluloses reversed this relationship and lead to a considerable enhancement of stress relaxation. The positive slope from approximately 5 to 32% hemicelluloses confirms this.

In respect to caustic steeped pulps, slope variation was less distinct. The slope covering the range from 0 to 6% hemicelluloses exhibits a somewhat steeper ascent than that for the range above 6%. Consequently, changes in hemicellulose content below 6% appear to have a more pronounced effect on rate of stress decay than variations above this level.

In the range from 6 to 32% hemicellulose similar slopes for both water and caustic treatment groups are evident. This indicates that effect of hemicellulose variation above 6% becomes independent of the steeping medium. As mentioned above, distance between the two regression lines originates primarily from phenomena which are inherent in alkaline swelling effects of cellulose.

Somewhat unexpected is the reverse relationship for water and 18.6% NaOH steeping in the range below 6%. It is obvious that hemicelluloses at such low contents resist stress relaxation when the pulp is soaked in distilled water, but contribute to stress dissipation when alkaline steeping is applied. This behavior, can be attributed particularly to qualitative features of residual hemicelluloses, in other words, to structural changes of hemicellulose molecules.

It seems reasonable to base the following discussion about the stress relaxation - hemicellulose relationship on a detailed analysis of characteristic features of pulp types or individual pulps, such as amount and molecular structure of hemicelluloses. This facilitates a better understanding of the hemicellulose contribution to rheological processes in the

fibre wall and, consequently, to the pulp mat. The discussion on this particular subject is subdivided according to pulp types.

4.3.2.1 Mechanical pulps

In the caustic swollen state groundwood pulps, which were found to contain the largest hemicellulose quantities (Table 3), exhibited the highest stress dissipation rates (Fig.22). This differs to some extent from observations made on water steeped samples. Here, the cottonwood holocelluloses appeared to dissipate energy at the highest rate, slightly more than groundwood pulps and hemlock holocelluloses. The superiority of groundwoods in stress dissipation, compared with low hemicellulose pulps, can be considered as strong evidence for involvement of hemicelluloses in rheological processes.

In groundwood, the wood polymers are more or less present in the native state (30). It means that the hemicelluloses - as in the undamaged wood fibres - are fully branched, amorphous and deposited on the fibril surface as matrix substance which surrounds the microfibrils (19,178,316). These polyoses are believed to form connecting layers between microfibrils and the encrusting lignin polymer system.

It is well known that lignin and cellulose vary widely in physical and mechanical properties. Consequently, in the stressed state, hemicelluloses acting as connecting links have to function as a stress adjusting system. Low DP, high degree of branching and hygroscopic nature make the hemicelluloses well suited to dissipate or distribute stresses uniformly in the cell wall. In wet condition, their strong tendency to swell, provides a gel system which, as a lubricant-like layer, allows at least some gliding along the fibril surface. An excessive gliding, however, may be hindered particularly by covalent bonds connecting them to the rigid three-dimensional lignin polymer system. The existence of such bonds has been proposed by several workers (36,272).

The low DP is expected to contribute to gliding or flow processes. Due to the gel-like state and numerous side branches, the strength and density of H-bonds is fairly low. This possibly facilitates flow between

adjacent hemicellulose or hemicellulose and cellulose molecules and, therefore, aids in dissipation of stress. The numerous side branches may not only contribute to the flow response, but may also be involved in stress distribution processes.

On the other hand, possible lignin-hemicellulose bonds and mechanical entanglement within hemicelluloses and between hemicelluloses and lignin may hinder the flow processes but certainly result in microscopic deformations of the lignin-carbohydrate complex. The complex, in turn, may be adapted better to provide uniform distribution and storage of energy. Both microscopic deformation in hemicellulose molecules and gliding processes may be part of the viscoelastic memory behavior.

In the case of compressive or tensile strains along the fibre axis, the microfibril angle, which is known to change between cell wall layers (148), may exert a considerable influence on the rheological processes between microfibrils in the hemicellulose matrix. The microfibril angle has been found to affect mechanical properties of wood parallel to the grain (83).

Interestingly, the contribution of hemicelluloses to the relaxation response does not seem to depend on any single hemicellulosic component. The function of various hemicellulose types in this regard appears to be very much the same. This is evidenced by the fact that, although profound differences in hemicellulose composition exist between angiospermous and coniferous groundwoods (Table 3), similar rates of stress relaxation were observed for all groundwood pulps. The slight differences in stress decay are caused by variations in total amount of hemicelluloses in the pulp as shown in Fig. 22.

The conclusion can be drawn that wood hemicelluloses in the native state, and/or even after chemical adjustment, function in stress adjusting systems. Moreover, they may control the rheological properties of wood fibres. It can be assumed that a minimum portion of hemicelluloses must be present in the cell wall to withstand sudden excitations in the living tree. The validity of this assumption is supported by the fact that wood

hemicellulose content increased considerably during evolution from coniferous to pored woods. These changes may have occurred to enhance the energy transfer system in woody cell walls.

Previously, the function of hemicelluloses in wood of the living tree has been rather obscure. Kollmann and Côté (148), for instance, consider hemicelluloses in wood cell walls as possible relicts of cell wall formation. According to them, these serve as a temporary matrix preceeding lignification. Hopefully, the findings of the present study will cause reconsideration of the role of wood hemicelluloses, which appear to have been underrated in importance or misinterpreted in the past.

4.3.2.2 Holocellulose pulps

The holocellulose preparations dissipated stress at somewhat lower rates than groundwoods when steeped in 18.6% NaOH, but exhibited more or equal stress decay in the water saturated state. This observation is not quite in accordance with expected results. Normally, the removal of lignin would be expected to increase the relative amount of hemicellulose in the pulp so that a higher rate of stress decay would seem likely.

The somewhat unexpected results must be primarily attributed to "overcooking" effects. Shimada and Kondo (264) reported that large chips, similar to those used in this study, cause fibre overcooking in outer portions of the chips. This, in turn, can be expected to result in considerable hemicellulose losses and, possibly, in severe degradation of the remaining carbohydrate portion.

The rather low hemicellulose contents for these preparations, compared with those obtained for groundwoods of the same species, provide evidence for this assumption. It is apparent from Table 3 that substantial portions of xylan and glucomannan were lost during pulp preparation. The losses were so high that, despite delignification which normally would have increased the relative amount of non-cellulosic carbohydrates, the hemicellulose portion was considerably below values obtained for groundwoods.

On the other hand, overcooking must have had a rather limited effect on sidebranches. As Table 3 suggests, degree of branching was still

fairly high.

It is conclusive from analytical data in Tables 3 and 4 that the lower rate of stress relaxation exhibited by caustic swollen holocelluloses, compared with that observed on groundwoods of the same treatment, was primarily due to hemicellulose losses. This observation can be considered as a further proof for the important role of hemicelluloses in wood and pulp rheology.

The residual hemicelluloses in caustic swollen holocelluloses may function essentially in the same way as described earlier for groundwood pulps. It is unlikely that the rather limited decrease in branching exerted a particular change. But it can be expected that the effect of branches might have changed to some extent due to the removal of lignin. Unfortunately, any conclusion on how delignification affects the rheological behavior of the hemicellulose complex is difficult to draw. The loss in hemicellulose during pulping makes it extremely difficult to evaluate effect of lignin-hemicellulose association on the stress dissipation mechanism in both caustic and water steeped pulps.

It can be assumed that the decrease in stress relaxation caused by loss of hemicelluloses is to some extent reduced by degradation effects on both cellulose and residual hemicelluloses. Pulping in both acid chlorite and peracetic acid media has been reported to cause decreased DP for all carbohydrates (4,164,292). As irradiation experiments, which will be discussed below, show, a decrease in DP enhances the viscoelastic response. Consequently, the degradation reactions can be expected to increase to some extent the contribution of remaining hemicelluloses in both water and caustic swollen pulps.

With respect to the water swollen state, cottonwood holocellulose was found to exhibit the highest rate of stress decay (Fig. 22) in spite of the lower hemicellulose content as compared to groundwood pulps. This phenomenon seems to be rather complex. Possibly, an "activating effect" on the branched xylan molecules may have taken place during the delignification process.

As Table 3 indicates, no severe loss of glucuronic acid side chains occurred during pulping treatments. It can be assumed that these side chains were closely associated with lignin and consequently exerted a retarding effect on swelling or viscoelastic behavior. By removing lignin this effect was eliminated and flexibility of the xylan molecule was considerably enhanced, possibly by the swelling tendency of the now unhindered glucuronic acid groups.

This assumption is supported by Pew and Weyna (234) who proposed that carbohydrate molecules are surrounded by lignin. In other words, they may be held in the gel-like lignin substance by molecular entanglement ("snake cage" structures).

The considerably lower relaxation of water steeped hemlock holo-celluloses, compared with cottonwood pulps, can be attributed to the lower content of acidic xylans in coniferous wood. Due to this quantitative difference the "activating effect" of acidic xylans, as caused by delignification, may contribute less to the total viscoelastic response of hemlock pulps. In addition, some removal of galactose side branches from glucomannans may have reduced to some extent the viscoelastic contribution of hemicelluloses.

4.3.2.3 Sulphite and sulphate paper pulps

As indicated by Table 4 and Fig. 22 the group of paper pulps ranked third with respect to hemicellulose content, which explains the lower rate of stress decay compared with that exhibited by groundwoods and holocelluloses. Again, the amount of residual hemicelluloses appeared to dominate the viscoelastic behavior of these pulps under compressive straining.

As indicated by Fig. 22, however, the corresponding data are rather scattered around the two regression lines showing that pulping method exerts an influence on paper pulp viscoelasticity. The variations between individual pulps within this group seem to be less due to quantitative, but more due to structural differences of the remaining carbohydrate complex. The rather similar hemicellulose content of these pulps (Table 3) confirms this. In addition, relative amount of lignin seems to be of some

importance for unbleached pulp stress relaxation.

The relaxation response of sulphite pulps in water and caustic swollen state is characterised by a number of factors inherent to this particular pulp type. It is apparent from Fig. 22 that the substantial loss of hemicelluloses during sulphite pulping was the major factor responsible for the generally lower rates of stress decay in comparison with groundwoods and holocelluloses. Other factors which may have enhanced or reduced sulphite pulp stress relaxation are: (i) removal of lignin to 0.7%; (ii) high degree of cellulose degradation within amorphous regions, particularly in the outer part of the fibre; (iii) low average DP of residual hemicelluloses; (iv) glucomannan redeposition; and (v) relative abundance of glucuronic acid groups.

That severe degradation of cellulose in sulphite pulping, as proven by Luce (171), may influence sulphite pulp viscoelasticity will be discussed in a later section. Similarly, hemicellulose degradation to a rather low average DP (174,217) may also contribute to the relaxation response. The considerably shorter chains might improve the "lubrication effect" of hemicelluloses and so that rate of stress decay is enhanced in both water and caustic swollen states.

The highly ordered structure of redeposited glucomannan (10) is believed to have played a subordinate role. It probably retarded stress decay to some extent in water saturated pulp, but exerted no effect on relaxation in caustic swollen samples. The relatively high amount of glucuronic acid (Table 3), indicating a high degree of residual xylan branching, may have influenced the stress decay process in a similar way to that described for holocelluloses. It may have enhanced relaxation particularly in the caustic swollen state.

In the case of caustic steeping, these physical and chemical changes of sulphite pulp hemicelluloses (factors iii to v) appear to be overshadowed by cellulose degradation effects caused by sulphite pulping. Similar rates of stress decay for caustic swollen sulphite pulp and holocelluloses (Fig. 22) provide this evidence. It seems that a reduction in

relaxation due to hemicellulose losses is at least partly compensated for by the cellulose degradation phenomena.

In the case of sulphate pulps, the following pulp characteristics, in addition to quantitative changes in hemicelluloses, are believed to have influenced stress decay: (i) removal of lignin; (ii) hemicellulose degradation; and (iii) xylan redeposition. This is confirmed by the scattered distribution of sulphate pulps around the regression lines which indicates considerable variation between individual pulps.

Figure 22 shows that pulps 7-1 and 8-2 in the caustic swollen state dissipated less stress than predicted from residual total hemicellulose contents. It is difficult to attribute this deviation to any particular factor. It seems likely, however, that in the case of pulp 7-1 the relatively high lignin content (9.1%) and probably lignin condensation are responsible for the comparatively low rate of stress decay.

Hemicellulose degradation effects may account most for the comparatively low relaxation rate observed for angiospermous pulp 8-2. It is known that the susceptibility of glucuronic acid and acetyl groups to loss in alkaline pulping media leaves the pored wood xylan without or with only few residues of side chains (53,54,97,191,216,291). This essentially linear xylan, which is the dominant hemicellulose in this hardwood pulp (Table 3), was substantially reduced in its capability to assist in stress dissipation.

In the water swollen state, the xylan degradation effect seems to play only a subordinate role in viscoelasticity of the same pulp. Further, the close location of this pulp to the lower regression line in Fig. 22 indicates also that effect of xylan redeposition, which could be expected to be particularly high for this pulp species, may not reach a significant level.

The considerably lower relaxation rate of bleached pulps in comparison with unbleached sulphate pulp 7-1 when steeped in water has to be considered as an indirect effect of lignin. It can be expected that removal of lignin and subsequent drying of pulp increased considerably the number of H-bonds in the remaining carbohydrate portion of the cell wall.

A certain portion of newly formed H-bonds in the close vicinity of crystallites may have been sufficiently strong to resist water swelling. This in turn may have reduced the viscoelastic response of the bleached sulphate pulps.

4.3.2.4 Viscose and acetate pulps

In viscose and acetate pulps the residual hemicellulose portion is reduced to less than 7%. In the caustic swollen state, this leads, as evidenced by Fig. 22, to less stress relaxation. The steeper slope of the regression line in the range of viscose and acetate pulps, in comparison with that of the remaining range, indicates that hemicellulose variations below 6% cause considerably greater changes in rate of stress relaxation. This phenomenon is considered to be the result of two factors: (i) increased viscoelastic contribution of hemicelluloses at lower contents; and (ii) cellulose degradation. The comparatively high stress relaxation values (groups of pulps lying above the regression line) obtained from sulphite pulps confirm the latter suggestion.

In the water swollen state, rate of viscose and acetate pulp stress relaxation is inversely related to residual hemicelluloses (Fig. 22). The unexpected behavior is believed to originate primarily from degradation and redeposition phenomena of hemicelluloses. The tendency of glucomannan and xylan to reprecipitate as highly ordered deposits on cellulose fibrils has been noted above. It is likely that a portion of redeposited hemicelluloses survived purification treatments, particularly in pulps of lower purity for which less severe purification treatments were employed. Further, it is also likely that part of the hemicelluloses remained in their original position in the fibre wall, but were subject to degradation (removal of side chains). During pulp drying the essentially linear chains formed H-bonds between themselves and with adjacent cellulose chains. These bonds can be expected to be sufficiently strong to resist water penetration. Consequently, a large portion of the relatively small amount of hemicelluloses in viscose and acetate pulps is not accessible to water and, therefore, does not assist, or only assists to rather limited extent, in stress dissipation. Since pulps with relatively large portions of hemicellulose residues

exhibited the lowest relaxation response (Fig. 22), the inaccessible hemicelluloses seem to be directly proportional to total amount of residual hemicelluloses.

In caustic steeping, however, the newly formed H-bonds are readily broken and the total remaining hemicellulose portion exists in a gel-like state which facilitates stress dissipation. This explains why these chemical and physical changes of polyoses do not affect the viscoelastic response of caustic swollen pulps.

It is obvious that the original function of polyoses in green or swollen wood fibres was almost entirely lost during pulping and purification treatments. This observation underlines again the importance of side branches in native hemicelluloses for maintaining the highly efficient energy dissipation and storage systems of wood fibres.

4.3.2.5 Alpha-cellulose pulps

No alpha-cellulose preparation was found to be free of residual polyoses. As indicated in Table 4 and supported by other work (55,87,304) alpha-celluloses from wood pulps still contain various amounts of hemicelluloses. The residual quantity seems to depend on the original hemicellulose content. The hemicellulose portions in the two alpha-pulps O-3 and O-4, which were prepared from viscose pulp 1-3 and acetate pulp 5-1, were found to account for 0.8 and 1.5% of pulp composition.

It is apparent from Fig. 22 that such low contents as the above contribute very little to stress decay in both water and caustic steeped mats. This is evidenced by the close location of the corresponding points to the intersections of the two regression lines with the Y-axis. The intersection points indicate stress decay following complete removal of hemicelluloses, i.e., the response contributed by pure cellulose as obtained by pulping and alkaline extraction treatments.

As in the case of viscose and acetate pulps the residual hemicelluloses are essentially linear (degraded) chains closely associated with cellulose. It is assumed that this residual portion originates primarily from degraded but non-redeposited hemicelluloses tightly embedded between

cellulose micro-fibrils. Even strongly alkaline extractions are not sufficient to remove this residual portion from the fibre wall. The contribution of these hemicelluloses to pulp viscoelasticity is believed identical to that observed for viscose and acetate pulps. They reduced stress decay in water steeped alpha-cellulose pulps, but enhanced the dissipation of stress in the caustic swollen state.

The alpha-pulps prepared from cottonwood and hemlock holocelluloses still contained considerable amounts of residual hemicelluloses (Table 3). This is reflected in their substantially different viscoelastic responses compared with those observed on the other two alpha-pulps. In the water saturated state they dissipated less stress, but exhibited a higher relaxation rate when steeped in caustic. As can be seen in Fig. 22, their response is essentially identical with that observed on bleached paper and viscose pulps of low purity. It appears that residual hemicelluloses affect the relaxation response of these two alpha-pulps in a way similar to that proposed in earlier discussions dealing with paper and viscose pulps.

4.3.3 Cellulose

The intersection of the two regression lines with the Y-axis in Fig. 22 provides evidence that cellulose plays the dominant role in viscoelastic behavior of both water and caustic treated pulps. It is apparent that cellulose accounts for at least more than 50% of total stress dissipation observed for the various pulp types. Its independent viscoelastic behavior and its contribution to relaxation in highly purified pulps is obtained from the intersection point.

In the case of paper grade, holocellulose and groundwood pulps the viscoelastic contribution of cellulose is more difficult to estimate. But it can be assumed that, in spite of complex interactions between the three wood structural polymers in rheological processes, the cellulose contribution is basically the same for all pulp types. This conclusion, however, is made on the assumption that the cellulose has not been subjected to serious degradation or does not contain degraded short chain fractions.

Variations in DP above 1000 are known to not influence significantly the pulp mechanical properties, which are drastically lowered as DP values fall below 1000 (251). Consequently, cellulose rheological properties can be expected not to be changed significantly by pulp processes which degrade cellulose uniformly to a DP level not lower than 1000. This implies that celluloses of groundwoods, holocelluloses and also of unbleached and bleached paper grade kraft pulps show essentially the same viscoelastic response.

In sulphate pulping the cellulose degradation is uniform and usually results in DP values above 1000 (171). This is reflected in the high strength properties of unbleached kraft pulps in particular (104). Based on this observation, it seems unlikely that cellulose viscoelasticity in unbleached and bleached kraft pulps differs significantly from that in groundwoods and holocelluloses. Consequently, not cellulose but instead the substantial quantitative and structural changes of hemicelluloses and possibly lignin must be responsible for the profound viscoelastic differences observed between groundwoods, holocelluloses and unbleached and bleached kraft pulps.

This leads to the conclusion that the high correlation between cellulose and rate of stress relaxation (Figs. 23 and 24) has to be considered as a secondary phenomenon. Thus, the decreasing order of hemicellulose content in groundwood to alpha-pulp preparations allows for a relative increase in cellulose content. The loss of hemicelluloses is accompanied by a proportional decrease in viscoelasticity (except for caustic treated viscose, acetate and two alpha-pulps) which is reflected in the negative relationship between fractional stress relaxation and cellulose content (Figs. 23 and 24).

As noted above, the contribution of cellulose to viscoelastic behavior in pulps of no or slight cellulose degradation is essentially the same. It appears that the cellulose response is based on molecular processes or rearrangements of cellulose chains or parts thereof found in the amorphous regions. In the caustic swollen state, molecular displacement in parts of the swollen cellulose crystal structure may be involved in viscoelastic processes.

In drastic pulping treatments, such as sulphite pulping or certain bleaching procedures which cause oxidative degradation, e.g. hypochlorite bleaching, cellulose is subject to considerable degradation (171,243,245). This is known to reduce pulp strength properties extensively (104). In sulphite pulping, the cleavage of the (1→4) glucosidic linkage between β -D-glucopyranose residues occurs preferentially in the amorphous regions thus creating weak areas in microfibrils. Since a great number of cellulose chains in amorphous regions, acting as connecting links between crystallites in the microfibrils, are cleaved, the former high resistance of the amorphous-crystalline system to straining is substantially reduced. Thus the crystallites, which can be considered as centres of energy storage and resistance to straining, become more or less ineffective without a sufficient number of connecting cellulose chains. They yield readily to mechanical excitation when chain degradation exceeds the critical level.

