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INDUSTRIAL DISPERSING AIDS BASED ON BARK AND WOOD EXTRACTS

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ABSTRACT

The object of this dissertation is to develop a cost effective plasticiser/water-reducer from tannin extracts which does not retard initial strength development. Model compounds of tannins indicated the suitability of substituted phenols for this purpose. Catechol with adjacent hydroxide groups gave a good combination of improved workability with compressive strengths equivalent to the control. Combinations with ammonia and formaldehyde resulted in some greatly improved performances, but also reduced stability of the additives. Urea and metabisulphite did provide some improvements and did not adversely affect shelf life.

Some of the tannin extracts tested on their own gave considerable improvements in workability and some strengths. To improve the stability of extract solutions, tannins were modified with urea, metabisulphite, small amounts of potassium hydroxide and a alcohol mixture used for pretreatment. Only the first two listed were consistently effective without producing any disadvantages. They even further improved the concrete performance of condensed tannins in particular. Small additions of TEA or its acetate salt resulted in better one day strengths of the modified tannins.

Analytical techniques such as infrared and nuclear magnetic resonance were used to monitor some modifications of the tannins and their result. A test representing early hydration conditions and X-ray diffraction provided clues to the additives mechanism in its interaction with cement. The additives performance was evaluated by comparison with a leading plasticiser/water-reducer, an independent concrete testing laboratory and conduction calorimetry by a research and testing council. A tannin based plasticiser made largely from local raw materials was quickly accepted during a recession by brick and precast manufactures.

DECLARATION

I declare that this dissertation is my own work and that any technical assistance has been acknowledged.

It is being submitted for the degree of Master of Science in the University of the Witwatersrand, Johannesburg. It has not been submitted for any degree or examination in this or any other University.

Hanno Kaspar

Hanno Rolf Erich Kaspar

28th of September 1994

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PREFACE

The manufacture of portland cement requires some of the largest plants in industry. It is a very capital intensive venture with high running costs. Increasingly admixtures are added to concrete to improve certain characteristics for a particular application. This means that fewer types of cement can be modified for a variety of purposes.

Tannin extracts have been used for drilling mud applications as have various lignosulphonate salts. The lignosulphonate salts have also been used for decades as cost effective plasticisers/water-reducers for concrete, but have had the disadvantage of retarding initial strength development. The potential application of a tannin based concrete additive means reduced dependency on imports with long transport lines, duties and exchange rates. A plasticiser obtainable from cheap widely available raw materials could for example be made from waste products such as pine bark from sawmills.

Standard concrete tests measuring workability of the fresh mix and compressive strength of the hardening concrete are used to evaluate straight additions and modifications of model compounds and tannin extracts.

Since the concrete tests in this dissertation were conducted over a full year, differences between cement batches and seasonal temperature variations come to effect. A direct comparison of samples from different groups is not possible, but within groups the standard serves as a comparison for the additives performance. In this way trends become apparent which can then be related to one another. Wherever possible, the numbering of tables and figures is the same as the section they refer to.

During the literature survey, some books used a different wording to describe the same chemical action. The words are "sulphonation" for some references or "sulphitation" for others. Both describe the attachment of sulphite or sulphonate (SO_3^{2-}) groups. The descriptions have been kept as they were obtained from their respective source; also in the results and discussion section when referring back to parts of the literature survey. For the experiments conducted the wording "sulphitation" was preferred.

LITERATURE SURVEY

PART 1

1. Cement and Concrete

1.1 General

The term cement is used to designate many different kinds of substances that are used as binders or adhesives. The cement produced in the greatest volume and most widely used in construction is portland cement. There are many other types of cement such as calcium aluminate extensively used for refractory concretes. All these are distinctly different from epoxies and other polymerisable organic materials. Portland cements are hydraulic cements, ie they set, harden and do not disintegrate in water. Therefore they are suitable for construction of underground, marine and hydraulic structures, whereas gypsum plasters and lime mortars are not. In this dissertation the term cement will be confined to inorganic hydraulic cements principally portland and related cements. The essential feature of these cements is their ability, on hydration with water, to form relatively insoluble bonded aggregations of considerable strength and dimensional stability[1].

Cements used for construction have both cohesive and adhesive properties[2]. Cement is used as a binder for bricks, precast units, and/or aggregates (stones and sand). The function of cement is to hold these together to form a rigid structure. The cement itself is unsuitable for load-bearing construction and too costly. This is because cement is structurally unsound, ie it changes its volume in accordance with moisture content and ambient temperatures. Therefore structurally stable materials such as sand and stones have to be incorporated into the mix, as restraining aggregates[2]. It is of utmost importance to keep the thickness of the cement interface between aggregates to a minimum possible for binding action to obtain maximum strength. Here lies the importance of dispersing aids. The aggregates themselves bear the weight of a structural component, for example a wall or a roof. This is due to their high compressive strength (granite: around 200 Mpa) and by interlocking and dispersing structural stresses. The cement holds the aggregates together forming a functional unit[5].

Concrete (latin: concretus "growing together") comprises cement, aggregates and water forming a building unit[3]. It is used for mass construction, load-bearing structural applications such as bridges, pillars, beams, roofing, foundations and harbours together with steel reinforcing. By chance it was found that steel has the same coefficient of expansion as concrete, making it particularly suitable as a means to improve tensile and flexural strength of concrete. This strength is about on tenth of compressive strength. The concrete bonds to the steel and protects it from corrosion, particularly when it is waterproof[1]. Other applications include foundations, roads, runways, water canals,

flooring and prefabrication of units such as cementitious bricks, paving tiles, wall panels, lintels, etc. the latter two are also reinforced with steel wire frames. Recently polymer fibres, such as polypropylene, have been used more extensively as reinforcing in the form of short fibres[9]. Mortar is made by adding cement, sand and water forming a paste. This cementitious dough-like mass is used with bricks, made of clay or cement, for housing, walls or precast applications.

1.1.1 History

The use of some material to cement small stones into a solid mass dates from antiqity. In Babylonia and Assyria clay mortar was used as a binder for building units. The Egyptians used lime and gypsum mortars for building structures such as pyramids[10]. Greeks and Romans used calcined limestone, later adding sand and stones or bricks and broken tiles. Th.. was the first concrete in history. However, lime (calcerous) mortar does not harden under water[2].

The Romans were first to discover hydraulic cement as we know it today. They found that quenched ground .ava, mainly silica originating from molten igneous rocks, mixed with calcined (burnt ie "hot") lime from chipped marble (named "caementum") and water gave a paste that hardened ; ie. a mortar[5] The lava was suddenly cooled when it entered the sea, preventing crystallisation and forming pozzolans (named after the village Pozzuoli near Vesuvius). The added lime gave the paste cementitous properties. Pozzolans contain reactive silica and alumina. The alumina reacts with hot lime and water by combining with the calcium hydroxide formed by the hydration of calcium silicates to produce additional calcium silicate hydrate ; while the silica similarly reacts with cement and water resulting in the same products[1,2].

This cement enabled the Romans to build harbours[11] and become a sea-faring nation. Ostia, to name one, was completed by Emperor Claudius in AD 52[5]. Now the Romans were able to conquer territories surrounding the mediterranean sea. Only much later in the 18th century further progress was made. John Smeaton of England found that the best mortar was produced when pozzolana was mixed with limestone containing a high proportion of clayey matter. By recognising the role of clay, until then considered undesirable, Smeaton was the first to understand the chemical properties of hydraulic lime[2]

Demand for cement in the United States in the 19th century led to process improvements in the calcination of certain (argillaceous) limestones for the manufacture of natural cements. The demand led to its gradual displacement by portland cement. This cement was so named by Joseph Aspidin in a 1824 patent because of its resemblance to a limestone quarried at the Isle of Portland in England[1].

This portland cement was prepared by heating a mixture of finely divided clay and hard limestone in a furnace until all CO_2 had been driven off. The temperature was much lower than that necessary for clinkering. The prototype of modern cement was made in 1845 by Isaac Johnson who burnt a mixture of clay and chalk until clinkering, so that the reactions necessary for the formation of strongly cementitous components took place. The name portland cement remains to this day to describe a cement obtained by intimately mixing together calcerous and argillaceous, or other silica, alumina and iron oxide-bearing materials, burning them at a clinkering temperature and grinding the resulting clinker. This is the definition of the current British Standard (B.S.12:1958) which stipulates also that no materials other than gypsum and water may be added after burning[2].

Research conducted in many parts of the world since then has provided a fairly clear picture of the composition, properties and fields of stability of the principal systems found in portland cement[1].

1.1.2 Portland Cement Types

Portland cement is made from raw materials recovered mainly in open-cast mines and often extended with undesirable industrial byproducts. Ordinary portland cement, the most widely used and basis of blended portland cements which are in widespread use, is made mainly of the following raw materials in varying proportions, depending on composition and physical properties of a suitable clinker to be obtained [2] and geographical location of the cement factory[5] :

Calcerous : limestone or chalk (mainly $CaCO_3$, etc)
Argillaceous : clay or shale (SiO_2, Fe_2O_3, etc)

These two materials, one rich in lime the other rich in silica, are carefully proportioned[2].

The process of manufacture of portland cement consists essentially of grinding the raw materials, mixing them intimately in certain proportions and burning them in a large rotary kiln at a temperature of approximately 1400°C when the material sinters and partly fuses into balls known as clinker. The mixing and grinding of the raw materials can be done either in water or in a dry condition, hence the names "wet" or "dry" processes. After burning the clinker are rapidly cooled to prevent crystallisation. These glassy clinkers are then ground to a controlled fineness to obtain cement, which is a powder of greyish appearance. Before the grinding process about 5% of raw gypsum is added to regulate the setting time of the cement and to enhance strength development. The purpose of milling is to provide the necessary large surface area for subsequent hydration of cement which results in its hardening[2].

During clinkering the raw materials react chemically to form hydraulic calcium silicates, aluminates, aluminoferrite and other compounds which modify to some extent the hardening and setting properties of cement. These mineral constituents of portland cement are different from those existing in the raw materials [7] ! There are other processes for cement manufacture. In one gypsum is used instead of lime together with clay, coke with sand and iron oxide, burnt in a rotary kiln the end products being portland cement and sulphur dioxide which is further converted into sulphuric acid[2]. Ordinary portland cement (OPC) is suitable for use in ordinary concrete construction when there is no exposure to sulphates[1].

Portland cement is a mineral mixture, the chemical composition being described by the quaternary system : CaO-SiO_2-Al_2O_3-Fe_2O_3 [5]. This system does not take into account other elements which are present in smaller concentrations , but which may be of considerable importance.

Table 1 Range of composition[12], in percent by weight, of portland cements

Oxides	content (%)
CaO	60-67
SiO_2	17-25
Al_2O_3	3-8
Fe_2O_3	0.5-6.0
MgO	0.1-4.0
alkali	0.2-1.3
SO_3	1-3
ignition	2
residue	0.5

[loss on ignition : extent of carbonation and hydration of the free lime and magnesia, due to the exposure of cement to the atmosphere ; B.S.12:1958 limits it up to 4%]
[insoluble residue : in concentrated HCl, due to impurities in gypsum ; B.S.12:1958 limits it up to 1.5%
alkali : such as Na_2O and K_2O]

Empirical moduli were introduced many years ago in attempts to provide a clear definition of chemical composition for factory control[5]. The most significant is the hydraulic modulus. It is given by :

$$\frac{CaO + MgO + \text{alkali}}{SiO_2 + Al_2O_3 + Fe_2O_3}$$

Experience has shown that a ratio of 2:1 of alkali to acidic constituents provides the best results ; it should be at least 1.7:1. This module in particular has proved to be of practical assistance in estimating the suitability of a particular raw mix composition [2]. The raw materials are so chosen that it is at all times possible to obtain, in a technologically simple manner, a blend which will result in a cement having a composition falling within the prescribed limits, see Table 2.

The abbreviations commonly used in cement chemistry include[1] :

$CaO = C$	$SiO_2 = S$	$Al_2O_3 = A$	$Fe_2O_3 = F$	$MgO = M$
$Na_2O = N$	$K_2O = K$	$H_2O = H$	$SO_3 = \overline{S}$	$CO_2 = \overline{C}$

The use of this notation and in table 2 does imply that the oxides exist as such in the structure of cement compounds. C_3S, for instance, is the cement chemist's notation for $(CaO)_3 + (SiO_2) = Ca_3SiO_5$ ie tricalcium silicate.

Table 2 Range of compounds formed during portland cement manufacture[5]

Compound	Formula	% by weight
C_3S	3CaO.SiO	35-55
C_2S	2CaO.SiO	20-40
C_3A	3CaO.AlO	5-12
C_4AF	4CaO.AlO.FeO	5-10
M	MgO	0.3-4.0
___	gypsum *	4-7
___	CaO (free lime)	0.5-2.5 #

* impurities, mainly $CaSO_4.2H_2O$

\# applies to clinker

C_4AF is really a solid solution ranging from C_2F to C_6A_2F but the description is a convenient simplification [13]. C_2S can exist in four crystalline forms, each with its own hydration characteristics[14, 15]. The beta-C_2S is the predominant form of C_2S and the inert gamma-C_2S has also been detected in portland cement[16]. Similarly other phases denoted above are also approxomations of composition and structure, which are nevertheless of real value in correlating cement properties. In addition to the compounds shown South African portland cements contain small quantities of sodium, potassium and traces of titanium, manganese and phosphorous.

Over the years there has been some changes in the characteristics of ordinary portland cement[17]. In particular, modern cements have a higher C_3S content and a greater fineness that 40 years ago but there has been no significant change in the quality of cement for a number of years. As a consequence, cements nowadays have a 28 day strength, but the gain in strength between 28 days and 10 years is unaltered ; approximately 20 MN/m^2 for continuously water cured concrete with a water/cement ratio of about 0.53[18].

Rapid hardening cement (RHC) is similar to ordinary portland cement (OPC) in composition and manufacture (also covered by B.S.12:1958 and SABS 47 '), but develops higher early strength ; see fig.1. It is ground much longer than OPC to obtain a greater fineness for increased reactivity. The rate of hardening must not be confused with the rate of setting, in fact, both cements have similar setting times. Setting occurs when the dough-like hydrated paste stiffens. From this stage the paste hydrates further developing strength. The strength developed by RHC at the age of three days is of the same order as the seven day strength of OPC with the same water/cement ratio. The increased rate of gain of strength of RHC is achieved by a higher C_3S content and by finer grinding of the cement clinker. This results in higher production costs : higher energy requirements, greater wear and tear of expensive rotary mills and increased production time. OPC occupies well above $225m^2/kg$ whereas RHC usually does above $325m^2/kg$, as prescribed by B.S.12:1958[3].

The requirements for soundness are the same as for OPC (eg ASTM C-151)[19]. A set cement paste is said to be sound if it does not undergo a large change in volume. An appreciable expansion under conditions of restraint could result in disruption of the hardened cement paste, making it unsound. The cause : free lime CaO, periclase (crystalline) MgO, gypsum $CaSO_4$ added in excess during manufacture undergo a delayed hydration. Slaked (hydrated) lime occupies almost twice the volume of free lime ; this is the principle of expanding grouts (used for demolition). Periclase MgO acts similarly while excess gypsum reacts with C_3A during setting[3].

The use of RHC is indicated where a rapid strength development is desired, for example, when formwork or moulds are to be removed early for re-use, or where sufficient strength for further construction is wanted as quickly as possible. Since rapid gain of strength means a high rate of heat development, RHC should not be used in mass construction or in large structural sections. On the other hand for construction at low temperatures RHC may prove a satisfactory safeguard against frost damage[3].

Portland cement is also intergroun: with other suitable materials such blast-furnace slag, flyash and fumes ; all of which are variable in composition. these substances show hydraulic activity when used with cements and the blended cements[20] bear special designations such as portland blast-furnace cement (PBFC).

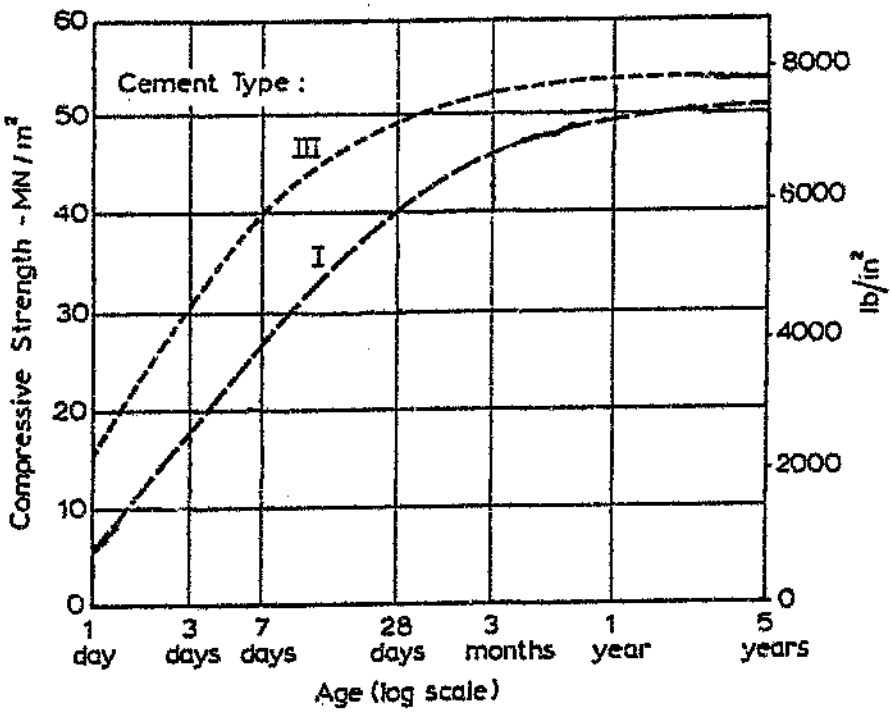


Fig. 1 Strength development of concretes with a water/cement ratio of 0.49 made with OPC (I) and RHC (III)[21]

Slag is a waste product (5000 t\day) from ISCOR's (Iron and Steel Corporation in South Africa) blast-furnaces. It contains a mixture of silica, alumina, lime and some flux. These oxides are reminiscent of those used to make OPC, but not in the same proportions. The slag, tapped as a molten stream at 1400-1500°C, has to be quenched so that it solidifies to a glass[5]. During this rapid cooling by water the material fragments into a granulated form. In this form slag can be used as a raw material, interground with limestone and some gypsum for the conventional manufacture of portland cement.

Alternatively it can be milled separately to the same fineness as the cement and blended with portland cement, as a partial replacement thereof, at a mixing plant. By either method the limestone or cement[5], serves to activate the slag, that is to accelerate the rate of strength development of the latter. Granulated blast-furnace slag is not ordinarily reactive with water, but in the presence of hot lime reactions occur with the silica framework. This break down of slag releases other components so that a variety of crystalline hydrate phases can also form.

The composition of slag varies considerably but usually falls within the following composition ranges[1] :

CaO	40 - 50%	MgO	0 - 8%
SiO_2	30 - 40%	S (sulfide)	0 - 2%
Al_2O_3	8 - 18%	FeO, MnO	0 - 3%

The chemical composition of local slags is unlike those of other origin as can be seen, for instance, by the different chemical requirements of SABS 526 and B.S.146-1958. Research undertaken in Germany and South Africa by Dr Elsener von Gronow and Dr Nico Stutterheim (CSIR) showed that a higher ratio of MgO:CaO as found in the South African dolomite is also acceptable[22].

Blast-furnace slag cements[23] improve economy, workability of the fresh concrete, reduce delitrious alkali-aggregate reactions[24] and can be resistant to sea water if the slag and cement compositions are suitably restricted. PBFC is similar to OPC and the B.S.146:1958 and SABS 471 requirements for fineness, setting times and soundness are the same. Both the blended and intergreund type hydrate and harden slower than OPC. This can be an advantage in mass concrete structures (it should then comply with B.S.4246:1968) where the lower rates of heat liberation may prevent excessive temperature rise, but when used at low temperatures the rate of hardening can be extremely slow. PBFC may be used to advantage in steam cured products, particularly precast, which develop strengths higher than OPC during the first 28 days. Although PBFC's fineness tends to be higher than OPC, the rate of hardening is somewhat slower, under ambient conditions, during the first 28 days and adequate curing is therefore of importance. The strength requirements of B.S.146:1958 are therefore lower than for OPC, for SABS 471 they are the same. However at later stages there is little difference between the strengths of PBFC and OPC[2,5]. Fig. 2 shows typical strength-time curves.

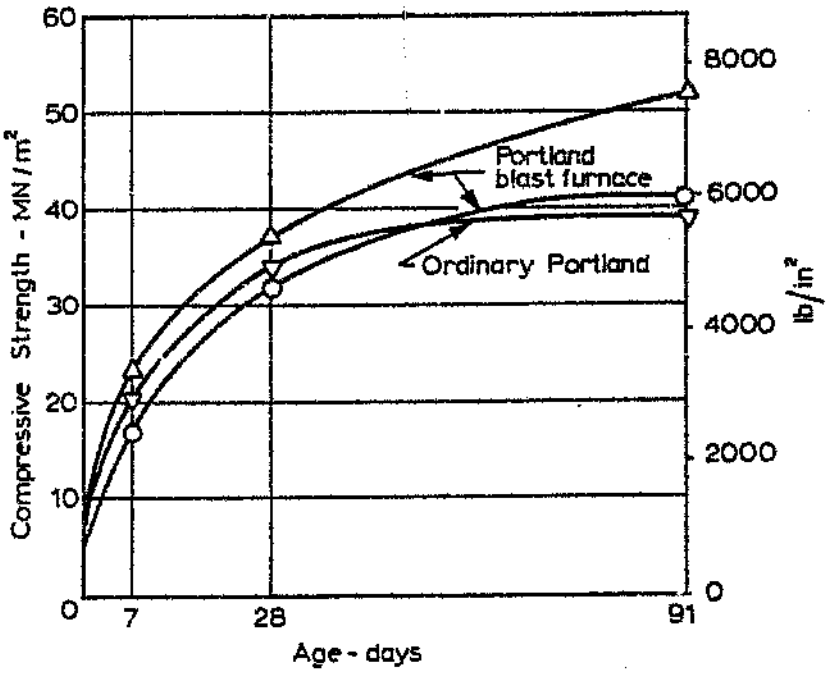


Fig. 2 Strength development of concretes made with OPC and PBFC, water/cement ratio = 0.6[25]

The pattern of low early and high late strength agrees with the influence of the initial framework of hardened cement on the ultimate development of strength : the more slowly the framework is established the denser the gel and the higher the ultimate strength (compare with fig. 1). Nevertheless significant differences in the important physical properties of cements of different types are found only in the earlier stages of hydration[26]. In well-hydrated pastes the differences are only minor.

When compared on a equal compressive strength basis, the flexural strength of concretes made with slag containing portland cement are already higher at seven days than corresponding concretes made with OPC. The higher shrinkage of the former is offset by this higher tensile strength in structural applications, providing resistance to cracking. PBFC also have a higher inherent resistance to chemical attack, for example to sulphates due to the low aluminate content of slag and C_3A content of the lower amount of portland cement[3].

Interground slag typically compromises 15% of the cement content, PC 15SL , complying with SABS 831 part I:1966 (B.S.146:1958 allows up to 65%). Slag can also be used together with lime as a raw material in the conventional manufacture of portland cement; in America the relevant standard is ASTM C595-72. PBFC is also used in Germany under the name "Eisenportland" (up to 30%) and "Hochofen" cements (31 to 85% slag). The physical properties of this cement are much the same as OPC and it is equally suitable for all normal construction purposes. The slag content can be as high as 30%[3].

Cemsave of South Africa uses the Slagment process, where the dry-ground granulated slag is added at the mixer as a partial replacement of portland cement ; PBFC is thus manufactured in situ. Portland cement/slag blends are usually proportioned 50/50 or over 50% of slag. The higher the amount of slag in blends the more the concrete becomes susceptible to inadequate curing, compared to the interground type. These high proportions of milled slag mixed with portland cement as activator improve the workability of the fresh concrete compared to the lower slag content of the intergound type, or OPC with the same water/cement ratio and aggregate content. This difference in behaviour is probably due to the difference in particle size distribution achieved by separate grinding (granulated slag is harder than portland cement clinker) as against intergrinding of the constituents. The difference in hardness of granulated slag and portland cement clinker has caused problems when intergrinding the components. Therefore they are generally ground separately and blended afterwards[5,1].

Flyash obtained from ESCOM's (Electricity Supply Commission in South Africa) power stations is also a waste product. It is a fine dust which is electrostatically precipitated in the chimneys of the coal fired boilers. This artificial pozzolan contains silica, alumina and ferric oxide ; together they should make up 70%. A more formal definition and tests on chemical activity are given in ASTM C618-72. ASTM C595-72 limits the pozzolana

content to between 15 and 40% of the weight of portland-pozzolana cement[27]. The silica reacts with the lime (liberated by the hydrating portland cement) in the presence of water to form stable calcium silicates which have cementitous properties. The flyash particles are spherical, which is advantageous from the water requirement point of view, and are approximately of the same fineness as portland cement. Considering pozzolans in general, one should note that it has to be amorphous as crystalline silica has very low reactivity. The rate of hydration and strength development of portland cement/flyash (PCFA) is synonymous to PBFC, except that lean mixes only surpass the OPC in compressive strength after three months[3,5].

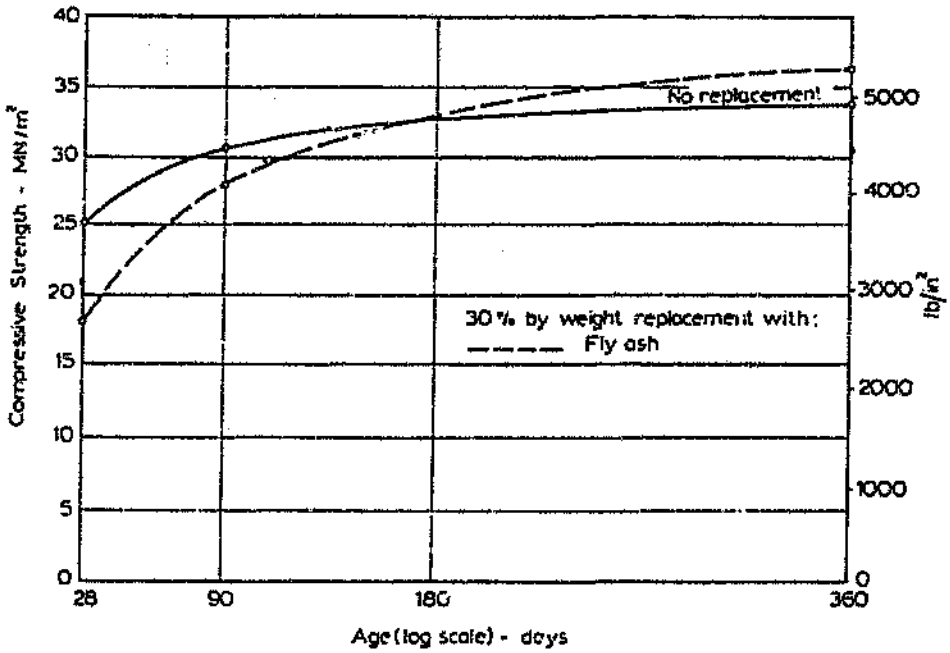


Fig. 3 Effect of partial replacement of portland cement by flyash on the strength development of concrete made with 167 kg cement material per cubic of concrete [28]

PCFA's characteristics and consequently applications are similar to PBFC. They are however slower in hydration but more resistant to destructive agents. Due to the continuing formation of hydrates, filling the pores and the absence of free lime which could be leached out partial replacement of portland cement by pozzolana reduces the permeability of the concrete up to seven to ten times[3].

Silica dust "fumes" is precipitated similarly to fly ash. It forms a waste product in the arc refining process of chrome in Siemens-Martin smelting ovens. Fumes also consist of a dust like fine powder (less than 0.25 mm). They are analogous in composition to fly ash being classified as artificial pozzolans. Correspondingly they are blended with portland cement resulting in a material with comparable characteristics, uses and applications[5].

All South African portland cements comply with the relevant South African (OPC : SABS 471:1959) and British standard specifications. These cements can also be regarded as complying with the requirements of the American Society for Testing Materials (ASTM C150-56) and U.S. Federal specifications for ordinary and rapid-hardening portland cements. Tests on South African cements have shown that they also comply with German and Swiss specification requirements[5].

Current interest in the use of blended portland cements is stimulated by energy conservation, rising cost of portland cement, solid waste utilisation and technological considerations[1]. Portland cements are manufactured to comply with the specifications established in each country[29]. In the United States several different specifications are used, those of ASTM, American Association of State Highway and Transportation Officials and various government agencies. The ASTM annually publishes test methods and standards[19] which are established on a consensus basis by its members, including consumers and producers. Portland cement is classified in five general types designated by ASTM C150-76. Chemical composition, physical and performance test requirements are specified for each type.

To summarise this chapter and provide a preview of the next :

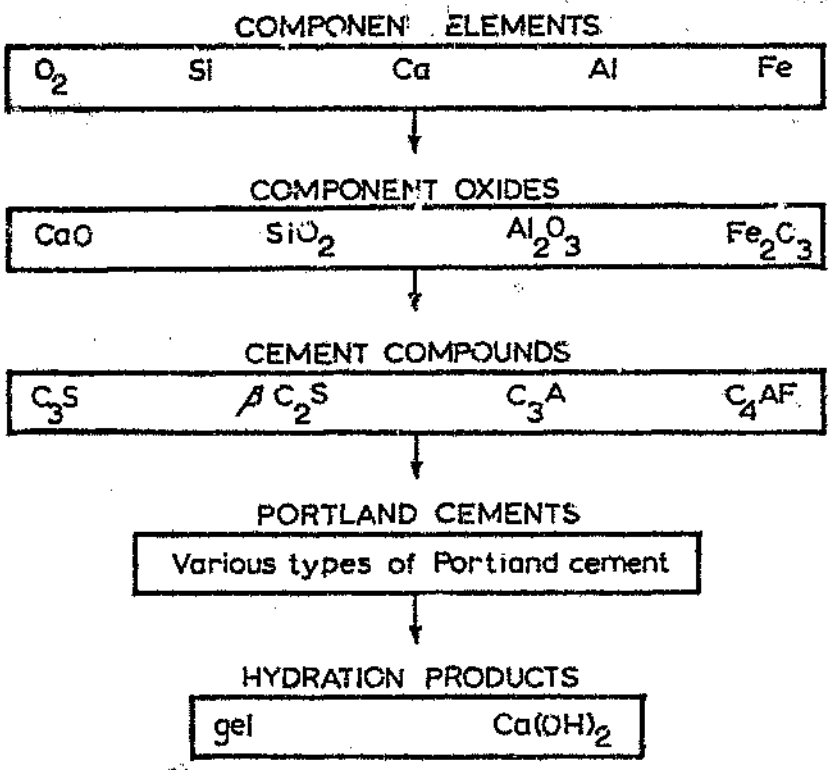


Fig.4 Schematic representation of the formation and hydration of portland cement[2]

1.1.3 Hydration of Cement

If there remains much to be learnt regarding the constitution of portland cement it is obvious that our knowledge of the system cement and water is even less complete. The reactions by virtue of which portland cement becomes a bonding agent takes place in a water-cement paste. In other words in the presence of water, the silicates and aluminates listed in Table 2 form products of hydration, which in time produce a firm and hard mass - the hardened cement paste.

There are two ways in which the compounds of the type present in cement may react with water. In the first a direct addition of some molecules of water takes place ; this being a true reaction of hydration. The second type of reaction with water is hydrolysis. It is convenient and usual, to apply the term hydration to all reactions of cement with water, ie to both true hydration and hydrolysis[5].

Early research indicated that the compounds in hydrated cement were those resulting from the independent reactions of the particular constituents with water. The assumption that "the reaction of portland cement and water was essentially the sum of reactions of the individual constituents " received considerable support from later investigations [31,32] and is still the basis of the dominant conception of cement hydration. There is evidence that during hydration a degree of interaction between the clinker compounds takes place, but the significance of such interaction has not been established. Similarly the products of hydration may influence one another or may interact with other compounds of the system[5].

In consequence research has been largely confined to studies of the systems : $CaO-SiO_2-H_2O$, $CaO-Al_2O_3-H_2O$ and $CaO-Al_2O_3-CaSO_4-H_2O$. The physical behaviour of cement during hydration is similar to that of the two calcium silicates alone[33]. From the study of literature it would seem that C_3S and $B-C_2S$ (the dominant form of C_2S), reacting independently with water, yield the same end products, consisting of calcium hydroxide and calcium silicate hydrates (CSH gel)[34], which are composed essentially of $3CaO.2SiO_2.3H_2O$ but may contain $2CaO.SiO_2.2H_2O$ or other compounds of less definite lime:silica ratios. The calcium silicate hydrate layers are bonded together by excess lime and interlayer water to form individual gel particles only 2-3 layers thick. Surface forces and excess lime on particle surfaces tend to bond these particles together into aggregations or stacks of individual particles to form a porous gel structure of low compressive and flexural strength[1,2].

On addition of water the cement hydrates with heat evolution forming crystals and gels. Based on the assumption that the silicate hydrate is compromised of essentially of $C_2S_2H_3$ and calcium hydroxide, the following equations[35] may be written :

$$2Ca_3SiO_2 + 6H_2O = Ca_3(SiO_2)_2(H_2O)_3 + 3CaO(OH)_2$$
$$2Ca_2SiO_2 + 4H_2O = Ca_3(SiO_2)_2(H_2O)_3 + CaO(OH)_2$$

These are the main reactions in portland cement since the two calcium silicates constitute about 75% of the cement. Thus on a weight basis both silicates require approximately the same amount of water for their hydration, but C_3S produces more than twice as much $Ca(OH)_2$ as C_2S. The above equations are over-simplified, since recent research has shown that the calcium silicate hydrates "probably comprise a range of phases of differing composition", depending on such factors as time, temperature and water:cement ratio. Temperature may affect the products of hydration of the two silicates as the permeability of the CSH gel (colloidal size below 0.1 um) is affected by temperature. Electron microscopes, however, show some crystalline character of calcium silicate hydrates. A considerable strength is attained long before the reaction of hydration is complete and it would seem that a small amount of the hydrate binds together the unhydrated remainder ; further hydration resulting in little or no increase in strength[1,2].

The amount of C_3A present in most cements is comparatively small but its behaviour and structural relationship with other phases in cement make it of interest. The tricalcium aluminate hydrate forms a prismatic dark interstitial material, possibly with other substances in solid solution. It is often in the form of flat plates individually surrounded by the calcium silicate hydrates. C_3A alone reacts violently with water producing a flash set accompanied by the generation of considerable heat[36] : $C_3A + 6H = C_3AH_6$. To prevent this from happening gypsum ($CaSO_4.2H_2O$) is added to the cement clinker. Comparing the molecular weights, C_3A requires a much higher proportion of water than that required by the silicates. When water is added to portland cement, a saturated solution of calcium hydroxide and calcium sulphate soon forms. The presence of C_3A in cement is undesirable : it contributes little or nothing to the strength of cement except at early ages. When hardened the cement paste is attacked by sulphates, expansion due to the formation of calcium sulphoaluminate from C_3A may result in disruption of the hardened paste. However C_3A acts as a flux and thus reduces the temperature of burning of clinker and facilitates the combination of lime and silica[2].

C_4AF also acts as a flux. Hydrated C_4AF probably forms solid solutions of tricalcium aluminate hydrate and an amorphous phase probably $CaO.Fe_2O_3$ aq. (analogous to C_3A hydrates with the iron oxide substituting for part of the alumina). The iron oxide also reacts independently to calcium ferric hydrates[37]. The calcium hydroxide formed in any of the above reactions rearranges with time to calcium carbonate. Other reactions taking place throughout the hardening period are substitution and addition reactions[38]. Reactions with the silicate hydrate result in the formation of additional substituted CSH gel at that expense of the crystalline aluminate, sulphate and ferrite hydrate phases. The above mentioned decomposition and rearrangement products form microscopically small interlocking crystallites or an amorphous gel. As time progresses the crystallites grow to

produce an increasingly solidifying structure. This concept of cement hydration implies additivity of hydration of its separate constituents, modified to some extent by interaction and possibly by interaction of minor constituents[1,2].

Additivity of the hydration process does not imply additivity of the rates of hydration. It has been shown[39] that pure compounds C_3S, C_2S, C_3A and C_4AF, when independently hydrated, react at different rates. At the age of one day the fractions hydrated are 35%, 5%, 80% and 90% respectively. X-ray diffraction, amongst other investigative techniques, has show that in portland cement the major portion of its C_3A and C_4AF constituents become hydrated at early ages.
C_3S reacts with water over months : $2C_3S + 6H = C_3S_2H_3 + 3Ca(OH)_2$,
whereas C_2S hydrates slowly over many years : $2C_2S + 4H = C_3S_2H_3 + Ca(OH)_2$[5].

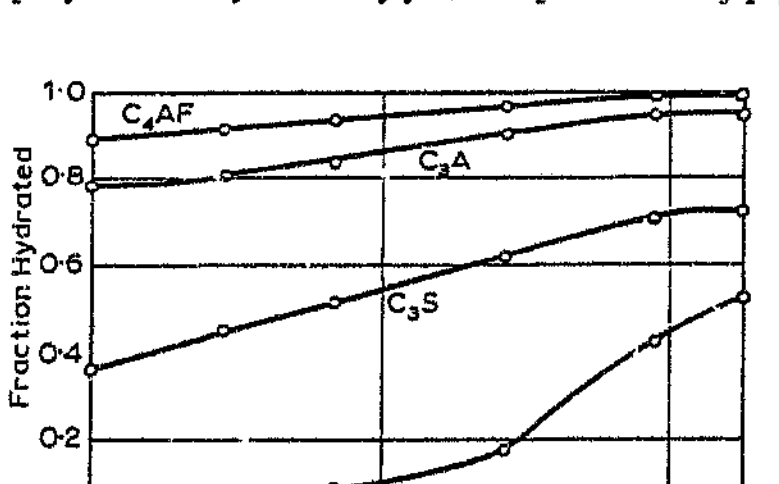


Fig.5 Rate of hydration of pure compounds[40]

Thus the exothermic hydration takes place at an exponential rate for an indefinite time (concretes placed by the Romans still hardens - albeit very slowly !). It would seem then that hydration proceeds by a gradual reduction in grain size of the cement particle. In fact unhydrated grains of coarse cement were found to contain C_3S as well as C_2S as the age of several months[41] and it is possible that small grains of C_2S hydrate before the hydration of large grains of C_3S has been completed. The various compounds in cement are gradually intermixed in all grains and some investigations suggested that the residue of a grain after a given period of hydration has the same percentage composition as the whole of the original grain[42]. However the composition of the residue does change throughout the period of cement hydration[43] and particularly during the first 24 hours selective hydration may take place.

Portland cement is generally used at temperatures ordinarily encountered in construction (5-40°C). The initial conditions for the hydration reactions are determined by the ratio

of the mixing water to the cement particles (0.2-100um) in the mixing water (0.3-0.7 water/cement on a weight basis) and the fineness of cement (2500-5000 cm^2/g). Upon mixing with water, the suspension of particles as shown in Fig.6 is such that the particles are surrounded by films of water with an average thickness of about 1 um. The anhydrous phases initially react by the formation of surface hydration products on each grain and by dissolution into the liquid phase. The solution quickly becomes saturated with calcium and sulphate ions and the concentration of alkali cations increases rapidly. These reactions consume part of the anhydrous grains, but the reaction products tend to fill that space as well as some of the originally water-filled space. The porous gel in its most dense configuration occupies about twice the volume of the reacted anhydrous material[44]. The hydration products at this stage are mostly colloidal (less than 0.1 um) but some larger crystals of calcium aluminate hydrates, sulphoaluminate hydrate and hydrogarnets form. As the reactions proceed the coatings increase in thickness and eventually form bridges between the original grains. This is the stage of setting. Despite the low solubility and mobility of the silicate anions, growths of the silicate hydrates also form on the crystalline phases formed from solution and become incorporated into the calcium hydroxide and other phases[1].

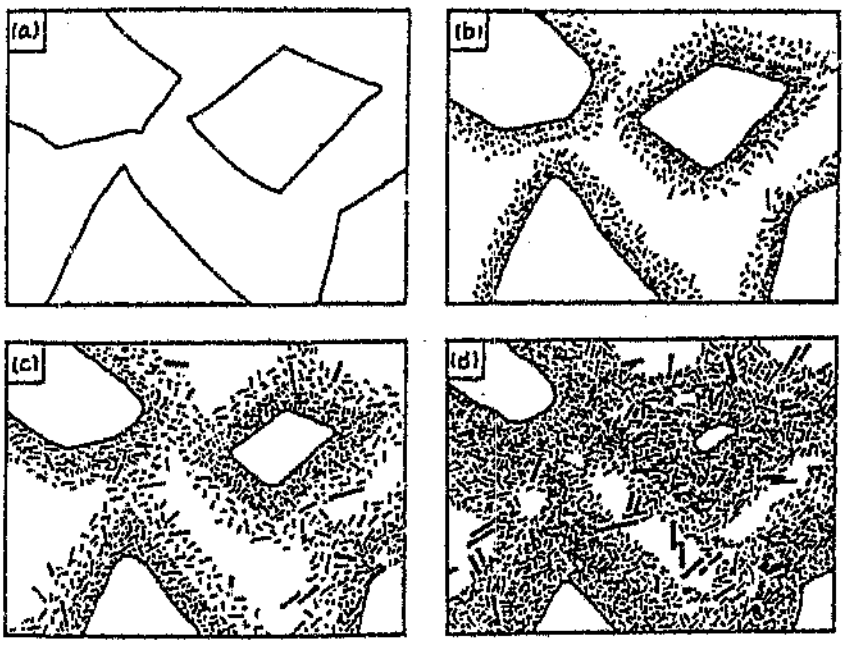


Fig.6 Four stages in the setting and hardening of portland cement : simplified representation of the sequence of changes. (a) Dispersion of unreacted clinker grains in water. (b) After a few minutes : hydration products eat into and grow out from the surface of each grain : (c) after a few hours : the coatings of different clinker grains have begun to join up, the gel thus becoming continuous (setting). (d) After a few days : further development of the gel has occurred (hardening)[45].

The composition of the liquid phase during the early hydration of portland cements is controlled mainly by the solution of calcium, sulphate, sodium and potassium ions. Very little alumina, silica, or iron are present in the solution. Calcium hydroxide (as calcium oxide) and gypsum (as calcium sulphate) alone have solubilities of about 1.1 and 2.1 g/l at 25°C respectively. In the presence of alkalis released by the readily soluble alkali sulphate phases in cements (as much as 70-80% may be released in the first 7 min), the composition tends to be covered by the equilibrium :

$$CaSO_4 + 2MOH = M_2SO_4 + Ca(OH)_2$$

Where M presents the alkalis. At advanced stages of hydration of low water-cement pastes, the alkali solution concentration may exceed 0.4 N with a pH above 13. Saturated lime-water has a pH of 12,4 at 25°C[1].

The products of hydration of cement have a low solubility in water as shown by the stability of the hardened cement paste in contact with water. The hydrated cement bonds firmly to the unreacted cement, but the exact way in which this is achieved is not certain. It is possible that the newly produced hydrate forms an envelope which grows from within by the action of water that has penetrated the surrounding film of hydrate. Alternatively the dissolved silicates may pass through the envelope and precipitate as an outer layer. A third possibility is for colloidal solution to be precipitated throughout the mass after the condition of saturation has been reached, the further hydration continuing within the structure[2].

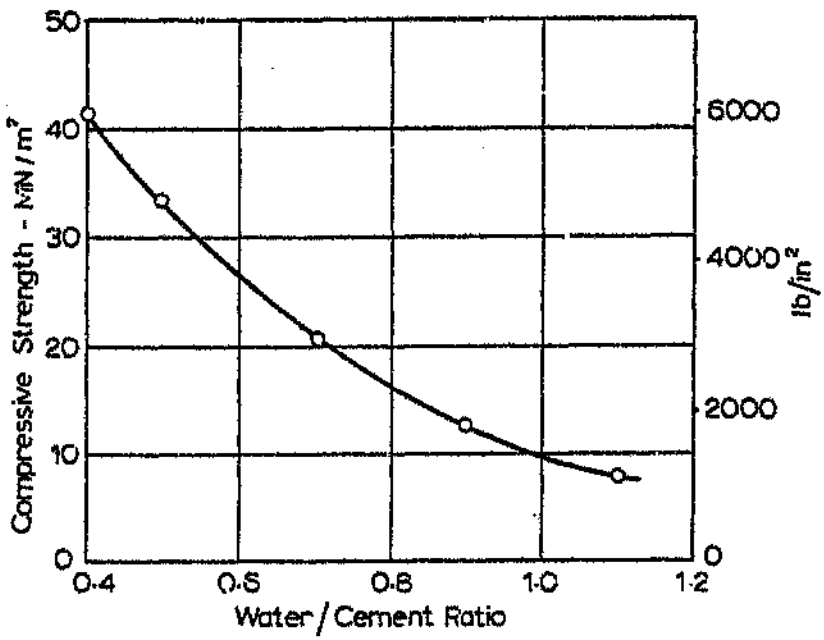


Fig.7 The relation between 7 day strength and water/cement ratio for concrete made with a rapid-hardening portland cement[46].

The rate of hydration and setting concrete is controlled by cement fineness, water content, concrete additives, curing temperature and humidity. For given aggregates the strength development, or curing, depends largely on cement components, water content, concrete additives and curing conditions. The cement components have been discussed, the curing conditions briefly mentioned and concrete additives will be addressed in part B of the introduction. This leaves the water/cement ratio, typically ranging from 0.3-0.7. The strength of the concrete decreases as the water:cement value increases from a minimum of 0.3. It is critical to the setting behaviour, ie the initial and final strengths that are expected to develop at a particular ratio. A variety of empirical water-cement ratio laws express the strength[1].

1.1.4 Cement paste structure and Concrete properties

When portland cement is mixed with water, the chemical reactions which take place bring about a change in structure of the plastic mass whereby it becomes rigid and hard. Immediately after the addition of water there is a short period of intense chemical reaction. Although immediately after mixing the rate of hydration is very high, this initial period is so short that the products have very little effect on the physical structure of the paste. With continued formation of hydrate the paste stiffens and attains rigidity, passing through the stages arbitrarily defined as "initial" and "final set. This reaction quickly subsides and is followed by a period of one to three hours, depending on the temperature and characteristics of cement, during which the reaction rate is slow. At the end of the dormant period the reaction rate increases rapidly, to reach a maximum in about 6-8 hours. Thereafter the rate of reaction decreases progressively, but provided the conditions are suitable, the hydration process will continue, although increasingly slowly for many years[5].

Many of the properties of concrete depend on the proportions and nature of several compounds present in cement. However the methods of manufacture (eg : wet or dry process) also have a considerable influence on cement properties. Both the method of cooling of the clinker and fineness of grinding are particularly important factors. Recent work has confirmed that cements of apparently identical composition may show different characteristics. The physical structure of the products of hydration, viewed at a level of colloidal dimensions, exert the greater influence on the hardened cement and concrete. The fresh paste consists of cement particles fairly uniformly distributed throughout the water-filled space. Fresh cement paste is a plastic network of particles of cement in water. The plastic viscosity ranges from 5000 to 500 mPa (=cP) as the water/cement ratio increases from 0.4 to 0.7. The viscosity value can be greatly decreased by the addition of organic water-reducing admixtures specially formulated for this purpose. The fresh paste, even in the dormant period, is normally thixotropic, or shear thinning, indicating that the structure is being continuously broken down and reformed during

mixing. It is evident that the average distance between cement particles depends on the fineness of the cement and the water/cement ratio[1].

Once the paste has set its apparent or gross volume remains approximately constant. At any stage of hydration the hardened paste consists of hydrates of various compounds, referred to collectively as gel (surface area : 220 m^2/g), of crystals of calcium hydroxide, some minor components, unhydrated cement and residue of water filled spaces in the fresh paste. These voids are called capillary pores, but within the gel itself there exist interstitial voids, called gel pores. Both exist in the hardened cement paste, the capillaries which, though considerably larger than gel pores, are still submicroscopic. These capillaries are the residue of the original water-filled space in the fresh paste. Initially the capillary pores form an interconnective system, but as hydration proceeds they tend to become blocked by the formation of cement gel. There are thus in hydrated pastes two distinct classes of pores represented in a diagram in fig.8[2].

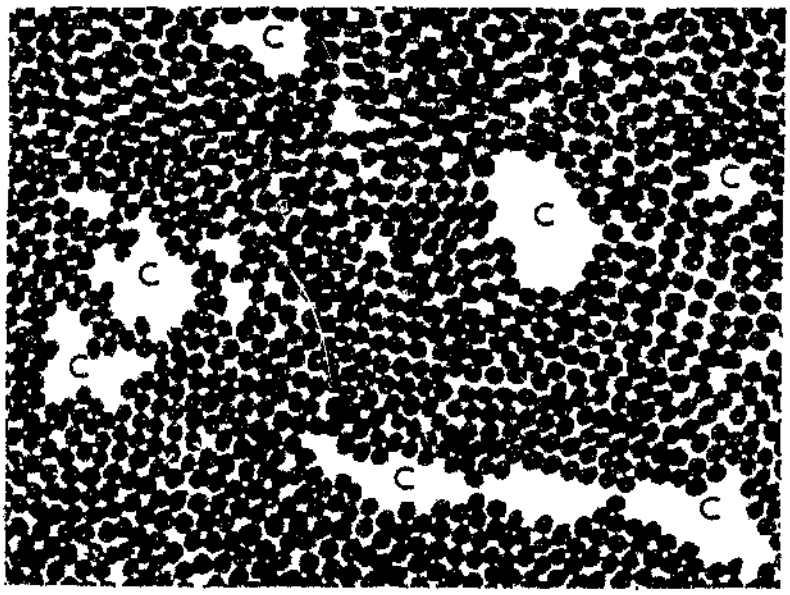


Fig.8 Symplified model of paste structure[47]
Solid dots represent gel particles; interstitial spaces are gel pores; spaces such as those marked C are capillary cavities. Size of gel pores is exaggerated.

Therefore chemical requirements must be supplemented with physical requirements defining such properties as soundness, fineness, setting time, and compressive strength. It can be seen from above that the mechanical properties of both fresh and hardened mortars and concretes depend mainly on the cement-water paste characteristics. Practical engineering tests are usually made with concrete specimens since their properties also depend on the proportions, size, graduation, and properties of the aggregates. Quality control testing and research on cement particles is usually done on cement pastes or cement mortars made with standard sands. The characteristics of hardened cements,

pastes, mortars and concretes are similar functions of the water/cement ratio and degree of hydration of cement. The properties of fresh concretes that determine the workability, or ease of mixing and placing into forms, also depend strongly on the cement paste rheological properties[48,49].

An important feature of the chemical reaction of portland cement and water is that the absolute volume of the hydrate is less than the sum of the absolute volumes of the water and cement of which it is composed. This contraction of the water\cement system must not be confused with shrinkage. Shrinkage refers to the diminution of the overall dimensions of the specimens consequent on drying. Contraction implies the reduction in absolute volume of the original paste components, with unchanged overall dimension. Since most of the products of hydration are colloidal, during hydration the surface area of the solid phase increases enormously and a large amount of free water becomes absorbed on this surface. If no water movement to or from the cement paste is permitted, contraction may involve emptying of the capillaries known as self-desiccation, to the degree that some shrinkage takes place. On the other hand if curing water is continuously available contraction results in the absorption of water. Since gel can only form in water filled space self-desiccation leads to a lower hydration compared with moist cured paste. However if the water:cement ratio is in excess of 0.5 the amount of mixing water is sufficient for hydration to proceed at the same rate as when moist cured[2,5].

After mixing and casting, sedimentation of the solid particles in the water results in the bleeding, (segregation) of water to the top surface and reduction of water/cement ratio in the paste. This is caused by the inability of the solid constituents of the mix to hold all of the mixing water when they settle downwards. Bleeding, known as water gain, is can be seen as a form of segregation[50]. At high water-cement ratios, some of the very fine particles may be carried with the bleed water to the top resulting in laitance (poor bonding area for subsequent layers) and perhaps the formation of flaws called bleeding channels. In concretes sedimentation may cause flaws under the larger aggregate particles resulting in a decrease in strength and durability. In reinforced concretes the bond strength and permeability may be seriously reduced by internal bleeding which results in the entrapment of water along the undersides of the reinforcement. The segregation is particularly serious if the water carries cement particles with it[1].

Bleeding can be avoided by increasing the fines content (ie a higher surface area to hold all the mixing water) with aggregate, cement (ie a rich mix), addition of an air-entrainer, or powdered additives. Their proportions are however chosen with regard to other factors. A poorly designed aggregate grading or simply a too high water content, undesirable from a strength point of view, could also be the cause (an increase of one fifth in the water content of a mix may multiply the bleeding rate 2.5 times). Chemical factors also influence bleeding ; there is less bleeding if the cement has a high alkali content, a high C_3A content, or when calcium chloride, pozzolans or an air-entrainer is

added[51]. A higher temperature, within the normal range, increases the rate of bleeding, but the total bleeding capacity is probably unaffected. The rate of bleeding may be intensified by vibration or tamping which encourages the settlement of the solid particles. Bleeding of concretes continues until the cement paste has stiffened sufficiently to put an end to the process of sedimentation. The bleeding capacity as well as the rate of bleeding can be determined experimentally using the test of ASTM C232-71[4].

If the fresh concrete is not protected from too rapid surface drying (for instance by a curing aid), capillary forces cause dry shrinkage which may cause plastic shrinkage cracks. Good construction practises are designed to minimize all these flaws. The engineering properties of concrete such as strength, elastic moduli, permeability to water and aggressive solutions and frost resistance depend strongly on the water/cement ratio and degree of hydration of cement[1].

1.1.5 Performance Tests

Tests can be made for different purposes but the main two objectives are control of quality and compliance with specifications. It should be remembered that tests are not an end in themselves. In the case of concrete they seldom lend themselves to a neat, concise interpretation, so that in order to be of real value tests should always be used against the background of experience[52]. We have seen that the properties of concrete are a function of time and ambient humidity and that is why, in order to be of value, tests on concrete have to be performed under specified or known conditions.

The strength of concrete of given mix proportions is very seriously affected by the degree of its compaction. Therefore it is vital that the consistence of the mix be such that the concrete can be transported, placed and finished sufficiently easily and without segregation. A concrete satisfying these conditions is said to be "workable". This, broadly defined, is a measure of its possible compaction to maximum density by mechanical means. Compaction is necessary to remove entrapped air bubbles thereby improving homogeneity of the mix and its strength. 5% Of voids can lower the strength of concrete by as much as 30% and even 2% voids can result in a drop in strength of more than 10% [53]. These unwanted air bubbles are more easily expelled from a wetter mix than a dry one. A concrete of high workability, ie low internal friction and surface friction to the mould is easily compacted. Aggregate maximum size, grading, shape and texture have a great influence on internal friction and voids. These influence not only the cement content (which contributes to the fines content), but also the water content, which is the main factor affecting workability of the mix[4].

Here it is worth mentioning the aggregate/cement ratio, a measure of the amount of binder compared to the structural component. The relationship of cement content to

strength is not linear but passes an optimum after which an increase in cement content will lower the strength. There is an optimal coating of the aggregates by the cement paste and the thickness of this coating depends on the dispersion of the cement grain which can be improved by dispersing agents. Ideally this ratio should be high ; less cement means increased soundness of the concrete and lower water demand coupled with higher strengths. A lower aggregate/cement ratio, eg 2, would produce the opposite effect, the increase in water demand being due to the fineness of cement particles (above 200 m^2/kg according to the Lea and Nurse method, or below 1mm particle size) with resulting high surface area. In practice this optimum is seldom reached because of the distribution in particle size, the compaction, the void content, the hardness of the aggregates and the performance of the plasticising agent are critical as well[4,54].

"Consistency" is defined as the firmness of form, or conversely the ease with which it will flow. In the case of concrete, consistency is taken to mean the degree of wetness. Within limits, wet concretes are more workable than dry concretes, but concretes of the same consistency may vary in workability[4]. "Mobility" is applicable to plastic concrete in the sense that fluidity is applied to liquids - the reciprocal of viscosity. "Plasticity" is the property of a material by virtue of which it can undergo moulding without rupturing[55].

In the following paragraphs a concrete two viscosity tests of the fresh mix and a compressive strength test on the hardened concrete will be explained. They serve to outline tests which are often related to literature concerning plasticisers (see Section 1.2.3. etc.) and extensively referred to in the discussion. There are a wide range of tests for each characteristic depending largely on local test specifications. The best known are B.S. (British Standard), ASTM (American Society for Testing Materials) and DIN (Deutsche Industrie Norm). SABS (South African Bureau of Standards) specifications have included parts of each of these. Specifications prescribe : type of material and dimensions of testing equipment (including moulds), water temperature, testing procedures such as method, type of equipment, and duration of mixing, placement into moulds, tamping or vibrating, conditions and duration of curing.

Unfortunately no test is known that will measure directly the workability as defined earlier. Numerous attempts have been made to correlate workability with some easily determinable physical measurement but none of these is fully satisfactory although they may provide useful information within a range of variation in workability.

The slump test is used to give an indication of workability. It does not measure it directly, but provides useful information in the form of an easily determinable physical dimension. There are various other tests, but none measures workability directly. The term consistency is widely used synonymously with slump. The slump test is used all over the world on construction sites for dough-like mixes. It is useful in detecting

variations in the uniformity of a mix of given nominal proportions. The degree of slump also gives an indication of compaction attainable. The mould used for the test is a frustum of a cone 300 mm high with handles to hold it firmly down during the test. It is moistened, placed on a smooth moistened surface with the smaller opening at the top and filled with concrete in four layers, each being tamped with a standard diame' steel rod 25 times. Finally the top surface is struck with a trowel. Immediately after filling the cone is slowly lifted, and the unsupported concrete will now slump. The decrease in height of the highest (B.S.; ASTM : the centre) part is measured. If, instead of slumping evenly all round as in a true slump (fig.9), one half of the cone slides down an inclined ne a shear slump has taken place and the test should be repeated. If shear slump persists, as may be the case with harsh mixes, this is an indication of lack of cohesion in the mix (ie poor consistency)[4].

Mixes of stiff consistence have a zero slump, so that in the rather dry range no variation can be detected between mixes of different workability. Rich (high cement content) mixes behave satisfactorily, their slump being sensitive to variations in workability. However in a lean mix with a tendency to harshness a true slump can easily change to the shear type, or even to collapse (fig. 9) and widely different slumps can be obtained in different samples of the same mix. It should be remembered that with different aggregates the same slump may be recorded for different workabilities, as the slump bears no unique relationship to the workability as defined earlier[4].

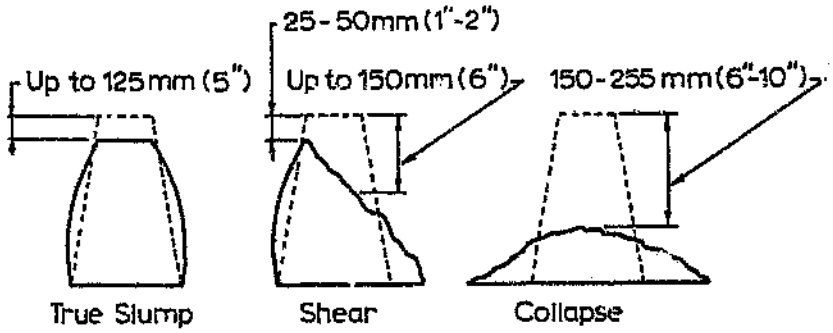


Fig. 9 Slump : true, shear, collapse[4]

Despite these limitations the slump test is very useful on site as a check on the day-to-day or hour-to-hour variation in materials being fed into the mixer. This also applies to laboratory testing or research on admixtures. An increase in slump may mean, for instance, that the moisture content of the aggregate has unexpectedly increased ; another cause would be a change in the grading of the aggregate, such as a deficiency in sand. Too high or too low a slump gives immediate warning and enables the mixer operator to remedy the situation. This application of the slump test as well as its simplicity is responsible for its widespread use[4].

The funnel-flow test is used to measure mobility or plasticity with flow characteristics. The equipment consists simply of a funnel of specified dimensions, material of construction, angles of the cone and a filling mark. A fresh concrete of low viscosity will run through the moistened funnel quickly and completely. The time taken, 10-30 seconds for suitable concretes, is measured with a stopwatch. Conversely a fresh concrete of thick consistency (low plasticity, ie high consistency) may not flow through completely. Here time and amount of the stationary mix are recorded. The funnel-flow test is useful for measuring liquid mixes and gives an idea of the suitability of a concrete for highly reinforced sections and pumping on site or in underground applications[22]. The test is often used to measure the effectiveness of water reducers/plasticisers, superplasticisers and retarders. Fresh concretes of very low viscosity can even be sprayed for tunnelling applications.

The most common of all tests on hardened concrete is the compressive strength test, partly because it is easy to make and partly because many, though not all, of the desirable characteristics of concrete are qualitatively related to its strength. The main reason being the intrinsic importance of the compressive strength of concrete in construction. The tests to destruction have been in use for a great number of years, but no universally accepted standard test is available. Different methods and techniques are used in different countries and sometimes even in the same country. As many of these tests are encountered in laboratory work and especially in research, a knowledge of the influence of the test methods on strength as measured is desirable[52].

The specimens are cast in steel or cast-iron moulds with prescribed dimensions, in this thesis 75 mm cubes, and planeness within narrow tolerances. The use of a rigidly connected base is essential when compaction is affected by means of vibration. The standard practise is to fill the mould in three layers. Since a check on the properties of the concrete as placed is required it is only tamped to ensure that it fills the corners of the cube properly. After the top surface has been finished with a trowel the cube is stored undisturbed at room temperature for 24 hours. At the end of this period the mould is stripped and the cube is further cured in water. Thus the potential quality of the concrete as on site can be determined as close as possible without the narrow limits of temperature, humidity and compaction given by specifications. This is important if one needs to know when formwork holding the cast concrete can be removed, or when further construction can continue[52].

In the compression test the mould is placed with the cast faces in contact with the platens of the testing machine, ie the position of the cube when tested is at right angles to that as cast. The load on the cube should be applied at the rate of 15 $MN/m^2/min$ according to B.S.1881:1970. Due to the non-linearity of the stress/strain relationship for concrete at high stresses, the rate of increase in strain must be increased progressively as failure is approached. This can only be done with a hydraulically operated machine. The

crushing strength is reported to the nearest 0.5 MN/m^2, a greater "accuracy" is usually only apparent. The set concrete quality is generally tested at the ages of 1,3,7 and 28 days. The one and three day strengths are of particular economic importance, allowing early removal of shutters and continuation of construction on previously completed sections[52].

1.2 Concrete Additives

Concrete additives, also called admixtures, are liquids or solids that are added to the concrete before mixing, generally premixed with the water for hydration. Lignosulphonate, liquid or spray-dried, is an example of a concrete plasticiser. Cement additives are added to the cement during manufacture either as a physical aid in production, such as a grinding aid, or to chemically control setting characteristics. TEA (triethanolamine) and gypsum respectively are examples. In this dissertation the term additives will be used to denote concrete additives, ie admixtures.