It appears from Figs.22 and 24 that some cellulose degradation effects may have contributed to rate of stress relaxation. All sulphite pulps (viscose, acetate and paper pulps) steeped in caustic dissipated stress at higher rates than prehydrolyzed sulphate pulps of similar residual hemicellulose content. All viscose and acetate pulps located above the regression line, representing the data obtained from caustic treated pulps (Figs.22 and 24) and pulp 6-1, are sulphite pulps.

Since cellulose degradation appears to relate to stress relaxation of low yield pulps, it was decided to provide more experimental evidence demonstrating relevance of cellulose DP to pulp viscoelasticity. For this reason, gamma-irradiation treatments at various dose levels (Fig. 25) were employed on two viscose pulps (3-2 and 3-4). These pulps were found to differ in both hemicellulose content and rate of stress relaxation. Radiation degradation effects on celluloses of these two pulps as followed by changes in alpha-cellulose, intrinsic viscosity and 10% NaOH solubility are shown in Table 5.

It is evident from Fig. 25, which presents the $1 - \frac{\sigma(t)}{\sigma(0)}$ - Mrad dose relationship at 6 sec and 35 min relaxation times, that gamma-irradiation changed relaxation responses of the cellulose. As the positive slopes show,

the time dependent resistance of pulps to straining decreased steadily with increasing dose level. Since this experiment was carried out without removing or reportioning initial carbohydrates the ascending slopes prove unequivocally that progressive degradation or shortening of cellulose chains leads to increased plasticisation of microfibrils and in turn to increased stress relaxation. As discussed above, the actual mechanism responsible for enhanced viscoelasticity of cellulose is increased mobility of crystallites caused by chain degradation in amorphous regions.

It is apparent that in pulps undergoing progressive degradation of carbohydrates the viscoelastic response changes according to both the hemicellulose portion and amount of low DP cellulose induced. Since hemicellulose molecules in low yield pulps are essentially linear, hemicelluloses and cellulose can be assumed to function similarly with respect to stress dissipation particularly in the caustic swollen state. This means that changes in viscoelastic responses of pulps, such as viscose, acetate and sulphite paper pulps, have to be considered as the result of variations in total short chain material in the fibre wall. The validity of this suggestion is supported by Fig. 26 illustrating the regression of $1 - G(35')/G(0)$ on 10% NaOH solubility of irradiated and untreated viscose pulps, and the corresponding statistical calculations given in Table 6.

As Fig. 27 indicates, the caustic solubility of non-irradiated pulps was primarily dependent on hemicellulose content. Consequently, the high correlation between $1 - G(35')/G(0)$ and caustic solubility of non-irradiated pulps (Fig. 26) is believed to be essentially caused by residual hemicelluloses. Testing of parallelism and coincidence for multiple curvilinear regression (Table 6) showed no significant differences in slopes and levels of the three regression lines in Fig. 26. This provides evidence that stress relaxation in highly degraded pulps seems to be solely a function of total amount of low DP carbohydrates and not of a specific carbohydrate component.

This observation is useful in explaining the relatively small chain length of native hemicelluloses. As proposed earlier, limited chain length and high degree of branching appear useful to viscoelastic processes

in the undamaged or slightly degraded fibre wall. In the water swollen state, severe chain degradation, particularly in low yield pulping, changes profoundly the original mechanical function of carbohydrates in the fibre wall. Highly degraded cellulose appeared to behave similarly to native hemicelluloses, whereas that part of the degraded hemicelluloses, which is redeposited in highly ordered form or remains after degradation (removal of side chains) in close association with cellulose, responded like crystalline cellulose.

4.4. Interchangeability of Stress Systems

When dry cellulosic materials are steeped in water or alkaline solutions, swelling takes place. This phenomenon is known to cause enormous swelling stresses which, in turn, can be assumed to induce rheological processes in the lignin-carbohydrate complex. Weakening, breaking and reformation of hydrogen bonds, bond angle changes, stretching of primary bonds, or even conformational changes can be expected to occur in cellulose under swelling stresses. Therefore, it was hypothesized that time of steeping in swelling reagents, i.e., the time period over which the sample is subjected to swelling stress, may significantly affect rheological behavior of ligno-cellulose under subsequent mechanical excitation.

Two experiments were carried out to study the effect of steeping (swelling) period on viscose pulp relaxation. In the first experiment this effect was investigated on samples steeped in water and 18.6% NaOH for short (1 min and 25 sec) and long periods (48 hr). For a more complete study of this interaction a second experiment with a sequence of tests following steeping periods in 18.6% NaOH ranging from 0.1 to 14400 min was undertaken. The data are shown in Figs. 28 and 29. Figure 28, in which fractional stress relaxation at 35 min is plotted against steeping time, compares stress dissipation in viscose pulps following short (one minute or less) and long (48 hr) term steeping in water or caustic. Figure 29 represents the data obtained from pulps steeped between 0.1 and 14400 min in 18.6% NaOH.

It appears from both figures that steeping time influenced residual stress dissipation. Extension of steeping time unequivocally resulted in reduced ability of the cellulosic material to absorb or dissipate energy.

This is true for both water and caustic steeping treatments. As exhibited in Fig. 28, approximately 10% less stress relaxation was observed with specimens steeped 48 hr in water or in 18.6% NaOH, compared to specimens steeped one minute in water or 25 sec in 18.6% NaOH. Since the effect occurred with water steeping, although to a lesser extent than with caustic, it is assumed that possible extractions of soluble fractions during steeping could not entirely cause the change. The residual solubles fraction following prolonged steeping was not examined in the present study.

In Fig. 29 a log-log plot is used for presenting data obtained with specimens treated over very short to long steeping periods. The two lines show the relationships between $\zeta(t)/\zeta(0)$ observed at 6 sec and 100 min after t_0 and steeping time. Again, it can be seen that the capability of pulp to dissipate energy decreased considerably with increased treatment time.

The dependence of stress relaxation on steeping period can be best expressed by a curvilinear relationship as indicated in Fig. 29. The slope reveals that short steeping periods (below one min) do not show large differences in stress decay. This implies that swelling stresses did not occur over a short time period or were less than the sensitivity of the test method. It appears to take at least five minutes steeping to observe the steeping effect at the temperature employed. The slopes of the curves in Fig. 29 show, furthermore, that increased steeping periods above approximately 5 minutes reduced both short (below 6 sec) and long time (above 6 sec) rates of stress dissipation. Both curves approach each other, indicating that after infinitely long steeping periods $\zeta(6 \text{ sec})$ will fall close to $\zeta(100 \text{ min})$. It may be proposed that after such a long steeping period the pulp is "conditioned" or "set" in a way that limits further chemical adjustment under temperature-concentration conditions of the system. Such setting or prestressing simultaneously reduces the time dependent physical-mechanical properties, at least as measured over short relaxation periods.

It is evident from the data presented in Fig. 29, that ability of cellulose to dissipate stress can be diminished by two types of excitation:

(i) by an infinitely long steeping time; (ii) by an infinitely long period of mechanical excitation; and that exhaustion should occur through a combination of both.

The inverse relationship between stress dissipation and steeping time in swelling solutions may be explained in the following way: The assumption can be made that cellulosic materials possess a maximum capacity for absorption or dissipation of stress under set conditions and according to their history. Steeping time adds a new component to that history. When, for instance, pulps are steeped in water or other swelling solutions, the enormous swelling forces induce rheological processes within the fibre walls. Under suitable conditions these kinds of strains may produce "internal chemical stress relaxation". The longer the pulp is kept in the swelling environment, the larger is this component. When the material is subsequently subjected to external physical-mechanical strain only a fraction of the initial capacity for relaxation can be observed. This assumes that adjustments in chemical components, such as alkali solubles, have not occurred during the chemical treatment, i.e., caustic steeping.

This phenomenon, as observed on viscose pulps, has to be attributed primarily to molecular processes in the amorphous regions of cellulose. The high swelling stresses may cause molecular motion of cellulose, probably involving the mechanisms mentioned at the beginning of the section. However, it can be assumed that these molecular rearrangements of amorphous cellulose are not of infinite extent due to the fact that cellulose chains leave and enter crystalline zones. Such dichotomy limits the linear cellulose chains from unrestricted motion. This means, that energy dissipation by reorientation of amorphous cellulose is of limited extent. In the swollen state the swelling stresses will entail molecular rearrangements which, in turn, reduce the capability of cellulose to dissipate stress. Under subsequent external straining the magnitude of cellulose reponse will be solely dependent on "residual" molecular rearrangements of amorphous cellulose.

These observations on interchangeability of chemical and physical stress systems carry the profound suggestion of a unifying concept for

adjudicating results of mixed systems. Both, as has been discussed, translate in to the same basic function: re-orientation of cellulose in amorphous zones. Difference lies only in the ways excitation is applied, i.e., "internal" or "external".

4.5 Application of Stress Relaxation Measurements for Characterising Pulps

Interrelationship between many chemical, physical and mechanical properties of cellulosic materials is frequently used for predicting material behavior by estimating related characteristics. Many cases are known where such indirect methods of material characterisations are employed with great success. In the following, an attempt is made to describe a few potential uses of stress relaxation as a tool for determining chemical and mechanical properties of various wood pulps and papers.

4.5.1 Estimation of viscose pulp alkali solubility

The highly significant correlation between fractional stress relaxation and alkali solubility of viscose pulps (Fig. 30) may be of practical importance. Determination of stress relaxation on pulp samples is done rapidly, easily and reproducibly, whereas customary multi-step solubility tests for determining viscose pulp qualities are time consuming. Consequently, relaxation tests may be suitable for replacing chemical methods with less costly procedures. Solubility values could be estimated by using the straight line relationship, such as between $1 - \sigma(t)/\sigma(0)$ and solubility in 10% NaOH as shown in Fig. 30, or other caustic concentrations. The inverse relationship of fractional stress relaxation between water and alkali steeped materials (Fig. 30) suggests that measurements done on water saturated pulps might be used also to predict alkali solubility.

The only uncertain factor remaining for application of the technique is the size of error in predicting solubility by using stress relaxation and relation of this to acceptability criteria. From this study, including numerous viscose pulp types, the accuracy of this new method was found to be reasonably good, as indicated by the standard error values in Fig. 30. Variation within any single pulp type under controlled manufacturing conditions could be much lower. The importance here could be the utilization

of rheology dynamics for "on machine" testing, thereby introducing a point of pulp process control not presently exercised.

Viscose pulp alkali solubility has meaning to viscose manufacturers as regards yield and possibly other viscose processing factors. It is likely that other useful parameters, as well as this, are associated with fractional stress relaxation.

4.5.2 Predicting viscose pulp pressing characteristics

The response of fibrous structures to compressibility has an important bearing on a number of fibre processing operations. Thus, the rate of water or alkaline solution flow from a fibrous mat should depend to a large extent upon its rheology in compression.

Compressibility of fibre mats or shreddings is of particular importance to the pressing of steeped viscose pulps, where it has been observed that time or pressure required to obtain the desired "press ratio" varies with individual pulps. The present work suggests that these variations are related directly to some intrinsic ability of the pulp to absorb and dissipate stresses, since it is found that viscose pulps exhibit differences in rate of stress decay corresponding to reported pressing behavior. Thus, high initial rate of stress decay shows rapid energy dissipation, which may indicate ease in pressing. A further study needs to be done for examining this relationship as regards its practical implications.

4.5.3 Predicting fibre response to machining

In pulp beating, the deformation of fibres can be considered as being of the relaxation type (271). Pulp fibres of high plasticity are said to deform readily and, therefore, respond easily to the beating treatment (272). It appears that a certain minimum low molecular fraction content, particularly of hemicelluloses, is necessary for good beating performance.

It is believed that new surfaces are formed in pulp machining only when some energy level critical to a given pulp is exceeded. This may be

accomplished by further loading of the molecular system already strained by swelling processes in the lignin-carbohydrate complex which, of course, reduces the energy absorption/dissipation ratio.

Based on this work, the suggestion is made that a high correlation should exist between beating response and rate of stress decay. This is demonstrated by the high correlation found between residual low-molecular fractions, i.e. hemicelluloses and low DP cellulose, and relaxation response. It would be of particular interest to examine the contents of this relationship, since the stress relaxation test could be applied as a dynamic system for "on machine" prediction of pulp beating response.

4.5.4 Predicting paper printability

Among other fibre machining operations, the possibility of employing stress relaxation for predicting paper printability is attractive. According to Ivarsson (124) and Steenberg (277), softness/hardness of a paper product correlates with its compression behavior and, together with other factors, the compression properties of a paper or board affect printing results. This implies that if paper is soft and capable of deforming readily under pressure, required intimate contact will be assured between the fibres and the printing plate, even at some variations in surface smoothness. It can be supposed that high rate of stress dissipation in steploaded operations would indicate a high degree of softness and, therefore, good printability.

Existing methods for assessing printing quality of various paper products are not always satisfactory (9,302). According to Ullman (303), current measurements can distinguish reliably only between papers of considerable differences. It is obvious from the great number of variables, which have been found to influence paper printability, that one testing method alone is not sufficient to supply accurate information.

For instance, current smoothness measurements of paper surface, widely practised for evaluating heavily coated paper surfaces (127), give some good indication regarding printing quality. However, due to the fact that this evaluation considers only surface characteristics and neglects

the compressibility behavior of the paper, the information is of limited value. It appears feasible to obtain accurate information by combining physical and mechanical testing methods, such as smoothness and stress relaxation measurements. Such a pair of measurements could be carried out simultaneously on the paper machine.

The same stress relaxation data may also furnish information about runnability of paper, a property extremely important in high speed printing. It is well known that the modulus of elasticity (E) is closely related to frequency of breaks and bagginess (303). Low E indicates an extensible paper which adapts smoothly to the printing rolls, thus limiting the number of breaks. Since viscoelastic and elastic properties are highly interrelated, stress relaxation measurements would be expected to be useful in predicting the runnability of various paper grades.

5.0 CONCLUSIONS

1. Rate of stress relaxation varied widely between individual pulps or pulp types. However, the relaxation measurements obtained from individual pulps, in particular when steeped in caustic, appeared to be highly consistent indicating good reproducibility.

2. Stress dissipation in water or caustic steeped pulp mats followed a similar pattern observed on wood and other ligno-cellulosics under constant compressive or tensile strain.

3. Two different mechanisms (M_1 and M_2) appeared to be involved in pulp mat stress relaxation following quasi steploading (1.0 to 1.5 sec). One dominated the initial short period (0.0 to approximately 1.0 min), while the other featured longer time response (from approximately 1.0 min to 35 min). It is thought that M_1 is mainly caused by inter-fibre processes, whereas M_2 comprises intra-fibre, essentially molecular processes.

4. Pulps dissipate stress at substantially higher rates in the caustic than in the water swollen state. This underlines the importance of inter-(in water and 18.6% NaOH) and intra-(in 18.6% NaOH) crystalline swelling phenomena which determine the molecular forces between individual molecules of the pulp polymeric system. These forces, in turn, control the relaxation response.

5. Pulp chemistry exerts a profound influence on stress relaxation of both water and caustic (18.6% NaOH) steeped pulp mats.

6. Lignin appeared to make no or only an insignificant contribution to pulp mat stress relaxation in compression. This is probably due to a "layer-effect" causing discontinued stress communication in the lignin-carbohydrate complex and due to the dominant role of hemicelluloses which seem to obscure a moderate contribution of lignin.

7. The hemicelluloses were found to be of extreme importance for stress dissipation or redistribution processes in water and caustic swollen pulp mats. Both quantitative and structural features of degraded or non-degraded residual hemicelluloses appeared to play an outstanding role in the

relaxation response. High hemicellulose contents in association with no or insignificant degradation provide a considerably higher degree of visco-elastic capacity than extremely low contents of highly degraded and redeposited hemicellulose residues. In water swollen low yield pulps, the highly degraded and redeposited residues were found to exert even a reverse effect, i.e. they retarded stress decay.

8. It is apparent from their rheological behavior in pulp mats that hemicelluloses must function as an extraordinary part in the stress dissipating system in living wood. This function is facilitated by the high degree of branching and the low DP.

9. It is evident that cellulose accounts for most of the dissipated stress in pulp mats steeped in water or caustic. In the native or only slightly degraded state its contribution to pulp mat rheology seems to vary only insignificantly between pulps of various hemicellulose contents. However, progressive chain cleavage leading to DP values below 1000 drastically changes the rheological behavior. This is indicated by considerably increased rates of stress relaxation of gamma-irradiation degraded pulps.

10. High degree of cellulose degradation and degradation and redeposition phenomena of hemicelluloses reverse the original function of these carbohydrates in rheological processes in the water swollen pulp mats. Degraded cellulose dissipated stress at increased rates, whereas degraded and redeposited hemicelluloses retard rheological processes.

11. In the caustic steeped state, pulp mat rheology appeared to be controlled solely by the short chain material present in the pulp. This implies that it does not depend on any specific carbohydrate component.

12. The profound effect of steeping time, observed on water and caustic (18.6% NaOH) steeped viscose pulps, on residual stress relaxation suggests the interchangeability of chemical and physical stress systems. Therefore, the capability of pulps to dissipate or redistribute stress can be diminished by two types of excitation: (i) an infinitely long steeping time; (ii) an infinitely long period of mechanical excitation; and a combination of both.

13. Fractional stress relaxation measurements on pulps and papers are suggested as useful tools for determining chemical and mechanical pulp properties, such as pressing characteristics and alkali solubility of viscose pulps, estimation of pulp fibre response to machining (beating) and evaluation of runnability and printability of paper.

14. Further studies need to be done for examining the relationship between stress relaxation and pulp mat characteristics as regards its practical implications.

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TABLES

All values in per cent of extractive-free wood.

Component	Red maple (<i>Acer rubrum</i> L.)	White birch (<i>Betula papyrifera</i> Marsh.)	Trembling aspen (<i>Populus tremuloides</i> Michx.)
Cellulose	45	42	48
Lignin	24	19	21
Glucuronoxylan	25	35	24
Glucomannan	4	3	3
Pectin, starch	2	1	4

Component	Balsam fir (<i>Abies balsamea</i> [L.] Mill)	White spruce (<i>Picea glauca</i> [Moench] Voss)	Eastern white pine (<i>Pinus strobus</i> L.)
Cellulose	42	41	41
Lignin	29	27	29
Arabinoglucuronoxylan	9	13	9
Galactoglucomannan	18	18	18
Pectin, starch	2	1	3

Table 1. The chemical composition of woods from three angiosperms and three conifers (after Timell (294)).

Table 2/a. Description of pulps used in the study.

Product Code No.	Wood source ^{a)}	Pulp type	Pulping process or method of preparation (and starting experimental material ^{b)})	Additional pulping treatments
0-1(9-1) ^{c)}	C	↑	↑ (W)	-
0-2(9-2)	A	Alpha-cellulose	TAPPI (W)	-
0-3(5-1)	C		standard (S)	-
0-4(1-3)	C		T203 os- 61 (S)	-
1-1	C	↓	↓	-
1-2	C	↑	Sulphate (S)	-
1-3	C		Sulphate (S)	-
1-4	C		Sulphate (S)	-
2-1	C		Sulphite (S)	-
2-2	C	Viscose pulps	Sulphite (S)	-
2-3	A		Sulphate (S)	-
2-4	C+A		Sulphate (S)	-
3-1	C		Sulphite (S)	-
3-2	C		Sulphite (S)	-
3-3	C		Sulphate (S)	-
3-4	C		Sulphate (S)	-
4-1	C		Sulphite (S)	-
4-2	C	↓	Sulphite (S)	-

a) Coniferous (C), Angiospermous (A).

b) Starting experimental material as wood (W), pulp fibre slurry (P) or pulp sheet (S).

c) Numbers in brackets refer to code No. of pulps used for alpha-cellulose preparations.

Table 2/b.

Product Code No.	Wood source ^{a)}	Pulp type	Pulping process or method of preparation (and starting experimental material ^{b)})	Additional pulping treatments
5-1	C	Acetate	Sulphite (S)	—
6-1	C	↑	Sulphite (S)	Bleached
7-1	C	↑	Sulphate (P)	Unbleached
7-2	C	Paper grade	Sulphate (P)	Bleached
8-1	C	↓	Sulphate (S)	Bleached
8-2	10% C+ 90% A	↓	Sulphate (S)	Bleached
9-1	C	↓	Chlorite (W)	—
9-2	A	Holo-cellulose	Chlorite (W)	—
9-3	C	↓	Peracetic acid (W)	—
9-4	A	↓	Peracetic acid (W)	—
10-1	C	↓	Mechanical (P)	Unbleached
10-2	C	Ground-wood	Mechanical (P)	Bleached
10-3	A	↓	Mechanical (P)	Unbleached
10-4	A	↓	Mechanical (P)	Bleached

Table 3/a. Summative data (in per cent of extractive-free wood) for chemical composition of pulps tested in the study. Values for cellulose and total amount of hemicelluloses have been adjusted according to ratios of glucose-mannose in isolated wood gluco-mannans (in conifers 1:3, and in pored wood 1:2(295)).