Outside of the laboratory, the realm of specifications and codes of practice, concrete is much abused. Years of use and familiarity overshadow the complexity of concrete. Concrete additives have therefore met with a general attitude of disbelief or disinterest. Coupled with a "witch doctor" chemistry surrounding concrete additives, their acceptance was slow and reluctant[6]. Even in the seventies the opinion of South African concrete authorities was that "the best additive for concrete is cement" ! Today admixtures have become widespread and virtually indispensable. In Germany each truckload of ready mixed concrete contains DM 50 of additives and the use of additives is still growing. This is due to higher cement manufacturing costs, a wider field of applications, and concern about durability and appearance of concrete[6]. The durability of concrete is its ability to maintain its aesthetic and constructional properties for which it is designed over a prolonged period of time. Any loss of durability may be ascribed to chemical attack, the action of freezing and thawing, or wetting and drying etc. The most important factor influencing durability is said to be the surface permeability of the system[56]. Other benefits include better workability, shorter setting times with increased strengths which result in shorter construction times or increased turnover of precast concrete. Conditioning to specific applications (slides, free cantilever); improved strength development against time (grouts, self-levelling floors, repairs); water proofing (roofing, monolithic structures, trench walling); gunniting (spraying).

There is very little which has not been added to concrete in order to improve its characteristics or simply to find a use for unwanted materials which at least do not interfere with the hydration. Examples range from lignosulphonates (an unwanted noxious by-product from the pulping of wood to make paper), polymers (for example melamine-formaldehyde), alkali metal salts ($CaCl_2$), to medicine production wastes[57] (antibiotics, insulin, geparin).

The purpose of additives is to modify the concrete, making it more suitable for certain applications. This applies to preparation, placing and curing. Reduction of water content, increased workability and improved strength development are the most common requirements. Unfortunately these properties of fresh concrete usually exclude one another. Additives generally have a great effect on the cement's hydration rate, often

causing drawbacks as the consequence of a desired characteristic. The disadvantages are minimised as far as possible and taken into account. For example nearly all plasticisers cause a retardation in the setting and early strength development of concrete. According to ASTM specifications a 10% reduction in 28 day compressive strength is allowed for plasticisers, compared to the unmodified concrete. Modern plasticisers merely cause a reduction of 0-5%. Tannin based plasticisers mentioned in the literature have high retarding properties and plasticising action similar to lignosulphonates, which are much cheaper. In the 1960's ITT Rayonier of USA investigated tannins to be used as concrete admixtures [58]. The product developed was withdrawn from the market due to poor sales. German specifications (DIN) require that an additive may not change in its effect on concrete at double the applicable dosage rate. This is in order to prevent adverse consequences of possible mistakes made particularly at construction sites. Concrete additives used skilfully can be a decisive factor in the economics of a given project.

Types of Additives

A wide range of types is available for various applications. Although the whole range of additives (in nine groups) and durability aids are shown in Table 3[6] page 27, only those applicable to this project will be addressed here. Included in the discussion are their modus operandi and benefits as well as their shortcomings. Curing and formwork aids due to their 'indirect' action on concrete are excluded.

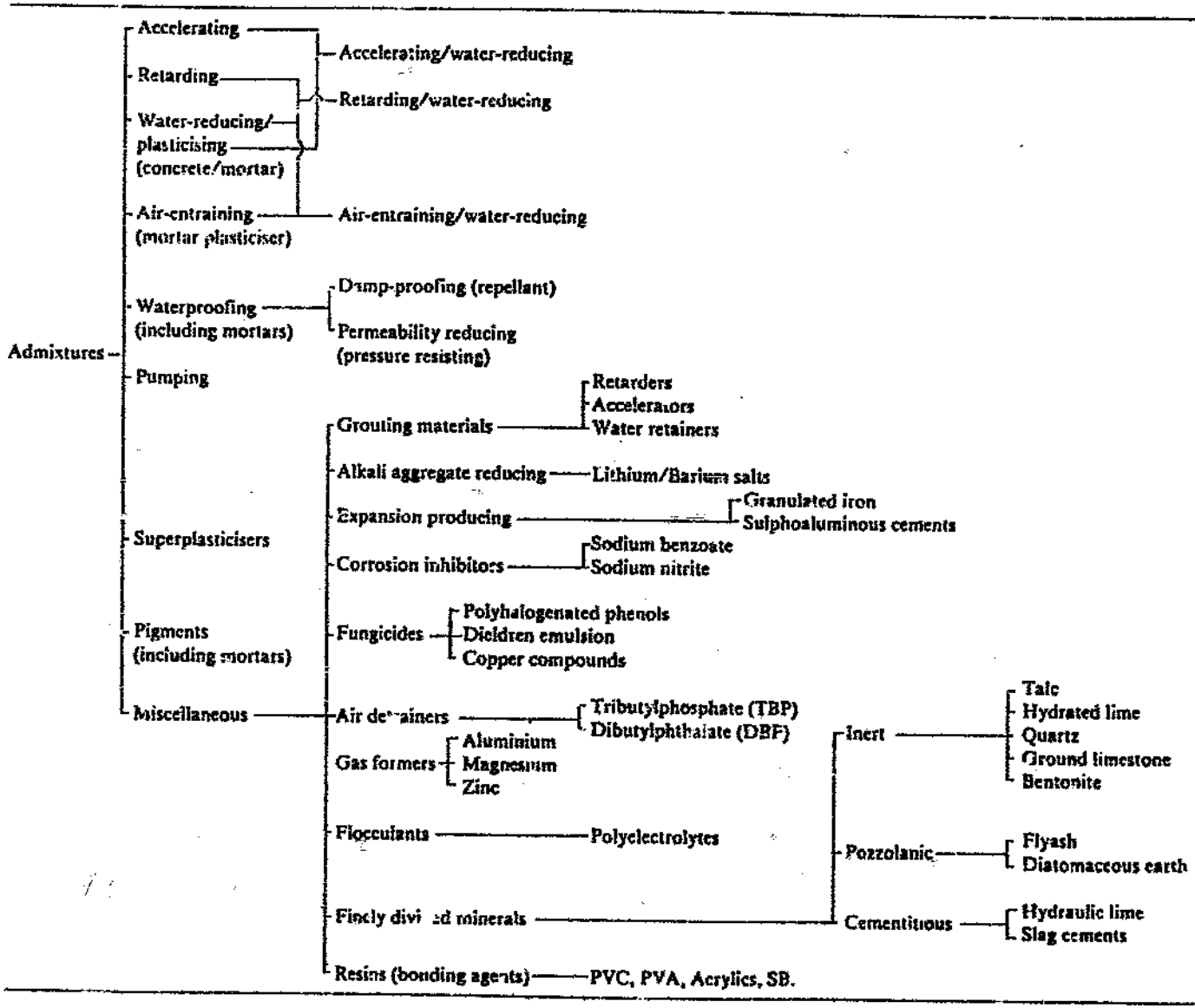
Those with more than one effect on concrete are divided into five subgroups, excluding those under miscellaneous. The nine main groups are listed in order of tonnage used. Obviously there are regional geographical differences, eg : cold areas may favour accelerators/air-entrainers and by contrast warmer zones favour retarders. Regions noted for poor or harsh aggregates (eg crushed aggregates) might endorse plasticisers.

The following two sections serve to introduce the concepts of "accelleration" and "retardation". Both descriptions are used extensively in conjunction with water-reducers/plasticiers in subsequent sections and throughout the discussion of this dissertation.

1.2.1 Accelerators

These materials shorten the setting time of cement and/or increase the rate of strength development. They help in maintaining contractors schedules particularly during cold weather working, allowing early removal of formwork. The products in this category are divided into chloride-containing or chloride-free materials. In the first group the accelerating chemical is calcium chloride, often used together with sodium chloride. In

Table 3 Classification of admixtures



the chloride-free group triethanolamine (TEA, added to cement during manufacture as a grinding aid), calcium nitrite, various formate or acetate, lithium oxalate and some aluminates[6]. Sodium carbonate has been shown to increase shrinkage and efflorescence (leaching out of $CaCO_3$). Another older type is sodium silicate. It too has undesired effects such as low and varying compressive strengths and is little used today. This is probably due to interference with the network of the hydrating cement causing only an apparent acceleration[59].

Alkali chlorides increase early strength at the expense of final strength. Chlorides in general have been much criticised over the last few years as a result of reinforcement corrosion. Although not directly responsible, they promote corrosion of exposed reinforcement. The volume increase due to the oxidation of the steel reinforcing breaks up the whole structure[60]. The corrosion mechanism is thought to be of the differential aeration type combined with stress corrosion. Other factors such as chloride overdosage, incorrect mix proportions, poor compaction, inadequate cover and poor detail design exacerbate the corrosion tendency. If immediate remedial action is not taken, as for instance cleaning and grouting of the whole affected area, crevice corrosion may result rendering the structure beyond repair and dangerous. Such degradation is particularly strong in reinforced load-bearing structures which are susceptible to water permeation.

Chlorides have therefore been banned from prestressed, reinforced concretes and concretes containing embedded metal. For these applications maximum chloride contents are prescribed in specifications. They do however remain acceptable in unreinforced concrete, being highly effective and economical to use. As an alternative chloride-free accelerators based on formates are widely being used[6].

The mechanism of how accelerators work is not fully understood, but it appears that both calcium chloride and formate tend to increase the rate of hydration of the different chemical constituents in cement. This interaction is complex being of both a chemical and physical nature. On a weight basis the chloride-free materials are less effective accelerators. At certain dosages, mostly overdosages, an accelerator can exhibit retarding properties instead. The performance of setting aids (accelerators an retarders) depends on cement properties and the water/cement ratio[6]. Dosages can be up to 2% by cement weight. The wetter the concrete the more agent is required. Initial and final strengths requirements are of the highest importance when selecting an accelerator. Tests also have to be conducted to determine dosages within which the accelerator remains true to type.

Some accelerators can be used to activate portland blended cements. A few chemicals having plasticising action are sometimes classed as accelerators, as a result of allowable water reductions on plastification, although they themselves do not speed up the cement hydration reaction[6]. This is of great commercial importance, combining the best of both worlds and saving a large amount in terms of construction time. Mixes containing

accelerators must still be protected from frost during the early stages of setting.

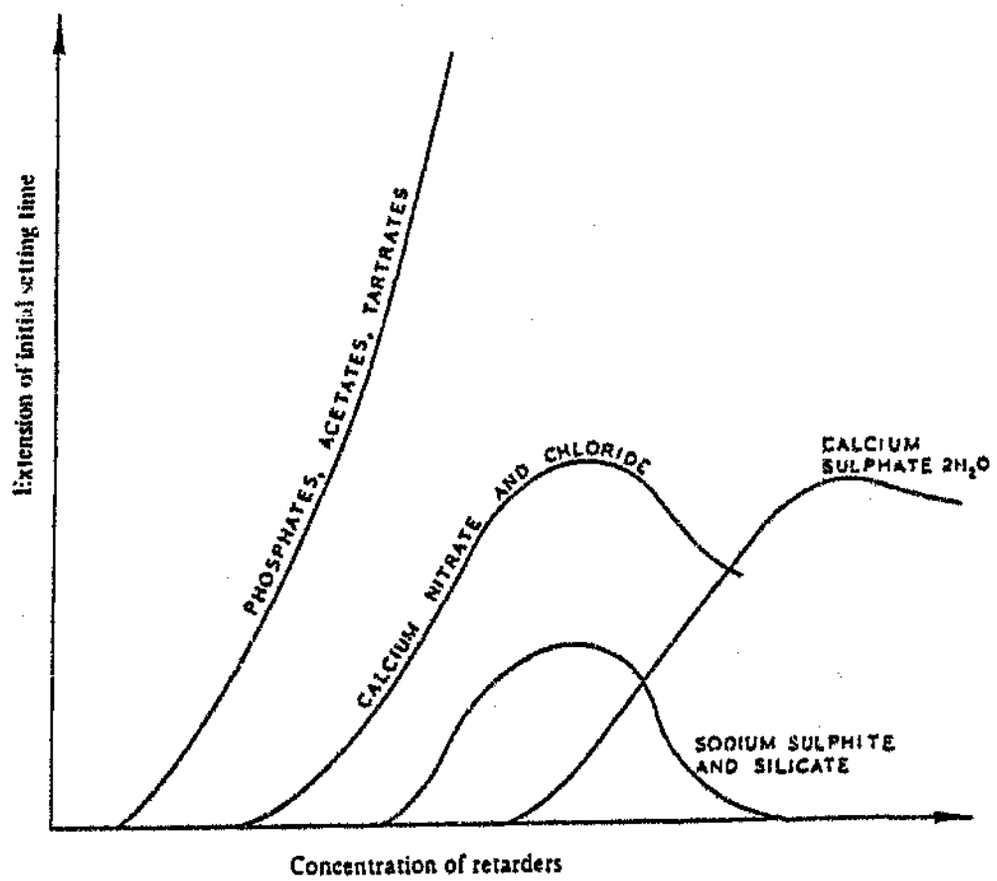


Fig. 10 Effect of various admixtures on initial setting time[6]

1.2.2 Retarders

Retarders, as their name suggests, have the opposite effect of accelerators. They slow down the rate of setting of cement and as with retarding/water-reducing admixtures they assist in hot weather concreting and casting. Retarders also prevent differential curing when many pours are needed for large concreting applications, allowing for monolithic structures. By extending vibration time, interfaces (cold joints) between consecutive pours are prevented. Once the reaction has gone past the initial setting stage the hydration continues at a normal rate and sometimes even faster compared to the unmodified concrete[6].

Retarders also offset heat build-up in mass constructions such as dam walls. This presumably is effected by slowing down particularly the early hydration reaction, which has the highest rate, allowing heat generated to dissipate before accumulating. Expansion and consequential shrinkage leading to stresses within the concrete structure, making it

unsound, are prevented. Total heat output during curing is not markedly altered[6].

It is thought that retarding admixtures are absorbed onto the C_3A phase (the first to hydrate, mainly responsible for initial set) in cement forming a film around the cement grains and preventing or reducing the reaction with water. Sugars and starches are quick in absorbing water, the shorter sugars later releasing the water to the cement. This may explain their retardation effect. The water-reducing ability is due to the lowering of the surface tension of water improving its wetting properties. It seems higher sugars ('gums') and carbohydrates hold on to a larger proportion of water more strongly for a longer period of time, increasing the water demand of the concrete. In both the film breaks down after a while and normal hydration can proceed[6]. This is a very simple picture and there is reason to believe that retarders also interact with the C_3S phase since retardation can be extended to a period of many days, which can not be accounted for by the C_3A water reaction alone. Another theory stipulates that the CSH gel is thickened by carbohydrates, increasing its viscosity and decreasing the mobility of the water molecules.

Some materials used are[6]:

(i) Various lignosulphonates containing, lignin, sugars and gums. The sugars are responsible for retardation.
(ii) Modifications and derivations of the above
(iii) Hydroxycarboxylic acids and their salts, for instance sodium tartrate
(iv) Modification of the above class
(v) Heptonates which are related to sugars and starches

Retarders together with a plasticising agent are used in large flooring applications, when the induced self-levelling effect of the modified concrete assists in placement, better compaction, less heat build up and less troweling required for finishing. Precise levelling is of particular importance to warehouse flooring where goods are stored on over 10 m high stacks by fork lifts with high vertical stacking capabilities. Types (i) to (iv) also have water reducing properties ; type (v) does not[6].

Analogous to accelerators, retarders can change in their effect on concrete reverting into accelerators as a result of incorrect dosages. Applied in unsuitable quantities retarders can completely inhibit the setting and hardening of concrete making it worthless. Recommended dosages are around 1-2% by cement weight[60]. Retarders do not react with ground blast-furnace slag. Retardation however can be obtained by mixing slag with OPC in ratios of 4:6 and 5:5. Concrete suitably retarded can be revibrated to achieve maximum compaction. This results in a more dense and more homogenous mass, which develops improved strengths and generates better impermeability. Thus a concrete of the highest possible quality is obtained. The retarding effect, as tested by a simple slump test, must be established before selecting a retarder. As with accelerators a dosage range has to be established within which the retarder remains true to type.

1.2.3 Water-reducers/Plasticisers

The normal water-reducing admixtures probably account for the largest tonnage value of organic materials used in concrete and has accordingly been the subject of fairly extensive fundamental and applied research work. Their necessity is given by the following reason : the relationship of cement content to strength is not linear but goes over an optimum after which an increase in cement content will lower the strength. There is an optimum coating of aggregates by the cement paste and the thickness of this coating depends on the dispersion of the cement grain which can be improved by dispersing agents[54]. In practice this optimum is seldom reached because of the distribution in particle size, the degree of compaction, the void content, the shape of the aggregates and the degree of performance of the plasticiser.

There are three main categories of water-reducing admixtures :
(i) Normal water-reducing
(ii) Accelerating/water-reducing
(iii) Retarding/water-reducing

The last will be mentioned only briefly. All three types can fulfil their function with OPC, PBFC and pulverised fuel ash and flyash modified cement concretes[7]. The difference between the types within the group lie in their effect on the set and strength development characteristics of the concrete into which they are incorporated. The criteria for classification according to the recently revised BS 5075, part 1,1982 - Specification for Accelerating Admixtures, Retarding Admixtures and Water-reducing Admixtures, are detailed in Table 4 page 32 which also indicates the product grouping according to the Cement Admixtures Association as wall chart[61].

The addition of plasticisers allows greater workability to be achieved for a given water:cement ratio or alternatively retains the workability or consistency whilst reducing the water content. The latter results in a denser and stronger concrete for a given cement content. This property has been used to effect cement savings whilst maintaining strength. At a cement content of about 300 kg/m^2 long term durability, permeability and porosity appear unaffected by up to 10% cement reduction in the presence of a plasticiser[6].

As a group water-reducing agents are characterised by having detergent-like properties. The surface active agents carry a slight negative charge at the high electron density atom or molecule balanced by a slight positive charge at the hydrocarbon tail. In water the surface active agents migrate towards the surface where they arrange themselves with the hydrophillic or active end pointing inward, while the hydrophobic hydrocarbon end is directed away from the water; see Fig.11[6].

Table 4/...

Table 4 Performance requirements of water-reducing admixtures according to BS 5075; Part 1; 1982 (Note: Test Mix A contains the admixture at the manufacturer's recommended dosage rate and in all other respects has the same composition as the control mix. Test Mix B contains the admixture at the manufacturer's recommended dosage rate and has the same composition as the control mix, except that the total water/cement ratio is reduced by 8%.)

Category of admixture	*CAA chart type*	*WORKABILITY* *Compacting factor relative to control mix*		*STIFFENING TIMES* *Time from completion of mixing to reach a penetration resistance of:*				*COMPRESSIVE STRENGTH* *Minimum compressive strength as % of control mix concrete at:*					
				0.5 N/mm²		*3.5 N/mm²*		*24 hours*		*7 Days*		*28 Days*	
		Test mix A	*Test mix B*	*Test mix A*	*Test mix B*	*Test mix A*	*Test mix B*	*Test mix A*	*Test mix B*	*Test mix A*	*Test mix B*	*Test mix A*	*Test mix B*
Normal water reducing	C3	At least 0.03 above	Not more than 0.02 below	—	Within 1 hour of control	—	Within 1 hour of control	—	—	90	110	90	110
Accelerating water reducing	C4	At least 0.03 above	Not more than 0.02 below	—	More than 1 hour	—	At least 1 hour less than control	125	125	—	—	90	110
Retarding water reducing	C5	At least 0.03 above	Not more than 0.02 below	—	At least 1 hour longer than control	—	—	—	—	90	110	90	110

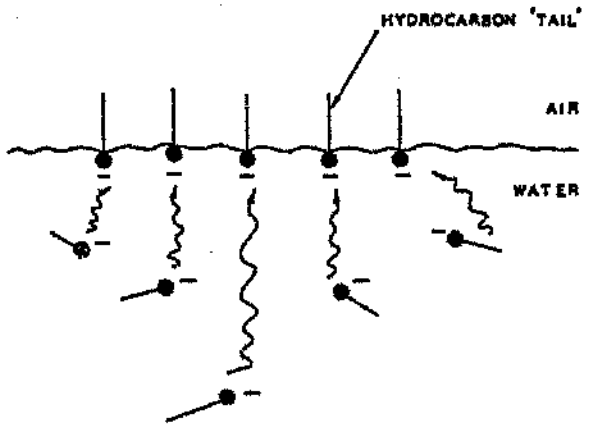


Fig. 11 Migration of water-reducing to the surface of water

In a suspension of cement particles a surface-active agent's hydrophobic tail is absorbed onto the surface of the cement with the negative protruding into the water. The surface electrostatic charges of the cement particles are then modified developing a sheath of orientated water molecules around each, reducing inter particle attraction and thus allowing increased wetting action of the water. This is due to the greater adhesive forces across the cement/water interface as compared to the forces of cohesion between water molecules and the cement particles themselves. Particle/cement interaction is also decreased. The water freed from the restraining influence of the flocculated system becomes available to lubricate the mix so that the workability is increased[62]. The combined effects, shown below, improve the workability by decreasing the viscosity of the fresh mix.

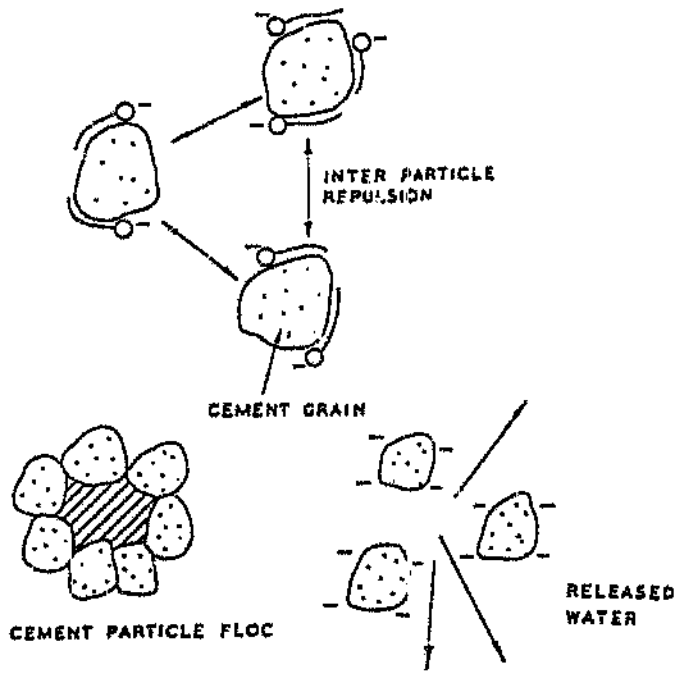


Fig. 12 Effect of surface-active agent on cement particle floc[6]

The admixture therefore changes the physico-chemical forces acting at the cement/water interface. As a result the cement particles do not agglomerate and therefore more surface area is available for the hydration reaction, which can now progress at a higher rate in the early stages. For this reason there is an increase in strength of the concrete compared to the control. A more uniform distribution of the dispersed cement throughout the concrete may also contribute to the improved strength[62]. There is also a greater statistical chance of inter-meshing of hydration products with fine and coarse aggregates on the micro scale and hence greater impermeability and higher strength. The increase in strength is particularly noticeable in very young concretes [63] but under certain conditions persists for a long time. The influence of the admixture varies considerably with the composition of the cement, the greatest increase occurring when used with cements of low alkali or low C_3A content. It should be noted that even though set is retarded, admixtures do not always reduce the rate of loss of workability with time [63].

Another effect is that entrapped air is more easily removed from the mix, by vibration and compaction, since orientation of the surface-agent agents prevents the air bubble from attaching to cement particles, as shown below. Plasticising water-reducers, due to their ability to migrate to the water/air boundary, reduce the surface tension at the boundary and can form very stable air bubbles. This is the principle behind air-entraining agents[6].

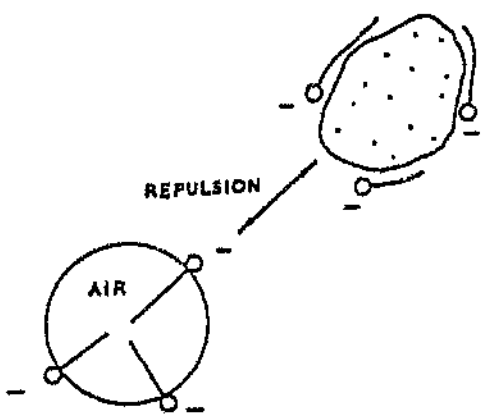


Fig. 13 Repulsion of an air bubble by surface-active agent[6]

Many plasticisers show wetting, dispersing and air-entraining properties and it is difficult to asses the effect of any single characteristic[64-66]. In plasticisers their tendency can be offset by introducing an air-detraining agent such as tributyl phosphate (see Table 3). Plasticisers can essentially be air-entraining or non air-entraining. The type selected depends on the fines content. Generally above 300 kg cement/m^3 of concrete the latter is employed, while below that amount entrained air is desired. The dispersed air bubbles thus compensate for the missing fines by occupying their spatial gaps instead of water, which would increase the water demand. Plasticisers of the non air-entraining type can reduce the water demand by up to 5-10%. A combination of plasticiser and air-entrainer reduce water demand by 15%[3] The stated figures are on a basis of equal workabilities

as measured by the slump test. If the entrained air stays below 3% by volume no loss in strength is experienced.

As the fines (aggregates below 0,25 mm) are increased above 300 kg/m^3 of cement a non air-entraining plasticiser must be used. It can only perform in the presence of excess fines. Plasticising agents can balance fines, which is mostly the case, but a minimum has to be maintained. If fines are to low an air-entrainer has to be combined with the plasticiser. Water-reducing agents can greatly benefit concrete containing harsh and/or poorly graded aggregates[54].

Table 5 Use of an air-detraining agent with a water-reducing agent[6]

Admixture	*Dosage (%)*	*Slump (mm)*	*Air content (%)*	*Water reduction (%)*
Control	0	89	2.0	—
Lignosulphate water-reducing agent (unmodified)	0.16	89	3.8	11.3
	0.26	114	5.0	14.2
	0.37	114	6.5	17.9
Lignosulphate water-reducing agent (modified)	0.16	102	2.5	5.8
	0.26	89	3.3	9.9
	0.37	102	3.8	12.8

1% Air entrained replaces about 50 kg/m^3 fines. Concrete with sufficient fines and non air-entrained plasticiser shows an increase of 15% in 24 hours strength, when used with RHC. The influence of admixtures on strength varies considerably with the composition of cement, the greatest increase in strength occurring when used with cements of low alkali or low C_3A content.

If concrete is made to a given workability, say slump value, then the addition of a plasticising water-reducing agent gives rise to the following possibilities[6]:

(i) Concretes having greater workability may be made without the need for more water so strength losses are not encountered

(ii) By maintaining workability, but with a lower water content, concrete strengths may be increased without the need for further cement addition

(iii) While maintaining the water/cement ratio and workability concrete can be made to a given strength specification at lower cement content than would otherwise be required

Generally a compromise between increased workability for a fixed water/cement ratio and a reduction in cement content is employed to obtain a certain strength for a fixed workability. Table 6[6] reports results of concretes of each of the possibilities given above.

Table 6 Purposes achieved by the use of water-reducing agents

Test	*Cement content (kg/m³)*	*Dosage rate (litres/50 kg)*	** W/C ratio*	*Slump (mm)*	*† UCS (N/mm²)*	
					7 day	*28 day*
Control	300	0	0.62	50	25.0	37.0
Workability increase	300	0.14	0.62	90	26.0	38.0
Strength increase	300	0.14	0.56	50	34.0	46.0
Cement saving	270	0.14	0.62	50	25.5	37.5

*Water: cement †Unconfined compressive strength

When selecting a suitable plasticiser the following should be tested[54]:

- Increase in slump against a standard for a given water/cement ratio
- Strengths, particularly 24 hours
- Reduction of water for a given slump
- Percentage air entrainment, can it be controlled
- Is the bubble size controlled

Types of materials used[6]:

(a) Lignosulphonate salts are made from naturally occurring lignins reacted with a lime and sulphurous acid mixture in the pulping of wood. They are usually described as calcium lignosulphonates although sodium, ammonium and magnesium SAICCOR (South African Industrial Cellulose Corporation) types are also available. Lignosulphonates used as admixtures may or may not contain sugars, varying amounts of gums, and a textbook of other plant extracted or derived metabolites[22]. If sugars are present retardation may occur depending on type and quantity. Sugars can be reduced by acid or alkali hydrolysis and gums broken down, the latter to reduce the viscosity of the liquor.

(b) Polyhydroxy compounds, ie carboxylic acid based, are similar in function to lignosulphonates and may lead to excessive retardation on overdosing.

1.2.3.1 Normal Water-reducers

This type of admixture is characterised by its ability to impart workability or permit water reductions without interfering significantly with the subsequent hydration of cement. The most traditional basis for these admixtures is lignosulphonic acid of the type mentioned earlier. The chemical formula of lignosulphonate is very complex but it can be said to be a large and essentially spherical polymeric sulphonate containing sufficient

groups (hydroxyl, methoxy, carboxylic acid and sulphonic acid) in the polymer backbone to allow adsorption onto cement particles without any significant interference with the hydration of those particles. The effect of calcium lignosulphonate in particular has been studied on the hydration process of portland cement[67] and it was found, although there is some evidence that the admixture may perhaps alter the rate of reaction, that the products of hydration are unaltered.

Normal water-reducing admixtures may also be formulated from wholly synthetic materials or chemically modified natural products, either as single component systems or blended formulations. Examples of such raw materials are polycarboxylic acids and their derivatives and certain polyhydroxy compounds such as starch hydrolisates. The chemical composition of this type may be controlled at the process of manufacture, giving the ability to "tailor make" an admixture to suit a particular set of applicational requirements[7].

At the manufacturer's recommended dosage rate, these admixtures due to their nature, do not affect the setting time of OPC to a degree significant enough to make any changes in concrete-placing practice necessary. At exceptionally high dosages certain products may cause retardation to an extent, most notably with the added effect of low temperature conditions. There is some indication that admixtures of this type may cause some slight increase in air content when used as a workability or water-reducing aid[68]. However this is usually only form 0.2 to 0.5% additional air entrainment and is more than compensated for by the additional strength possibilities. Materials are occasionally blended with a plasticiser to prevent this additional air entrainment.

Increased workability by the addition of a normal water-reducing plasticiser depends on a number of factors including the following[7]:

(i) dosage level of the admixture
(ii) cement content
(iii) cement type
(iv) aggregate type

When used as workability aids or water reducers admixtures of this type do not adversely affect shrinkage, either due to volume effect of hydration products under saturated conditions or due to moisture loss under non-saturated conditions, in comparison with mixes of similar workability and strength characteristics produced at higher cement contents. Creep is essentially design factor and since it has been stated that it is associated with water movement at the molecular level then the surface active nature of admixtures has led to some examination on its effect on this property. There is now a significant volume of data on the influence of plasticising admixtures on shrinkage and creep of concrete[69] to show that they have no deleterious effect on the creep of concrete.

Table 7 Examples of various concrete mixes with normal water-reducing admixtures[7]

Mix number		*1*	*2*	*3*	*4*
Purpose of use		*Control mix*	*Increased workability*	*Increased strength*	*Cement economy*
Mix proportions:					
Cement (OPC)	By weight	1.00	1.00	1.00	1.00
Sand (Zone 2)		1.80	1.80	1.80	1.93
Gravel (20–5 mm)		4.05	4.05	4.05	4.55
Water/cement ratio		0.55	0.55	0.50	0.55
Admixture		0	Normal dosage	Normal dosage	Normal dosage
Properties:					
Slump (mm)		75	135	75	75
Density (kg/m³)		2480	2480 (4%)	2495	2480
Compressive strength (N/mm²) at:	7 days	24.0	28.5 (118)	30.0	23.5
	28 days	30.5	33.0 (108)	38.5	32.5

The following list summarises the main applications for admixtures of this type[7]:

(a) The effective plasticising action of normal water-reducing admixtures increases the workability of most types of concrete mixes without reducing the compressive strength. This is particularly useful when concrete pours are restricted due to either congested reinforcement or thin sections.

(b) When harsh mixes are experienced, as those produced with crushed aggregates, then considerable improvements in plastic properties of the concrete can be obtained.

(c) When used for its water-reducing effect, higher strengths at an early and subsequent age can be obtained. This may be applied where required strengths are difficult to obtain within specified maximum cement contents and where early demoulding is required.

(d) When used for water reduction, concrete of lower permeability and correspondingly greater durability to the action of aggressive agents may be produced.

(e) By modifying the concrete mix design in conjunction with the addition of an admixture of this type, cement reductions of about 10% can be obtained. As a rough guide it can be generally stated that for each 1p spent on the admixture, then approximately 4-5p worth of cement can be saved.

1.2.3.2 Accelerating Water-reducers

Two categories are now available : those containing chloride and those not. Chloride based accelerators/water-reducers are mixtures of the familiar calcium chloride (which is the accelerating component) blended with a plasticiser/water-reducing agent. Chloride containing admixtures have been much criticised as explained in section 1.2.1 Accelerators. The chloride-free admixtures contain one or more of the following

materials: calcium formate, calcium nitrite, triethanolamine as the accelerating component[7]. The water-reducing ingredient is normally a lignosulphonate, although hydroxycarboxylic acids in lower proportions can be utilised and tend to produce solutions less susceptible to sedimentation, especially in the case of chloride containing products. All accelerators/water-reducers increase the rate of hydration of cement resulting in a more rapid build-up of strengths, which is particularly useful at low ambient temperatures as shown in Tables 8,9[6] below.

Table 8 Effect of accelerating/water-reducing admixtures at low ambient temperatures

Temperature of casting or curing	*Mix (300 kg/m³) slump — 50 mm*	*W:C ratio*	*UCS (N/mm²)*			
			1 day	*3 day*	*7 day*	*28 day*
2°C	Control	0.65	—	3.6	12.8	26.1
	Admixture	0.60	—	7.2	19.3	32.0
5°C	Control	0.65	—	5.4	16.7	30.9
	Admixture	0.60	—	8.0	21.0	35.9
18°C	Control	0.65	5.6	15.5	28.1	38.6
	Admixture	0.60	7.9	19.2	32.9	41.6

Table 9 Effect of an accelerating/water-reducing admixture on setting time

Mix	*Setting time (mins)*	
	Initial	*Final*
Control	140	200
Admixture (normal dose)	75	115
Admixture (double dose)	65	95

In the case of the chloride containing admixture acceleration is achieved by the calcium chloride reacting with the C_3A/C_3S phases in cement (these phases are responsible for the early setting characteristics of the cement and later strength development respectively)[6]. From B.S. requirements (Table 4) it can be seen that the stiffening time, ie set, to reach 3.5 N/mm² of mortar sieved from concrete should be at least 1 hour less than the control mix. There is normally no increase in the air content of mixes containing admixtures of this type. An accelerating water-reducing admixture can be used to produce a concrete possessing greater workability to allow easier placing in congested areas and yet provide high early strength. As an example, at a normal dosage of such a material, 40 mm slump would be expected to increase to approximately 70 or 80 mm[7].

Development of high strengths of the initial stages is the main application. Although these

admixtures can be used as a straight addition to obtain higher workability with some increase in initial strength, it is more usual to combine some slight water reduction with the acceleration effect to achieve very significant increases in strength. Table 10[7] illustrates the use of straight addition and, for general interest, a comparison is also made with the lignosulphonate plasticiser of the normal water-reducing type. Table 11 illustrates the use of an accelerating/water-reducing capability in comparison with calcium chloride solution itself.

Table 10 Achievement of increased workability from accelerating water-reducing admixtures

Admixture type	*None*	*Normal water reducing*	*Accelerating water reducing*	
Mix proportions:				
Cement (RHPC)	1.00	1.00	1.00	
Sand (Zone 2)	1.24	1.24	1.24	
Gravel (20–10 mm)	3.20	3.20	3.20	
Water	0.48	0.48	0.48	
Admixture	—	Normal dosage	Normal dosage	
Properties:				
Slump (mm)	40	65	70	
28-day density (kg/m³)	2480	2480	2480	
Average compressive strength (N/mm²) at				(%)
7 day	33.5	32.5	40.5	(121)
28 days	49.0	52.0	56.5	(115)

As far as permeability is concerned there is some evidence[70] that the effective pore diameter distribution is changed by the addition of calcium chloride and that there is some change in the hydration species of tricalcium silicates. It appears generally that the permeability is reduced by the calcium chloride and together with the water reduction by the admixture produce a more impermeable concrete (increased durability). When the admixture is used to produce high early strength with the simultaneous reduction of the water/cement ratio, generally the shrinkage due both to hydrate volume changes and to moisture removal will be slightly higher than for the control concrete. Where a straight addition is made to provide a more workable yet quicker hardening concrete there will be a greater increase in shrinkage. There are indication that accelerators/water-reducers should not be used in creep sensitive situations[7].

Table 11/...

Table 11 Achievement of maximum strength from accelerating water-reducing admixtures[7]

Admixture type	*None*	*Calcium chloride solution*	*Accelerating water-reducing admixture*
Mix Proportions:			
Cement OPC	1	1	1
Sand (Zone 2)	2.2	2.2	2.2
Gravel (20–10 mm)	4.5	4.5	4.5
Water	0.58	0.56	0.52
Admixture	—	Normal dosage (1.5% by weight of cement)	Normal dosage
Properties:			
Slump (mm)	15	15	15
28-day density (kg/m³)	2450	2465	2450
Average compressive strength (N/mm²) at			
7 days	27.1	29.0	32.5
28 days	42.0	45.5	53.2

As outlined earlier, products of this type can impart workability whilst giving high early strength, or even higher early strengths at similar workability to the control. In view of this they will find applications as follows :

(i) To impart higher early and ultimate strength to concrete, enabling forms to be stripped sooner in site-cast concrete and earlier demoulding in the precast applications. This effect is particularly useful at low temperatures, when it also lessons the susceptibility to frost damage.

(ii) The effective plasticising action of this product will give increased workability to many concrete mixes to enable easier placing yet to raise early compressive strength. Water reductions can be made without affecting the workability with consequent increases in strength, impermeability and durability.

(iii) Earlier finishing of concrete floors and screeds (adding layers to existing floors). These advantages result in savings in production time, labour and materials costs. It is interesting to note that plasticising accelerators are of particular use in flooring and screeding applications where time between initial and final trowelling can be reduced by as much as 50%[6].

1.2.3.3 Retarding Water-reducers

As the name suggests this admixture is intended to produce the opposite effect to accelerators/water-reducers as far as setting and initial hardening are concerned as shown in Table 12. As with other admixtures in the water-reducing group it allows increased

workability or water reductions, but retards the set and initial hardening of concrete. Strength development thereafter follows closely that of a control. B.S. specifications (Table 4) state that the retarding influence at normal dosage should be at least 1 hour longer than for the control mix; this, of course, depends on the mix ingredients, cement type and dosage level.

Table 12 Effect of retarding/water-reducing admixtures on setting time and strength build up[6]

Admixture addition (litres/50 kg)	*Setting time Proctor needle (hrs)*		*W:C ratio*	*UCS (N/mm²)*		
	Initial	*Final*		*3 day*	*7 day*	*28 day*
0	4.5	9	0.68	20.3	28.0	37.0
0.14	8	13	0.61	28.0	36.5	46.8
0.21	11.5	16	0.58	29.6	40.1	49.7
0.28	16	21	0.58	30.1	41.6	54.1

Table 13 Strength development with retarding/water-reducing admixtures[7]

Mix number	*1*	*2*	*3*	*4*
Mix purpose	*Control mix*	*Increased workability*	*Increased strength*	*Cement economies*
Mix proportions:				
Cement OPC	1.00	1.00	1.00	1.00
Sand (Zone 2)	1.8	1.8	1.8	1.93
Gravel (20–5 mm)	4.05	4.05	4.05	4.55
Water	0.55	0.55	0.50	0.55
Admixture	—	Normal dosage	Normal dosage	Normal dosage
Properties:				
Slump (mm)	75	150	75	75
Density (kg/m³)	2480	2480	2495	2480
Compressive strength (N/mm²) at 7 days	24.0	30.5	31.5	25.5
28 days	31.0	37.5	40.5	34.0

These products are based normally on hydroxycarboxylic acids which contain a considerable amount of hydroxyl groups which are absorbed on the surface of cement, thereby retarding initial hydration. They also possess carboxyl groups which are negatively charged and cause deflocculation of cement particles, as discussed earlier. Lignosulphonates containing retarding ingredients are also utilised, either fortuitously by the use of products of lesser purity (wood sugars) or intentionally by the addition of phosphate or sugar-based retarding species[7]. Retarding/water-reducers are, in their effect,

hybrids of retarders and plasticisers. Their uses bridge the applications of both groups.

Applications include :

(a) Long hauls of ready-mixed concrete
(b) High cement content mixes
(c) High ambient temperatures conditions and prevention of "cold joints" (compare with section 1.2.2. Retarders).

If the water content is reduced significant increases in strength are obtained, which can be used to allow cement economies in a mix. Table 13 illustrates three different mixes in comparison with a control mix. The air content can increase on addition of these materials, but can be offset by adding an air-detrainer. Durability is increased since the delayed rate of early cement hydration leads towards a more dense crystalline network of hydration products. Volume changes in the hardened state is due to the amount of water in the mix, which in turn is affected by the cement content[7]. Therefore, if retarding plasticisors are used to decrease the water content (increased strength) or lower the cement content, shrinkage will be reduced. There is no deleterious effect on creep under water-saturated conditions.

1.2.4 Superplasticisers

Superplasticisers are comparatively new (since the late 1960's) and are far more effective in decreasing the viscosity of the fresh concrete mix than ordinary plasticisers. This extreme workability without the addition of extra water results in "flowing concrete", ie the water content can be reduced without loss of workability, or strength and workability can be increased simultaneously at no substantial extra cost. It should be noted that in each case the scale of the effect goes far beyond that obtained from normal plasticisers and to achieve it much higher dosages of superplasticiser are used (see Fig.14) . In practice it is also important that use of the admixture at this dosage level does not result in adverse side-effects that will result in gross retardation of the set and initial low strength[8].

Chemically they are based on synthesised partial condensates and comprise a group of formaldehyde derivatives such as melamine-formaldehyde, naphthalene sulphonate-formaldehyde and partial condensates of sulphited sugars. The remarkable plasticising action is demonstrated by slumps of 200 mm without an increase in water content. Alternatively water reductions as high as 30% may be achieved[6]. Superplasticisers can turn dough-like mixtures into fluids. Many are high in basic cost, although each product should be judged on its cost-in-use. Chemicals capable of imparting high fluidity to a concrete should also offset bleeding and segregation in order to be totally effective. Dosage rates can vary from a fraction of a percent to 1.5% of the cement weight.

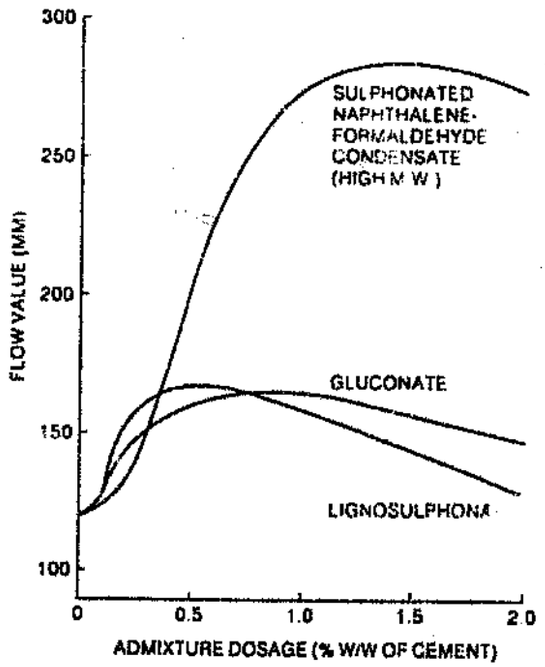


Fig. 14 Fluidity of cement paste containing various dispersing agents at constant water/cement ratio[8]

Several distinct types of superplasticiser are available , base. ifferent chemicals, although they purport to have similar functions in concrete. ..ey are all organic compounds of high molecular weight, some being synthetic and others derived from natural products. In 1976 a CAA/C&CA Working Party[71] defined the following categories of superplasticiser :

A. Sulphonated melamine-formaldehyde condensates

These are polymers with the structural formula shown in Fig.15. According to the literature[8] the value of '*n*' is usually in the range of 50-60, giving a molecular weight in the region of 20 000. However sources for other uses of melamine-formaldehyde resins would consider an *n* value of 4 or 5 more realistic[72]. These condensates are usually employed in the form of the sodium salt illustrated, which is very soluble in water due mainly to the sulphonate groups on the side-chains.

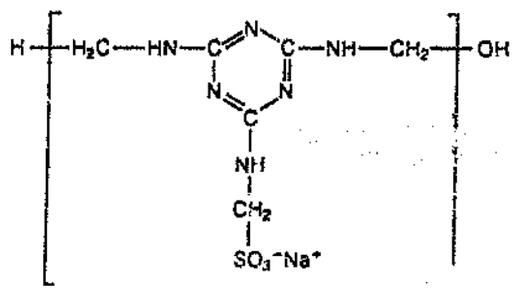


Fig. 15 Sulphonated melamine-formaldehyde

B. Sulphonated naphthalene-formaldehyde condensates

These are polymers similar in many ways to the previous category, with a simple repeating unit as shown in Fig.16. Again the sodium salt is usually employed, solubility being due solely to the sulphonate groups. The value of n is in this case is typically in the range 5-10, giving a molecular weight in the order of 2000.

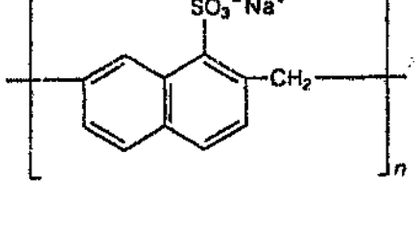


Fig. 16 Sulphonated naphthalene-formaldehyde[8]

C. Modified lignosulphonates

The lignosulphonates derived from wood-pulping are commonly used as plasticisers and in order to improve their effectiveness they are further refined and modified. The processing involves the more thorough removal of sugars and other unwanted impurities, selection of a higher molecular weight fraction and optionally, further sulphonation or partial polymerisation. The calcium or alkali metal salts are employed in the admixture, the latter having a superior water-reducing ability. The basic repeating unit of the lignosulphonate molecule has a rather complex phenyl-propane skeleton. Substituent groups vary and may include phenolic, carboxylic and methoxy in addition to sulphonate. In solution the molecule coils into a spherical configuration, with ionised groups at or near the surface ; Fig.17[8].

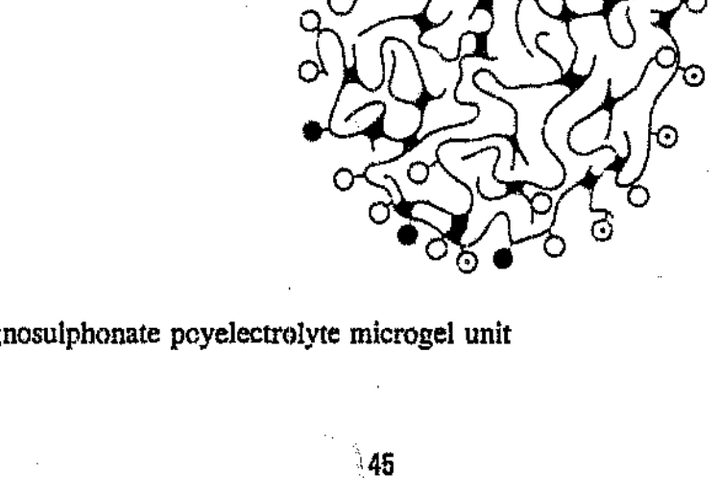


Fig. 17 Lignosulphonate polyelectrolyte microgel unit

D. Various chemical or mixtures

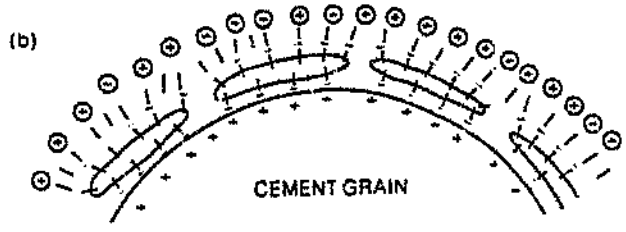
Acid amide/ploysaccharide mixtures and other high molecular weight hydroxylated polymers and copolymers are examples. This is not a very important category as yet, but current research could give rise to new types of superplasticising admixture in the near future.

In recent years the distinction between these categories has become rather blurred, as attempts have been made to blend B and C materials in order to produce a cheaper but effective plasticiser. Also a new class of "retarding superplasticiser" has gained acceptance for applications where longer retention of high workability is required. They are usually a blend of retarding plasticiser and category A or B superplasticiser and will be covered by B.S.5075:part3. They are already included in the ASTM C-494 specification[8].

The only superplasticiser/accelerator admixture currently available is Melment. It is a partial condensate of melamine-formaldehyde and has to be used at dosages ranging from 0.5 to 1.5% of solid material[22]. This makes it very expensive to use allowing only specialised high cost applications, for example such as grouting. Melment shortens the working time to 5-7 min after which the flow is lost. Its disadvantages therefore are : high cost, high dosage, working time too short for normal application and being based on melamine the cost of which keeps rising[22]. The aim of this project is to replace Melment completely or partly with a product which has the following characteristics : low cost, low dosage, normal working time and based on readily available raw materials.

1. Mode of action

The mechanism by which superplasticiser produce their effect is very similar to that of normal plasticisers. The main difference is that the former consist of very large molecules (colloidal size) which dissolve in water to give ions with a high negative charge. Although the configuration of the anions is not known (except in the case of lignosulphonates) they may be represented as in Fig. 18[8] with the sulphonate groups oriented outwards into the water (a). These anions are attracted to the surface of cement grains (b) and at normal levels of admixture usage, are absorbed in sufficient numbers to form a complete monolayer around them.



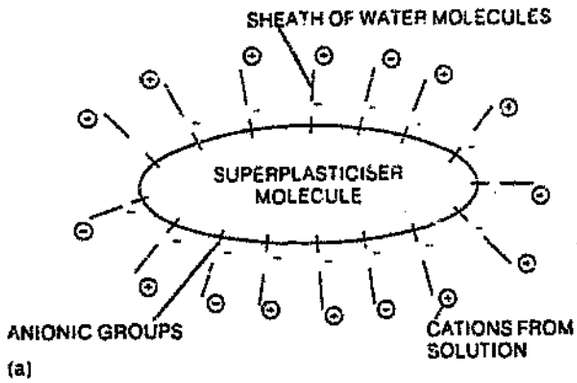


Fig. 18 Representation of a superplasticiser molecule and mode of absorption on cement (after Kreijger[73])

The combination of electrostatic repulsion and large ionic size (which provides physical separation) brings about a rapid dispersion of the individual cement grains. In doing so water trapped within the original flocs is released and can then contribute to the mobility of the cement paste - and hence to the workability of the concrete. Superplasticisers do not cause much reduction in the surface tension of water, therefore there is little tendency to excessive air entrainment even at high dosage. The adsorption of the anions on the surface of the cement grain is also less tenacious than in the case of retarders (eg. hydroxycarboxylic acid salts) and the course of hydration reactions is not hindered at normal dosage levels. Hence, for normal superplasticisers there should be no significant retardation of setting and hardening[8].

2. Effect on fresh concrete

The properties of fresh concrete containing a superplasticiser are affected by both the category of the superplasticiser and by the initial workability of the mix. It is therefore convenient to compare the properties of a control mix with those of a superplasticised mix which has been water-reduced to give equal workability and also with a mix of unchanged water content which will produce a high workability flowing concrete.

At high levels of water reduction workability may be lost rather more quickly than would be expected with a normal concrete mix having the same initial workability. When used to produce flowing concrete, particularly at the highest end of the range, cohesion can be adversely affected : segregation of the coarse aggregate during placing and bleed and segregation *in situ*. These undesirable properties can be avoided by careful choice of superplasticiser type, mix design, aggregate shape and grading. Category C superplasticisers, because of their tendency to slightly increase air-entrainment, may enhance the cohesion of the mix. Category B generally have little effect on air, while category A usually reduce the natural air-entrainment thus slightly reducing the cohesion. This generally applies to both high workability mixes, when the stability of the entrained

air is low and to water-reduced mixes. With flowing concrete an over-cohesive mix is generally preferable and if a pump mix design to produce a 75 mm control slump is used, this will normally produce good flowing concrete when superplasticised[8].

The dosage required to give a particular level of fluidity is dependant on the category of the superplasticiser and on the concrete mix design and its constituents. A plasticiser which gives satisfactory flowing concrete in one mix will not necessarily, at the same dosage, do so on another mix design using different sand and aggregate. Fig. 19 shows a typical set of results of flow vs dosage for three categories of superplasticiser[74].

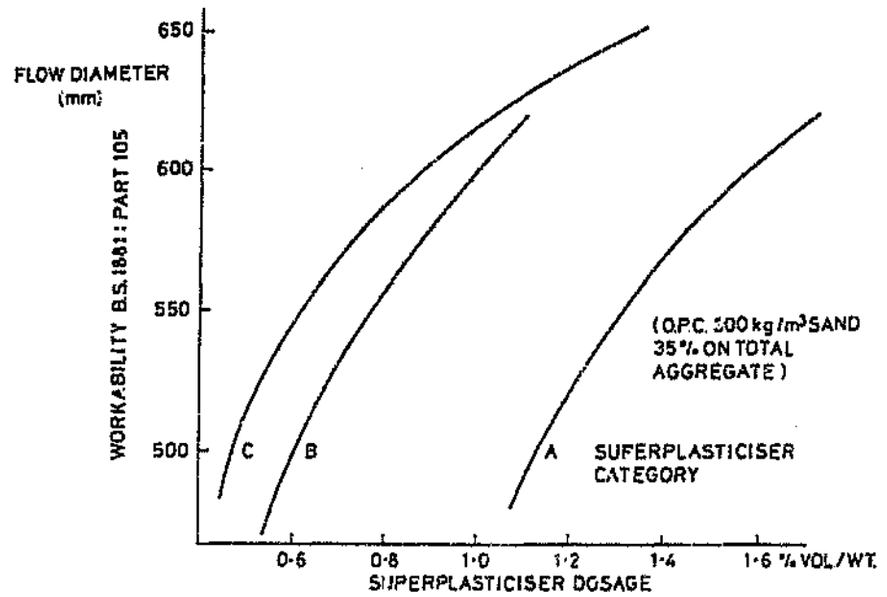


Fig. 19 Typical workability vs dosage results for three categories of superplasticiser

For a given application, the period over which it is desirable for a superplasticiser to retain its fluidity will depend on several factors. These include ambient temperature, likely time delay between the addition of the superplasticiser and placing of the concrete and time delays to subsequent pours if self-compaction is required or if early access onto the still plastic concrete is required in order to add a topping. The workability retention period is significantly affected by the initial workability but Fig.20[8] gives typical results for three categories of superplasticiser.

When used as a workability aid, those categories which give extended periods of high workability will also result in extended setting times[76]. Setting times of the water-reduced mixes, having the same workability as the control mix vary from -30 minutes for category A superplasticisers to +60 minutes for category C, relative to the control (see Table 12[74]). This needs to be borne in mind when selecting the category of superplasticiser for a certain application, particularly at very low or very high ambient temperatures.

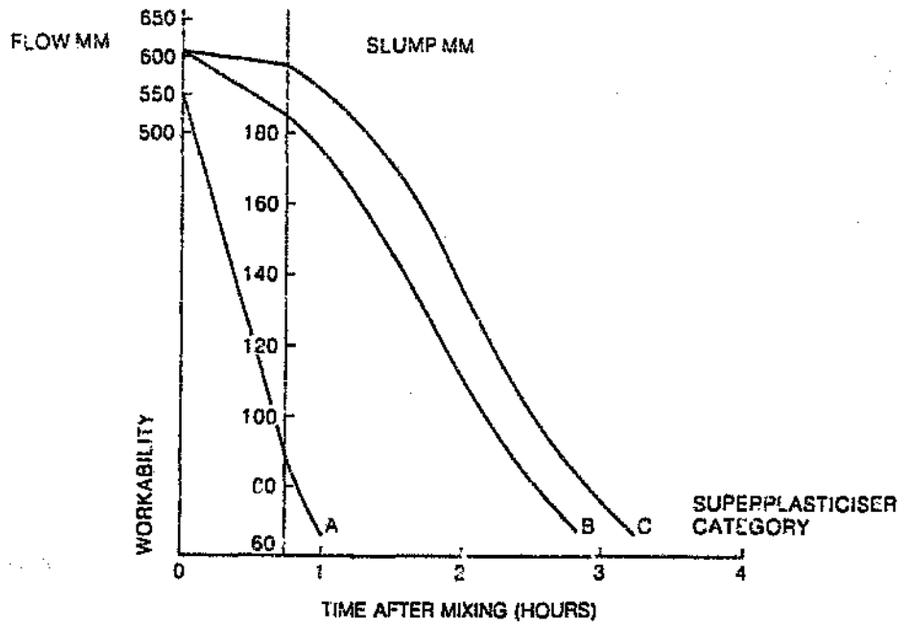


Fig. 20 Retention of high workability by different categories of superplasticiser[75]

Table 12 Typical results of workability loss and setting time. (Note the extension of initial stiffening time when the sample is taken 2 hours after mixing)

Superplasticiser	*Initial workability slump/flow*	*Workability at 2 hours slump*	*0.5 N/mm² Initial stiffening time. Relative to control mix*	
			Sample taken after mixing	*Sample taken at 2 hours*
Control	75 mm slump	15 mm slump	3 hr: 10 min	—
Category A	600 mm flow	45 mm slump	+ 0 hr: 25 min	+ 1 hr: 00 min
Category B	550 mm flow	95 mm slump	+ 0 hr: 55 min	+ 1 hr: 30 min
Category C	570 mm flow	110 mm slump	+ 1 hr: 30 min	+ 2 hr: 05 min

3. Effect on hardened concrete

The properties of superplasticised concrete, whether of the high strength or high workability type, depend mainly on the mix design and particularly on the water:cement ratio. Bearing in mind the essentially physical action of the admixtures in fresh concrete this is to be expected, but the high degree of dispersion of the cement does have an effect on early strength. Due to the greater accessibility of the cement grain surfaces, early hydration is more complete and 24 hour strengths of concrete are generally higher than in the case of non-superplasticised concrete of the same water:cement ratio [77]. By 28 days these effects have diminished and long term there is no deviation from the accepted strength - water:cement relationship.

As in the case of normal plasticisers, these admixtures can be used to produce a wide range of concretes. These will include concretes with improved workability, reduced water content, reduced cement content, or a combination of such benefits. In flowing concretes category A plasticisers generally give early and final strengths slightly higher than the control mix, but category B superplasticisers may cause a slight reduction in early and increase in final strength. Category C gives similar results. Where the maximum water reduction is the main intention (this can vary between 20 and 35%[8]) it is possible to achieve very high early and ultimate compressive strengths, as indicated in:

Table 14 Compressive strengths of water-reduced concretes containing a category B superplasticiser[79]

Cement content (kg/m³)	334	355	378	404	434	471	512
Water: cement ratio	0.55	0.50	0.45	0.40	0.35	0.30	0.25
Admixture dosage* (% Weight of cement)	None	0.70	1.00	1.40	1.80	2.20	2.95
Slump (mm)	93	96	94	97	96	106	108
Air content (% by volume)	1.2	1.2	1.4	1.5	1.5	1.5	0.8
Compressive strength (N/mm²) at:							
1 day	11.4	12.9	17.6	19.7	29.6	41.5	47.2
3 days	21.1	31.0	36.9	45.6	61.6	74.0	82.6
7 days	32.3	42.8	51.0	59.0	75.1	85.3	93.8
28 days	41.6	52.7	58.6	70.0	85.6	96.6	110.8
365 days	49.6	60.8	72.8	85.8	100.2	112.8	120.6

*The admixture used was a 42% solution of a Category [illegible] condensate.

However the question of long term concrete performance is often raised, particularly with respect to durability, creep and shrinkage. In reply to this genuine concern, it can be stated that all the available evidence indicates that superplasticisers have no adverse effects on the engineering properties of concrete. Tests carried out over a one-year period on flowing concrete (both air-entrained and non-air-entrained) and water-reduced concrete show that, compared with control concretes of identical water:cement ratio, strength, drying shrinkage, swelling, modulus of elasticity and durability in sulphate solutions were not significantly affected by the presence of a category B superplasticiser [78-80]. Other data are also available which confirm that there is no fall off in strength over period of eleven years for plasticised concrete containing a category B plasticiser[79]. Freeze/thaw durability is also no worse than that of comparable normal concrete, also in the case of air-entrained concrete. Other properties of concrete relevant to long-term durability are permeability and the protection of reinforcement from corrosion. Again, all the valuable evidence indicates that no deleterious effects are caused by the use of superplasticisers. In the case of water-reduced concrete there is a beneficial effect on permeability and a reduction in the rate of carbonation. Superplasticisers, being chloride free do not chemically promote corrosion ; this has been confirmed by exposure tests in Japan[79], see:

Table 15 Rusting of reinforcement embedded for 5 years in prestressed autoclave concrete piles[8]

Admixture	*Dosage (% wt of cement)*	*Rust coverage (%)*
None	—	0.25
Category B superplasticiser (42% solution)	0.60	Trace
Calcium lignosulphonate plasticiser	0.25	0.10
Calcium chloride	0.05	0.30
	0.50	0.60
	1.00	11.70
	2.00	19.60

4. Practical considerations

Each superplasticiser type gives its own characteristic to the concrete. In the following paragraphs the main characteristic of each superplasticiser is highlighted. Category A shows little or no retardation and may therefore be preferred at low temperatures when high early strengths are required or in flowing mixes for floor slabs where early access for finishing equipment is desirable. Loss of workability with this category, particularly with water-reduced concrete, is very much more rapid than with other categories which, while having advantages on floor slabs at low temperatures, can give very short periods of placing at normal or elevated temperatures. The workability of a flowing mix may fall to only a 70 mm slump in less than 15 minutes at 40°C. It is therefore preferable to add this category of superplasticiser directly into the ready-mix truck at the job site and then place the concrete as quickly as possible. If workability is lost before placing, a second dose of this admixture may be added to restore workability without significant loss physical properties within the hardened concrete. This procedure is not normally recommended with other categories of superplasticiser[8].