Component	Alpha-cellulose preparations			
	0-1	0-2	0-3	0-4
Acetyl	-	-	-	-
Uronic anhydride	-	-	-	-
Residues of:				
Galactose	-	-	-	-
Glucose	92.9	97.1	99.5	99.2
Mannose	6.2	2.0	0.5	0.8
Arabinose	40.1	0.1	-	-
Xylose	0.6	1.3	0.2	0.5
Rhamnose	-	-	-	-
Cellulose	90.8	96.1	99.3	99.0
Hemicelluloses	8.9	4.4	0.9	1.5
Lignin	-	-	-	-
Total	99.7	100.5	100.2	100.5

Table 3/b.

Component	Viscose pulps			
	1-1	1-2	1-3	1-4
Acetyl	-	-	-	-
Uronic anhydride	-	-	-	-
Residues of:				
Galactose	-	-	-	-
Glucose	95.1	97.0	96.6	97.5
Mannose	2.4	2.0	1.8	2.0
Arabinose	<0.1	0.1	<0.1	<0.1
Xylose	1.9	2.4	0.8	0.7
Rhamnose	-	-	-	-
Cellulose	94.3	96.3	96.0	96.8
Hemicelluloses	5.1	5.2	3.2	3.4
Lignin	-	-	-	-
Total	99.4	101.5	99.2	100.2

Table 3/c.

Component	Viscose pulps			
	2-1	2-2	2-3	2-4
Acetyl	-	-	-	-
Uronic anhydride	-	-	-	-
Residues of:				
Galactose	-	-	-	-
Glucose	92.5	97.3	94.2	96.3
Mannose	2.3	1.5	1.0	0.7
Arabinose	<0.1	<0.1	0.1	<0.1
Xylose	1.8	1.9	2.6	1.2
Rhamnose	-	-	-	-
Cellulose	91.7	96.8	93.7	96.1
Hemicelluloses	4.9	3.9	4.2	2.2
Lignin	-	-	-	-
Total	96.6	100.7	97.9	98.3

Table 3/d.

Component	Viscose pulps			
	3-1	3-2	3-3	3-4
Acetyl	-	-	-	-
Uronic anhydride	-	-	-	-
Residues of:				
Galactose	-	-	-	-
Glucose	93.1	92.4	96.1	96.5
Mannose	1.8	3.5	1.6	1.6
Arabinose	<0.1	<0.1	<0.1	<0.1
Xylose	1.7	1.4	1.9	0.6
Rhamnose	-	-	-	-
Cellulose	92.5	91.2	95.6	96.0
Hemicelluloses	4.1	6.1	4.0	2.7
Lignin	-	-	-	-
Total	96.6	97.3	99.6	98.7

Table 3/e.

Component	Viscose pulps		Acetate pulp	Bleached sulphite pulp
	4-1	4-2	5-1	6-1
Acetyl	-	-	-	3.1
Uronic anhydride	-	-	-	0.9
Residues of:				
Galactose	-	-	-	0.2
Glucose	97.0	93.9	97.0	86.5
Mannose	2.3	2.2	2.2	7.2
Arabinose	40.1	40.1	40.1	0.3
Xylose	1.5	1.5	1.2	(3.9) (3.3)*)
Rhamnose	-	-	-	-
Cellulose	96.2	93.2	96.3	84.1
Hemicelluloses	4.6	4.4	4.1	17.9
Lignin	-	-	-	0.7
Total	100.8	97.6	100.4	102.7

*) values indicate total xylose residues as obtained from gas- liquid chromatography measurements (in brackets) and corrected for xylose residues in aldobiouronic acid groups which resisted acid hydrolysis (according to Meier and Wilkie (192) and Zinbo and Timell (327)).

Table 3/f.

Component	Unbleached. sulphate pulps	Bleached sulphate pulps		
	7-1	7-2	8-1	8-2
Acetyl	-	-	-	-
Uronic anhydride	1.1	0.7	0.7	1.6
Residues of:				
Galactose	0.3	0.3	0.2	0.2
Glucose	74.6	83.4	83.1	83.0
Mannose	7.5	8.4	7.2	1.5
Arabinose	0.5	0.5	0.3	0.5
Xylose	6.0 (5.3)*	6.0 (5.5)*	7.4 (6.9)*	14.7 (13.6)*
Rhamnose	-	-	-	-
Cellulose	72.1	80.6	80.7	82.2
Hemicelluloses	17.9	18.7	18.2	19.3
Lignin	9.1	1.0	0.3	0.5
Total	99.1	100.3	99.2	102.0

Table 3/g.

Component	Holocellulose pulps			
	9-1	9-2	9-3	9-4
Acetyl	5.1	6.0	3.8	5.6
Uronic anhydride	3.0	3.0	2.6	2.2
Residues of:				
Galactose	0.9	0.6	1.1	0.7
Glucose	72.4	75.1	71.7	73.8
Mannose	11.9	4.3	12.0	4.6
Arabinose	0.4	0.3	0.5	0.3
Xylose	5.4 (3.4)*	13.3 (11.3)*	5.7 (4.0)*	12.3 (10.8)*
Rhamnose	-	0.1	-	0.1
Cellulose	68.5	73.0	67.7	71.5
Hemicelluloses	30.6	29.7	29.7	28.1
Lignin	0.3	0.4	0.3	0.4
Total	99.4	103.1	97.7	100.0

Table 3/h.

Component	Groundwoods			
	10-1	10-2	10-3	10-4
Acetyl	3.7	3.8	4.7	4.7
Uronic anhydride	2.8	2.8	4.0	4.0
Residues of:				
Galactose	1.2	1.1	1.0	1.2
Glucose	47.0	46.5	50.5	50.8
Mannose	12.4	12.7	2.9	2.9
Arabinose	0.5	0.6	0.7	0.6
Xylose	5.4 (3.6)*	5.7 (3.9)*	16.4 (13.8)*	16.8 (14.2)*
Rhamnose	0.1	0.1	0.3	0.2
Cellulose	42.9	42.2	49.0	49.3
Hemicelluloses	30.1	31.0	31.5	31.9
Lignin	30.5	30.3	21.7	21.6
Total	103.5	103.5	102.2	102.8

Table 4/a. Summary of fractional stress relaxation results on pulps tested in the study as read after 35 min relaxation time ($1 - \zeta(35 \text{ min}) / \zeta(0)$) following steeping in water or caustic.

Product Code No.	.1 - $\frac{\zeta(35 \text{ min})}{\zeta(0)}$					
	H ₂ O, distilled			18.6% NaOH		
	Single Measur.	Mean Value	Std. Dev.	Single Measur.	Mean Value	Std. Dev.
α-cellulose pulps						
0-1	.495	.497	.026	.667	.657	.008
	.480			.655		
	.479			.652		
	.592			.661		
	.487			.648		
0-2	.510	.492	.017	.702	.701	.003
	.498			.705		
	.492			.698		
	.494			.699		
	.464			.702		
0-3	.534	.537	.010	.625	.630	.009
	.543			.618		
	.550			.628		
	.537			.638		
	.523			.639		
0-4	.527	.528	.015	.582	.579	.002
	.546			.576		
	.515			.579		
	.541			.580		
	.513			.577		
Viscose Pulps						
1-1	.436	.461	.020	.648	.653	.017
	.443			.634		
	.477			.642		
	.470			.673		
	.477			.668		
1-2	.481	.461	.017	.654	.649	.021
	.456			.615		
	.470			.659		
	.435			.669		
	.461			.649		

Table 4/b.

Product Code No.	1 - $\frac{\delta(35 \text{ min})}{\delta (o)}$					
	H_2O , distilled			18.6% NaOH		
	Single Measur.	Mean Value	Std. Dev.	Single Measur.	Mean Value	Std. Dev.
Viscose Pulps						
1-3	.485 .485 .506 .500 .486	.492	.010	.610 .616 .622 .618 .621	.617	.005
1-4	.509 .482 .512 .497 .496	.499	.012	.576 .611 .619 .618 .614	.608	.018
2-1	.468 .487 .400 .467 .443	.453	.034	.720 .730 .714 .725 .734	.725	.008
2-2	.503 .448 .487 .422 .514	.475	.039	.683 .702 .702 .716 .759	.712	.029
2-3	.484 .482 .530 .520 .500	.503	.021	.677 .682 .679 .676 .690	.681	.006
2-4	.532 .554 .534 .549 .562	.546	.013	.599 .569 .594 .593 .601	.591	.013
3-1	.533 .506 .496 .470 .497	.500	.023	.642 .644 .647 .643 .628	.641	.007

Table 4/c.

Product	1 - $\frac{G(35 \text{ min})}{G(o)}$					
Code	H ₂ O, distilled			18.6% NaOH		
No.	Single Measur.	Mean Value	Std. Dev.	Single Measur.	Mean Value	Std. Dev.
Viscose Pulps						
3-2	.474 .461 .428 .461 .465	.458	.018	.695 .690 .716 .699 .706	.701	.010
3-3	.508 .527 .511 .505 .496	.509	.011	.617 .613 .615 .622 .622	.618	.004
3-4	.517 .520 .524 .537 .529	.525	.008	.600 .590 .608 .617 .610	.605	.010
4-1	.466 .497 .512 .498 .491	.493	.017	.704 .709 .727 .725 .746	.722	.017
4-2	.486 .456 .416 .458 .485	.460	.029	.707 .741 .713 .724 .751	.727	.019
Acetate Pulp						
5-1	.527 .529 .543 .525 .547	.535	.010	.682 .633 .673 .701 .701	.678	.028

Table 4/d.

Product Code No.	1 - $\frac{G(35 \text{ min})}{G(o)}$					
	H ₂ O, distilled			18.6% NaOH		
	Single Measur.	Mean Value	Std. Dev.	Single Measur.	Mean Value	Std. Dev.
Sulphite Pulp						
6-1	.506 .559 .519 .518 .513	.523	.021	.795 .807 .797 .809 .798	.801	.006
Unbleached Sulphate Pulp						
7-1	.574 .572 .583 .570 .586	.577	.007	.735 .723 .731 .724 .734	.729	.006
Bleached Sulphate Pulps						
7-2	.533 .533 .548 .532 .526	.534		.782 .769 .781 .775 .785	.778	.006
8-1	.510 .530 .545 .506 .524	.523	.012	.811 .804 .810 .802 .808	.807	.004
8-2	.539 .538 .506 .496 .538	.524	.021	.741 .744 .735 .748 .735	.741	.006

Table 4/e.

Product Code No.	1 - $\frac{G(35 \text{ min})}{G(o)}$					
	H ₂ O, distilled			18.6% NaOH.		
	Single Measur.	Mean Value	Std. Dev.	Single Measur.	Mean Value	Std. Dev.
Holocellulose Preparations						
9-1	.669 .695 .642 .670 .641	.643	.022	.823 .793 .810 .811 .829	.813	.014
9-2	.703 .725 .730 .706 .712	.715	.012	.872 .858 .869 .821 .872	.858	.022
9-3	.652 .658 .596 .647 .663	.643	.027	.820 .771 .778 .783 .808	.792	.021
9-4	.695 .686 .702 .672 .709	.693	.014	.817 .820 .826 .820 .814	.819	.005
Groundwood Pulps						
10-1	.661 .671 .633 .651 .653	.654	.014	.865 .874 .870 .855 .875	.868	.008
10-2	.643 .673 .685 .639 .657	.659	.020	.845 .845 .847 .868 .867	.855	.012

Table 4/f.

Product Code No.	1 - $\zeta(35 \text{ min})$ $\zeta(o)$					
	H ₂ O, distilled			18.6% NaOH		
	Single Measur.	Mean Value	Std. Dev.	Single Measur.	Mean Value	Std. Dev.
Groundwood Pulps						
10-3	.672 .662 .664 .653 .663	.663	.007	.888 .890 .890 .893 .891	.890	.002
10-4	.648 .644 .649 .685 .677	.661	.019	.903 .900 .899 .902 .874	.896	.012

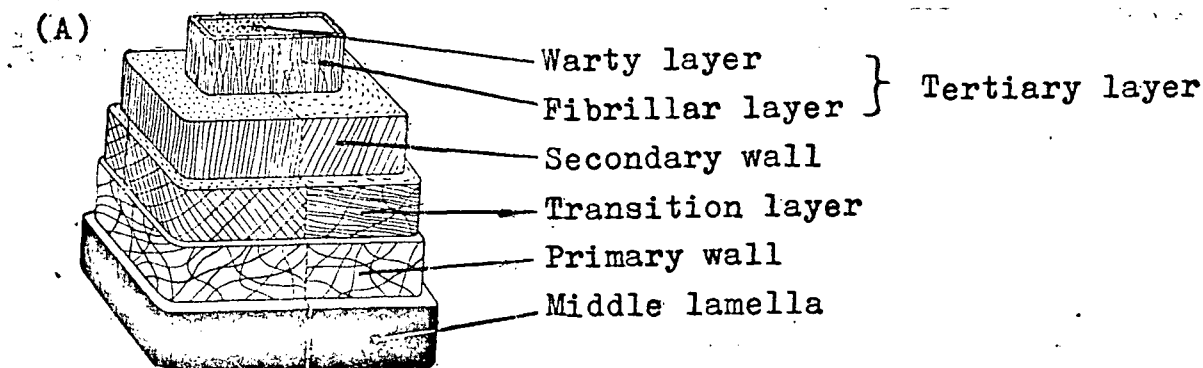
Table 5. Properties of viscose pulps treated with various doses of gamma-radiation.

Product Code No.	Treatment, Mrd	Alpha-cellulose, %	Intrinsic Viscosity, $[\eta]$	10% NaOH Solubility, %
3-2	0.0	90.3	12.8	9.5
	0.5	90.0	6.0	9.9
	1.0	88.4	4.5	12.6
	2.0	82.4	3.0	15.5
	4.0	63.2	2.1	25.2
	6.0	47.5	1.3	43.1
3-4	0.0	97.5	13.2	1.6
	0.5	97.5	6.2	1.8
	1.0	96.0	4.7	3.3
	2.0	91.1	3.1	5.1
	4.0	75.9	2.1	14.1
	6.0	66.5	1.3	32.9

Table 6. Multiple curvilinear covariance analysis for the relationship between 10% NaOH solubility and fractional stress relaxation of irradiated and untreated viscose pulps.

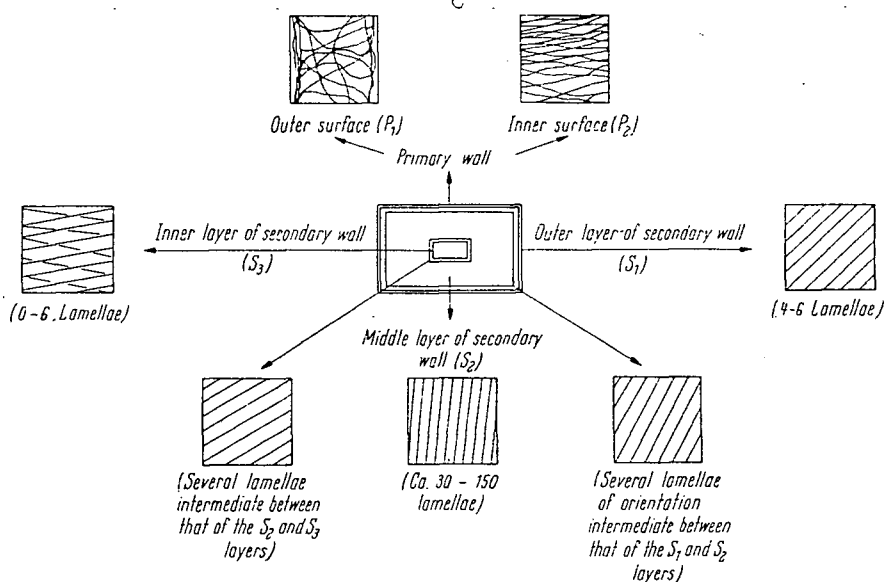
<u>Groups</u>	<u>DF</u>	<u>F</u>
Set 1 (untreated pulps)	11	
Set 2 (irradiated pulp No. 3-2)	3	
Set 3 (irradiated pulp No. 3-4)	<u>3</u>	
Total	17	
Difference for testing slopes	<u>4</u>	1.343 N.S.
Sums	21	
Difference for testing levels	<u>2</u>	3.074 N.S.
Combined regression	23	

FIGURES



Angiospermous wood (birch) | Coniferous wood (spruce)

(B)



(C)

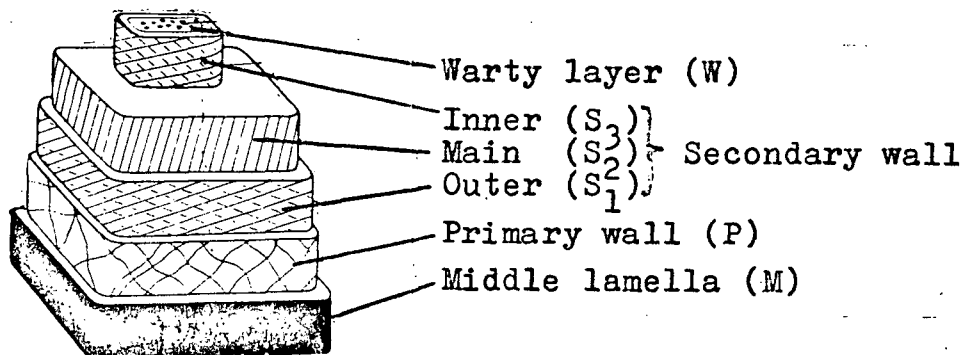


Figure 1. Schematic representation of the cell wall organisation in a coniferous tracheid and/or angiospermous wood fibre, with respective microfibril orientation: (A) after Meier (187); (B) after Wardrop and Harada as in Wardrop (316); after Tsoumis (301).

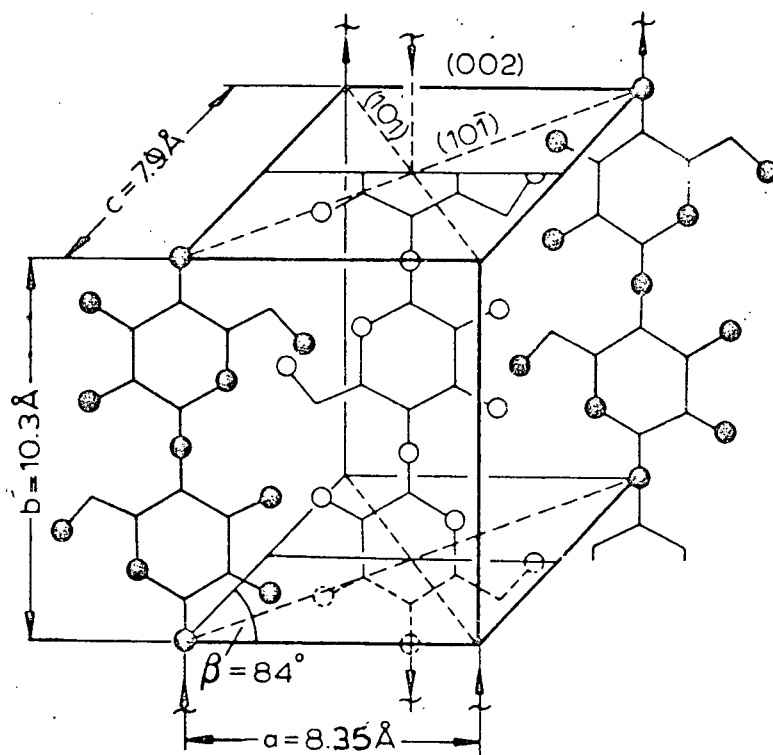


Figure 2. The unit cell as proposed by Meyer and Misch (197).

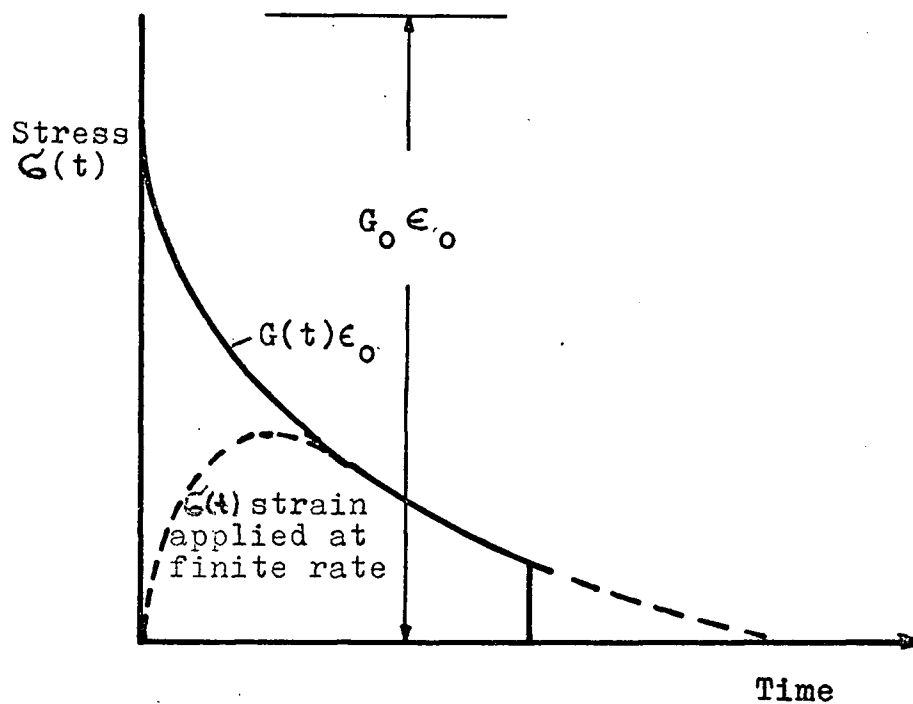


Figure 3. Stress relaxation under constant strain (after Leaderman (161)).

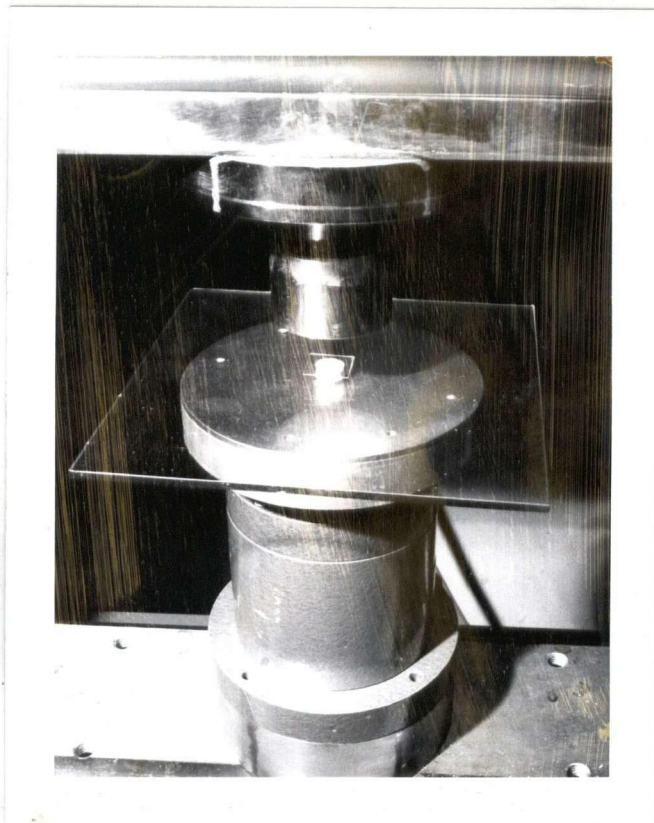


Figure 4. Steeped pulp specimen mounted between glass plates for testing of relaxation in compression.

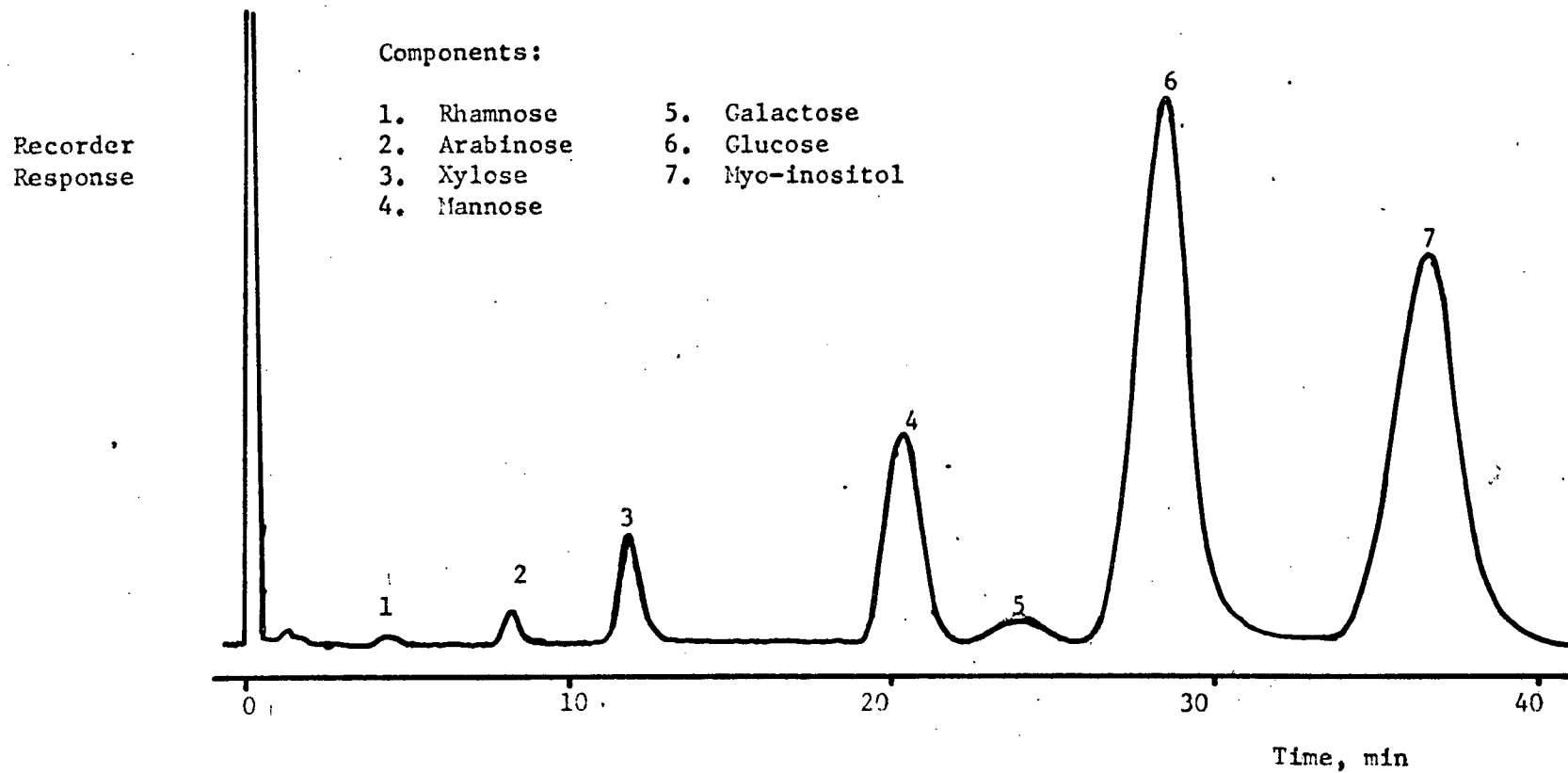


Figure 5.

Gas chromatogram of the acetylated hydrolysates of western hemlock groundwood pulp No. 10-2 (brightened).

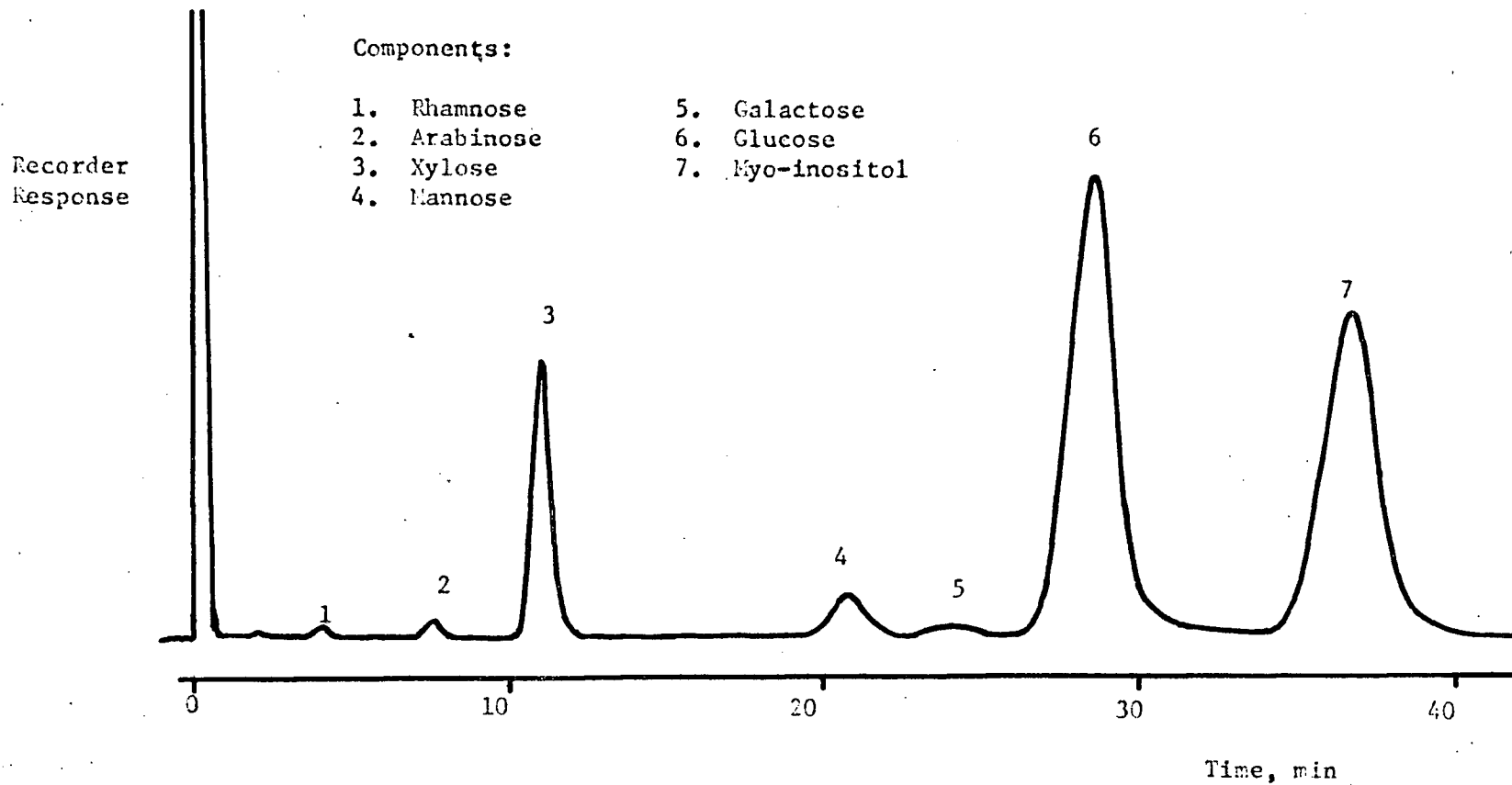


Figure 6. Gas chromatogram of the acetylated hydrolysates of western cottonwood groundwood No. 10-4 (brightened).

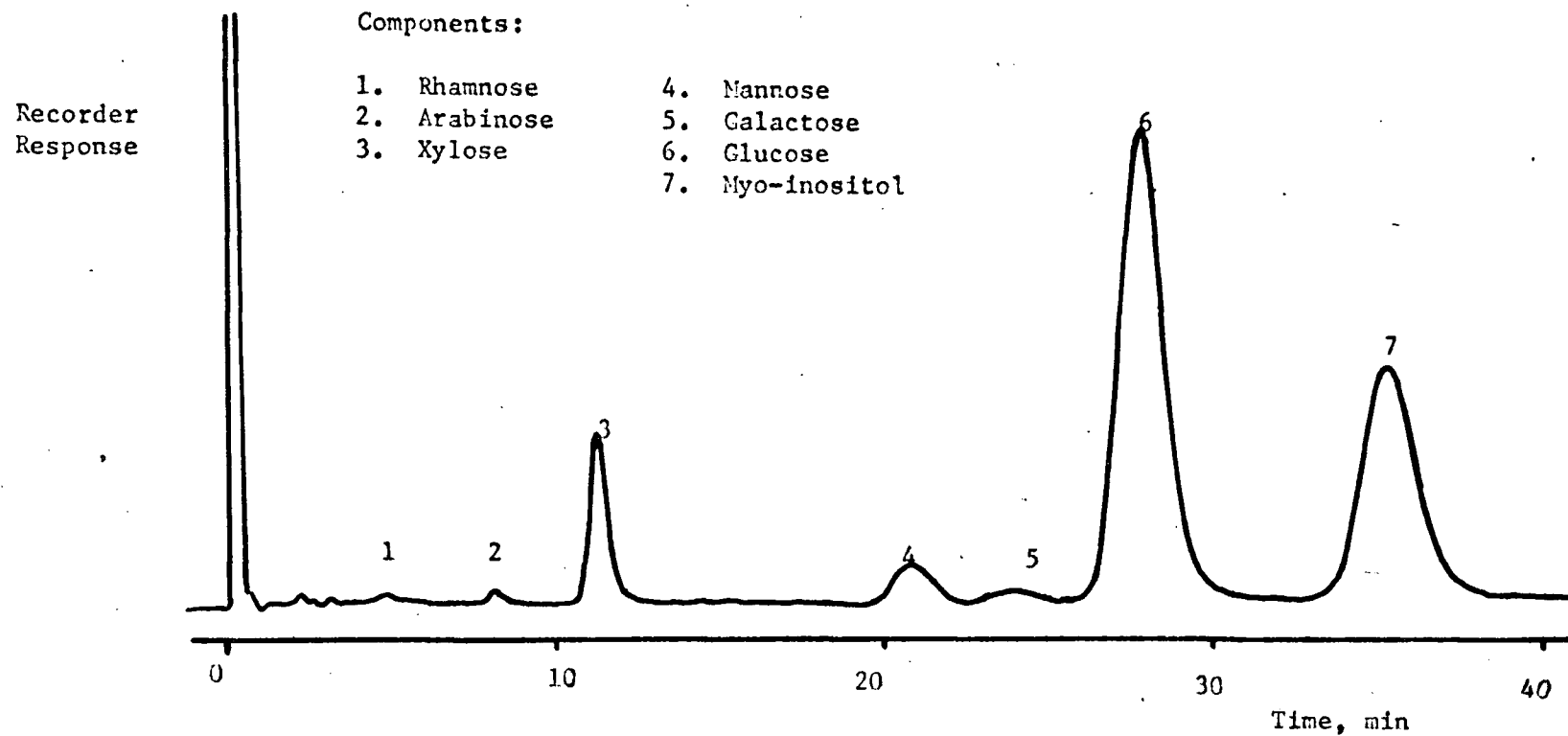


Figure 7. Gas chromatogram of the acetylated hydrolysates of western cottonwood peracetic acid holocellulose No. 9-4.

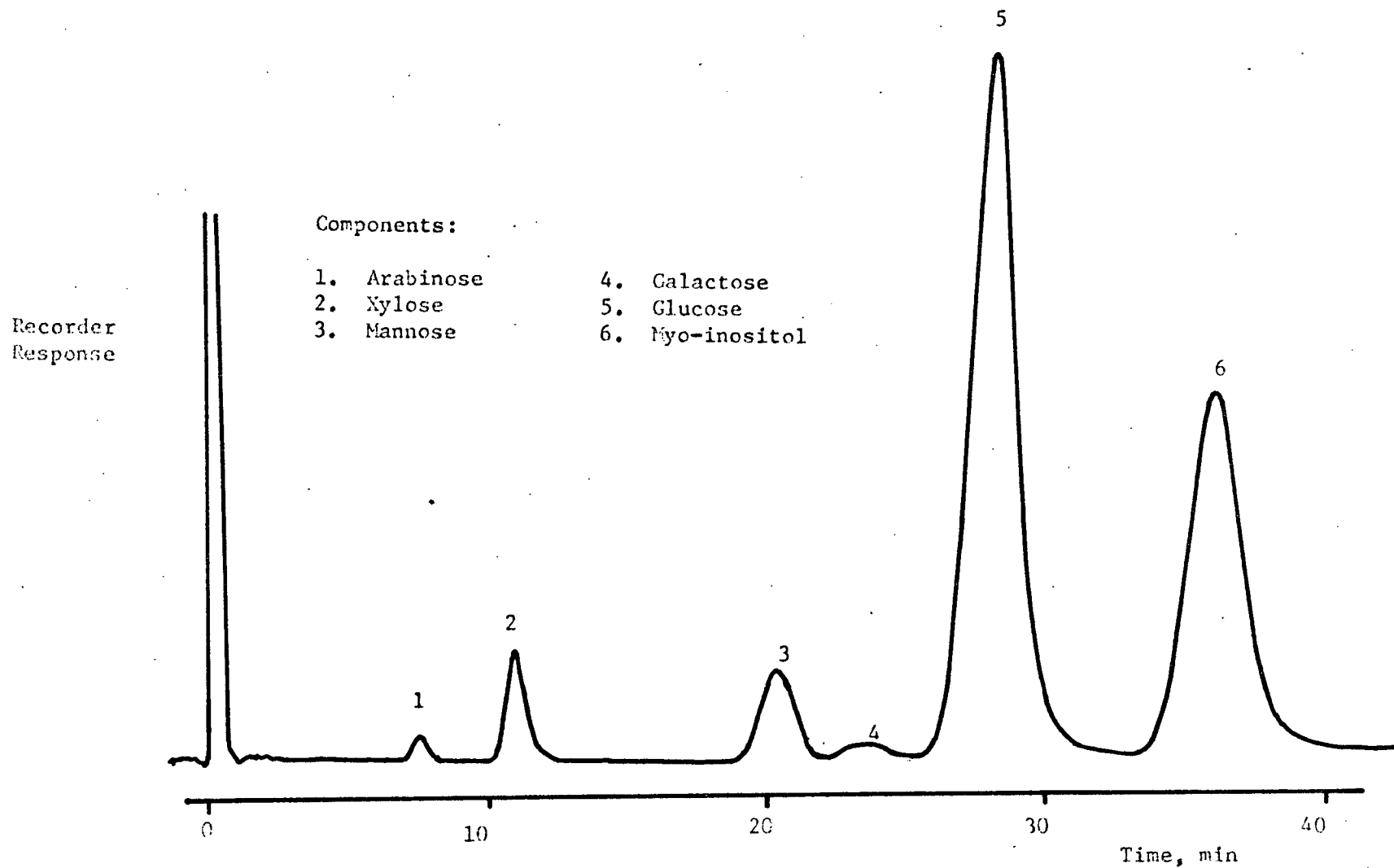


Figure 8. Gas chromatogram of the acetylated hydrolysates of unbleached coniferous sulphate pulp No. 7-1.

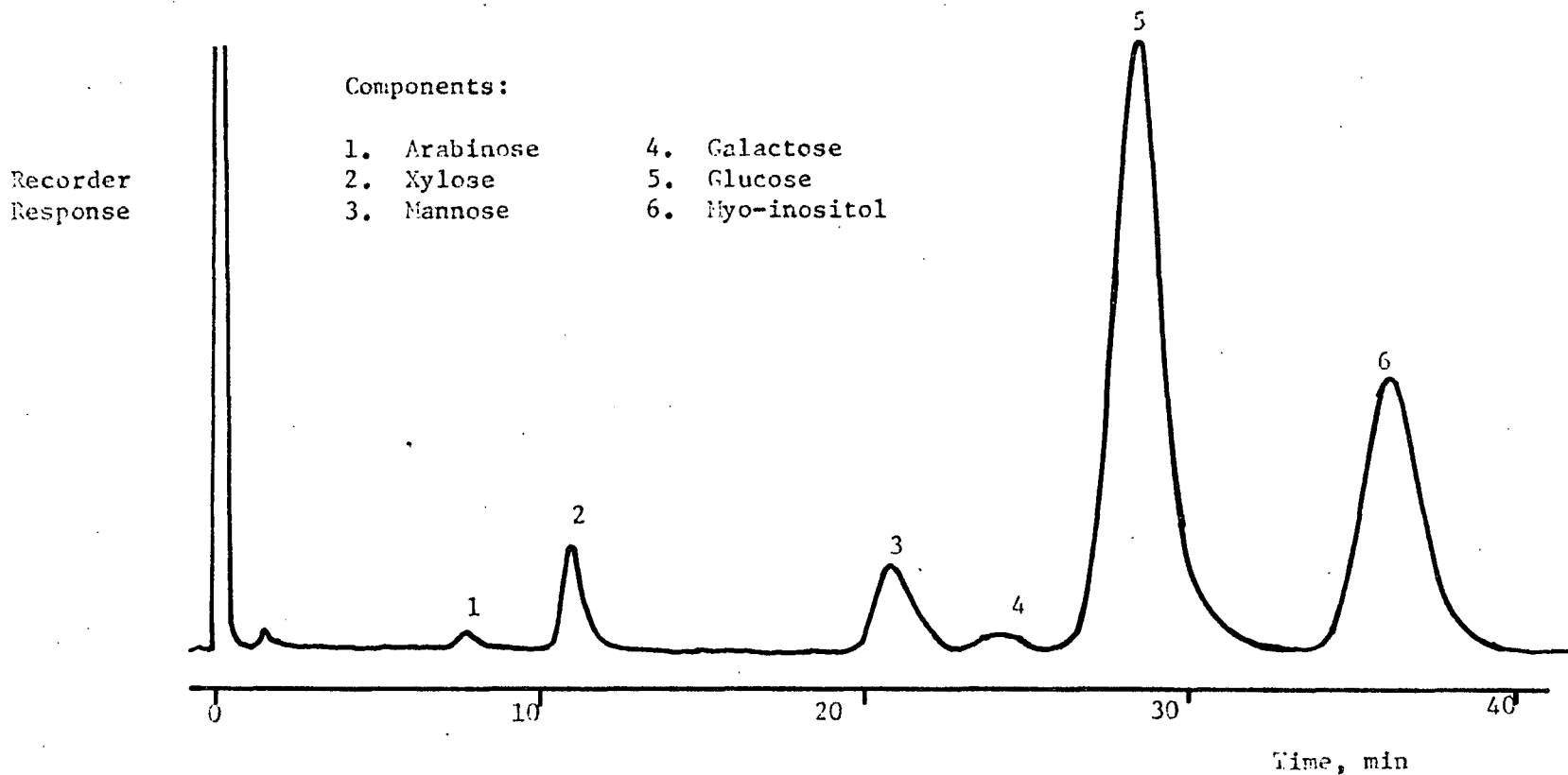


Figure 9. Gas chromatogram of the acetylated hydrolysates of bleached coniferous sulphate pulp No. 7-2.