Category A superplasticisers tend to reduce air-entrainment resulting in a mix which may be prone to bleed and segregation, so a higher than normal sand is desirable to improve the cohesiveness of themex. At very high workability levels the mix may still show signs of segregation and transportation and vibration should therefore be kept to a minimum. 24-Hour strength is typically in excess of 150% of the control. Category A[8] should preferably be used for:

- low temperature concreting
- casting floor slabs where early access for finishing equipment is required
- where high early strength is required

Category B superplasticisers give slightly higher levels of set retardation and air-entrainment than those of category A, but also give significantly longer periods of

workability retention. This makes it possible for the admixture to be dosed at ready mix plant prior to trucking to site. The increase in the level of air-entrainment is too low to affect the cohesiveness of the mix, so a high sand content is desirable with the high workability mixes to prevent bleed and segregation. At normal to high ambient temperatures the benefit of the longer period of workability retention becomes an important advantage. This, coupled with a retardation of 20 to 40 minutes in high strength water-reduced mixes, makes this category of superplasticiser very effective for pre-cast concrete at ambient temperatures between 15 and 40°C, as well as on plants where a heating cycle is used. Category B[8] superplasticiser should preferably be used for:

- precasting at normal and elevated temperatures
- floor slabs laid at normal or elevated temperatures
- casting mass concrete with heavy reinforcement where self compaction and some workability retention is required

Category C superplsticisers give the highest retention of workability and is therefore very effective at high ambient temperatures or where long trucking distances and placing delays may occur. Conversely they also give the most set retardation and therefore generally give the lowest 24 hour strengths. Since category C give an increase of between 1 and 2% in the level of entrained air in the mix, an increase in the sand content of high workability mixes reduces the likelihood of bleed and segregation. These features make this category particularly suitable where superplasticisers are being used with aggregates having a poor grading profile or where the superplasticiser is being batched in a ready-mix plant before trucking to site[8].

When category C superplasticisers are being used to produce a water-reduced mix, the mix may become over-cohesive and prevent the full water-reducing potential of the admixture from being realised. In this situation the sand content can often be reduced by between 3 and 5%. Category C[8] superplasticisers should preferably be used for :

- concreting at high ambient temperatures
- concrete where the admixture is being added at the ready mix plant and then transported long distances to site
- mass concrete with heavy reinforcement where self-compaction and some workability retention is required
- high workability mixes where poor aggregates are likely to lead to problems of bleed or segregation

PART 2

2. Tannins

2.1 General

Tanning of animal hides and skins to make leather is the oldest application of tannins. Over centuries, with the application of empirical methods, reasoning, improvisation, trial and error, it has developed into a highly skilled craft. In recent times tannins have consistently lost ground to metal salts (chomium[58], etc.) in the manufacture of leather.

A great deal of fundamental scientific study has now unequivocally established the structures of many of the key plant polyphenols and has defined, at least in broad outline, the manner in which they are formed in plants and how they are inter-related to other important groups of natural products. This surge in knowledge of a fundamental chemical and biochemical nature has given rise in the last fifteen years to a burgeoning practical interest in the influence and role of plant polyphenols in diverse areas such as agriculture, foodstuffs and nutrition, beverages, traditional medicines and herbal remedies, chemical protection in plants, and the potential use of plant polyphenols as sources of important industrial organic chemicals[102]. Other new applications of tannins include partial replacement in phenolic resins[86], use in drilling muds, cooling water treatment, mineral dispersion, chemical grouting, and as concrete additives[58].

Polyphenols (vegetable tannins) constitute a distinctive and unique group of higher plant metabolites. Their uniqueness lies not only in their polyphenolic character but also in their relatively large molecular size (M.wt. up to 20 000)[102]. From a botanical point of view they represent a distinctive example of the general phenomenon of secondary metabolism in plants. Substantial accumulations of vegetable tannins can be found in almost any part of a plant: seed, bark, wood, leaves, fruit, pods, root, or even in secondary plant growths, like galls.

> "Tannins" were originally defined as those astringent vegetable substances which had the property of tanning leather. Other definitions mention their ability to form coloured solutions and precipitates with iron and other metals. Tannins are also precipitated from solution by forming complexes with macromolecules[102] such as proteins (as in tannage), polysacharrides and alkaloids. These loose definitions incorporate two important classes of naturally occurring complex, amorphous phenolic-based compounds - namely: hydrolyzable tannins and condensed tannins.

Neither term (hydrolyzable or condensed) is very meaningful since examples of both types can be degraded by acid (see section 2.6.4). Therefore condensed tannins are now

more correctly referred to as proanthocyanidins[117] or more broadly as polyflavonoids and hydrolyzable tannins as gallo- or ellagitannins, or derivatives thereof[116]. However, the terms have become firmly entrenched and are still widely used.

2.2 Hydrolyzable Tannins

Compared with condensed tannins hydrolyzable tannins are of relatively limited distribution in nature[102]. They are abundant in various parts of dicotyledonous plants, such as oak, but have not been detected in monocots[118].

Hydrolyzable tannins are mixtures of simple phenols, such as pyrogallol and ellagic acid, with oligomers of gallic acid derivatives as esters (M. wt. in the region of 3 000)[102] of simple sugars, such as glucose[81]. They obtained their name from the ease of their hydrolysis to gallic acid and its dimer ellagic acid, in the presence of precific enzymes or dilute hydrochloric acid (figures I, II, III, IV, page 58[82]). Hydrolyzable tannins occur naturally in such species as:

- myrobolans (*Terminalia* and *Phyllantus* species)
- dividivi (*Caesalpina coraria*)
- and in trees of the chestnut species[84].

These tannins have not been isolated in conifers[81]. Hydrolyzable tannins have been successfully employed in the production of phenol-formaldehyde resins where they can be used to partially substitute the phenol. This can be achieved since they are analogous to simple phenols in their low reactivity with formaldehyde. They are, however, of little economic importance owing to their limited availability, low worldwide production, high cost, lack of macromolecular structure and low nucleophilicity[64].

2.3 Condensed Tannins

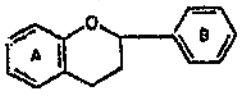
Condensed tannins and their flavonoid precursors are the second most abundant classes of natural phenolic compounds after lignin and are found extensively throughout the plant kingdom[85]. They constitute approximately 90% of the worldwide production of tannins (± 350 000 tons per year). Commercially, these are currently extracted from *Acacia* (wattle or mimosa) bark and *Schinopsis* (quebracho) wood, predominantly in the southern hemisphere[84]. These have taken the form of large scale afforestation (well over half a million acres planted with wattle in South Africa[58]) and/or industrial extraction mainly for the use in leather tanning.

Other potential sources of fairly high concentrations of polyphenlic type compounds include *Tsuga* (hemlock bark extract) and *Rhus* (sumach extract)[86]. The lack of commercial production of condensed tannins in the northern hemisphere is probably

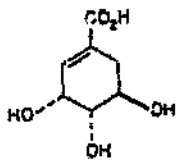
attributed to the limited distribution of the wattle and quebracho species in addition to the extraction problems experienced with the tannin rich conifer species. Despite the problems experienced in the extraction of condensed tannins from these trees, the extraction of condensed tannins from the bark of various *pinus* (pine) was recently commercialised in Chile[87].

2.4 Biosynthesis of Tannins

The biosynthesis of plant phenolics ("hydrolyzable") and polyphenols ("condensed tannins") is highly complex. Only the basics will be briefly outlined. It has been firmly established[105] that benzenoid ring systems of condensed tannins arise by two main pathways, (a) from acetic acid and (b) from shikimic acid. Thus A-rings of the flavonoid type (1) are acetate derived and the B-ring has shikimic acid (2) as its precursor[103].

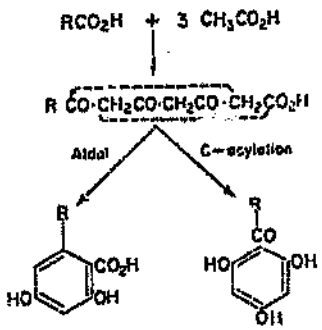


(1)



(2)

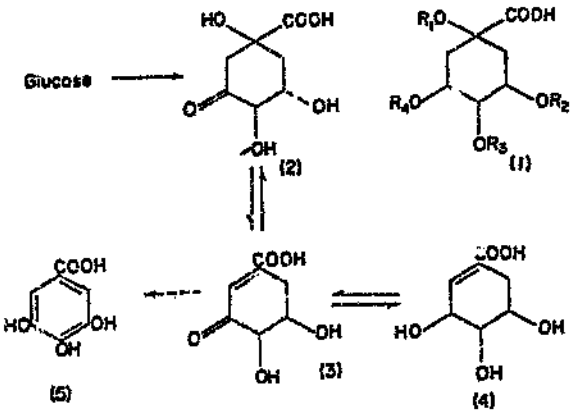
Hypothetically, acetic acid units (biologically activated for acylation) are joined by formal elimination of water in head-to-tail linkage with each other or with naturally occurring carboxylic acids. Ring closure by aldol condensation or C-acylation would then produce phenols of the orcinol or acyl-phloroglucinol type, respectively[104].



Further reactions lead to the generation of carbon-oxygen skeletons which can undergo secondary structural modifications, occurring either before or after cyclization. These modifications include principally the introduction and removal of oxygen, alkylation notably with methyl and isoprenoid groups and halogenation. This enables the extension of the acetate hypothesis to many natural substances[104].

The biosynthesis of gallic acid (5), a hydrolyzable tannin precursor, occurs by the dehydrogenation of 5-dehydroshikimic acid (3). Growth experiments with *Phycomyces blakesleeanus* have supported this conclusion. These experiments also indicated that 5-

dehydroquinic (2) and shikimic (4) acids are near but not immediate precursors of the acid. In addition, both 5-dehydroshikimic (3) and shikimic (4) acids were isolated by ion exchange chromotography from old culture media of *Phycomyces blakesleeanus*, and the former is transformed to gallic acid in good yield by several methods of chemical oxidation[107].



The biosynthesis of proanthocyanidins is one of the most expensive major metabolites next to lignin and protein, i.e. their formation contributes significantly to the utilization of captured photosynthetic energy[116]. Although the functions and uses of tannins have not as yet been fully elucidated, they are thought to be involved in several defence mechanisms, protecting the plant from both pathogens and/or herbivores and in some cases increasing the plants' drought resistance[85].

2.5 The Chemistry of Condensed Tannins

Condensed tannins, consist of flavonoid units which have undergone varying degrees of ionic-based self-condensation. Naturally, these polyflavonoid structures are often found in association with their immediate precursors, including flavan-3-ols, flavan-3,4-diols and other flavonoid analogues (see figures V-XIX, page 58)[88]. Over 4 000 flavonoid structures have been listed of which only 143 are proanthocyanidins[113]. Extracts containing condensed tannins and their precursors are also associated with simple carbohydrates (hexoses, pentoses, disacharrides) and glucuronates (hydrocolloid gums) whose presence is sufficient to affect the viscosity and sometimes, other physical properties[88].

Condensed tannins or proanthocyanidins are classified according to the combinations of resorcinol and phloroglucinol (A-rings) with catechol, phenol and pyrogallol (B-rings). Two major classes are generally defined[110]:

(i) Those containing predominantly resorcinol-type A-rings - confined to tropical and sub-tropical hardwoods (including wattle) and until recently the only ones of economic importance (see 2.5.1)

(ii) Those containing predominantly phloroglucinol-type A-rings - very common in monocotyledonous and dicotyledonous plants (including conifers) which recently became economically important (see 2.5.1)

2.5.1 Monoflavonoids

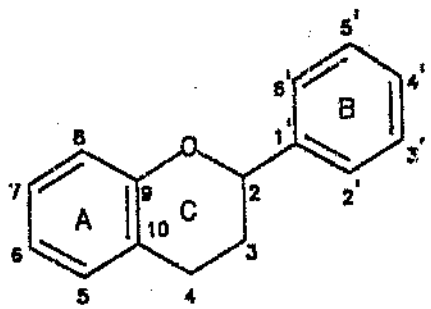
Monoflavonoids are classified as 'phenolic nontannins' and owing to their relative simplicity, are the most widely studied group in the tannin extracts. They include flavan-3-ols (catechins), flavan-3,4-diols (leucoanthocyanidins), dihydroflavonoids (flavonols), flavanones, chalcones and coumaran-3-ones (see figures V-XIX, page 58)[86].

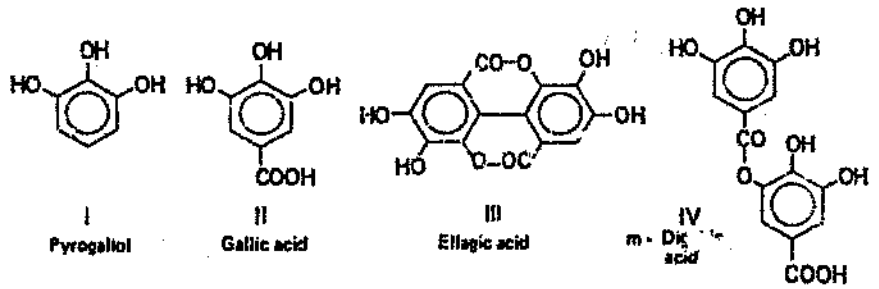
Condensed tannins appear to be formed by flavan-3,4-diols and some flavan-3-ols whilst the remaining structures do not appear to be involved in tannin formation.

In black wattle bark extract the main polyphenolic patterns are represented by flavonoid analogues on resorcinolic A-rings. Approximately 70% of the extract consists of resorcinol A- and pyrogallol B-rings (XX), page 60, and 25% is represented by the resorcinol A- and catechol B-rings (XXI). Small amounts of phloroglucinol A-pyrogallol B (XXII) and phloroglucinol A-catechol B (XXIII) are also present[110].

In contrast, however, pine tannins have completely different patterns and relationships. In general, most coniferous species (including *pinus radiata, taeda, sylvestris, patula* and *pinaster*) present only two main patterns. The more important pattern is based on phloroglucinol A- and catechol B-rings (XXIII), page 60. Also known as procyanidins, these phloroglucinol-catechol condensed tannins have been established to be the most widely spread condensed tannins in the plant kingdom. A lesser evident pattern is based on phloroglucinol A- and phenol B-rings (XX V). The complete lack of resorcinol A-rings has important consequences in the use of these tannins in adhesives[110].

Labelling and numbering systems for a typical condensed tannin monomer unit[121]:





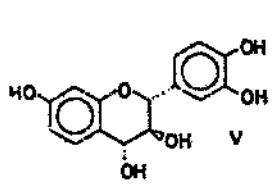
I Pyrogallol

II Gallic acid

III Ellagic acid

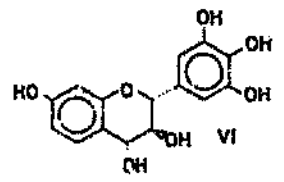
IV m - Di[illegible] acid

A. Flavan-3,4-diols



V

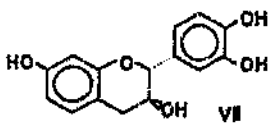
(+) - leucofisetinidin



VI

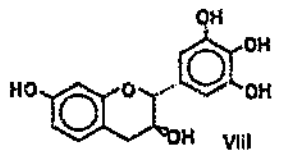
(+) - leucorobinetinidin

B. Flavan-3-ols



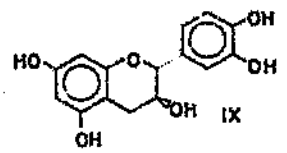
VII

(–) - fisetinidol



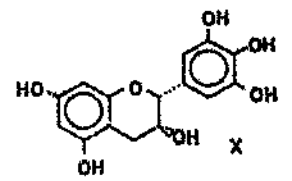
VIII

(–) - robinetinidol



IX

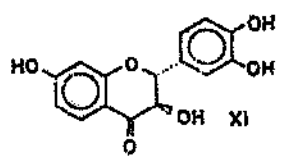
(+) - catechin



X

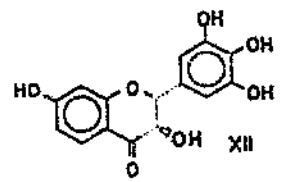
(+) - gallocatechin

C. Dihydroflavonols



XI

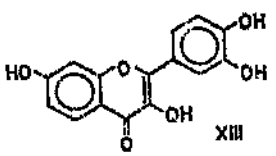
(+) - fustin



XII

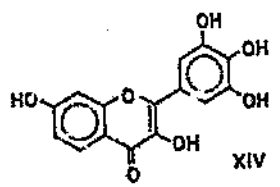
(+) - dihydrorobinetin

D. Flavonols



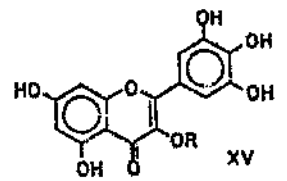
XIII

fisetin



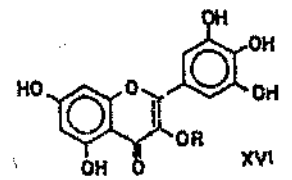
XIV

robinetin



XV

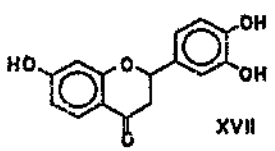
quercetin (R = rhamnose)



XVI

myricitrin (R = rhamnose)

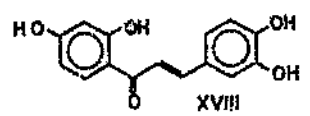
E. Flavanones



XVII

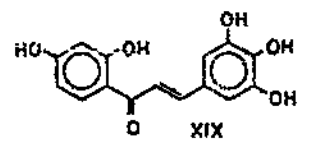
(±) - butin

F. Chalcones



XVIII

butein



XIX

robtein

2.5.2 Biflavonoids

Flavan-3-ols and flavan-3,4-diols participate in tannin formation via an autocondensation process which relies on the nucleophilicity of the A-rings and available reactive positions. Since the other flavonoids are all substituted at position 4 on the heterocyclic ring, the nucleophilic character of the A-rings is reduced and inhibition of autocondensation occurs.

In the flavan-3-4-diols and flavan-3-ols the *meta*-substitution of hydroxyl groups and the heterocyclic oxygen cause strong nucleophilic centres in the C6- and C8- positions on the A-rings. In addition, charge delocalisation stabilises the benzylcarbonium ion formed at the C4-position of the heterocyclic ring (XXV), page 60. Together, these enhance the possibility of autocondensation based on an ionic mechanism[88].

Since there are two positions for attack on the A-ring, namely the 6- and 8-positions, two types of biflavonoid are expected. Both products, 4→6 (XXVI) and 4→8 (XXVII), have been isolated although the 4→8 product does predominate under ideal conditions. In phloroglucinol derived condensed tannins, or procyanidins, 4→8 interflavonoid linkages are more common and are found in an approximate ratio of 3:1 (4→8 : 4→6), in comparison with the predominance of the 4→6 linkage in wattle extracts[110].

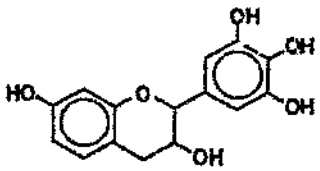
2.5.3 Oligomeric and Polymeric Flavonoids

Some oligomeric flavonoid structures have been elucidated and found, in general, to be an extension of the low molecular weight flavonoid structures. Thus the 4→6 and 4→8 linking patterns have been found to continue in the higher oligomers[89].

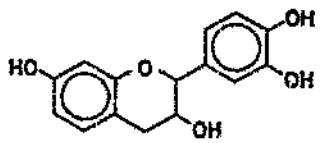
In pine extracts, as all the flavonoids are phloroglucinolic in nature, the condensation pattern is accepted to be via 4→8 interflavonoid linkages only, forming linear chains (XXVIII), page 60[110].

With the 8- and 6-positions providing the nucleophilic function in the phloroglucinolic and resorcinolic flavonoids respectively, self-condensation continues as the 4-carbonium ion electrophile is generated from the flavan a-3,4-diols. This mechanism results in oligomeric units with greater than 10 linked flavonoids resulting in high molecular weight tannins. Wattle tannins have a number average mass of 1250 compared with 1784 for quebracho and in the case of pine a number average mass of 4300 has been established[84].

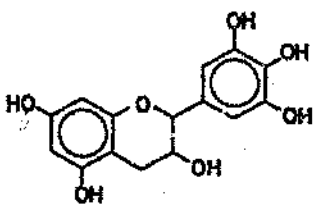
The first two listed (procyanidins and prodelphinidenis) are thought to have an average degree of polymerisation of about 4 to 5[88]. Similarly pine tannin (profisetinidins and prorobinetinidins) are thought to have a number average of 9-11.



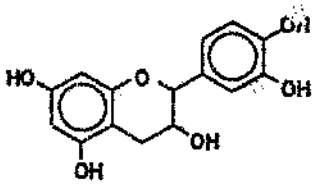
XX



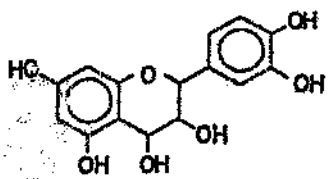
XXI



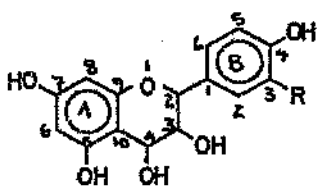
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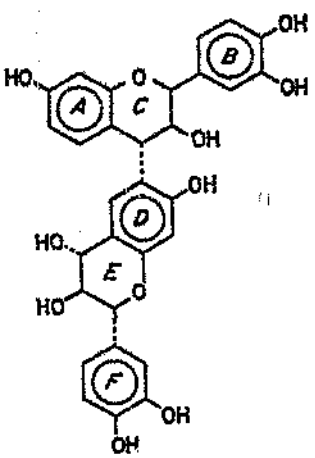
XXIII



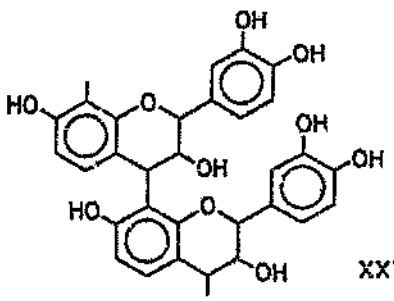
XXIV



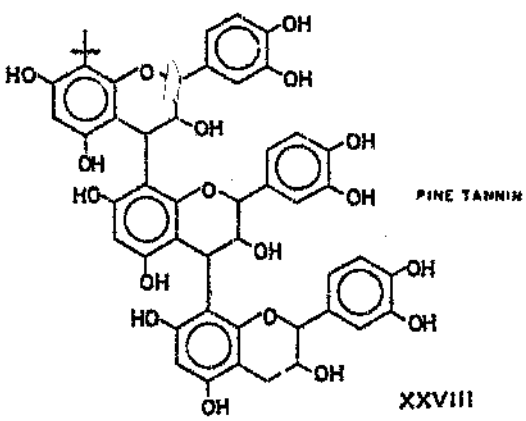
XXV



XXVI



XXVII



PINE TANNIN

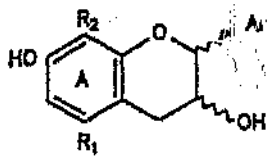
XXVIII

Polyflavonoids also contain the familiar flavonoid skeleton, linked together in apparently infinite arrangements, depending on the nature of the interflavonoid linkage, hydroxylation pattern, stereochemistry at carbons 2,3 and 4 of the pyran ring, as well as the presence of additional substituents (eg: ester linked gallic acid). Hence, well over 100 oligomeric and polymeric proanthocyanidins with subtle but well defined structural variations have been isolated from many different plant species. For the most part, interflavonoid linages occur at C-4, C-6 and C-8[116].

2.6 The Reactivity of Macromolecular Tannins

Compared to lignins, polyflavonoids are exceptionally reactive compounds[115]. In addition to the reactions expected of flavan-3-ol units and some reactions of phenols, such as oxidation[102], condensed tannins exhibit unique reactions due to their macromolecular structure. The chemistry of condensed tannins is dominated by the properties of the A- and B-rings.

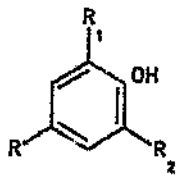
The hydroxylation patterns of the A-ring play an important role (by steric and electronic effects) in determining both nature and rate of reaction that occur on the A-ring and B-ring as well as the interflavonoid bond of condensed tannins[106]. To recap the A-ring[121]:



$R_1 = R_2 = H$; resorcinolic
$R_1 = OH$, $R_2 = H$; phloroglucinolic
$R_1 = H$, $R_2 = OH$; pyrogallic

The presence of the hydroxy groups on the A-ring results in structures that are activated toward electrophilic aromatic substitution. The phenolic hydroxyl is a powerful electron donor, especially under basic conditions, increasing the electron density in the ring and thereby making it a better nucleophile as well as stabilizing carbocation intermediates that result from electrophilic attack on the positions *ortho* and *para* to the hydroxy groups. Thus, one observes reactions that are typical of activated ring systems, such as alkylation (methylolation) and condensation with alehydes, among others[106].

To recap the B-ring[121]:



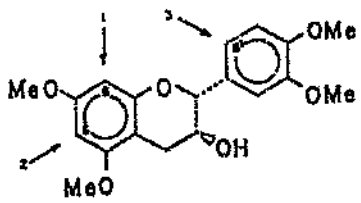
Phenol related – $R_1 = R_2 = H$; (Propelargonidins, Proquibourtinidins)
Catechol related – $R_1 = H$, $R_2 = OH$; (Procyanidins, Profisetinidins)
Pyrogallol related – $R_1 = R_2 = OH$ (Prodelphinidins, Prorobinetinidins)
R = Remainder of flavanoid monomer unit

The chemistry of the condensed tannin B-ring is closely related to that of the parent phenols. Amongst others, the reactions include electrophillic addition, oxidation and metal chelation[85] (see section 2.6.3). In general, the degree of reactivity of the phenol and the complexity of its reactions increase with the addition of hydroxyl groups to the benzene nucleus. Comparing phenol to catechol to pyrogallol, there is an increase in acidity, reactivity to electrophiles in addition and substitution reactions and reducing power[85].

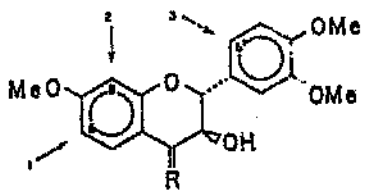
The pyran ring's (often referred to as C-ring) reactivity is a function of how A and B-rings affect its electronic structure. The chemical properties of condensed tannins are also influenced by the location of the interflavonoid bond. Reductive cleavage results in significant yields of flavan-3-ols and low molecular weight proanthocyanidins[111] Consequently, tannin physical properties are highly sensitive to temperature, solvent effects, pH conditions, solution concentrations and presence of salts[114].

2.6.1 Positional Selectivity of Electrophilic Substituents on Flavonoids

Selective bromination was used to examine the relative accesibility and reactivity of the flavonoid units. (+)-Tetra-o-methyl catechin (XLIII), representing a phloroglucinol-type flavonoid, was reacted with pyridine hydrobromide perbromide[90]. Bromination, with displacement of hydrogen, occurred preferentially at the 8-position and only commenced at the 6-position once the former was filled. The B-ring was found to be very unreactive, although in the presence of excess brominating agent a low degree of substitution was noted at the 6' position[91]. Thus for phloroglucinol based tannins the positions of reactivity are 8>6>>6'.



XLIII



XLIV

Using (+)tri-o-methylfustin as a model for resorcinol, the substitution sequence for the A-ring was found to be 6>8>>6' [(XLIV), R=0][86]. The preferentail 8- and 6-substitution in phloroglucinol- and resorcinol-type flavonoids, respectively, appear to be related to the greater accesibility of these positions in each instance.

2.6.2/...

2.6.2 A- and B-ring Reactions with Aldehydes

Tannins, being phenolic in nature, undergo the same well-known base- or acid-catalysed reactions of the phenols with formaldehyde. The nucleophilic centres on the A-rings of the flavonoid units tend to be more reactive than those on the B-rings[86], since in addition to the hydroxyl substituent activation of the ring, the A-ring has localised effects causing further activation.

Formaldehyde reacts with tannins producing polymerisation through methylene linkages to reactive positions of the flavonoid units, mainly on the A-ring (tannin-CH_2-tannin). In condensed tannins, the A-rings of the oligomeric flavonoid units retain only one reactive nucleophilic centre with the remaining active centres being involved in interflavonoid bond formation. Increasingly alkaline conditions lead to progressive activation of the phenol as a nucleophile, especially above pH 8 where phenate ions are formed[110].

Under acid conditions, rate increases are also observed for many of these electrophilic aromatic substitution reactions. Such rate increases are most likely a result of formation of a more reactive electrophile (e.g., a carbocation from a methylophenol). Reaction rates are slowest at near neutral pH where there is limited ionization of the electrophile or nucleophile[106].

Due to their great size and bulky shape, tannin molecules become immobile at low levels of condensation with formaldehyde. This ensures that the available reactive sites become too far apart for further methylene bridge formation, resulting in incomplete polymerisation[110].

Formaldehyde is generally the aldehyde used in the preparation, setting and curing of tannin adhesives, despite the problem of incomplete cross-linking. The formaldehyde is normally added to the tannin extract solution at the desired pH, both as liquid formalin solution and in its polymeric form of paraformaldehyde. The latter is capable of fairly rapid depolymerisation in the aqueous conditions normally employed in adhesive preparation.

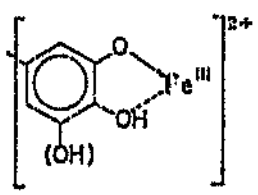
2.6.3 Metal Ion Complexation

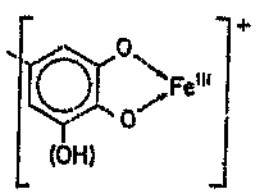
A considerable amount of information is available in the literature on the complexing of monomeric flavonoids, particularly flavonols (see page 58), with metal ions.

There are three possible metal complexing sites within a flavonol containing hydroxyls at C-3,5,3' and 4'. These are between the C-3 hydroxyl and the carbonyl, the C-5

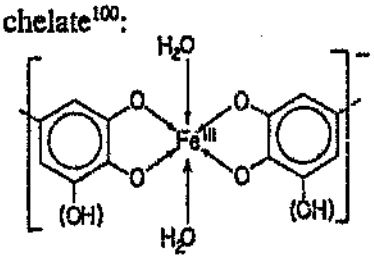
hydroxyl and the carbonyl, and between the *ortho*-hydroxyls in the B-ring. It has been determined that the first site listed is normally the first occupied, whereas, the latter two sites have about the same complexing ability under neutral conditions. An important conclusion that came out of this type of work is that the complexing ability of a catechol-type B-ring increases as the pH becomes more alkaline[108,109].

Complexation has been found to occur with a wide range of metals of various oxidation states[85]. It might be expected, for instance, that the Fe^{III} complex would contain the structure (a) in which only one of the hydroxyl groups is ionized. However, despite the high pK_a value for the hydroxyl group of the C_4 position of the strongly ionized anion, the greater stability of the doubly ionized chelate leads to the formation of an *ortho*-diphenol complex of the type (b)[100].

(a) 

(b) 

The violet Fe^{III} tannate formed between Fe^{3+} (hexa-aqueous) and mimosa (wattle) tannin under acid conditions is the bis chelate[100]:



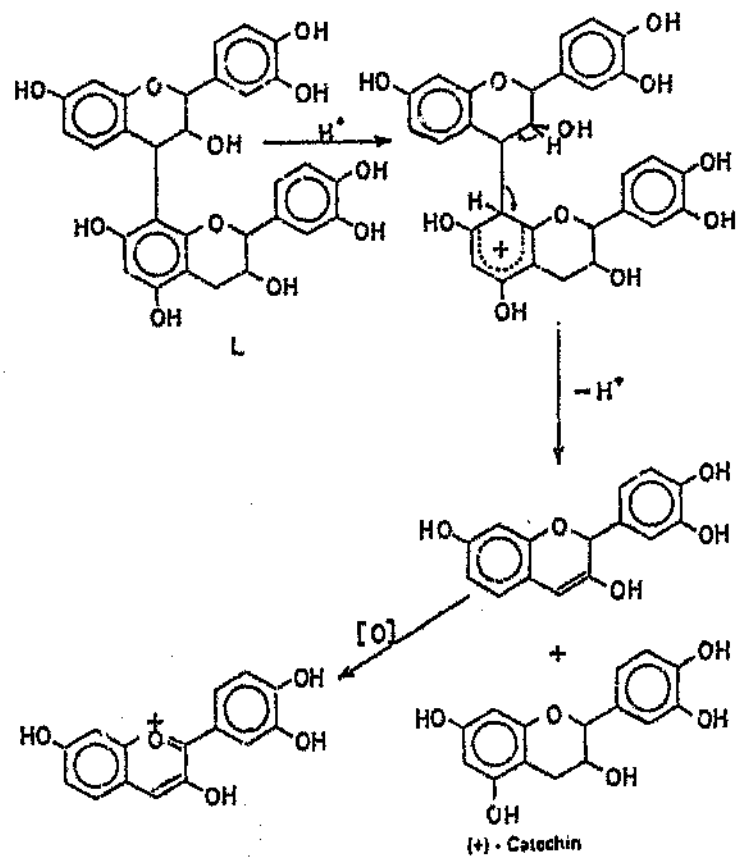
This tris chelate is not likely to form, except under alkaline conditions.