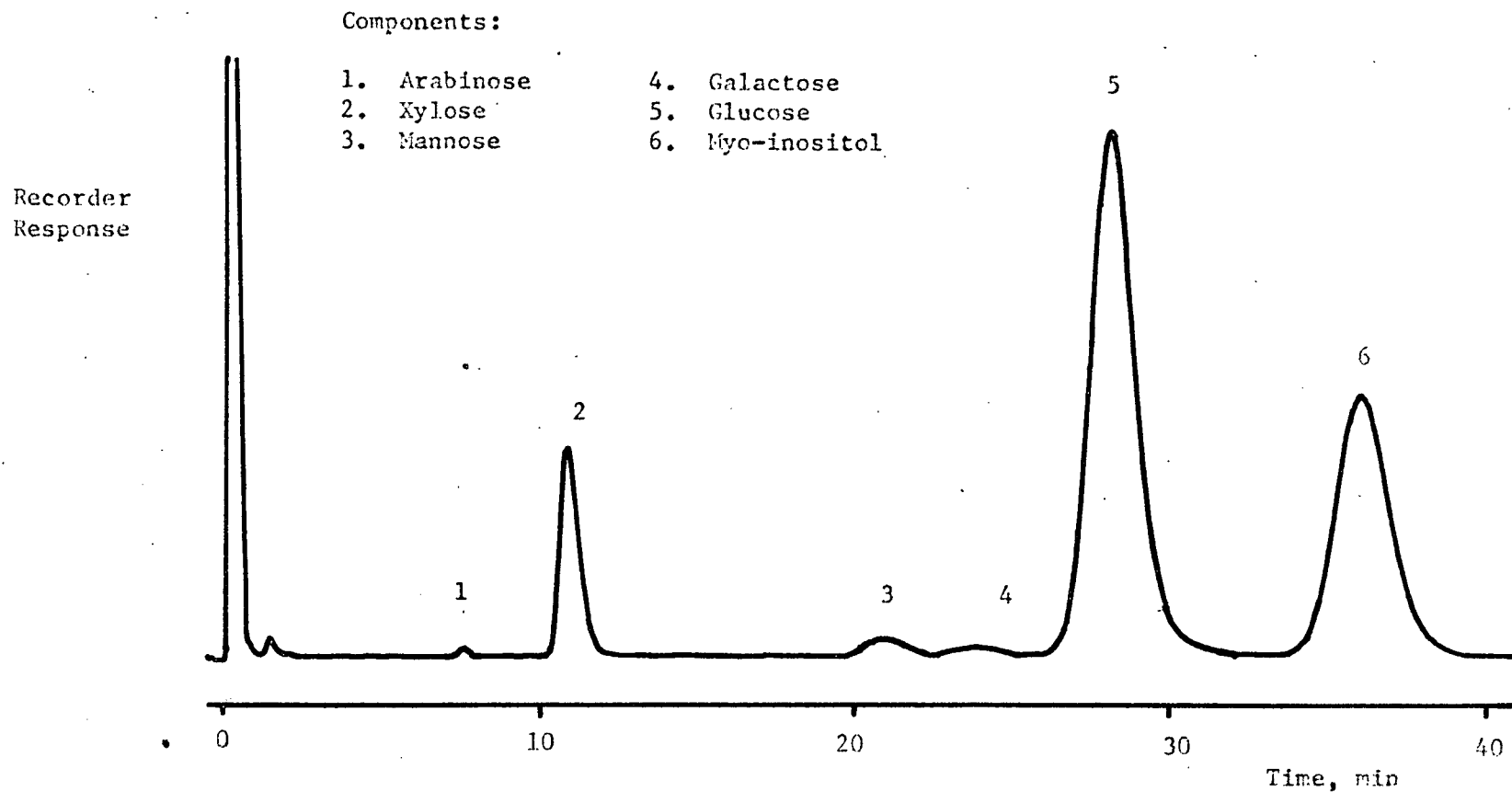


Figure 10. Gas chromatogram of the acetylated hydrolysates of bleached predominantly angiospermous sulphate pulp No. 8-2.

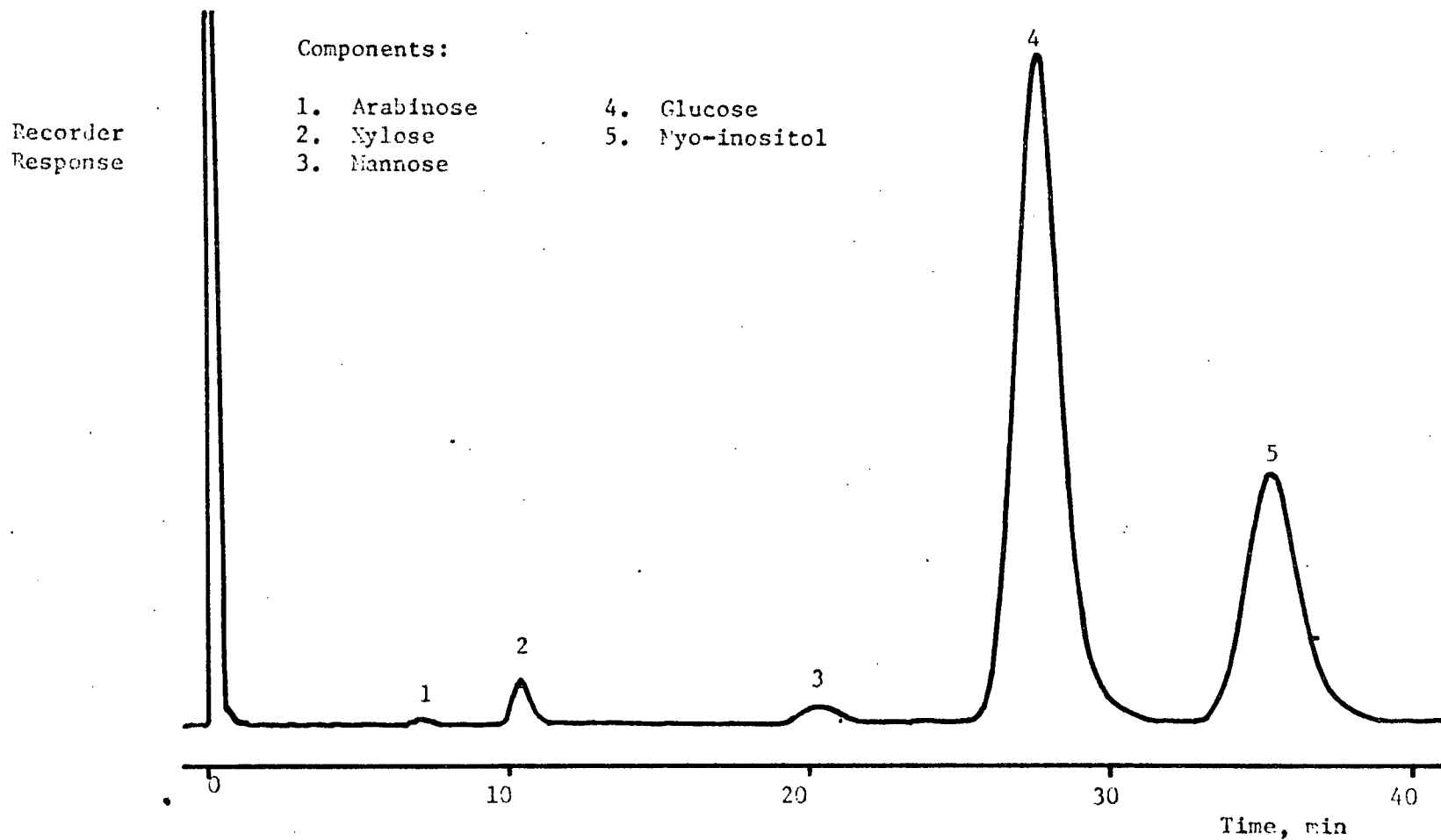


Figure 11. Gas chromatogram of the acetylated hydrolysates of coniferous viscose pulp No. 1-2.

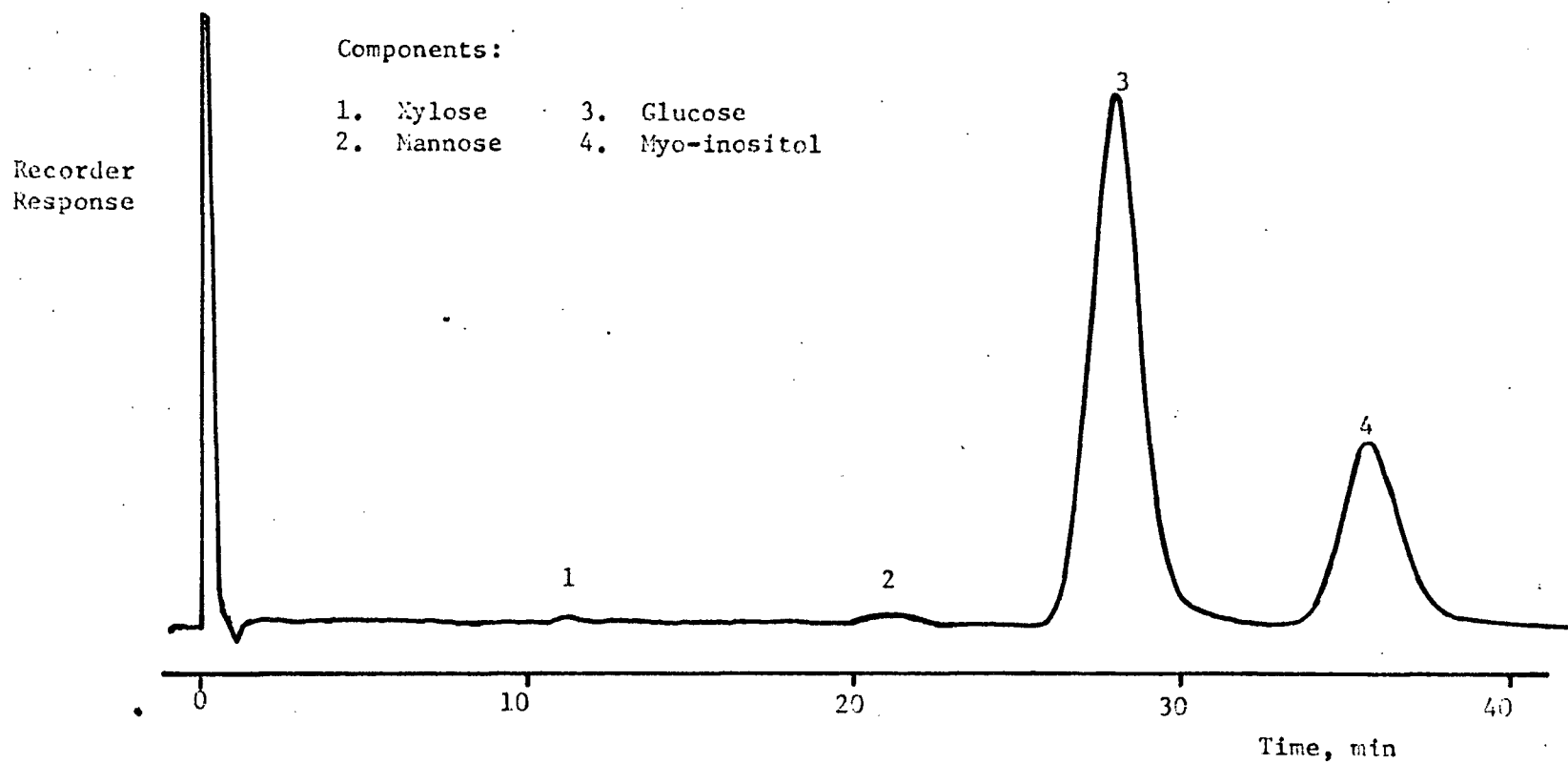


Figure 12. Gas chromatogram of the acetylated hydrolysates of alpha-cellulose pulp No. 0-3.

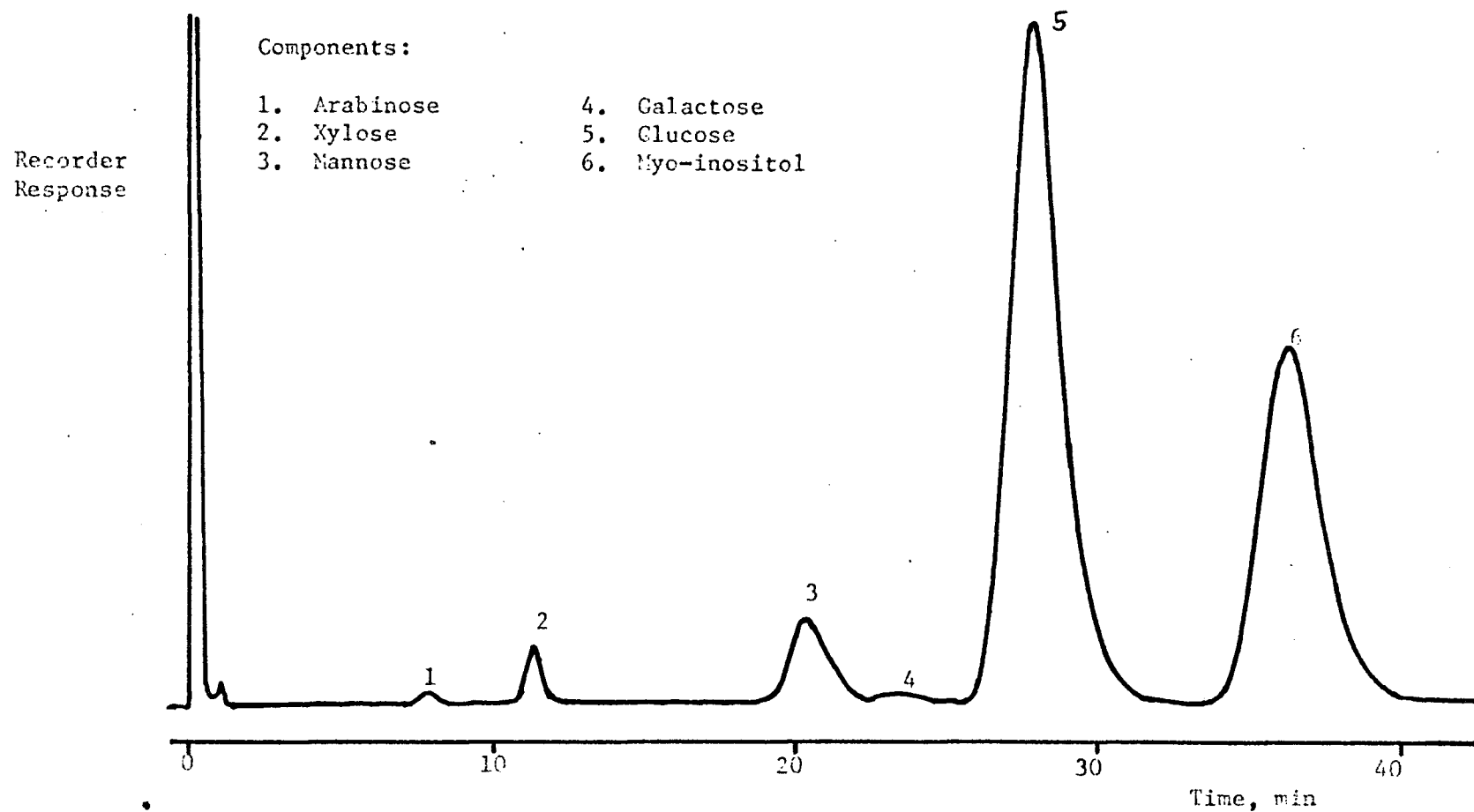


Figure 13. Gas chromatogram of the acetylated hydrolysates of bleached coniferous sulphite pulp No. 6-1.

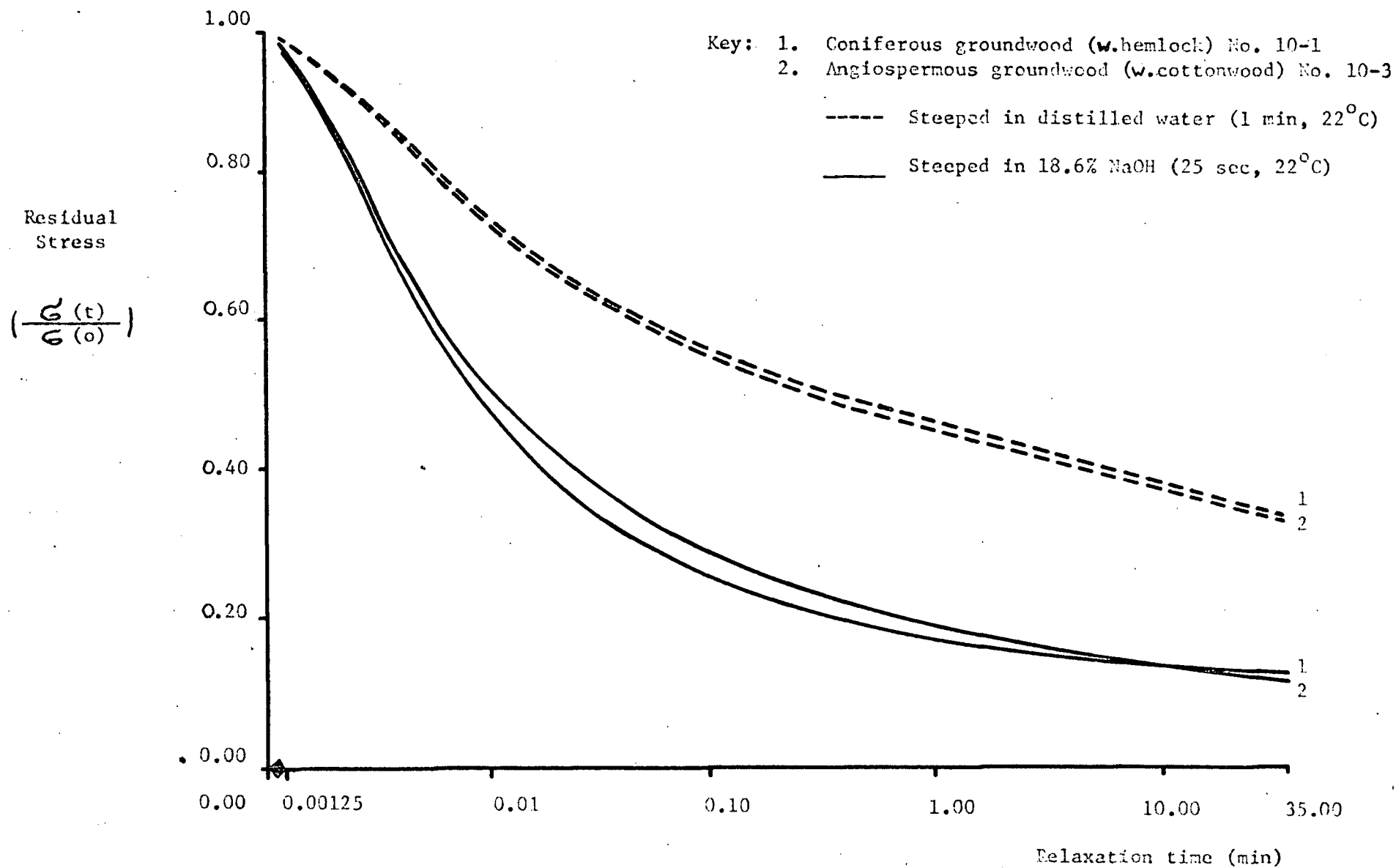


Figure 14. Fractional stress relaxation curves for groundwood pulps following water or caustic steeping ($n = 5$).