2.6.4 Hydrolysis and Autocondensation

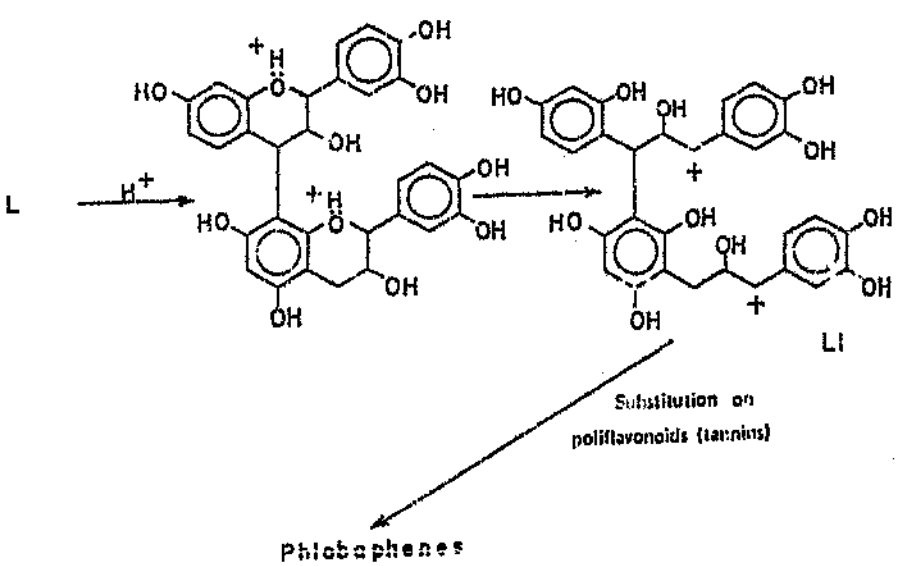
Tannins are subjected to two competing reactions when heated in the presence of strong, mineral acids. Degradation occurs in the one where fission of the interflavonoid bond leads to anthocyanidin and catechin formation[88] (see L). Whilst this reaction should cause a decrease in the overall molecular weight, it has been noted that a secondary reaction occurs where the anthocyanidins formed can condense forming angular triflavonoids and higher oligomers[92]. These can precipitate as the condensation increases, forming a red insoluble mass of higher than expected molecular weight[93].

The second reaction is condensation, occurring as a result of hydrolysis of the heterocyclic rings. The resultant p-hydroxylbenzylcarbonium ions (L1) condense randomly with the nucleophilic centres on other tannin units forming high molecular weight, insoluble "phlobaphenes" or "tanner's reds" (see L to L1)[94].

Some phlobaphenes are formed naturally (assumed to occur by oxidation and/or polymerisation of condensed tannins[102]) and are complex mixtures of high molecular weight condensed tannins which have, in some instances, been found associated with carbohydrates and which contain higher proportions of methoxyl groups[95]. There is speculation as to the differences between phlobaphenes formed naturally, which could include extraneous matter and which are therefore variable, and those formed by acid treatment[95].



Under aqueous conditions, the phlobaphene formation or formation of insoluble condensates is preferred[88]. In strongly alkaline conditions, partial autocondensation takes place. This has been observed by the considerable viscosity increases at high pHs[88].



Theoretically this is thought to be due to reactions of the flavonoids C-4 of the lower terminal units with C-6 and/or C-8 of flavonoid units in other tannin polymers, according to which of the latter two is available. This is due to the reactivity of the hydroxy-group-carrying C-4.[133]

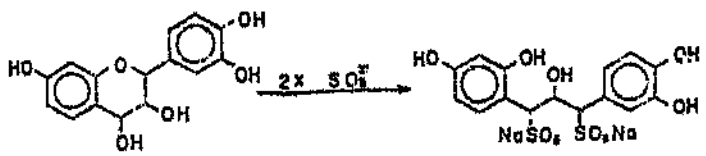
2.6.5 Sulphitation

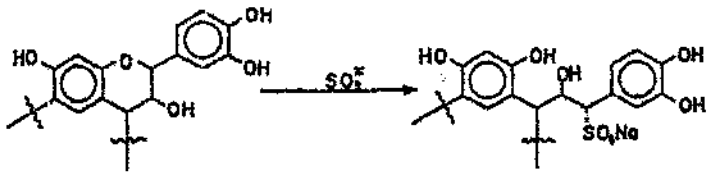
One of the oldest and most useful reactions in flavonoid chemistry is the sulphitation of tannins. Sulphitation affects both the physical and chemical properties of the tannin extracts such as increased solubility and a decrease in the viscosity of the resultant solution[94].

> Both effects are due to 1) the elimination of the etherocyclic ether group which is water repellent (it is well-known that tannin extract water solutions are not true solutions but hydrocolloids suspensions in which part of the tannin molecule keeps the tannin in solution while other parts tend to push the tannin out of solution[98]); 2) the introduction of sulfonic groups[88] and another hydroxyl group, both hydrophilic; 3) the decrease in polymer rigidity, in steric hindrance, in intermolecular H-bonding resulting in decreased viscosity[84] by the opening of the etherocyclic ring; 4) interflavonoid bond cleavage, decreasing the molecular weight and viscosity[96]; and 5) the acid hydrolysis of the hydrocolloid gum.

The total effect of all the modifications indicated, particularly in the introduction of sodium sulfonate groups lead to the important advantages of increased tannin yields when barks are sulphite-extracted[112] and higher concentration of tannin phenolics due to enhanced solubility and decreased viscosity[56]. The former advantage is due to the well-known solubilizing effect of sulfite treatment on phlobaphenes.

Sulfitation is frequently applied during or after the extraction process, although usually only to a small degree. Condensed tannins with phloroglucinolic A-rings are particularly susceptible to interflavonoid bond cleavages under mild acidic[119] or alkalyne[120] conditions (ie. pH 9 and ambient temperatures). In addition, sulphited tannins are more reactive to formaldehyde, due to the enhancement of their nucleophilicity by the opening of the ring, and they are more readily available for the reaction with formaldehyde because of the increased mobility of the tannin molecule as a whole[85].





2.7 Tannin Extracts

As with most other biomass chemicals, tannins are intrinsically a variable resource. Their structure and properties depend on the particular plant species being used, the time of harvest during the year, and the age of the material being extracted[85]. The purity of vegetable tannin extracts varies considerably. Pine bark yields an extract containing only 50 to 60% active phenolic ingredients compared with 70 to 80% for commercial wattle extracts[97]. The heartwood of quebracho contains up to 25% tannin and yields a product with 80 to 85% tannin content. Chestnut extracts have a very low nontannin content[58].

The nontannin fraction consists mainly of sugars and high molecular weight hydrocolloid gums. Sugars have been found to retard the early strength development of concrete[99]. The viscosity of the tannin solution is strongly dependent on the concentration and increases rapidly above a concentration of 50%. Extracted pine tannins have a higher viscosity than the equivalent mimosa extracts, a result of the higher average molecular weight of the pine tannins compared with wattle tannins[110].

The reactivity of pine tannins toward formaldehyde is considerably greater than experienced by mimosa or quebracho tannins. The increased reactivity is attributable to the more reactive phloroglucinolic A-ring in the structural monomer of the pine tannin. To date little research has been done to investigate the exact chemical composition of quebracho tannin. However, practical experience, particularly in the field of fortified tannin adhesives, has shown very close chemistry to that of wattle tannin extracts[101].

GLOSSARY OF TERMS

Workability/Flow

The workability of a fresh concrete mixture changes with time as setting progresses. Depending on the intended application a workable concrete may have an appearance from seemingly dry to fluid. In this project the degree of workability of a desired low viscosity mix is expressed as flow time measured in seconds with a flow funnel (see 1.1.5 of the literature survey).

For placi equirements a minimum working time is needed during which the workability remains approximately the same. In this project it is expressed by the flow test after 5 minutes ("initial") and 15 minutes ("final workability") of mixing.

Standard/Control

A concrete mix identical in composition and water/cement ratio to a test mix, but not containing any additive. The compressive strength results of concrete vary with the seasons and cement batches, but they follow the same pattern when related to their respective standard.

Flash set

An early and sudden stiffening of the fresh concrete mix. Reworking does not restore workability.

RESULTS AND DISCUSSION

3.1 Model Compounds of Tannin Extracts

Some typical raw material components of tannin extracts were tested for their particular effect on fresh and hardened concrete. Resorcinol and phloroglucinol are typical of the A-ring component in condensed tannin extracts (pine, wattle, quebracho), where it is fused with a six membered etherocycle. Catechol is representative of their B-ring component. Following the straight addition of the model compounds are tests with various modifications to the same chemicals as discussed. Modifications include various amounts of ammonia, paraformaldehyde, sodium metalbisulphite, urea and combinations thereof.

3.1.1 Model Compounds tested on their own

Resorcinol greatly hindered the flow of the fresh concrete mix compared to the standard. Its one day compressive strength was significantly higher than the standard - as expected from the poor flow results. This points to early setting and strength development due to the improved wetting of cement grains. At three days resorcinol still gave a significantly higher compressive strength, one and a half times the standard. Toward the seventh day the rate of strength development decreased to give a similar result as the standard (Table 3.1.1).

Catechol greatly improved the workability without retardation in one day strength development compared to the standard (Table 3.1.1). The improved workability may be due to opening of cement particle flocs, releasing water to lubricate the mix (see Figure 12, p.33 of the literature survey). The good strength points toward improved dispersion of the cement particles and a better coating of the cement grains with water. Strengths at three and seven days curing were slightly higher than the standard, but these results are probably equal within the experimental error.

The phloroglucinol addition showed no change in workability and lower strengths throughout seven days of curing, compared to the standard (Table 3.1.1). The one day result was almost half, the three day similar to and seven day result a little lower than the control. Adding phloroglucinol and catechol in a 1:1 mass ratio combination gave very poor results. The workability was worse, three day strength lower, seven days strength slightly lower than the control and one day strength non existent. This flash set indicates interference between the effects which phloroglucinol and catechol induce in the cement mix.

As a comparison a test was done with a commercial superplasticiser (SPC) which is well

established on the local market. Chemically this superplasticiser is a sulphited partial formaldehyde condensate of molasses.

The catechol gave less though comparable workability to SPC but at the same time had the same one day strength as the control whereas SPC had none. A similar effect is only obtained with a sulphonated melamine formaldehyde condensate (sulph. MF) which requires a much higher dosage than the 0,25% used with catechol and also causes a too early loss in workability (Table 3.5 and 3.6).

Comparative values are: an 11 second faster flow result than the control for the catechol 0,25% solid addition corresponding to the solid content of a 40% (m/m) solution (Table 3.1.1) and for the 1.5% sulph. MF 30% (m/m) solution an initial, only partial flow of 7 seconds compared to its control (Table 3.5). The second workability test for the sulph. MF gave no flow at all. The one day strength was 28% below the control, while for catechol it was equal. Although the catechol addition was not tested for its second workability (after 15 minutes of mixing), its fast initial result strongly suggests a good second flow result; ie. no great loss in workability can be expected.

[During the course of this project two new improved sulph. MF became locally available. Their results, applied at 1% addition of a 40% (m/m) solution are as good as that of the catechol 0,25% solid addition corresponding to the solid content of a 40% (m/m) solution (Table 3.1.1). The new sulph. MF's show no loss in workability and almost no one day strength retardation (SPC Table 3.6 top)].

All other superplasticisers cause retardation of the setting of the concrete, consequently the early (one day) strength is much lower than the control, often showing a reading only after the second day of curing[122] (Table 3.1.1; see also Section 3.8).

The commercial SPC superplasticiser used clearly demonstrates the effect of good dispersion of cement particles on later (seven day onward) strength development with the highest seven day result of the series. This is typical of low viscosity (high workability) mixes[4,7] which have a better self-compacting property resulting in a more dense curing mass with higher strengths after one week. Catechol shows a similar but lesser tendency compared to the standard, but has also shown as mentioned, good early strength development.

A 9:1 mass ratio combination of SPC and catechol respectively resulted in flow similar to the standard and worse than that of the two constituents separately. This indicates that some interference between the mechanisms of the two has occurred (Table 3.1.1). One and three day strengths were between that of SPC and catechol alone. The seven day strength did not follow the intermediate trend and was lower than both constituents separate but still equal to the control. Mixing the two did not provide any benefits as was

hoped for : better flow by SPC combined with the good strengths of catechol. The interference was probably due to a reaction between the catechol and modified molasses. Tannins are known for their complexation reactions with sugars which can lead to the formation of precipitates[123].

3.1.2 A Model Compounds reacted with Paraformaldehyde and Ammonia

Catechol, having given the most promising results so far, was reacted with paraformaldehyde and ammonia. Formaldehyde is widely used in the manufacture of polymers, amongst others, phenol formaldelhyde resins. In Section 1.2.4 of the literature survey it was mentioned that the majority of current superplasticisers are based on a polymer backbone to which a hydrophillic sulphonate group is attached. An example is the partial formaldehyde condensate modification of molasses to make superplasticiser.

Ammonia is a strong base and its hydroxide group converts phenols into phenate ions which are more susceptible to electrophilic attack by formaldehyde. Pizzi[86] has shown that if one or both neighbouring hydroxide groups on phenols are ionised they can form complexes with metals (see Section 2.6.3 of the literature survey). This complexation may help to prevent or open up agglomerations of cement particles (see Section 1.2.3).

The molar ratios as quoted from the Table 3.1.2 A are catechol : paraformaldehyde : ammonia, the first being 1:0:1. After dissolving catechol in the ammonia solution for ten minutes the colour changed from clear to murky yellow and the pH was 10,89. One hour later at 70°C the solution darkened to beige brown and the pH dropped slightly to 10,81. These observations appear to indicate that a reaction has taken place with some ammonia being consumed.

Molar ratio 1:1:1 : the ammonia and paraformaldehyde addition to catechol resulted in a light red solution with a pH of 10,46. After one hour at 70°C the solution became reddish-black and the pH dropped to 10,08. This is a much greater pH change compared to that observed with the catechol: ammonia 1:1 reaction discussed above. It may indicate a stronger reaction of ammonia with catechol in the presence of paraformaldehyde, or hydroxyl groups being consumed in the breaking up of the paraformaldehyde polymer.

However, the very different colour shown by this solution suggests an interaction involving formaldehyde. This may be a reaction between ammonia and formaldehyde or of ammonia and methylol groups formed on catechol. Either or both of these reactions could explain the pH drop. The extent of the reaction/s is/are small, since the decrease in pH is relatively low.

Both preparations (1:0:1 and 1:1:1) showed much improved flow over the standard and

better strengths throughout the seven days curing (Table 3.1.2 A). The combination of better workability with improved one day strengths compared to the standard provides a very useful advantage. The paraformaldehyde ammonia type gave a 20 second flow result compared to the ammonia-only type of 18 seconds, but also had a one day strength almost one and a half times higher than the control. Three day strengths were virtually equal to the standard. The much higher seventh day compressive strength of the paraformaldehyde ammonia type over the standard and ammonia-only type is thought to be due to better dispersion of the cement grains. This can also be seen in the lower viscosity of the fresh mix and is induced by water freed from cement particle flocs (see 1.2.3) of the literature survey.

The improved dispersion may be due to the formation of an imine group on the catechol by a reaction between ammonia and a methylol group. The possibility of this reaction was pointed out in the previous paragraph. The imine group is more water soluble than the catechol to which it is attached. The compound could arrange itself at the interface between the water and cement particles. The imine group would point into the water and the adjacent hydroxide groups, partially ionised by the alkaline cement/water suspension, could form a complex with the calcium of cement particles. The surface electrostatic charge between the cement particles would change resulting in a dispersion of agglomerations and improving homogenous hydration.

The ammonia-only modification hardly improved the results already obtained with catechol itself in Table 3.1.1., giving only slightly higher strengths at one and three days of curing. This is likely due to ionisation of one or both hydroxide groups improving complexation and early hydration of the cement.

It was also tested at double dosage and gave even better flow than at normal dosage, as expected, while one and three day strengths were only slightly lower than at normal dosage. The seventh day compressive result was higher, probably due to the same reasoning as mentioned earlier. Compared to the standard the one and three day strengths were equal and on the seventh day higher.

An additional two samples of the catechol : paraformaldehyde : ammonia type were made with a half (2:1:2) and a quarter (4:1:4) molar content of paraformaldehyde. The quarter content type had a more reddish colour on dissolution and a slightly higher pH : 10,68 vs. 10,39 of the half content type. The stronger red colour of the 4:1:4 type is due to the relatively higher ammonia content. The slightly lower solution pH of the 2:1:2 type is probably due to more ammonia being required to break up the relatively higher content of paraformaldehyde polymer. After one hour at 70°C the 4:1:4's pH decreased to 10,57 and the 2:1:2's to 10,35. The changes in pH during heating for the different types can be summarised as follows from highest to lowest : 1:1:1 >> 4:1:4 > 2:1:2.

No apparent trend in pH changes is evident unless at different ratios ammonia - catechol and ammonia - paraformaldehyde interactions take place at different rates and the sum of these effects prevents the pH measurements from showing the trend of one of the reactions.

The half paraformaldehyde content type (2:1:2) gave the best one day strength of the series, almost double that of the standard. Workability and later compressive strengths remained the same as those of 1:1:1. At a quarter content of paraformaldehyde (4:1:4) of the original (1:1:1), workability was still the same and one day strength intermediate between the 2:1:2 and 1:1:1 type additives. Three and particularly seven days strength of type 4:1:4 were lower than for the other ratios but still equal and only slightly lower respectively compared to the standard (Table 3.1.2 A).

Therefore the additive with catechol : paraformaldehyde : ammonia in a 2:1:2 molar ratio presented the best strength results. It is interesting to note that, irrespective of the paraformaldehyde content of the additives, their workability effects on concrete hardly changed, which means that catechol's affect is maintained. Paraformaldehyde in addition to ammonia greatly improved the one and from lower than 4:1 moles catechol : paraformaldehyde, the seven day strength compared to the catechol tested on its own in Table 3.1.1. The disadvantage was that almost five months later all the samples showed some form of precipitate, indicating a low stability and shelf life of the additive. This shows that a degradation occurred regardless of whether paraformaldehyde was present or the quantities in which it was used.

As a comparison to the catechol : ammonia 1:1 a test sample was made with phloroglucinol and ammonia in the same ratio. Phloroglucinol has three hydroxide groups meta positioned to one another while catechol has two adjacent to each other. Phloroglucinol was used in preference to resorcinol, because on its own it provided a much better flow result than resorcinol alone (see Table 3.1.1).

It formed a much darker red solution than the catechol equivalent did, probably showing a greater sensitivity to either ammonia itself or alkalinity in general. On dissolution the pH was 9,68 which dropped to 9,38 after one hour at 70°C and colour of the solution changed to black-red. The stronger colour and pH changes may indicate a more complete reaction than that of the synonymous catechol and ammonia.

The test results showed a poorer flow than the catechol equivalent, but more seriously the one day strength was only equal and from the third day onward slightly below those of the standard. The ammonia addition did however considerably improve workability and one and seven day strength when compared to the phloroglucinol-only testing in Table 3.1.1. On storage the additive also showed the greatest tendency of the series to agglutinate. After five months it presented a considerable amount of precipitate.

This may have been due to the formation of ammonia-phloroglucinol complexes which, over time, combined to greatly increase their molecular weight. A large molecule made up of several phloroglucinal units, which by themselves are not very soluble in water, could then precipitate from the solution. Ammonia with more than one removable proton and a single lone pair of electrons could have reacted with a carbocation centre (formed in the alkaylne solution) on phloroglucinol. The resulting NH_2- phloroglucinol complex could further react with another ionised phloroglucinol to form a phloroglucinol -NH-phloroglucinol complex of greatly decreased solubility. Catechol can be expected to have reacted similarly with ammonia, although judging by the lower amount of precipitate formed during the same time, catechol has shown a lower reactivity toward ammonia than phloroglucinol. A similar explanation has been put forward for a tannin-ammonia interaction leading to increased molecular weight and agglutination[124]. Since tannins are less reactive than their component phenols, the above proposed mechanism seems plausible.

The stronger tendency to agglutinate of the phloroglucinol 1:1 ammonia over the catechol 1:1 ammonia molar ratio additive is in line with the experience that meta positioned hydroxide groups more strongly activate the phenolic ring toward electrophilic substitution than hydroxide groups positioned ortho to each other.

3.1.2 B The Formation of an Insoluble Product from Catechol and Ammonia

In the preceding section it was noted that all additives made with ammonia developed some sort of precipitate after a few months storage. This occurred roughly to the same extent independent of the amount of paraformaldehyde used or whether it was included at all.

A 2:1 molar ratio catechol : ammonia sample was prepared and heated for three hours at 70°C. The progress of the reaction was monitored by taking four sample lots at half an hour intervals for two hours and spotting them on TLC plates (Table 3.1.2 B). The final samples were taken at the end of three hours heating. The developer used was benzene : ethyl acetate : methanol in a 3:2:1 by volume ratio. Catechol on its own has a Rf value of 0,67 and ammonia a weak spot at 0,15.

From the first reading, half an hour into the reaction, the Rf value decreased from 0,85 to 0,79 after an hour (Table 3.1.2. B). The first value may show that the ammonia had ionised the catechol, which was then carried further by the developer than unmodified catechol would have been. The second lower Rf value (0,79) may indicate a reversal of some of the phenate-type catechol ion to non-ionised catechol. The latter did not separate from the former, instead slowing it down a little, which may explain the lower Rf value after an hour.

The next Rf value observed after one and a half hour was identical to the one hour value. It seems that a kind of equilibrium between the formation of ionised catechol and its reversal to catechol has been established. Samples taken from one-and-a-half hour up to three hours after starting the reaction all showed a very small gradual increase up toward 0,84. This points toward a related small increase in the ionisation of the acidic catechol by the basic ammonia. However, these latter Rf value increases are so small, that they could well be within the accuracy of TLC spotting and developing.

Subsequent NMR analyses support the expected catechol hydroxide group - ammonium ion interaction. This can be seen on the carbon 13 NMR (Fig 3.1.2 B) which is identical to that obtained with catechol alone (see bibliography of spectra) and proves that the benzene-like ring itself is unaffected. The proton NMR (Fig 3.1.2 C) shows, apart from catechol's characteristic peaks at 7 and 5 ppm, two very small peaks at 2,8 and 2,9 ppm. These could only correspond to a ($-O^-NH_4^+$) group, since the deprotonated acidic hydroxide group is the only site for attack by the basic ammonium ion on an otherwise stable benzene ring.

The extent of the reaction is very small since the two new peaks each have an integrated intensity of 2/183 compared to the double peak at 7 ppm and 2/133 compared to the peak at 5 ppm. The ionic interaction would increase the solubility of catechol and the formation of precipitate after a few months storage seems only possible if the reaction is of a temporary nature. It may also be possible that with time new products form with a $-NH_2$ group attached to catechol's ring. This could in turn progress to form -NH- links between two catechols which could well be less soluble than catechol. An amine group and -NH- link were proposed by V J Sealy-Fischer as possible products between ammonia and tannin[124].

3.1.3 A Model Compounds reacted with Metabisulphite, Urea and Ammonia

Various metabisulphite salts have been used to facilitate the extraction of tannins[125] and to decrease the viscosity of their concentrated solutions (See Section 2.6.5 of the literature survey). Further, the majority of currently available plasticisers and superplasticisers have one common chemical feature : hydrophillic sulphonate groups attached to a polymer backbone (See 1.2.3/4) of the literature survey.

Urea has been used to stabilise lignosulphonate solutions and may have a similar effect on tannin extracts. Urea has a highly reactive carbocationic centre. Ammonia is a cheap alkali which appears to activate adjacent hydroxide groups on phenols for complexation with metals. Unlike urea its reactive centre is the amine group with a single lone pair of electrons.

As in Section 3.1.2 A, modifications were carried out with catechol and phloroglucinol.

The catechol : metabisulphite 1:1 molar mixture was light brown on dissolution and had a pH of 3,96 which remained almost constant during the heating. After one hour at 70°C the pH was 4,01 and the colour of the solution had changed to golden brown. The intensification in colour may be due to a complexation of a sodium ion with both of the adjacent hydroxyl groups where one proton or both protons have been displaced or a simple replacement of a proton by a sodium ion. A better explanation for the constant pH during the reaction would be the oxidation of catechol, which would also account for the slight colour change typical for oxidised phenols.

Comparing the results obtained with this additive (Table 3.1.3 A) with the standard it can seen that they are almost identical to the results obtained with the catechol-only addition in Table 3.1.1. The only exception is the higher three day strength obtained with this metabisulphite modified catechol. The test results and the experimental observations lead to the conclusion that no catechol - metabisulphite product was formed. The metabisulphite ion hydrolyses in water to form two bisulphite ions. Since these are anions they are nucleophilic and can not undergo electrophilic addition to catechol. The similarities are greatly improved workability over their respective standards, same one day and slightly higher seven day strength than their respective standards.

The phloroglucinol : metabisulphite 1:1 molar mixture was yellowish white, but only after a 2 molar ammonia addition making the ratio 1:1:2 did the phloroglucinol dissolve completely. The pH after the ammonia addition was 9,30 and the solution still yellow. After one hour at 70 °C the pH dropped to 8,30 and the solution became amber in colour.

The more reddish colour and part of the pH decrease (see also phloroglucinol ammonia 1:1 of Section 3.1.2 A) during the heating may indicate a reaction between phloroglucinol and ammonia. The major part of the high drop in pH may have been due to the exchange of a proton of one of the hydroxide groups with a sodium cation. The proton would form water with the hydroxide of the alkali.

Workability was considerably improved over the standard and to the same extent as the previous additive. One and seven day strengths were exactly the same as the standard, with the third day strength slightly lower. In comparison to the phloroglucinol only addition of Table 3.1.1 one can see that the metabisulphite and ammonia modification greatly improved flow, one and also seven day compressive strength. Considering that metabisulphite hardly affected catechol's performance and that equimolar amounts of phloroglucinol and ammonia in Table 3.1.2 A already showed the same trend in improvements as metabisulphite and ammonia here, these results are mainly due to the ammonia itself.

The catechol : metabisulphite 1:1 solution remained stable over four months later, whereas the phloroglucinol with metabisulphite and ammonia (1:1:2 solution) presented a

considerable amount of precipitate. The solution however did not solidify completely probably prevented by the metabisulphite, considering that the phloroglucinol ammonia 1:1 mixture of Section 3.1.2 A became completely solid.

Catechol and urea 1:1 by mole gave an orange solution with a pH of 3,30 which changed drastically to 5,08 at the end of one hour heating at 70°C, but retained the same colour. This may point toward a salt formation between the strongly acidic catechol and weakly basic urea. The protonated urea may be coordinated at the site of a deprotonated hydroxyl group: $-O^{-}C^{+}(NH_2)_2OH$. The urea may also have undergone hydrolysis under the strongly acidic conditions forming ammonium ions and carbon dioxide.

V J Sealy-Fischer postulated the following: "The reaction between the urea and ... tannin could have been a reaction similar to that occurring between formaldehyde and tannin". Since tannins are less reactive than their component phenols, catechol should show a similar but stronger tendency. "The alcoholic groups could leave the phenolic ring under acidic conditions and the urea could react via its nucleophilic carbonyl, attaching to the ring as a $-C(NH_2)_2OH$ functionality"[126]. The above coordination or less likely the proposed bonding may explain the very strong pH increase. Urea is a known buffer and in this case acted as a Lewis base.

This urea modification had such a detrimental effect on flow that the fresh mix did not move at all. The advantage was a one day strength one and a half times that of the standard. Three day strength was a little higher and at seven days a little lower than the control. Therefore urea with catechol resulted in a setting aid which accelerated early strength development, compared to catechol alone (see Table 3.1.1).

Phloroglucinol mixed with urea and ammonia in a 1:1:1 molar ratio had a pH of 10,05 and a yellow colour. After the usual heating the solution changed to a reddish black and the pH decreased to 9,83. The characteristic red colour and lower pH may indicate the reaction of phloroglucinol and ammonia as observed in Section 3.1.2 A.

Similar to the previous additive there was again no flow of the concrete mix but the dough-like fresh paste was less stiff. A similar trend of much higher one day, slightly higher three day and lower seven day compressive strength occurred. Urea and ammonia combined with phloroglucinol gave an accelerator in contrast to the phloroglucinol addition itself (see Table 3.1.1).

With both additives the urea modification has resulted in accelerating properties which may be due to urea acting as a buffer, interfering with complexation and deflocculation. In the second its action offset that of ammonia as discussed previously. After four and a half months storage the catechol urea sample had almost no precipitate. Urea therefore did not cross-link with catechol as formaldehyde would have. This shows that urea does

not cause agglutination as ammonia does (see Section 3.1.2 A). The phloroglucinol/urea/ ammonia additive at that stage showed a lot of precipitate, which apparently could not be prevented by the urea. A few weeks later the sample became completely solid similar to the phloroglucinol ammonia sample of 3.1.2 A.

In both additives a high early strength development seems to have impaired subsequent hydration. The lower later strengths (seven day) compared to the control mix are typical for accelerators[127].

3.1.3 B The Interaction of Catechol and Urea

In the previous section it was stated that there could be two types of reaction between catechol and urea: of the acid-base type or less likely related to that of phenol and formaldehyde. A 1:1 molar ratio sample was made and heated for three hours at 70°C. The development of a reaction was followed by taking four samples lots at half hourly intervals for two hours and spotting them on TLC plates (Table 3.1.3 B). The last samples were taken at the end of the three hours heating. The developer used was again benzene : ethyl acetate : methanol in a 3:2:1 by volume ratio. With this solution catechol on its own has an Rf value of 0,67 and urea a difficult to detect spot at 0,20.

The first Rf value, half an hour into the reaction, was 0,86, which increased to about 0,90 after an hour (Table 3.1.3 B). Both values may indicate ionisation of the catechol with protonation of the urea. The oppositely charged chemicals seem to have been carried further together by the developer than the uncharged chemicals would have been. The slightly higher Rf value after an hour indicates that further hydrogen ion exchange had taken place, but to a much lower extent than during the first half hour.

One and a half hours into the reaction the Rf value was 0,92, which indicates a slower continuation of the above proposed reactions. The two hour samples gave a slightly reduced value of 0,91. This suggests that an equilibrium in the deprotonation of catechol had already taken place, with some reversal of the reaction. However, the change is so small that it could well be within the accuracy of TLC spotting and developing.

At the end of the three hours heating the Rf value decreased to 0,89. This is still higher than the first value of 0,86 (½ hour) and appears to be an equilibrium value after the reaction had reached its peak of 0,92 one and a half hour from the beginning.