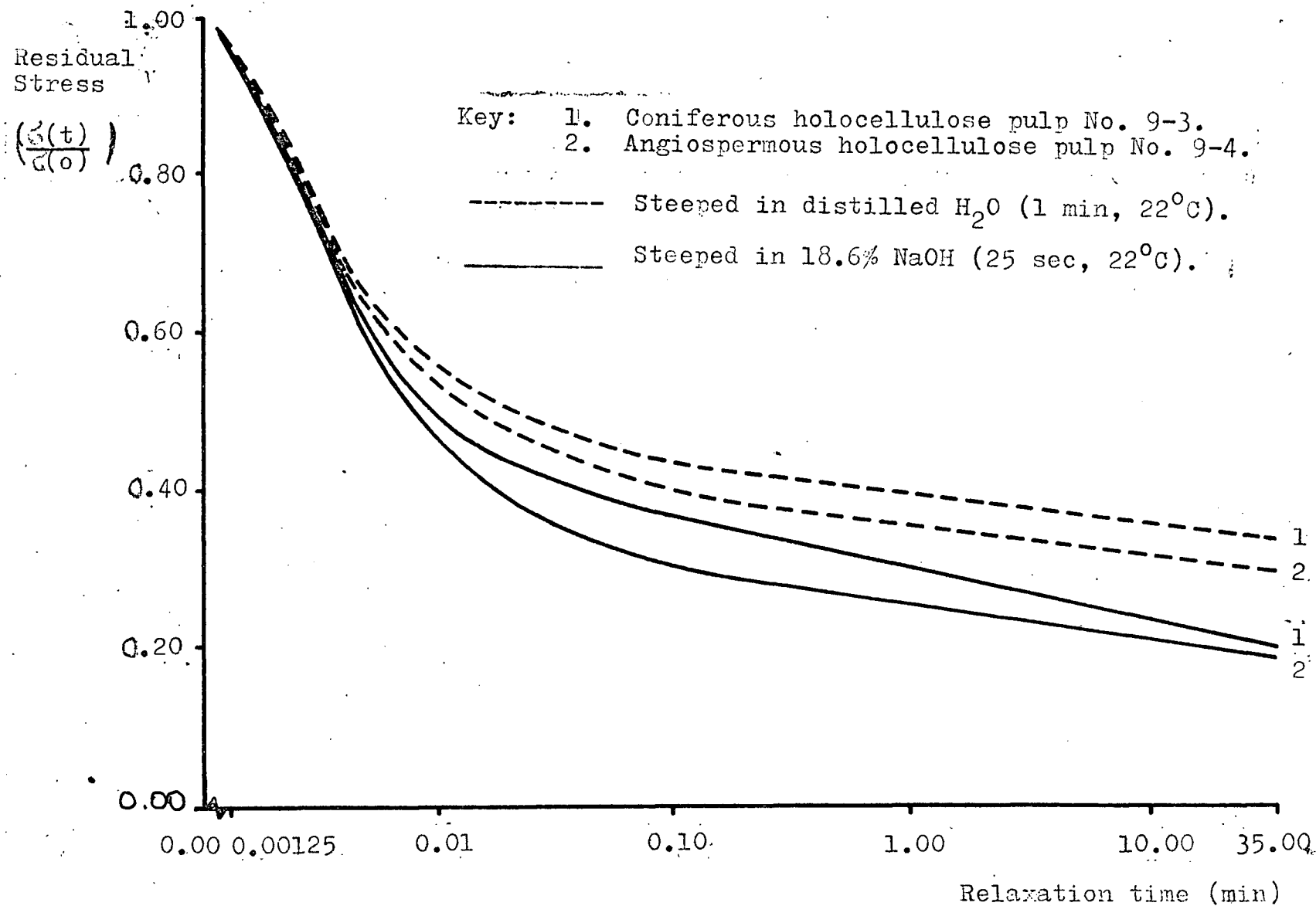


Figure 15. Typical fractional stress relaxation curves for holocellulose pulps following water or caustic steeping ($n = 5$).

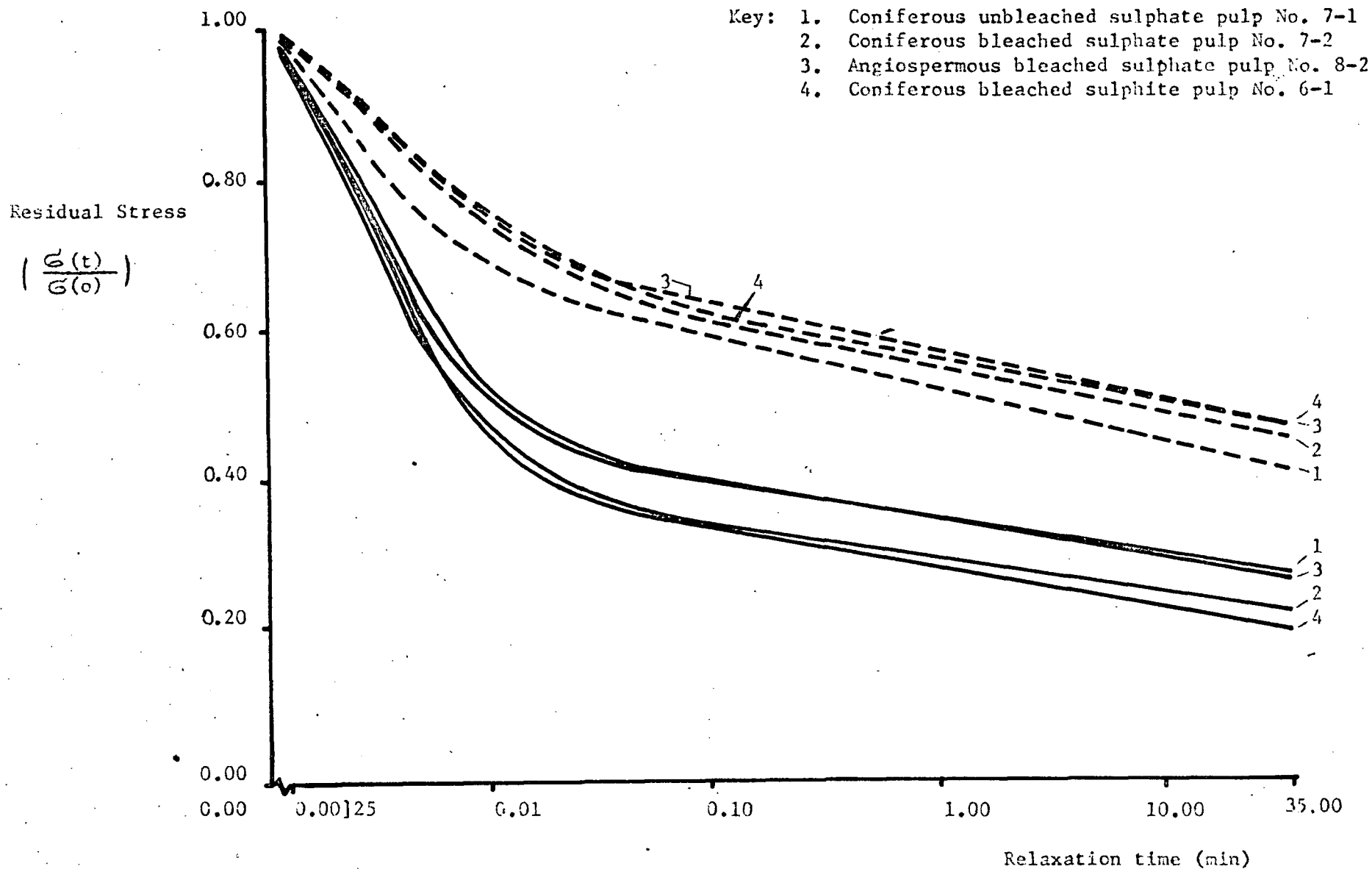


Figure 16. Fractional stress relaxation curves for paper pulps following water or caustic steeping ($n = 5$).

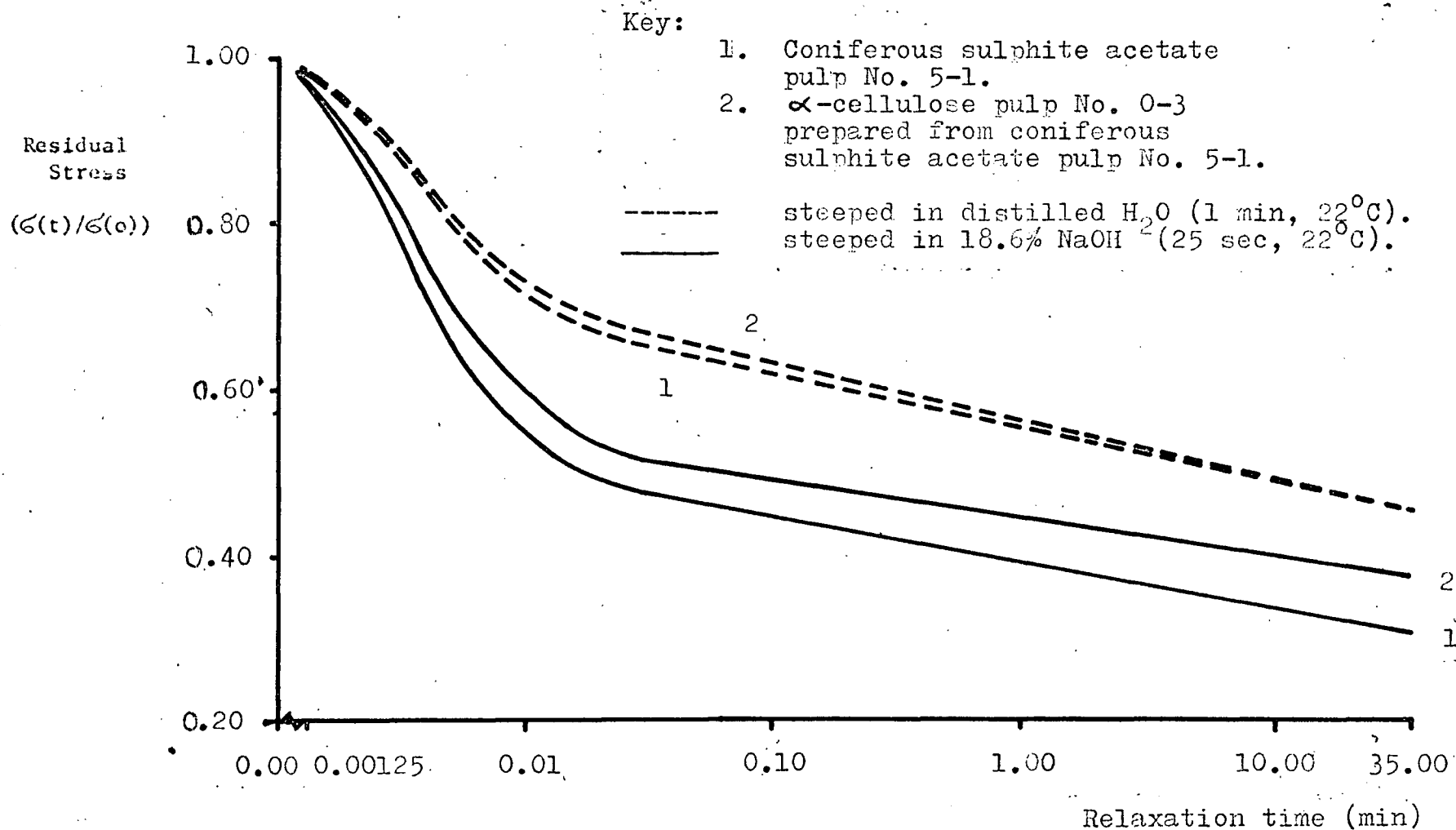


Figure 17. Fractional stress relaxation curves for acetate and α -cellulose pulps following water or caustic steeping ($n = 5$).

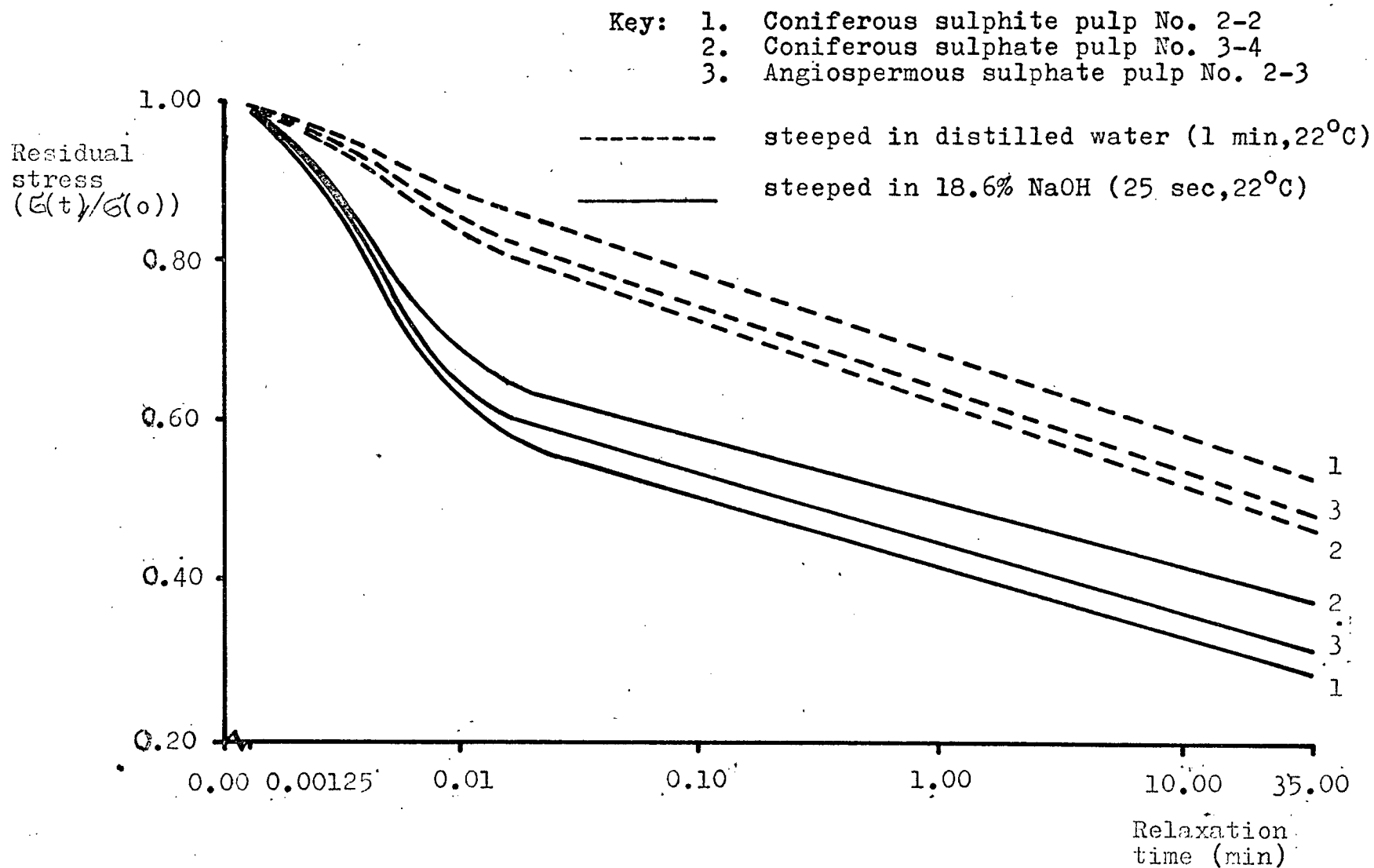


Figure 18. Typical fractional stress relaxation curves for three viscose pulps following water or caustic steeping ($n = 5$).

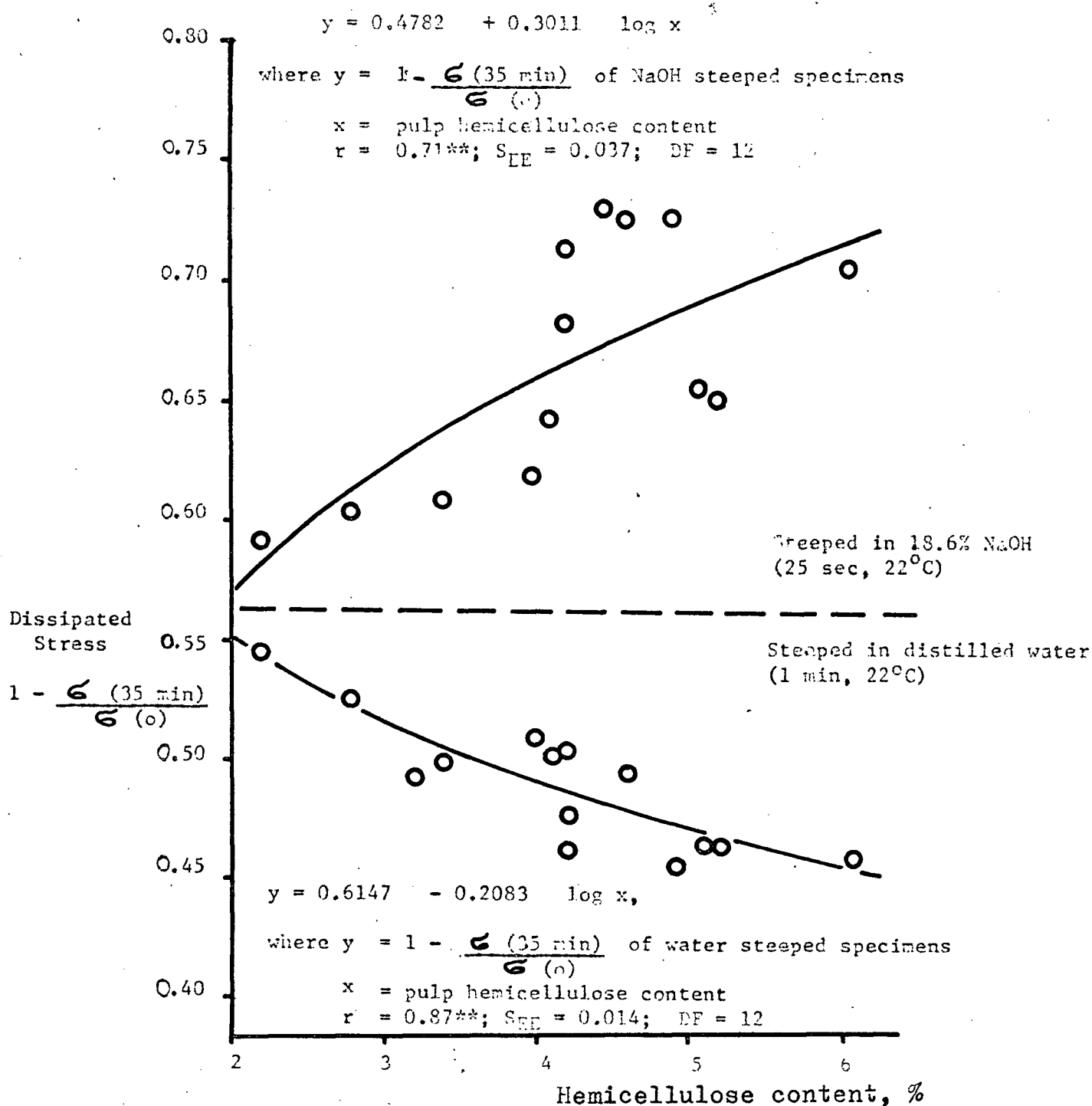


Figure 19. Correlation between fractional stress relaxation of 14 viscose pulps read after 35 min relaxation time following steeping in water or caustic and pulp hemicellulose content.

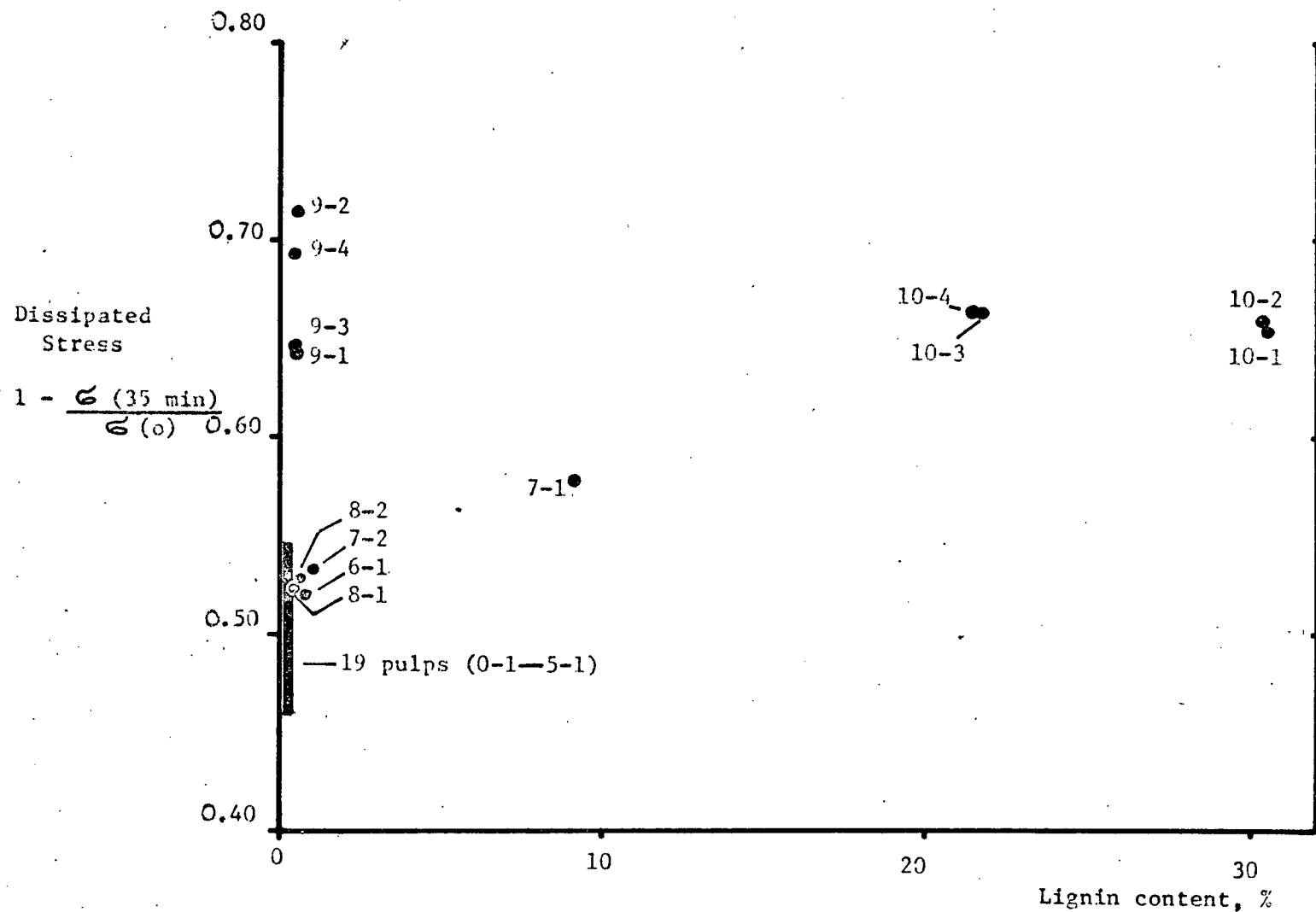


Figure 20.

Relationship between fractional stress relaxation ($n = 5$) and lignin contents as observed on water steeped samples of various pulp types after 35 min relaxation time. Code numbers refer to pulps listed in Table 2.

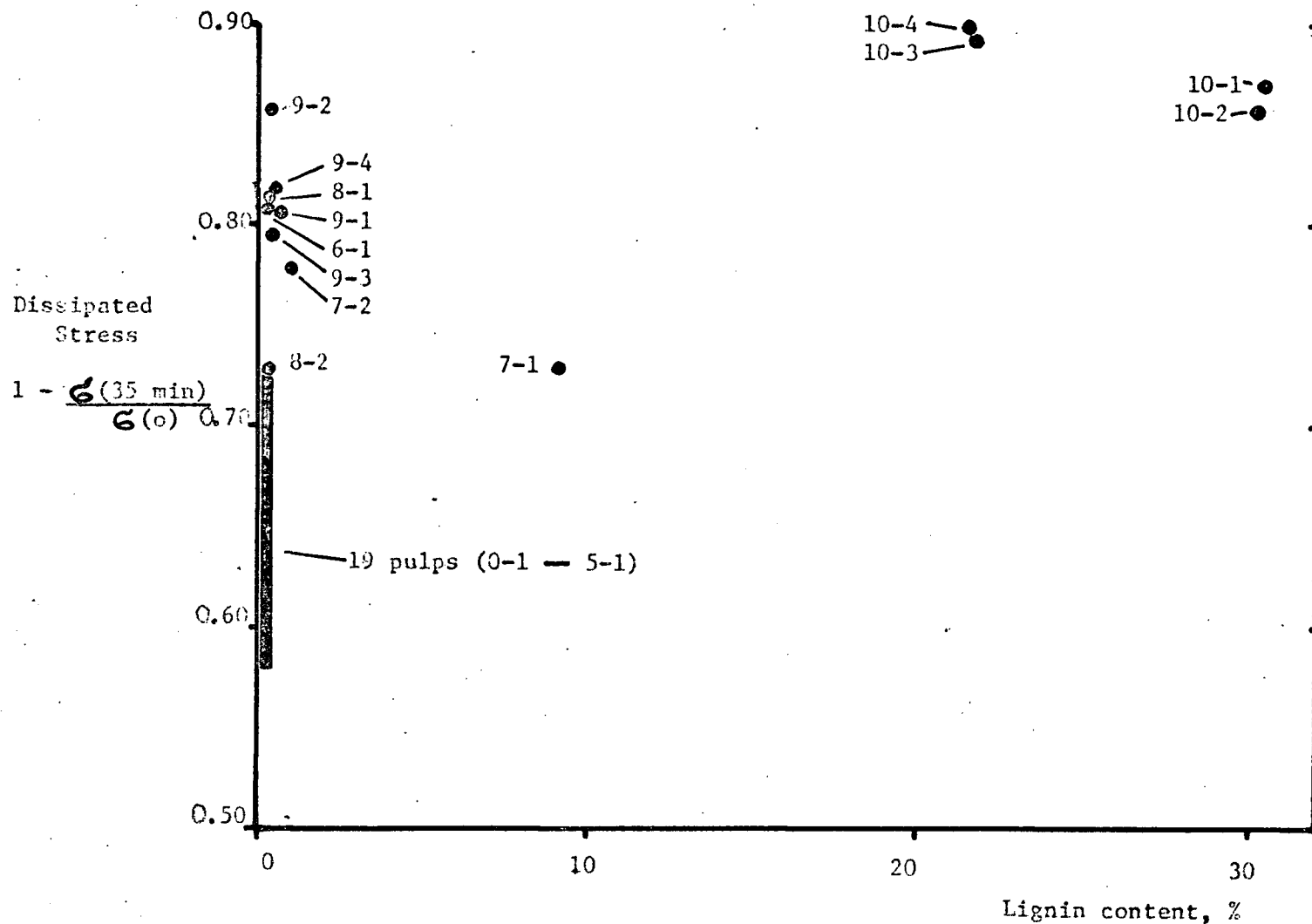


Figure 21. Relationship between fractional stress relaxation ($n = 5$) and lignin contents as observed on caustic steeped (18.6% NaOH) samples of various pulp types after 35 min relaxation time. Code numbers refer to pulps listed in Table 2.

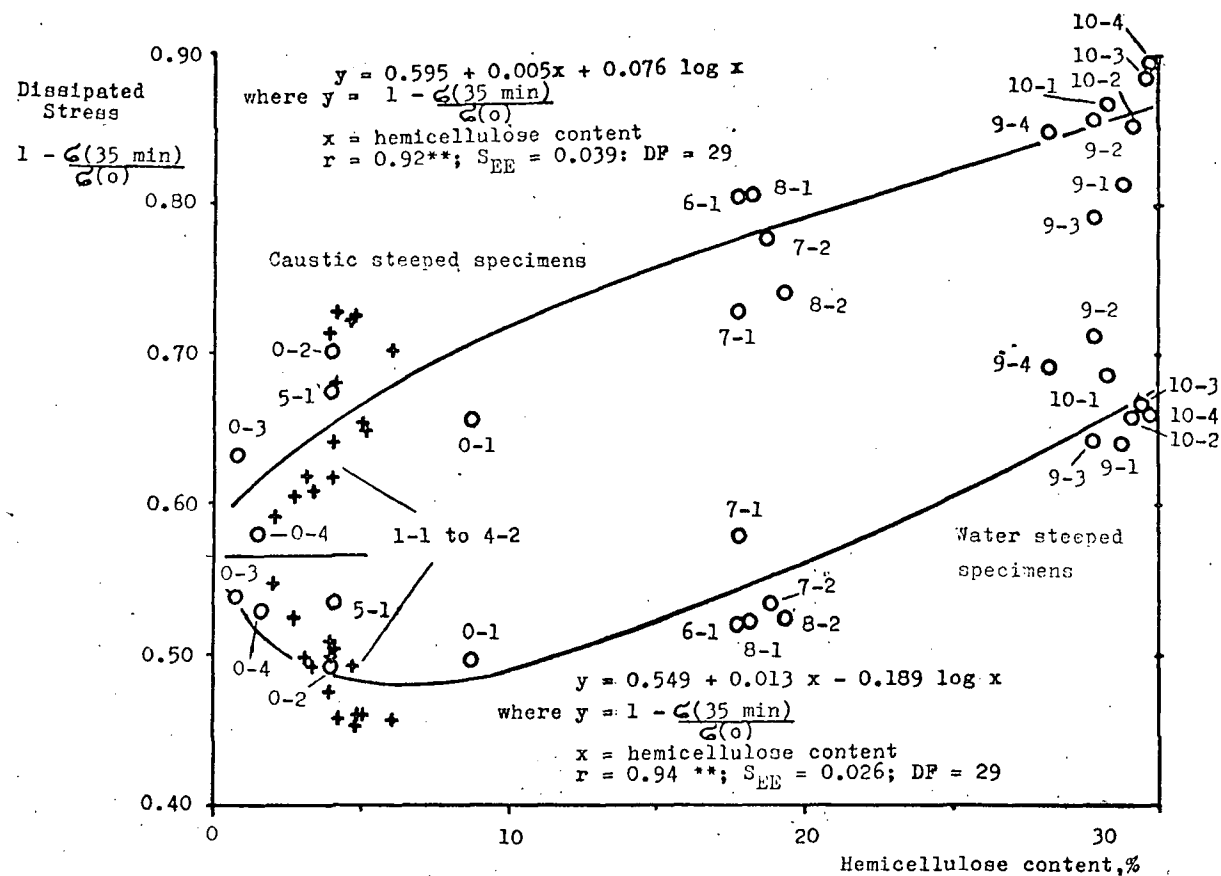


Figure 22. Relationship between fractional stress relaxation ($n=5$) and hemicellulose contents as observed on water and caustic (18.6% NaOH) steeped samples of various pulp types after 35 min relaxation time.

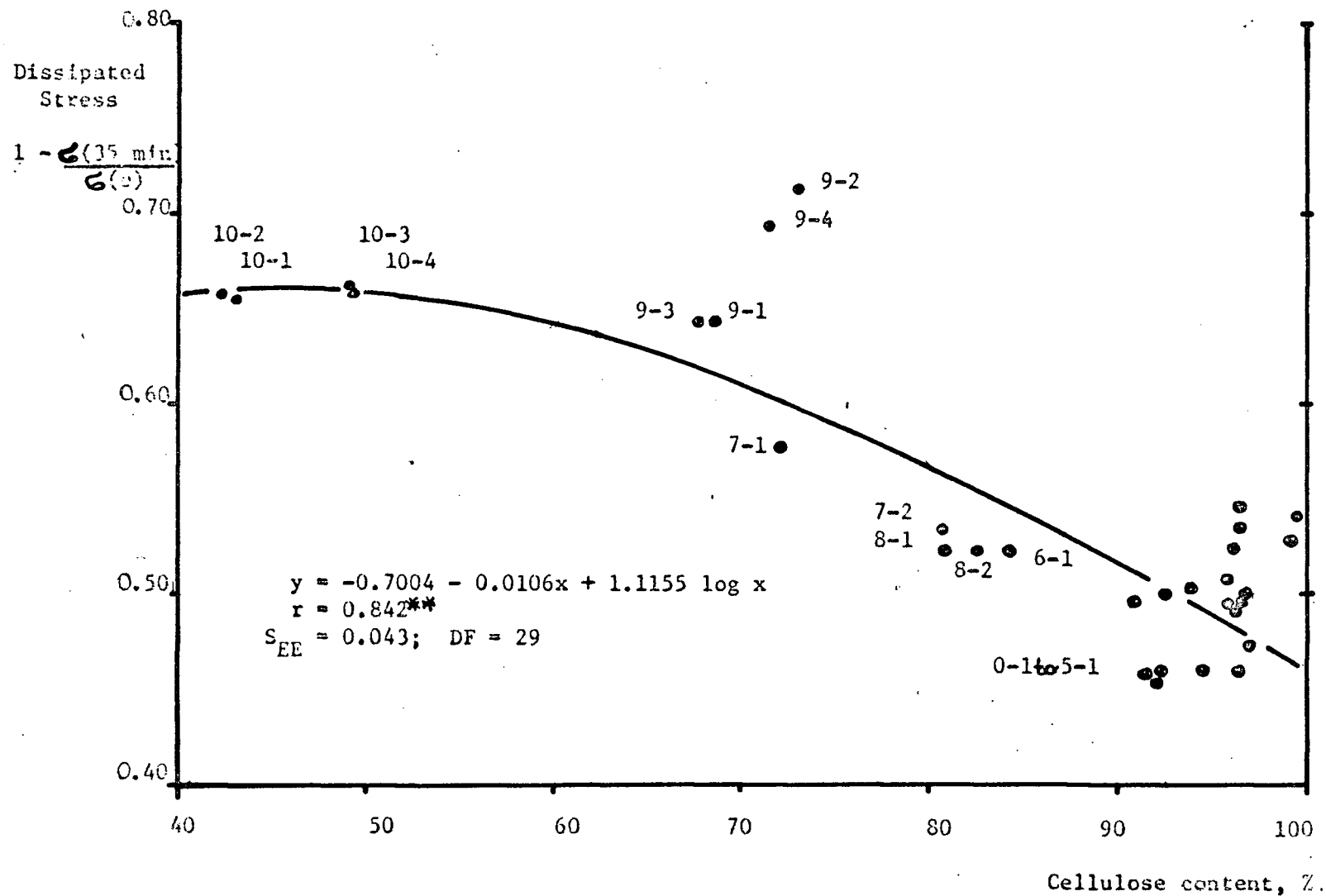


Figure 23. Relationship between fractional stress relaxation ($n = 5$) and cellulose contents as observed on water steeped samples of various pulp types after 35 min relaxation time. Code numbers refer to pulps listed in Table 2.

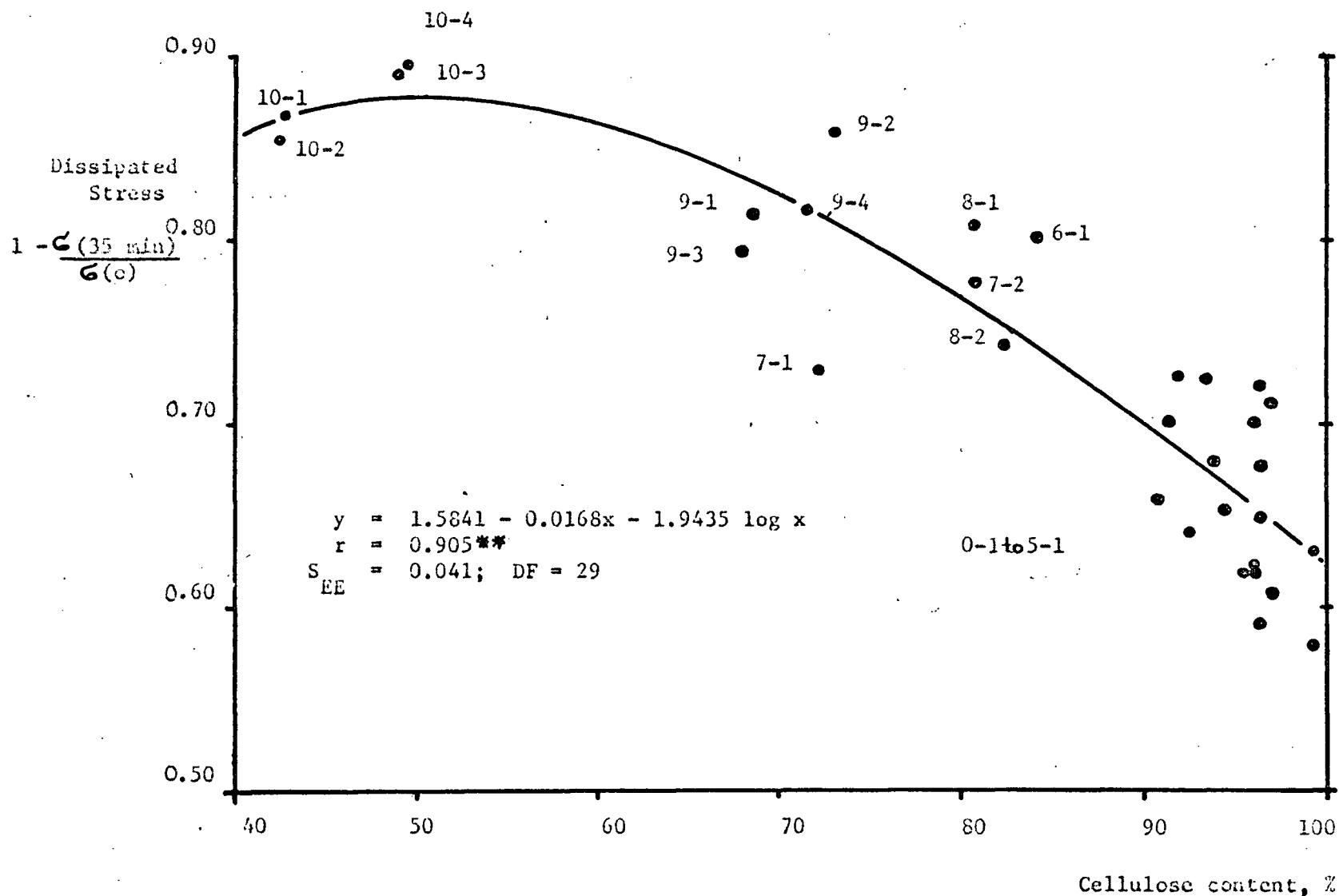


Figure 24. Relationship between fractional stress relaxation ($n = 5$) and cellulose contents as observed after 35 min relaxation time on caustic steeped (18.6% NaOH) samples of various pulp types. Code numbers refer to pulps listed in Table 2.

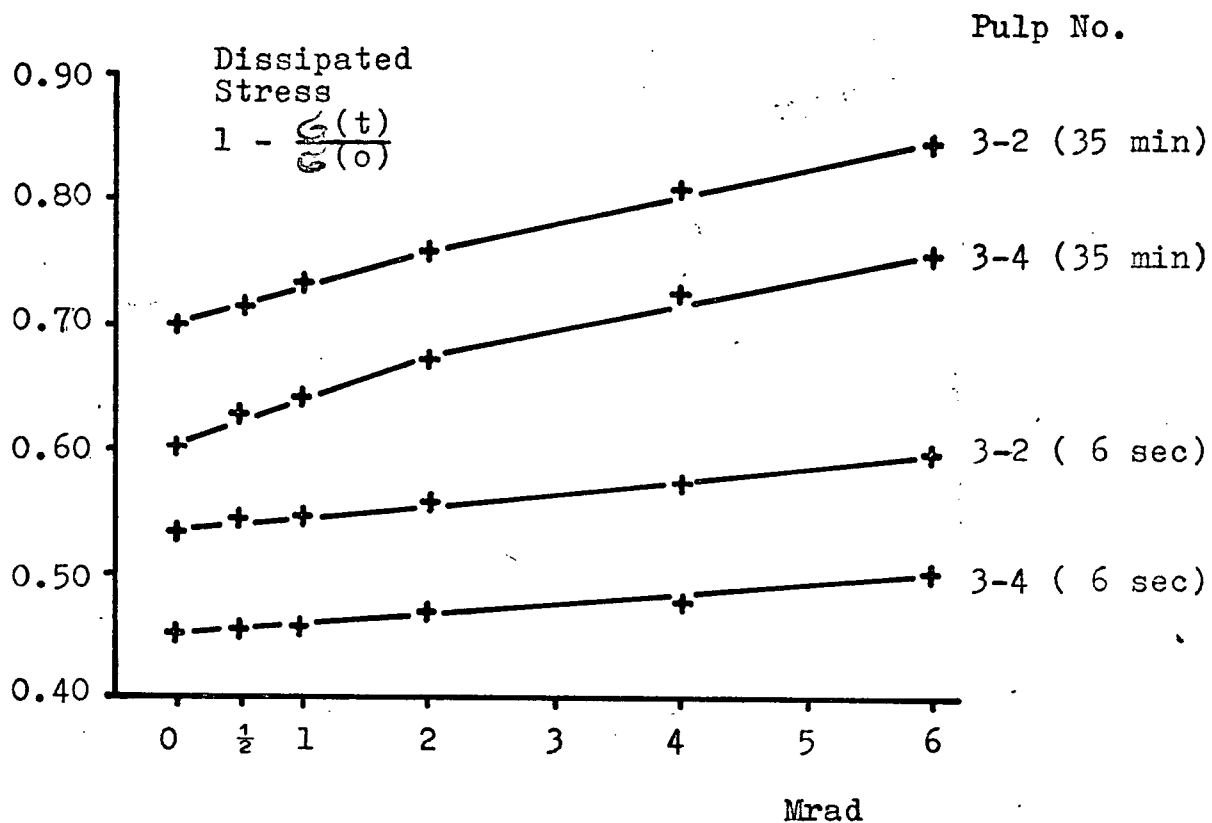


Figure 25. Short and long time response in fractional stress relaxation ($n = 5$) of two viscose pulps exposed (air-dry) to different gamma-radiation levels and then steeped in 18.6% NaOH (30 sec, 22°C).