Carbon 13 NMR analysis of the test shows that the ring of catechol is unaffected, with the typical peaks of catechol present at 119, 124 and 147 ppm (Figure 3.1.3 B and bibliography of spectra). The very small peak at 167 ppm represents the carbon of ureas carbonyl and indicates a very small amount of unreacted urea. Two slightly more

prominent peaks at 40 and 34 ppm appear to indicate a reaction between two ureas. This may be an ether like oxygen linkage of the carbonyl carbons of two ureas, where one urea has undergone reduction in the presence of easily oxidisable catechol. The extent of the reaction is very small, the product probably being present as around 1% of the sample analysed.

The proton NMR (Figure 3.1.3 C) has the typical phenolic double peak of the catechol at 7 ppm and a water peak at 5 ppm. At 7,8 ppm there is a very small peak indicating an amine group. Its integrated intensity is only 4 compared to a value of 64 and 66 of the catechol double peak. This very small peak could be related to the very small peak at 167 ppm in the carbon 13 spectra, which represented the carbonyl of a small amount of unreacted urea. At 2,8 and 2,9 ppm there are two peaks with intensities of 13 and 15 respectively. These may be related to the 34 and 40 ppm peaks of the carbon 13 spectra, which showed two ureas linked together.

The above results show that no phenol-formaldehyde-like reaction has taken place between catechol and urea. Closer examination of the chemical shifts and their intensities of the proton NMR spectra with that of catechol alone reveals some important differences. The phenolic hydrogen double peak of the sample has ppm values up to 7,0361, whereas catechol has values up to 7,0845. The lowest values do not show this marginal shift which may be caused by the buffering effect of urea on the acidic catechol. More importantly, the sample has 12 peaks in the region of 7 ppm compared to 15 of catechol and the relationship in intensity of these peaks to one another is quite different for the two spectra compared. This observation supports the acid-base interaction of catechol and urea, as proposed for the changing Rf values measured earlier and in Section 3.1.3 A.

3.2 Sugars, Polyalcohols and Ethers

Sugars are well known for their retarding effect[99] on the setting and early hardening of concrete. They are sometimes used as plasticisers when improved workability is desired. Most sugars are reducing sugars and a simple test can determine their content in, for instance, plant extracts. The presence of sugars may require changes in the manufacture of additives based on plant extracts to reduce or eliminate any subsequent retardation.

Since tannin extracts comprise up to 20% by mass of mono- and polysacharrides, the effect of sugars on cement mixes was tested to gain background information. Three sugars common in plants were tested. Maltose has a double six ring configuration. On acid hydrolysis it would break up into two monosacharrides, in the form of two glucose units. Maltose greatly improved the workability of cement mixes, but had no one day strength as with all the other sugars tested. At three days curing its strength surpassed the standard and even more so on the seventh day.

Sucrose consists of a glucose and a fructose unit linked together. It is therefore also a disacharride, but unlike maltose it is a non-reducing sugar. Sucrose showed a similar trend of results, although it provided slightly less flow and lower strengths than Maltose. At three days the strength of the sucrose modified concrete was still lower than the standard and only managed to equal it on the seventh day. Therefore, not only reducing sugars act as retarders, but apparently to a lesser extent.

The lowest grade of molasses as used for concrete addition, is a mixture of sugars and various other naturally occurring materials in lower proportions. It gave the least improved workability of the sugars, but still a cohesive mix as indicated by the long 36 second flow times and complete run-through. As with the other sugars there was no one day strength. Three and seven day strengths were the best amongst the sugars, but only by a small margin compared to maltose.

Glycerol and ethanediol were tested to investigate the effect of three and two neighbouring hydroxide groups respectively. From the test results it appears they function as accelerators resulting in a stiffer fresh mix and higher one day strengths than the standard. At three days the strengths were still higher, but at seven days they were equal to the control. This decrease in the rate of later strength development is typical for accelerators[127]. Both glycerol and ethanediol showed very similar results which are within the accuracy obtained with the flow and compressive strength tests. Glycerol with its one day strength one and a half times that of the standard could qualify as an accelerator.

Glycerol and ethanediol have demonstrated that neighbouring hydroxide groups on a aliphate do not improve workability as was the case for catechol in Table 3.1.1. This may be due to the ability of an aromatic ring to better stabilize an oxide ion, which is likely to form from a bonded hydroxide in the alkaline environment of concrete. They did however give very good strengths up to the third day of curing, possibly by complexing with cement particles resulting in accelerated early strength development. Since glycerol and ethanediol showed very similar text results, it appears that the three neighbouring hydroxide groups do not form two complexes. Instead both probably only form one complex with two of their hydroxide groups.

Tetrahydrofurane (THF) is a five membered etherocyclic ring similar to that contained in sucrose. There are no hydroxyl or methyl groups attached to the ring, which is the case for sucrose. Workability was lower than the standard but one and three day strengths higher. The seven day strength was, surprisingly, lower than the control, although only by a very small margin.

Diethylether was tested for the effect an oxygen atom has on concrete when bonded to carbon atoms as part of an aliphatic chain. Workability was lower than the standard and one day strength slightly higher. Both compressive strengths from the third day onward

were higher than the control. Therefore it too had no real advantages as a concrete additive.

Both ethers, whether aliphatic or alicyclic have as their most pronounced result a higher three day strength than the control. The improved three day result is however not unique, glycerol and ethanediol have shown a similar improvement. The ethers have neither resonance of electrons nor any group which could form complexes. It appears that oxygen as part of a carbon chain is not an important feature for concrete additive.

Neither adjacent hydroxide groups or an ether like bonded oxygen atom can explain the behaviour of sugars on concrete. Both these configurations do not reduce the viscosity of fresh concrete and only glycerol and ethanediol could be used as mild accelerators.

The sugars, which combine the above features of neighbouring hydroxide groups and cyclic ethers have shown quite different results : the workability was very much improved and there was no early strength. The improved workability may be due to sugars decreasing the surface tension of water by interacting with the hydrogen bonds between water molecules. Water molecules could be freed from the constrained system and become available to lubricate the concrete water mixture. At the same time the sugars with their complex structure could hold on to water molecules, initially slowing down the hydration and strength development of the concrete.

3.3 Bark and Wood Tannin Extracts

The model compounds have shown that two hydroxide groups on a resonating phenolic ring have resulted in a good combination of improved workability with good early strengths (catechol) or higher early strengths than the control (resorcinol, both Table 3.1.1). Good to very good results were also obtained with catechol reacted with ammonia or both ammonia and formaldehyde (Table 3.1.2). However the solutions continued to react in the sample bottles forming precipitates. Their shelf life was therefore limited. In a follow up experiment the formation of an insoluble catechol-ammonia product could not be observed, only an acid-base reaction (Section 3.1.2 B).

Sulphitation did not adversely affect the results of the phenols. Urea reacted with catechol resulted in a greatly improved one day strength at the expense of workability (both Table 3.1.3 A). The amount of the urea, equimolar, may have been too high. A subsequent investigation showed an acid-base reaction, with the phenolic ring unaffected (Section 3.1.3 B). Both urea and metabisulphate were anticipated to be useful in improving the performance and solubility of the non-phenolic (sugars etc.) constituents of tannin extracts. This was based on the effect of urea and metabisulphite on a molasses-based superplasticiser (compare workabilities Table 3.1.1 and 3.2 of superplasticiser and molasses respectively) and relevant literature (Section 2.6.5, reference 126).

Adjacent hydroxide groups on a aliphate have shown very different results (Table 3.2) from those of catechol in Table 3.1.1. This implies that the adjacent groups are not the only criteria for good overall results. Instead the resonating phenolic ring may assist in stabilising a negative charge from one of the hydroxide groups which has been deprotonated in the alkaline environment of concrete.

In the following sections tannin extracts are reacted with the same chemicals, because either the stability disadvantages caused by ammonia and formaldehyde had not been noticed, or it was hoped smaller amounts and the tannin's lower reactivity would provide the benefits without the disadvantages. Urea, metabisulphite, small amounts of alkali or an alcohol mixture are used to improve the solubility, effectiveness and stability of the tannin extract solutions as concrete additives.

3.3.1 Tannin Extracts as Additives

In this section, chestnut, quebracho and two types of wattle extracts were tested on their own as additives for concrete.

Wattle extract improved the workability slightly, but had lower one and three day strengths. At seven days curing the compressive strength was almost the same as the

standard. The somewhat retarded early strength development (Table 3.3.1 A) may have been caused by sugars contained in the wattle tannin extract. In particular gums contained in the extract may have decreased the more marked improvement in flow found with catechol by itself in Table 3.1.1, or sugars in Table 3.2. The gums may have held water molecules by intermolecular hydrogen bonding, thereby restricting them from lubricating the fresh concrete mix and hydrating the cement during early strength development.

However the tannin content of commercially available tannins is over 80% by mass. It is therefore plausible that the wattle tannin itself prevented the complete retardation of the one day strengths caused by the sugars as seen in Table 3.2. The tannin, with its neighbouring hydroxide groups on the catecholic B-ring, may have complexed calcium ions and therefore deflocculated cement particles and improved their hydration. This is thought to be similar to that observed with catechol in Table 3.1.1.

Conditioned wattle is a grade of wattle extract which has undergone alkaline hydrolysis. This results in the breaking down of higher sugars and gums, which in turn increases the solubility and reduces the viscosity of the extract in water solution. It showed better flow and only slightly lower one and two days strengths than its standard. These results were better than those of the wattle extract equivalent. On the third and seventh day the strengths were considerably lower compared to both its standard and the wattle tannin tested above.

The sugars, resulting from hydrolysed higher sugars and gums, and the tannin appear to have greatly reduced the viscosity of the fresh mix (Table 3.3.1 A). The much lower early strength retardation may have been due to an acceleration effect by the tannin itself and the absence of gums. Catechol itself has shown very similar results in Table 3.1.1. The unusually low three day strength seems to be due to a testing error. This result and the early high strength development of the low viscosity concrete mix probably contributed to the relatively low seven day strength.

The quebracho extract at 0,25% dosage rate considerably improved the workability and was slightly more beneficial in its strength results than its standard; more so at seven days. At a 0,50% double dosage quebracho extract, as expected at this double dose, improved the workability even more with consequential lower one day strength. The one day strength was not much lower than the standard considering the great improvement in workability. The three and seven days strengths were very similar to those of the normal 0,25% addition.

Since wattle and quebracho tannins are said to be chemically very similar (Section 2.7) and the conditioned wattle tannin has shown that a lower content of higher sugars and gums improves workability and early strengths (Table 3.3.1 A), it appears that the quebracho extract contains less higher sugars and gums than the wattle extract. The

greatly improved workabilities of quebracho extract may be due to the presence of less complex sugars, as with the conditioned wattle; or the amount of simple sugars may have been low enough not to affect early strength development.

Yoguslavian chestnut extract provided only slightly better workability, but the concrete had the same one and seven day compressive strengths as the control (Table 3.3.1 B). Very significant is the much higher three day strength obtained with the chestnut addition.

The poor flow result may be attributed to esters of sugars (see Section 2.2, p.54) holding water molecules, by hydrogen bonding, which would otherwise be free to reduce the viscosity of the fresh concrete mix. The much higher three day strength is a unique characteristic of this hydrolysable tannin. It could then be associated with the high content of pyrogallol and its derivatives. Complexes of three neighbouring hydroxide groups with two calcium atoms are not apparent since this should have effectively deflocculated cement particles resulting in a low viscosity fresh mix. With a stoichiometrically equal pyrogallol - calcium complex one of the hydroxide groups would have been relatively unaffected. This group may have via hydrogen bonding, favourably positioned a water molecule toward a complexed cement particle for hydration or toward a developing crystal for growth.

This "directing effect" should be most significant after setting and during the first days of strength development when small crystals and calcium silicate hydrate gel in the set concrete hinder movement of water (see fig. 6(c) and (d) of 1.1.3 of the literature survey). The marked three day strength is not simply a result of three neighbouring hydroxide groups. A comparison with glycerol in Table 3.2 will support this. As pointed out in Section 3.2 an aromatic ring can better stabilise an oxide ion/s to from complexes.

Pine extract was mixed with a 10% by mass catechol to improve the workability. Catechol itself greatly improved the flow while maintaining early strength, as seen in Table 3.1.1. Together they gave very good flow and better three and seven days compressive strength compared to the standard. The one day strength was only slightly below the control, which is impressive considering that with the additive the fresh concrete flowed through the testing funnel in half the time of the control mix.

These strength results compared to the control show the same trend as catechol by itself compared to its control in Table 3.1.1. The close correlation suggests that the predominantly catecholic B-ring of pine tannin is the more active than the A-ring as a concrete additive. The initial flow result was even better than for catechol alone, which is probably due to some sugars contained in the pine extract (the effect of sugars on flow can be seen in Table 3.2).

In a similar attempt to improve the workability of a 0,25% quebracho addition a 10% by

weight superplasticiser was added. The result was no flow and no early strength, which indicates a flash set. Three day strength was considerably better than the control, but at seven days lower by an equal measure. Evidently the quebracho extract and the molasses based superplasticiser had interfered very strongly with one another. A possible explanation could be a precipitation of the superplasticiser by the tannin analogous to that of sugars[128].

The above results show that important characteristics of fresh and hardening concrete can be altered without strongly and adversely affecting other properties. The most important result is that of the quebracho which combines improvements in workability with equal or higher compressive strengths at all stages of curing. Therefore it functions as a plasticiser without retarding strength development at any stage. The latter effect applies not only to one day but also to higher seven day strengths, which are thought to be due to improved dispersion (as seen by the lower viscosity of the fresh mix) and more homogenous hydration of cement particles.

Similar results in both workability and early strengths are only obtainable with the newest German sulph.MF (see Table 3.6). Chestnut extract alone improves workability somewhat and greatly improves three day strength. It functions mainly as a hardener although at later stage of curing. The pine and catechol result show that properties of extracts can be much improved with small additions of other chemicals. It would qualify as a superplasticiser but doesn't retard early strength development as is commonly the case[8].

3.3.2 Sulphited and Semi-Sulphited grade Quebracho Extracts reacted with Urea and Paraformaldehyde

Quebracho of the sulphited (5% by mass) and semi-sulphited (2,5%) type were reacted with urea and paraformaldehyde was added cold to half of each sample after the one hour heating at 70°C.

During the one hour heating of the sulphited and semi-sulphited quebracho with urea 2:1 by mass the pH of each solution dropped from 5,56 and 5,00 to 5,04 and 4,83 respectively. The sulphited extract had therefore reacted more strongly with the slightly alkaline (Lewis base) urea than the semi-sulphited type.

As pointed out in Section 2.6.5 of the literature survey the higher sulphited quebracho extract would contain more tannins with opened etherocycles and newly formed additional hydroxide groups. Together with a greater amount of sulphite groups it would be more acidic and reactive towards the slightly alkaline urea.

Then each sample was split in half and to one half of each paraformaldehyde was added

as one tenth of the extract content. A pellet potassium hydroxide was added to improve the dissolution of the solid formaldehyde. Forty minutes later at room temperature the pH was 6,62 and 6,25 for the sulphited and semi-sulphited type; these increased to 7,12 and 6,54 respectively after another twenty minutes. In this second reaction the sulphited type again showed a stronger change in pH, this time an increase. Since the added potassium hydroxide was not measured accurately it is difficult to follow the series of events.

The urea and paraformaldehyde reacted semi-sulphited extract solution foamed more at the end of the reactions. This often gives an indication of good surfactant properties which was confirmed later in the flow test by results showing better workability than the sulphited type.

The samples with the paraformaldehyde addition had a gluey consistence already twenty-four hours later. In each bottle the inner of the lid stuck to the top of the bottle and the sample itself did not run off the sides when the bottle was tilted. Therefore both samples, with one tenth addition of paraformaldehyde compared to the extract content, were polymerising. The sulphited type was completely solid three months later, while the semi-sulphited one was three quarter solid. The attachment of sulphite groups increases the mobility of the molecule and the reactivity of the A-ring with meta positioned hydroxide groups, which activates the phenolic ring toward electrophillic substitution. For this reason the sulphited tannin appears to have reacted more strongly with the formaldehyde which would have been protonated in the acidic solution. This would suggest an attachment to the C-6 or C-8 position of the A-ring followed by cross linking. Both types of quebracho extract treated only with urea showed no precipitate at that stage.

The plastification of the concrete can be summarised as : sulphited/urea > semi/urea > > semi/urea/formaldehyde > sulphited/urea/ formaldehyde from highest to lowest (Table 3.3.2). None provided a marked improvement and it seems no improved dispersion of cement particles, resulting in more uniform hydration and better strength development had taken place. Consequently compressive strengths were generally very similar to the control with the exception of the three day tests which were all a little lower. The sand used for these tests was not graded and had a high clay content. Therefore the water demand for the concrete was higher than usual which resulted in slower strength development, as can be seen by the low results obtained for the standard. A direct comparison with test results from other series can not be made.

3.3.3 Tannin Extracts modified with Ammonia

Yugoslavian chestnut extract was reacted with ammonia in a 1:1 mass ratio in the resulting alkaline solution of pH 12,48 for one hour at 70°C. After heating the pH had dropped to 12,01 proving that some alkaline ammonia had been consumed. Two further

observations were made: foam formed during the dissolving of the chestnut extract completely disappeared half an hour into the reaction. This is usually a sign of low surfactant properties since the foam is no longer stabilised. Secondly, lumps formed in the additive twenty-four hours after the completion of the heating. The pyrogallol content of the extract must have been high and the pyrogallol reactive enough to agglutinate with the relatively high amount of ammonia in the additive.

The chestnut ammonia additive was nevertheless tested with resulting poor findings (Table 3.3.3 A). The flow was worse compared to the standard, one day strength the same and three and seven day strength a little lower. The ammonia addition had not provided any advantages to the chestnut extract as an additive. These results were similar or poorer than those obtained with the tannin alone in Table 3.3.1 B. In particular the much higher three day strength given by the Yugoslavian chestnut was completely lost when modified with ammonia. Four and a half months later a third of this additive had solidified.

The same procedure was used to react quebracho extract and ammonia in a mass ratio of 3:1. The lower ratio of ammonia and the lower reactivity of the quebracho polyphenol were supposed to prevent the occurrences experienced with the previous experiment. The pH meter gave faulty readings, however the solution was alkaline, tested with litmus paper and a similar if less pronounced drop in pH during the reaction is to be expected.

The results were far more encouraging, the additive giving much improved flow, slightly lower one day strength and at three days a little higher and seven days higher than the standard. Therefore the ammonia modification improved the workability of the quebracho extract (see Table 3.3.1 A) and also the seven day strength a little. The drawback came almost four months later, when the sample had completely solidified.

The thickening of both additives which led to the formation of a solid mass is similar to that observed in Section 3.1.2 A of the model compound studies. There catechol was reacted with ammonia in various molar ratios and so was phloroglucinol. The latter showed a greater tendency to agglutinate. In this section chestnut extract (mainly pyrogallol) and quebracho tannin (similar to wattle[101] : mainly resorcinolic A- and pyrogallic or catecholic B-ring) showed a similar tendency toward agglutination when reacted with ammonia. This confirms an ammonia-phenolic interaction. Again meta positioned hydroxides (mainly A-ring of quebracho) contributed toward a stronger agglutination with ammonia than adjacent hydroxide groups (chestnut) on storage. V J Sealy-Fischer proposed the formation of NH_2-tannin complex which would further react with another tannin molecule to form a tannin-NH-tannin compound, resulting in increased molecular weight leading to agglutination[124]. This phenomenon was discussed on the last page of Section 3.1.2 A.

Lower Concentrations of Ammonia

The supplier of wattle tannin extract suggests in their information pamphlet that small amounts of ammonia improve the solvation of the tannin.

Wattle extract reacted for one hour at 70°C with a very small amount of ammonia (2,5% by mass) gave very good flow compared to the standard and even slightly higher one and three day strengths (Table 3.3.3 B). The seven day strength was equal to the control. Pine extract modified similarly with the same dose ammonia gave, as expected from the similar chemical make-up, very similar results with one and three days compressive strengths between the wattle counterpart and the standard. The seven day strength did not follow the intermediate trend and was a little lower than the wattle additive and the standard.

Compared to the wattle extract tested on its own in Table 3.3.1 A, the ammonia modification greatly improved the workability and the one and three day compressive strengths to just above the standard. It can be assumed that a similar effect has taken place with the addition of the ammonia to pine tannin.

The same modified pine extract was mixed cold 1:2 parts by mass with catechol to combine the good strength results obtained above with the very good workability of catechol (see Table 3.1.1.). The results did show very good workability, better than the modified pine by itself, but slightly lower one day strength also compared to the standard. The three day strength was slightly higher than the modified pine itself and higher than the standard. At seven days curing the strength was unaffected by the additional catechol and remained a little lower than the standard's. The improvements were not good enough to justify the high content of catechol.

All the last three additives showed typical characteristics of a superplasticiser, i.e. lower viscosity of the fresh mix but without high losses and with the wattle based addition even a slight improvement in one day strength. The only characteristic not evident is an expected higher later strength. It may have developed after seven days of curing.

All the condensed tannins (quebracho, wattle and very likely also the pine extract) have given much improved flow results to the fresh concrete mix with ammonia additions ranging from 2.5% to 33% by mass. The 2.5% addition to wattle and pine extract provided generally greater improvements than the 33% addition to quebracho extract. In both cases of additions some strength results improved a little, but those of the wattle tannin were more significant. The performance of the chestnut tannin became worse with the 1:1 by mass ammonia modification and it also exhibited the fastest tendency to agglutinate.

3.3.4 A Various Tannin Extracts Sulphited

Tannin extracts, in particular that of wattle, have been sulphited in order to reduce the viscosity of concentrated tannin solutions used as raw material for adhesives[26]. The sulphitation breaks open the etherocyclic ring of condensed tannin molecules, which then have improved solubility in water (see Section 2.6.5 of the literature survey). Sulphitation may also reduce the hydrophobic nature of other extract constituents such as higher sugars and gums.

Pine and mimosa extracts were both reacted with sodium metabisulphite in a 3:1 by mass ratio in order to improve their solubility and therefore be able to keep their solution stable over longer periods or increase the solid content of the tannin extract in water. Sodium metabisulphite was used because it is known not to have side effects on concrete as it has long been used in the sulphitation of the molasses based superplasticiser.

In addition to the metabisulphite a small amount of potassium hydroxide was added to the mixture. The alkali is known to assist the sulphitation of molasses and may activate the tannin molecule by hydrolysing some hydroxide groups to form phenate ions.

The pine extract appeared to dissolve quicker in water than the wattle, but its solution became more viscous during the one hour heating at 70°C. Both sulphited extracts provided much improved workabilities over the standard and had the same flow time (Table 3.3.4 A). The sulphited wattle tannin provided strengths slightly higher than the control from the first day onward. On the seventh day its compressive strength was considerably higher than the standard. The sulphited pine extract had the same strength as the standard on the first day and from then on slightly higher. Its strength results were intermediate between the wattle counterpart and the standard, a similar trend to that observed in Table 3.3.3 B when both tannin extracts were treated with a small amount of ammonia. This indicates that each tannin's characteristic is retained and that they respond similarly to modifications.

Compared to the results of the wattle extract only addition in Table 3.3.1 A, the sulphitation of the tannins in the presence of the small amount of alkali has resulted in greatly improved workability of the fresh mix and an increase in compressive strengths at all stages of curing from a little below to slightly above the standard.

These results indicate the suitability of modified tannin extracts as plasticisers. In particular their advantage lies in providing lower viscosity of the fresh concrete mix with equal or slightly higher strengths from the first day of curing. This leads to the thought that the cement grains are better deflocculated and dispersed by complexation in the wet mix and hydrate more homogenously to give higher strengths particularly from the third day onward.

In a different series Italian chestnut extract was sulphited 10:2 by mass with sodium metabisulphite, a small amount of potassium hydroxide and also heated for one hour at 70°C. The chestnut tannin was less soluble and could only be dissolved as a 9% solid content solution, whereas the pine and wattle extracts did as a 39% solid content solutions. On dissolving the solution pH was 5,27 which rose to 5,95 after the reaction indicating the consumption of protons from the pyrogallol molecules of the extract. However the pH reading was wandering, so the accuracy of the measurements is debatable. Three quarters of an hour into the reaction foam still present from dissolving the chestnut, had disappeared. The presence of foam on the additive is usually a good indicator of its surfactant properties. The workability was not much better than the standard, but at least strengths were equal apart from that of the first day, which was much better than that for the standard. Four and a half months later the additive showed some precipitate, presumably chestnut extract precipitated from the solution.

Following the good one day strength results obtained with the sulphited Italian chestnut extract another two samples were made but this time with Yugoslavian chestnut in a 10:5 and 10:2,5 extract : metabisulphite ratio, heated one hour at 70°C. Both were made without the usual small amount of potassium hydroxide and the latter was also intended as a comparison to the sulphited Italian chestnut extract. The additive made with the lower ratio gave a slightly lower one day, much higher three day and higher seven day strength compared to its standard than the 10:2 Italian ratio type discussed previously. Workabilities were the same.

The big difference in three day strength can not be ascribed to the potassium hydroxide content of the 10:2 Italian type since the Yugoslavian chestnut tannin has already shown this property on its own also in Table 3.3.4 A. The Italian type is more difficult to dissolve in water. This and its apparent different composition may explain the poorer resulted obtained.

At the higher metabisulphite content (10:5) workability was as above, one day strength was marginally higher and three and seven days slightly lower compared to the 10:2,5 type. Apart from the higher three day strength, one and seven days compressive strengths were equal to the control. The higher sulphitation therefore showed no general improvements in the properties of concrete. The unmodified Yugoslavian chestnut extract previously mentioned gave very similar results to those of the 10:2,5 and 10:5 type, so that the sulphitation does not provide significant advantages from a concrete performance point of view. The metabisulphite may however be necessary to stabilise the extract solution on storage. In the case of the Italian chestnut extract the sulphitation, in the presence of a small amount of potassium hydroxide, may have led to a much higher one day strength.

Based on the success of the earlier sulphited pine and wattle extracts in particular,

quebracho and pecan nut shell extracts were modified in the same way with metabisulphite and a small addition of potassium hydroxide. The ratio of extract to metabisulphite used for both samples was 10:3.

The water content of the solution had to be increased to three times the usual amount because dissolving the quebracho extract in warm water was problematic. The pH of the quebracho sample dropped from 6,50 to 5,78 during the one hour heating at 70°C possibly indicating the breaking open of the etherocyclic ring of the tannin, as indicated in the sulphitation of tannins in Section 2.6.5 of the literature survey. In the process the oxygen from the opened etherocycle forms an additional hydroxide group, which may explain the decreasing pH. Three days later some sticky residue formed, probably due to the formation of phlobaphenes brought about by too high sulphitation. V.J. Sealy-Fischer states that sulphitation of tannin with large quantities of sodium sulphite leads to auto-condensation[129]. The additive was nevertheless tested to establish the effect of the formation of insoluble constituents on the performance of concrete.

The performance of the lified quebracho extract was very good as far as the workability is concerned (Table 3.3.4 A). However after fifteen minutes of mixing no stiffening took place and the one day strength was half of that of the standard. These are typical results of the sulphited molasses based superplasticiser. Sugars in the quebracho extract may have been sulphitised. The main reason for the poor one day strength is probably the degradative autocondensation of the tannins. By the third day the retardation in strength development was overcome and strengths from then on were slightly above the standard. After almost four months storage the additive showed only a little precipitate.

Compared to the quebracho extract addition on its own in Table 3.3.1 A, the sulphitation in the presence of a small amount of alkali has greatly improved the flow of the fresh mix but also halved the one day compressive strength. The poorer early strength of the sulphited quebracho extract can only be due to oversulphitation leading to the degradative autocondensation of the tannin, rendering the modified tannin largely ineffective. Three and seven day strength results did not change.

The 20g pecan nut shell extract would have dissolved in 40ml water, but was diluted to the same concentration as the above mentioned quebracho extract sample. The pH of the pecan type remained virtually constant during one hour of heating at 70°C, changing slightly from 5,83 to 5,89. This additive had the opposite effect on concrete compared to its quebracho counterpart. It showed no measurable improvement in workability, but a higher one day compressive strength than its standard. Three day strength was a little lower and seven day strength slightly below the control.

Of all the sulphited extracts tested wattle, pine, quebracho and Yugoslavian chestnut are listed in order of their suitability. Chestnut extract of Italian origin was inferior both in

handling and performance to the Yugoslavian type. Quebracho would require further modifications to improve its solubility and chestnut also to some extent. The series of tests in Section 3.3.5 A were done for this purpose. The workability characteristic of chestnut extract would also have to be improved. Pecan nut shell extract, by contrast, had shown no real advantages.

3.3.4.B Investigation of Sulphite treated Chestnut Tannin

The previous section has shown that many concrete performance characteristics of most tannins could be considerably improved by sulphitation. In the literature numerous references are made to the structural changes condensed tannins are subjected to when sulphited (see Section 2.6.5 of the literature survey). This is not the case for hydrolysable tannins. For this reason Yugoslavian chestnut extract was reacted with metabisulphite in a 10:1 molar ratio for two hours at 70°C.

The carbon 13 NMR (Figure 3.3.4 B) analysis shows two distinct changes when compared to the natural Yugoslavian tannin of the bibliography. The spectra have different resolutions, but a significant decrease in the area of the peak at 84 ppm can be seen for the sulphite treated extract. It is roughly equal to two peaks neighbouring it and much smaller than the broad peak at 71-80 ppm. In the spectra of the natural chestnut the peak at 84 ppm covers a greater area than its two neighbours and is larger compared to the broad peak. This decrease may indicate that some polymeric carbohydrates were broken down by the sulphitation, since the peak is within the region of the -C-O- backbone of sugars.

Another peak, at 59 ppm, shows a small increase in the spectra for the sulphite treated extract. It relates to CH_3-O- and -CH_2-O-groups. These could be the result of the above proposed reaction, where some of the resulting sugars could have reacted with phenols of the extract.

The phenolic ring appears to be unaffected by the sulphitation. This correlates with an observation made in Section 3.1.3 A when a catechol: metabisulphite 1:1 molar additive was concrete tested and found to essentially perform as catechol on its own.

3.3.5 A Quebracho and Wattle Tannin Extracts Sulphited and treated with Urea or Ammonia

The first two samples of this series are quebracho extracts reacted with sodium metabisulphite in a 10:1,5 ratio and with a small amount of potassium hydroxide. One was treated with an additional 1,5 parts of urea to establish its effect on the performance

of the additive on concrete. Both samples were heated for one hour at 60°C.

The non-urea type gave only a small improvement in initial workability (Table 3.3.5). After fifteen minutes of mixing the flow of the fresh mix became much better. This is however impractical and often leads to retardation. The one day compressive strength was slightly lower and at three days even more so compared to the standard. Surprisingly the strength was considerably higher than the control on the seventh day.

The sample with the additional urea gave better workabilities with test results after five and fifteen minutes close to each other. At least the very long flow times and complete run-through demonstrate a very good cohesiveness of the fresh mix. One day strength was just above the control and the three day strength below, similar to the non-urea result. At seven days curing this additive also had higher strengths than the standard, but not as high as that without the urea.

The lower three day strength of both additives may have been caused by the relatively low metabisulphite content, since the 10:3 type sample of the Table 3.3.4 A had shown a slightly higher strength than its control. The 10°C lower temperature of 60°C applied here is not thought to have been responsible.

As a comparison two more samples were made with same formulation and in the same way as the above two, but with a different batch of quebracho tannin extract.