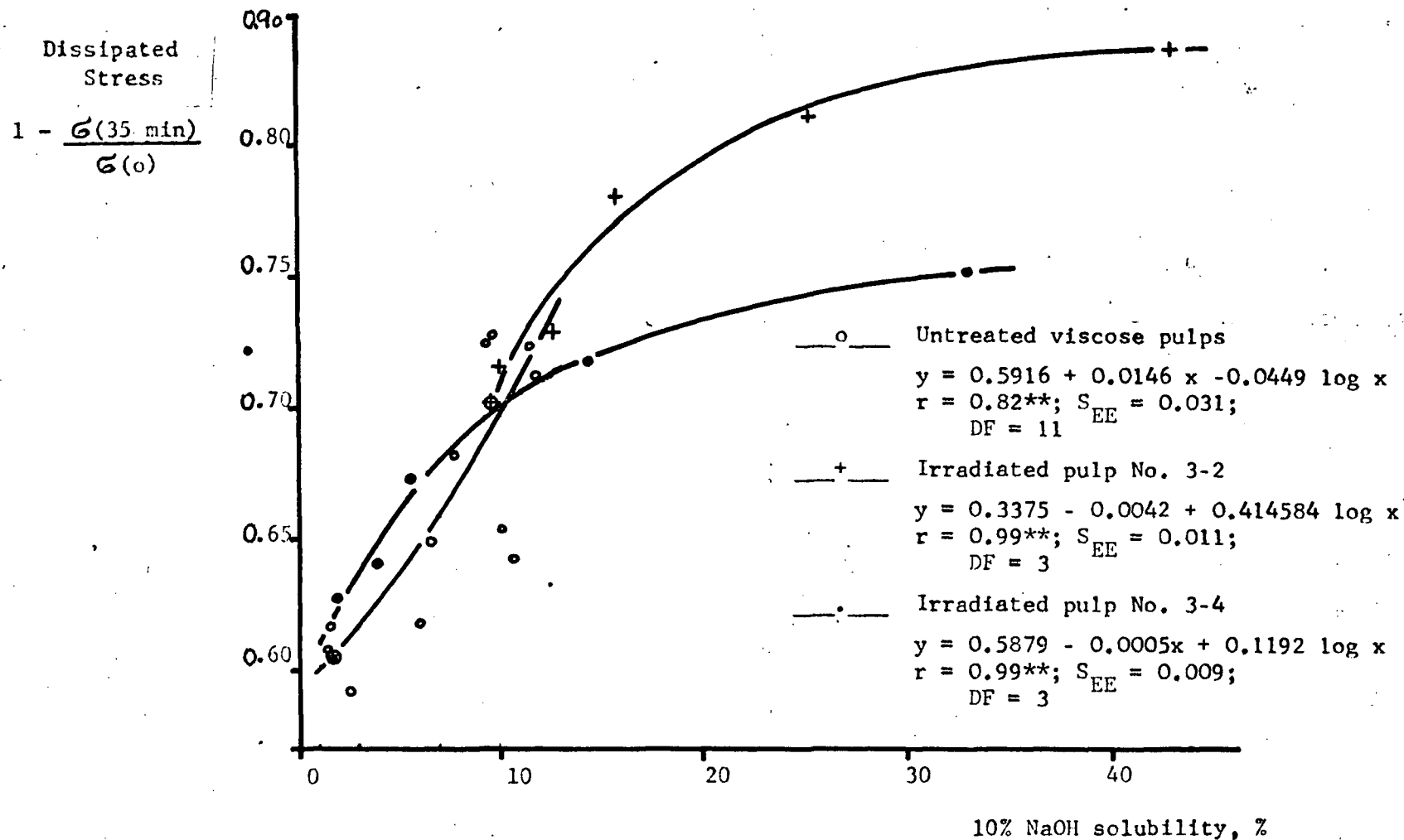


Figure 26. Correlation between fractional stress relaxation ($n = 5$) of irradiated and untreated viscose pulps read after 35 min relaxation time following steeping in 18.6% NaOH and pulp caustic solubility.

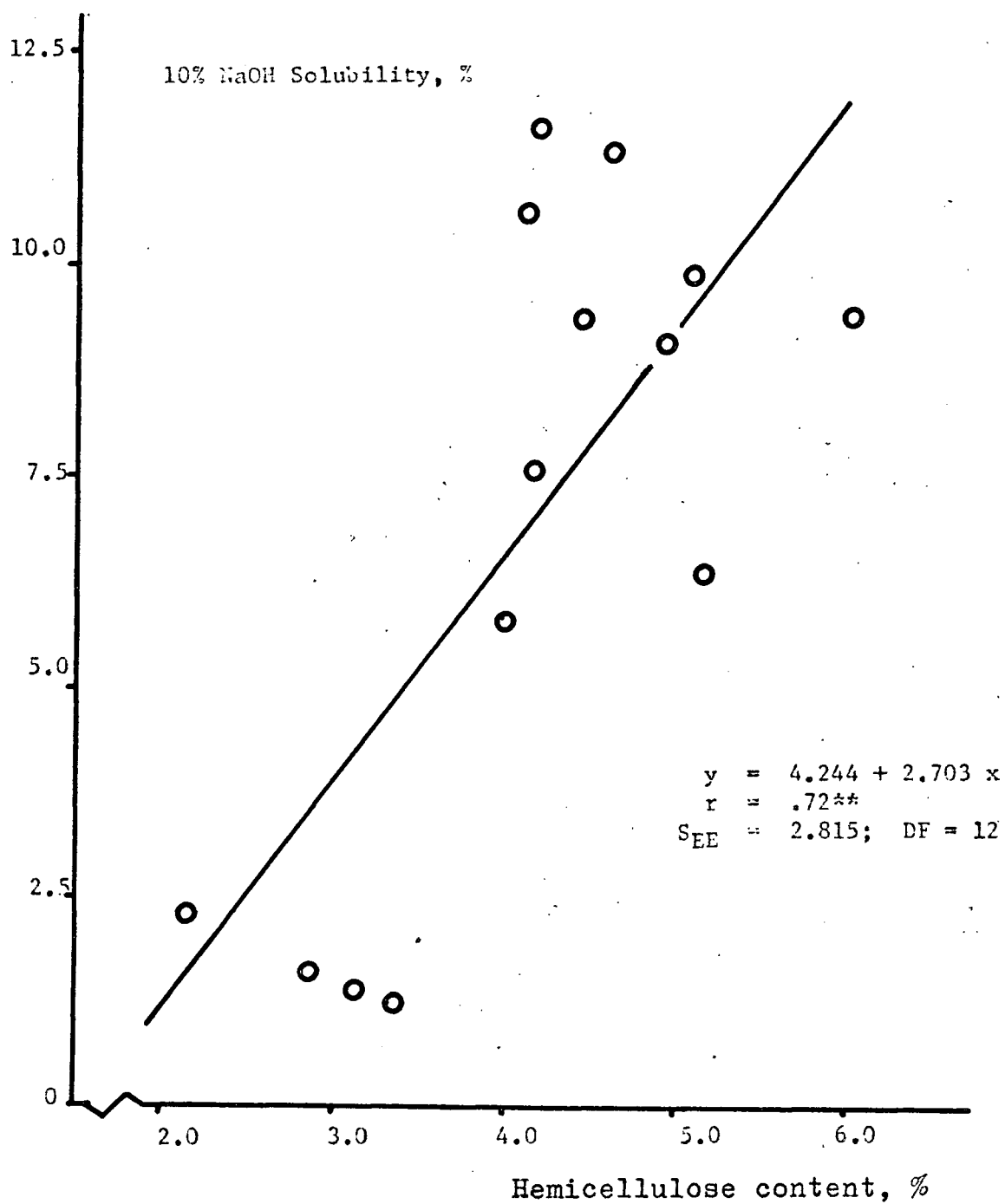


Figure 27. Relationship between caustic solubility and relative amount of hemicelluloses of 14 viscose pulps.

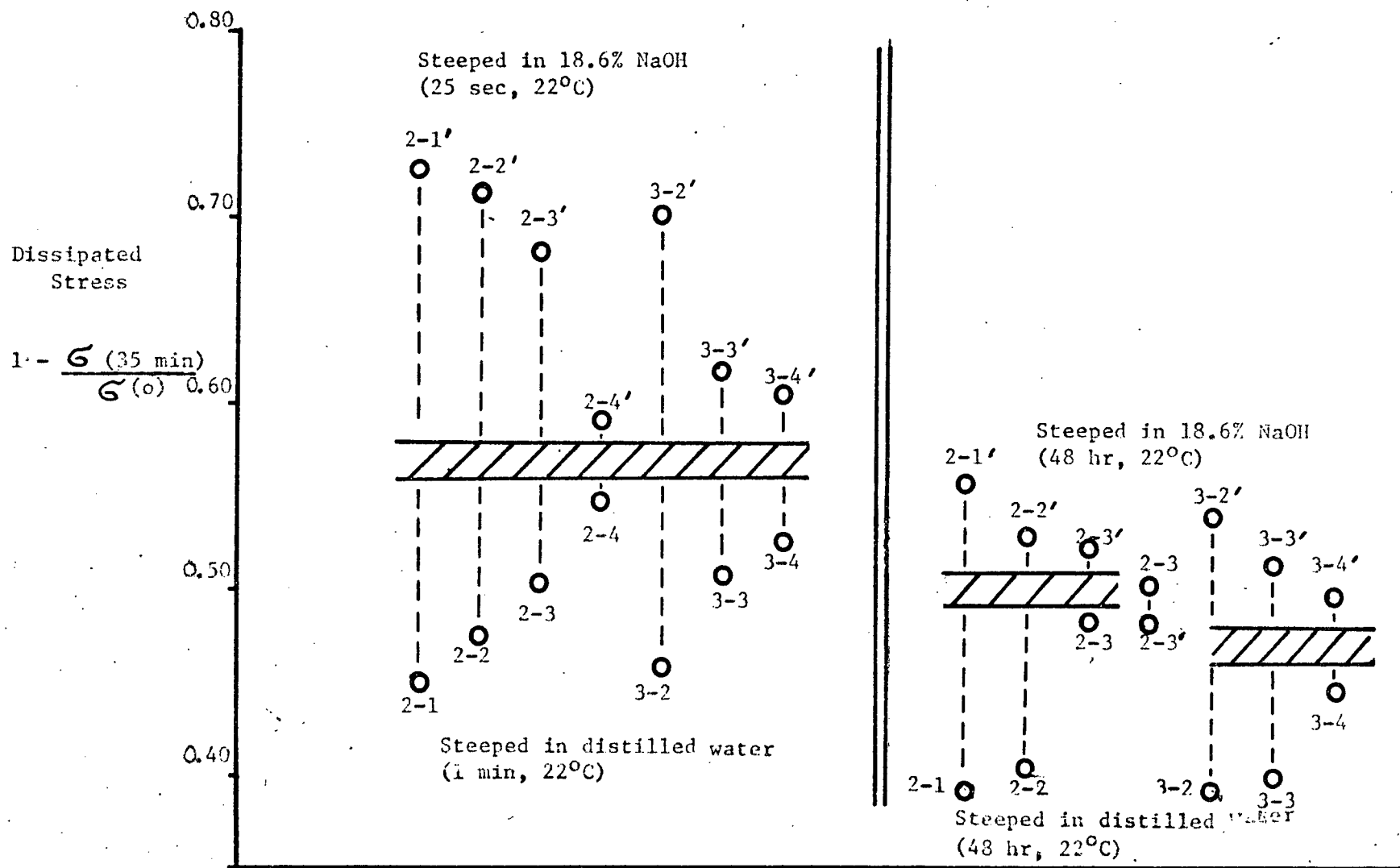


Figure 28. Fractional stress relaxation results ($n = 5$) on seven viscose pulps as read after 35 min relaxation time following short and long time steeping in water or caustic.

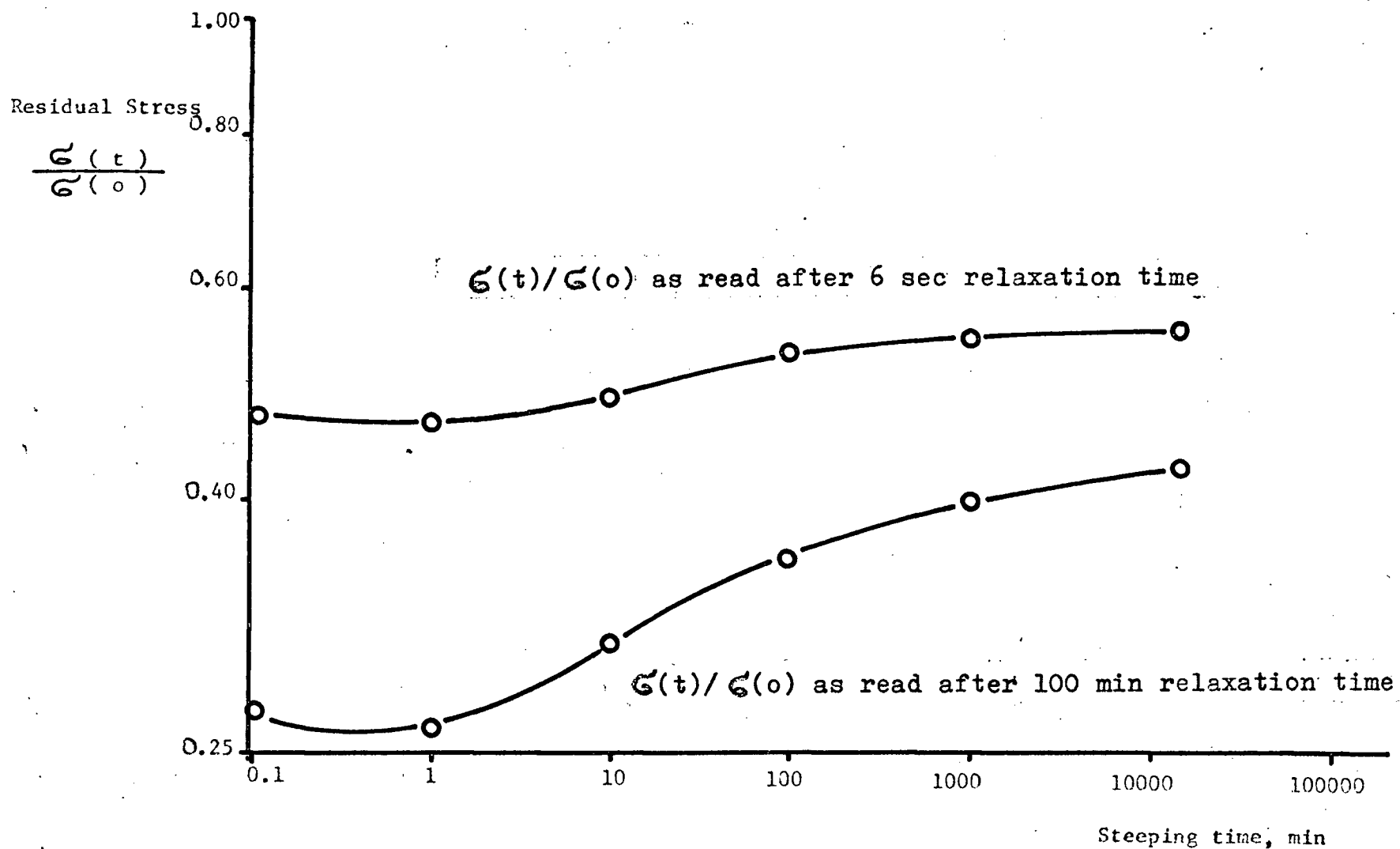


Figure 29. Effect of steeping time in 18.6% NaOH (22°C) on residual stress relaxation (n = 5) of viscose pulp No. 3-2.

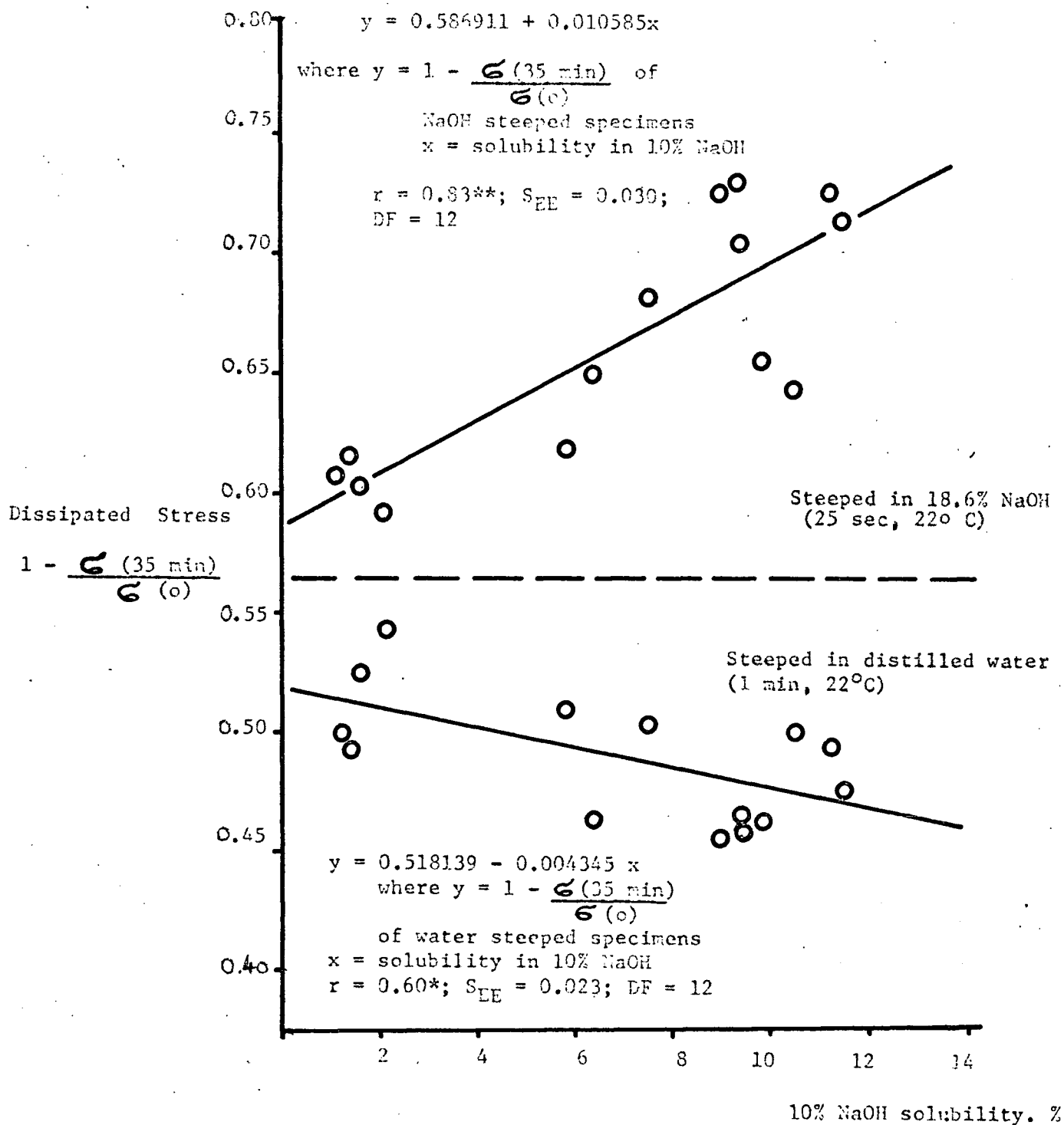


Figure 30. Correlation between fractional stress relaxation ($n=5$) of 14 viscose pulps read after 35 min relaxation time following steeping in water or caustic (18.6% NaOH) and caustic solubility.