This newer batch powder was much lighter, i.e. very bulky, more difficult to dissolve in water and foamed considerably more. This time the non-urea additive gave an initial workability well below that of its standard and in both flow tests some of the fresh concrete remained in the funnel. The one day compressive strength was slightly below the control and at three days considerably higher, the latter result being in contrast to that of the previous quebracho based additive. Similarly, the seven day strength was not as much higher compared to its control as the previous batch equivalent additive.

During the flow test of the additional urea type again only some of the fresh concrete flowed through (Table 3.3.5). This happened with both tests and also shows lower workability and cohesiveness of the fresh mix than the standard and the equivalent previous batch quebracho additive. The first day strength was slightly below the control in contrast to the slightly higher strength obtained with the previous batch quebracho equivalent. Three day strength was again higher than the standard and the previous batch counterpart and at seven days similarly above the control.

Although the newer quebracho extract had an advantage in providing higher three day strengths, it was far less beneficial from a workability and cohesiveness of the fresh mix point of view. With the longer flowing times an accelerated early strength development

was expected, but did not occur as can be seen by the normal one day strengths. The gain in three days strength of the newer batch quebracho came at the expense of higher seven day strengths. Other disadvantages are the more difficult handiing of the extract when preparing additives and the stronger cloudiness of the resulting solutions. The minute white particles which form, are not truly soluble in water and are responsible for a large part of the glue-like precipitate formed on storage.

To improve the solubility of the newer quebracho extract it was again reacted with sodium metabisulphite as 10:1,5 parts by mass, but with double the urea making its addition 3 parts. The raw materials were heated twice as long as previously, this time two hours at 60°C and included the usual small amount of potassium hydroxide.

Strengthwise the results were generally better than the 10:1,5:1,5 type made with the older batch quebracho extract. Workability was still much lower than the standard but cohesiveness was high. The one day strength was higher than the standard and on the third day too, the latter a characteristic of this newer quebracho extract. These strength results present an improvement obtained with the 10:1,5:3 type. Seven day strength was still higher than the standard, almost as good as that of the 10:1,5:1,5 type of the older quebracho extract. The higher three day compressive strength of the newer quebracho extract is retained with the higher urea modification and longer heating.

Comparing the 10:1,5:3 of the newer quebracho extract with the higher urea and longer heating time with the 10:1,5:1,5 of the same quebracho batch, there is a great improvement in workability. The second workability, after fifteen minutes, of the 10:1,5:3 shows a quicker stiffening of the fresh concrete mix has taken place and the one day strength is one and a half times that of the 10:1,5:1,5 type. The three day strength is slightly higher and the seven day result slightly lower than that of the 10:1,5:1,5 additive.

The above comparisons clearly demonstrate the variations in the chemistry of different batches of the same extract. Some changes in formulation and in production of the additive can compensate for certain undesirable characteristics, but not all. A consistent raw material and regular testing of batches is required for practical purposes.

In a direct comparison between the older quebracho and wattle tannin extract, the latter was modified in the same way as described in the beginning of this Section (3.3.5). The non-urea type showed better initial but lower final workability than the quebracho counterpart. In relation to the 10:3,5 sulphited wattle tannin of Table 3.3.4 A the lower metabisulphite content used here appears to have decreased initial workability. The cohesiveness of the fresh mix was high, as indicated by the long flow times and complete run-through. The one-day strength was considerably higher but later results only equal to the control. The results of both urea and non-urea types were an improvement over the

standard. In one day strength the non-urea wattle based additive showed a result one and a half times higher than the quebracho equivalent or the standard. Compared to the quebracho equivalent the three and seven day compressive strengths were higher and considerably lower respectively.

The inclusion of urea in the second modified wattle additive resulted in a similar trend. The initial workability was a little better than without the urea addition and the final workability result showed the onset of setting. The strengths were hardly affected compared to the sulphited wattle tannin. They were slightly lower up to the third day and on the seventh day slightly higher. Compared to the quebracho urea equivalent, one and three day strengths were again higher and respectively higher and close to those of the standard. The seventh day strength was slightly higher this time than the control, but not as high as for the quebracho equivalent.

The wattle extract based additives were equivalent to the quebracho extract i.t.o. workability but much higher in one and three day strengths, which are the most important for practical applications. The quebracho based additives have an advantage in their higher seven day strengths, but tend to be less stable on storage. The performance of sulphited quebracho tannin can be greatly improved with urea, whereas the sulphited wattle extract appears hardly affected.

In Section 3.3.4 A sulphited quebracho extract showed a strong tendency to form a residue. This was attributed to auto-condensation (phlobaphene formation) of the tannin resulting from too much sulphitation. The other extracts, including wattle did not show this strong tendency. V.J. Sealy-Fischer found that urea used in the sulphite extraction of pine bark reduced the formation of phlobaphenes and attributed that "to the presence of the urea on the tannin molecules"[125].

The urea could be protonated in the acidic solution (see pH values of around 6 in section 3.3.4 A, despite small amounts of alkali). With its carbocation, the protonated urea could act as a strong electrophile and attach to either position 6 or 8 on the A-ring (see figure XLIV of Section 2.6.1, literature survey) similar to that of phenol and formaldehyde interaction in acidic solution. This proposed mechanism is based on the fact that meta positioned hydroxide groups activate the phenolic ring more strongly toward electrophillic substitution than adjacent groups such as catechol in Section 3.1.3 B. It would thus effectively block some of the two most common sites for interflavonoid bonds (see figures XXVI and XXVII, p.60) and phlobaphene precipation (see Section 2.6.4). The tannin would remain water soluble and be able to perform better as a concrete additive.

The urea could therefore prevent tannin auto-condensation at the A-rings which are activated by sulphitation (Section 2.6.5). It appears the wattle tannin, due to different chemical make-up and composition, is less susceptible to sulphite induced phlobaphene

formation, as was also noted in Section 3.3.4 A. The effect of urea on wattle tannin is therefore less noticeable than on quebracho extract.

3.3.5. B Time monitored interaction of Quebracho Tannin with Metabisulphite and Urea

Additives of Section 3.3.5 A demonstrated that many important concrete characteristics of wattle and quebracho tannin could be improved when treated with metabisulphite and urea. A sample with quebracho: metabisulphite: urea in a 3:1:6 molar ratio was heated for an hour at 70°C. The progress of the reaction was monitored by taking samples for infra red analysis when the constituents were mixed, after one hour heating and 24 hours later (Figures 3.3.5 A-C). The last sample was tested to obtain information on previous observations that additives concrete tested after a maturing period gave different results to those tested fresh (for example Table 3.3.8 B).

Comparing the two spectra before (Figure 3.3.5 A) and after heating (Figure 3.3.5 B), one can see that two very small peaks have developed at around 2900cm^{-1} which are characteristic of a secondary amide. 24 hours later (Figure 3.3.5 C) a second type of carbonyl group bond appears at 1660cm^{-1}. Apart from the major reaction, the opening of the etherocyclic ring by the sulphite (See Section 2.6.5 of the literature survey), the three peaks suggest a related mechanism. The sulphitation may not continue after the heating, but a small amount of the etherocyclic rings may have been opened up by acid hydrolysis (see Section 2.6.4) by the acidic solution, or by hydroxide groups formed by the sodium ion of the metabisulphite salt. This may have resulted in a carbocation being formed (at originally the C-2 position, see p.57) with urea probably attaching itself at that site. The blocking of the carbocation site may prevent self condensation of tannins with opened etherocyclic rings. By avoiding this phlobaphene precipitate formation, the storage life of the additive would be much improved. The three abovementioned peaks and other smaller peaks suggest that the amine group of urea has changed to form a -NH- link with the tannin. The 24 hours spectra (Figure 3.3.5 C) shows an increase of a peak at 970cm^{-1} apparently indicating the presence of a less substituted aromatic ring opening. This implies cleavage of the interflavonoid bond.

In a second experiment a sample was made with quebracho : metabisulphite : urea in a 3: 1,3 :6 molar ratio and also heated for one hour at 70°C. The peculiar ratio comes from a mass ratio in which the metabisulphite is one third of the mass of quebracho tannin. In the previously discussed experiment the salt is a quarter of the mass of the tannin.

Again, the events of interaction were monitored by taking infra red samples as previously, this time with an additional sample taken one hour after the heating (Figures 3.3.5 D-G). Once more the sulphitation with opening of the etherocyclic ring represents the major

reaction. A very small peak at just under 3000cm^{-1}, representing a secondary amide, shows an increase toward one hour after heating and remains 24 hours later. This lends support to the proposed mechanism and timing of the reactions involving urea in the previous sample.

There are also two bands which gradually change in intensity during one hour heating and after, but more noticeably during the 24 hour 'maturing period'. The first is at 1520cm^{-1}, indicating the C-4 and C-8 interflavonoid bond (see Section 2.5.3 of the literature survey), decreases and the second bond at 1040 cm^{-1}, indicating the C-4 and C-6 interflavonoid bond, increases. This could be due to the changing of one type of interflavonoid bond to another resulting in a rotation or recyclation of flavonoids. The proposed structures of the two types of interflavonoid bond (XXVI and XXVII, p.60) show that the C-4 and C-6 linkage offers a geometry in which the B-ring is more readily available to act as a dispersant by complexing with calcium ions of the cement. Since the recyclation is most noticeable toward the 24 hour sample, it could be the reason why the same additive tested a day later, instead of fresh, gives improved concrete performance (see Table 3.3.8 B).

3.3.6 Pine and Wattle Tannin Extracts reacted with Metabisulphite, Urea and Paraformaldehyde

It has been observed that sulphitation with sodium metabisulphite has been beneficial to the solubility of condensed tannin extract. There was no interference with the curing of concrete and the storage life of the additive was extended i.t.o. the stability of the solution (Section 3.3.4 A). Urea too is known not to have any detrimental effects on concrete. At this stage the agglutination of tannin extracts with even a low amount of formaldehyde had not been noticed (see Section 3.3.2).

Two samples, wattle and pine, were heated with metabisulphite for one hour at 70°C. Then urea was added and stirring continued without heating for an hour. Afterwards paraformaldehyde and potassium hydroxide was added to improve its dissolution. Stirring continued for another hour without heat. The ratio of the constituents was 10:3,5:5:0,5 by mass, in the order as described.

Initially the wattle dissolved better than the pine extract, which formed a more viscous solution. This has been observed in previous experiments, for instance in Section 3.3.4 A and also in subsequent ones. Both solutions, after the first stage of reaction, had a bean like odour which is typical when sulphitation with metabisulphite has taken place, as in the reaction with molasses in the production of superplasticiser.

Workabilities for both the pine and wattle based additives were much improved and one day strengths both slightly above the standard (Table 3.3.6). These early strengths were

the same although the second flow test showed a higher retention of workability with the wattle based additive. It also showed the highest three day strength, with the pine type intermediate between it and the standard. The much higher three day strength of the wattle type over the standard showed a marked drop to just below the standard toward the seventh day of curing. The pine based additive, by contrast, showed a much higher strength development between the third and seventh day with a result just above the control.

Depending on whether the three day curing or the seven day cured compressive strength is more important, the wattle based or pine based additive respectively would be more suitable. After three months storage the pine type still showed no separation, while the wattle equivalent had only a little thick precipitate. The pine tannin extract may have reacted more strongly with the metabisulphite and urea in the first stage of preparation, thereby becoming more soluble than the wattle tannin extract. It could also be that pine extract contains less poorly soluble constituents than wattle extract. Sodium metabisulphite and urea together stabilise the tannin extracts and would not be responsible for precipitation or separation.

Paraformaldehyde generally presented problems as far as storage life of additives was concerned (see Sections 3.3.2 and 3.1.2 A). In this section a very small application of 5% resulted in no such disadvantage. Conversely, this low amount of paraformaldehyde showed no advantages either. It was therefore decided to abandon its use altogether.

3.3.7 Yugoslavian Chestnut and Quebracho Tannin Extracts at various stages of modification

The chestnut solutions, numbers 1 to 4 Table 3.3.7 A, were tested at the usual 0,25% by cement weight addition. Two dry additions, number 5 and 6, of unmodified chestnut extract were added at 2g and 1g respectively. These amounts correspond to the tannin extract contained in solutions applied at 0,25% and 0,125%. Modifications of the tannin included : potassium hydroxide, sodium metabisulphite and urea (ie 10:0,1:1:2 by mass). Each of these was added to the chestnut extract in addition to the previous modification in a successive manner as listed and heated for one hour at 60°C. Irrespective of chemical modification no significant improvements in workability were obtained. Also characteristic for chestnut based additives were three day compressive strengths well above the standard.

Plain chestnut extract, predissolved in water, gave no surprises apart from a slight improvement in flow and the characteristic much higher three day strength. The potassium hydroxide addition to the above solution decreased the slight flow and increased all strengths slightly. This leads to the thought that the phenate like ion formed from the

pyrogallol of the chestnut extract had assisted strength development by forming complexes with the calcium ions of cement.

Another addition, this time metabisulphite, resulted in a slightly better flow but also a little lower one and seven day strength. This sulphitation is known to improve the solubility of condensed tannins. In Section 3.3.4 B a sulphited chestnut extract showed that some polymeric carbohydrates had been broken down to sugars. The tannin itself appeared unaffected. Hence the slightly improved initial workability may be due to the increased presence of sugars as a result of sulphitation of higher sugars.

A further addition, to the previous ones, of urea reduced the flow and improved strengths, with a seventh day result the highest of the series and higher than the standard. This full modification corresponds to the formulation of condensed tannin extracts which have given the best results. The other advantage of urea is its ability to keep extract solutions stable for longer periods of time.

Next, Chestnut tannin extract was added as a dry powder to the mixing water corresponding in mass to that of the extract contained in the previously discussed solutions. A direct comparison can be made to the same amount of unmodified extract predissolved before being added to the mixing water. The dry addition resulted in the same slight improvement in flow and the same three day strength. However, the one day strength was lower, even than the standard and the seven day strength slightly higher, also compared to the predissolved type. Since the one day strength is more important for most practical applications, predissolving the dry extract powder is vital. It seems to improve the dispersion of the powder in water. Generally the powder would have to be modified further in water in any case to improve characteristics of the additive.

A similar addition of half the dry powder still gave a very small improvement in flow. Apart from the usual higher three day strength, the one and seven day results were only equal to the standard. It is interesting to note that at half the dry powder addition the one day strength was higher and the three and seven days strength lower by an equal measure than the previous dry chestnut addition. It is possible that the higher addition of dry extract had not dissolved to the same degree and therefore hindered the one day strength development.

In the next series (Table 3.3.7 B) quebracho tannin extract was modified with the same chemicals in the same proportions and stages as the chestnut extract. The quebracho extract alone gave better workability but poorer strengths up to the seventh day, when it had improved to equal the standard. Together with potassium hydroxide workability was lower, but the strengths were slightly better from the third day onward. Apart from a slightly decreased one day strength, this is a similar trend to that of chestnut modified with the same alkali and confirms the thought that the presence of the phenate type ion does

improve strength development.

A further addition, metabisulphite, improved the flow of the fresh mix, but decreased the third and seventh day strength a little. The one day compressive strength was still below the standard. The improved workability may be due to the sulphitation of sugars, as in the molassis based superplasticiser and/or the recyclation of interflavonoid bonds observed in Section 3.3.5 B. The next addition, urea, decreased the workability and improved the one day strength to just above the standard. Three day strength was equal and seven day strength a little higher than the standard at this full modification of the quebracho extract. Again a similar trend to chestnut tannin : workability down and strengths all up a little. The same additive, tested at double the normal dosage i.e. 0.50% by cement weight, gave very good all round results. Despite the very good workabilities obtained the one day strength was only slightly lower than that of the standard. Three and seven days compressive strengths were both considerably higher than the standard and the highest of the series.

This series has shown that quebracho tannin extract does improve the workability of the fresh mix, particularly when fully modified. An interesting observation are two very high flow rates of above one minute. This is very unusual and demonstrates the good cohesiveness of the fresh concretes treated with a quebracho based additive. The roughly similar trends in concrete performance by : potassium hydroxide and urea modifications on both hydrolysable and condensed tannin based additives suggests some similar reactions with both tannins and similar mechanisms for their influences on fresh and hardening concrete. These respectively appear to be of the acid-base type and complexation of calcium ions of cement resulting in deflocculation and improved dispersion. The sulphitation had a greater effect on the condensed tannin probably due to recyclation which does not apply to the hydrolysable tannin.

3.3.8 Improving the solubilities of Wattle and Quebracho Tannin Extracts with small amounts of Alcohol

As pointed out in Section 2.6.5 of the literature survey tannin extracts in water form hydrocolloid suspensions. Very short chain alcohols have a polarity just lower than that of water and closer to that of organic solvents. A commercially available alcohol mixture containing approximately 70% ethanol and 30% by mass methanol was used in this and the next section to improve the solubility of tannin extracts. Since alcohol, or any other organic solvent, interferes with the hydration of cement, only a small amount of the alcohol mixture was added to the tannin at a dosage of 5% by mass. This mixture was left standing overnight before being used. Also new in this test series is the addition of sugar, which was intended to improve the workability, but instead completely retarded the one day strength development.

The first two samples were made with a alcohol mixture treated quebracho extract which was modified with sodium metabisulphite and urea in mass ratios of 10:1,5:3 and 10:2:4 respectively and heated for one hour at 60°C. The first additive gave much improved workability over the standard, but only a third of its one day strength (Table 3.3.8 A). At three days the compressive strength was still below the standard and at seven days in line with plasticisers improving later strengths due to improved dispersion of cement grains and their more uniform hydration.

The second test sample, the 10:2:4 type, generally showed very similar results. This was to be expected since the first additive had a similar ratio of constituents 10:1,5:3. The flow times were marginally slower and the one day strength barely measurable. Three and seven days compressive strength showed a slower strength development to the previous additive and, of course, also compared to the control. The higher chemical modifications of the alcohol treated quebracho with metabisulphite and urea therefore did not improve the effect the additive had on the characteristics of the concrete.

The next two samples were made with wattle tannin treated with the alcohol mixture analogous to the quebracho tannin discussed previously. This wattle extract was then modified with metabisulphite, urea and sugar in a ratio 10:3:2:5 by mass. A second sample was made without urea, i.e. 10:3:0:5 and also heated for one hour at 60°C. Both additives were tested at double dosage, that is 0,50% by cement weight.

The first type, with urea, gave very good workabilities but no one day strength could be measured. On the third day the compressive strength was a little lower than the standard and on the seventh day considerably lower. It is not clear why there was only a small strength development between the third and seventh day of curing. The non existent one day strength is probably due to a too high sugar content in the additive and/or the higher dosage used, which caused a high retardation in one day strength development.

The second modified wattle, without urea, showed the same workabilities and the same non-existent one day strength. At three days the strength was still considerably lower than the standard, but surpassed it slightly on the seventh day. The high retardation in one day strength is likely again due to the relatively high sugar content and/or higher dosage, as with the previous sample.

Without the urea there was a higher early strength retardation, but with the urea it appears the seven days strength was decreased. In both cases the effect of the sugar must be taken into account and double dosage at which the additive was applied.

Following on the previous series wattle tannin was again treated with the alcohol mixture in the same way but reacted with half the amount of metabisulphite. One sample was made without urea and the other with a slightly lower amount than that used in the

previous series.

The urea type w[illegible]e without the small amount of potassium hydroxide, which was included in the non-urea type. The ratios of wattle extract : metabisulphite : urea were 10:1,5:1,5 and 10:1,5 respectively (see Table 3.3.8 B). The major difference in this series is that no sugar was added and the reagents were heated two and a half hours at 70°C, after which the solutions did not show any more cloudiness. Both solutions were tested immediately after preparation and after a twenty four hour maturing period.

During preparation and heating the non-urea retained the foam formed on dissolving the extract. The urea counterpart remained cloudy much longer. The fresh 10:1,5 additive did not change the workability and provided strengths slightly lower than the standard throughout the seven days of curing. The fresh 10:1,5:1,5 type gave a slightly better workability than the above, but no flow was measured. Its one day strength was the same as the standard, but both three and seven days compressive strengths were equal to the non-urea type.

After a twenty four hours maturing period the 10:1,5 type still showed no changes in workability, but one and seven day strengths slightly higher than that of the standard. The third day compressive strength was even more pronounced in its increase.

The 10:1,5:1,5 type showed a similar tendency after twenty four hours : workability unchanged and [illegible]e day strength equal to the standard. From the third day onward the compressive strength was even a little higher than for the above type, providing a considerable advantage over the standard.

The much higher strengths obtained with both additives after a days maturing shows that important reactions leading to significant changes in the characteristics of an additive, take place after the heating process. This is probably even more pronounced in additives heated for one hour at 70°C. The above observed changes were expected to occur, since in the preparation of samples, slow organic reactions take place. One of these has been identified as the recyclation of the interflavonoid bonds in Section 3.3.5 B. All the additives tested in this project were only tested at least a day after their preparation. Experience has shown little changes in performance after twenty four hours maturing.

None of the alcohol modified wattle based extracts showed any appreciable improvement in workability whether tested immediately or after the usual twenty four hour maturing period. Results of Table 3.3.8 A show that this is not due to the alcohol modification. The different amounts of chemicals in Table 3.3.8 B can not account for such a radical change. The major difference has been the much longer heating time, one and a half hours longer than usual, which must have changed the chemistry of components of the additive responsible for inducing improved workability in fresh concrete mixes. This

could have been the formation of phlobaphenes which would prevent effective complexation and deflocculation by tannins.

3.3.9 Quebracho Tannin Extract at various stages of Alcohol treatment

Unmodified quebracho tannin extract was reacted in varying proportions with sodium metabisulphite and urea in ratios of 10:3,5:5 and 10:2:5 by mass as listed. Two samples followed with identical formulation but were prepared with quebracho extract treated with an alcohol mixture and left standing for three days prior to modification.

The first two without alcohol pretreatment required a little heating to dissolve the chemicals. When the first sample of the unmodified quebracho tannin was dissolved it had a pH of 5,62 which dropped to 5,09 after one hour heating at 70°C. The second type of the first lot showed a much lower pH change from 5,61 to 5,43 after the heating. It had a lower amount of metabisulphite and therefore less etherocyclic rings of tannin molecules could be broken by sulphitation to give a more acidic product (see Section 2.6.5).

On testing, the 10:3,5:5 type showed much improved workability over the standard (Table 3.3.9). The much higher second flow time measured indicated that stiffening of the fresh paste already took place during the fifteen minutes of mixing. This lead to a one day strength only slightly below the standard and three and seven day strengths considerably higher.

The 10:2:5 type showed very similar results. Its workabilities were slightly lower than for the above, but still much better than the standard. The second flow test also indicated an early setting with only part of the fresh mix flowing through the funnel. This did not lead to a higher early strength as for the 10:3,5:5 type, instead it was the same. The three day compressive strength was slightly higher than for the previous type, giving even more of an advantage over the control. The final strength, at seven days was identical to the previous type.

The higher metabisulphite content in the 10:3,5:5 type had lead to a greater improvement in workability possibly due to recyclation as pointed out in Section 3.3.5 B. The advantage of the 10:2:5 type was a even better improvement in three day strength over the standard.

The next two samples were identical to the above two as far as heating and chemicals are concerned. In this case the quebracho extract used was treated with a 5% by mass alcohol mixture and left standing three days before being used. Both treated extracts with their chemicals dissolved completely at ambient temperature, in contrast to the previous two samples which would not without a little heat.

The 10:3,5:5 type this time showed a much smaller change in pH during the heating, with a decrease from 5,59 to 5,43. The 10:2:5 type's pH remained virtually constant, with a slight increase from 5,14 to 5,18 diving the one hour at 70°C. This is in contrast to the slight decrease observed with the equivalent additives made with the non alcohol modified quebracho tannin. The above findings show a considerable change in chemistry of the extract brought about by the alcohol mixture.

The most obvious change in the alcohol treated extract 10:3,5:5 type was that it showed much lower improvement in workability over the standard than its non alcohol equivalent, both Table 3.3.9. The alcohol treatment hardly had any effect on compressive strength, with one and seven day results identical to the non alcohol counterpart. The only beneficial change was a slightly higher three day strength, which was also considerably higher than the control.

The 10:2:5 type showed no improvement in workability over the control and slightly lower strengths which decreased from the first day onward, compared to its non alcohol counterpart. In relation to the control the one day strength was lower, the three day result still higher and the seven day strength equivalent.

The alcohol treatment over the three days had therefore drastically reduced or eliminated the quebracho extract's ability to improve the flow of fresh concrete. In both the above additives the strengths were roughly equal or poorer compared to their counterparts based on quebracho tannin not treated with the alcohol mixture. It seems possible that the alcohol could have formed ether links with hydroxide groups from the tannin in an acid-base type reaction. In Section 3.2 diethyl ether showed similar results : no improvement in workability and approximately equal strengths to the control. However, the alcohol treatment did provide a great advantage by greatly increasing the solubility of the tannin extract on handling. Irrespective of alcohol treatment all four additives showed a little precipitate after three months storage.

The next two additives were made with quebracho tannin also treated with 5% by mass alcohol mixture overnight before being used. The ratio of constituents was not equal to the previous four, instead 10:2:2,5 and 10:1:5 alcohol - extract : metabisulphite : urea, by mass. Both dissolved quickly in water at ambient temperature. The first one took longer to dissolve probably due to its higher sodium metabisulphite content, which has a negative enthalpy for solvation.

The pH of both remained constant during the one hour heating at 70°C, 5,45 and 5,43. Generally all four alcohol treated extract based additives showed little or no pH changes compared to the untreated extracts.

The 10:2:2,5 type showed much improved workability over the standard, but only a third

of its one day strength (Table 3.3.9). By the third day the rate of strength development of the additive modified concrete was so high, that the strength was considerably above the standard. Toward the seventh day of curing the strength development had decreased considerably to give a value slightly below that of the standard.

The 10:1:5 type also showed a very good improvement in workability over the standard. It was the best result of the series. Early strength retardation resulted in a strength slightly below even that of the above mentioned. By the third day the early strength development had increased to give a result equal to the standard and on the seventh day slightly higher. After three months storage the 10:2:2,5 additive showed some precipitate while the 10:1:5 had none. The higher urea content of the latter appears to have a greater effect on the stability of the quebracho extract solution than the higher metabisulphite content of the 10:2:2,5 type.

Although the ratios of constituents of the last two additives does not equal those of their preceding four some generalisations can be made. The first two sets of results, with identical formulations apart from no alcohol treatment and alcohol treatment for three days, show that the long maturing time with the alcohol mixture almost eliminated the improved workability effect of the additives. Overnight treatment of quebracho extract with the alcohol mixture has maintained or improved the workability, but also considerably decreased the one day strength (see also Table 3.3.8 A). The alcohol treatment of quebracho tannin, whether overnight or for three days made no difference to the stability of additives on storage, but improved the solubility of the extract when mixed with water during the preparation of the additives. The alcohol pretreatment was abandoned.

3.3.10 Quebracho Extract modified with various dosages of Metabisulphite and Urea

The first sample was made to exactly the same formulation, 10:3,5:5. as the first from Table 3.3.9 apart from being made with a new batch of quebracho extract. A difference in chemistry to the older extract is evident by the much lower change in pH of the newer type 4,87 to 4,83 during the one hour heating at 70°C vs 5.62 to 5.09 for the older equivalent. The differences in appearance and handling of the powders have already been pointed out in Section 3.3.5 A.

This additive showed no improvements in flow over the standard (Table 3.3.10) compared to the high workability induced by the counterpart in Table 3.3.9. This confirms the observation made from Table 3.3.5 that additives based on the newer batch of quebracho gave much lower workabilities. The one day compressive strength was almost as high as the standard and the three and seven days result a little lower and slightly higher respectively.

The next two samples were made in a 10:2,5:5 ratio by mass representative of the familiar quebracho extract : metabisulphite : urea. The difference was in the method of preparation. For the first the chemical powders were mixed dry before the addition of water; the usual procedure. For the second the metabisulphite, urea and extract were successively dissolved as listed. The first two chemicals dissolved quickly while respectively causing a 1°C and 2°C drop in solution temperature until their solvation was complete. The quebracho extract, added last, was fairly difficult to dissolve probably due to less free water molecules for solvation. This seemed to have a greater effect on its solubility than the lower enthalpy available when all powders were mixed at once.

During the one hour heating at 70°C both showed the same changes in pH : 4,56 to 4,52 for the dry premixed and 4,60 to 4,51 for the stage dissolved type. This shows that a small change in procedure does not affect the individual chemical reactions. Both additives showed no improved workability and equal one day strengths which were only two thirds of the control. The three day results were similar to each other and still a little lower than the control. On the seventh day the dry premixed type had a slightly higher compressive strength and the stage dissolved equivalent a little lower result than the standard. The low seven day result of the stage dissolved type may be due to a testing error.

The 10:2,5:5 dry premixed type was also tested at double the normal dosage rate, i.e. 0,50% by cement weight. At this addition it showed good improvements in workability over the standard, while giving the same one day strength. Three and seven day compressive strengths were slightly higher and lower respectively than the standard. The main strength development took place from the setting of the fresh mix up to the three days, when it surpassed those results obtained at 0,25%. From the third day to seventh day there was only a small strength increase, the time range where the normal addition performed best.

It is surprising that almost none of the additives applied at normal dosage showed any improvement in workability, unlike the 10:3,5:5 and 10:2:5 types of Table 3.3.9 whose compositions are not that different from those in this series. The standard concrete mix of this series could have been very stiff and the plastification of the additives at normal dosage not strong enough to induce flow. The 10:2,5:5 sample tested at double dose did increase flow as expected, but still did not show any retardation in one day strength as would also have been expected with an average concrete mix. It can be expected that with an average mix the additives applied at normal dosages would have induced flow.

A higher content of metabisulphite than urea in a ratio of 10:5:3,5 gave unsatisfactory results (Table 3.3.10). The flow of the fresh mix improved a little but the one day compressive strength was a little lower than the standard. The three and seven day curing result were only slightly lower.

An equal dosage of metabisulphite and urea added to quebracho tannin in the 10:2,5:2,5 type sample gave good improvement in flow compared to its standard. This standard's fresh mix was less stiff than that for the preceding additives, which can also be seen in its generally lower strengths. The additive gave only two thirds of the one day strength, but on the third day increased to almost the same result as the control. The seventh day strength was considerably higher than the standard.

The final two tests are two very low modifications of quebracho extract with metabisulphite and urea; the ratio is 10:0,5:1 quebracho : metabisulphite : urea. At normal dose the flow improved a little and all strengths including one day were all slightly above the standard. At double dose workability improved a lot, as expected, but at the expense of one day strength. Later strengths were in line with the standard, so that the retardation was overcome by the third day. The best flow result at double dosage was measured after 15 minutes of mixing, which is too long for practical purposes and led to the very low one day strength.

In this section none of the various metabisulphite and urea contents tested were particularly successful. In order of suitability the quebracho tannin : metabisulphite : urea ratios can be listed as 10:2,5:2,5; 10:0.5:1; 10:2,5:5; 10:5:3,5. Two types tested in Table 3.3.9 were both much better all round performers, namely 10:3,5:5 and 10:2:5. Taking a small variation in cement quality into account, one can still see that a high metabisulphite than urea content is not beneficial. An equal content of both gave much better results, apart from a lower one day strength. A very low modification of quebracho tannin resulted in good strengths but very poor workability. The two additives from Table 3.3.9 appear the closest to an ideal formulation

3.4 Various additions to improve the performance of modified Tannin Extracts

Some modifications of tannins have greatly improved important characteristics. Sulphitation of condensed tannins has resulted in improved workabilities, an increase in most compressive strengths and generally an improved storage life. This is most likely due to opening of the etherocylic ring and interflavonoid bond cleavage. In the case of hydrolysable tannins minor improvements appear to be a consequence of sulphitation of non-tannin constituents (Section 3.3.4 B).

Urea improved the solubility of extract solutions and appears to have prevented sulphite induced autocondensation of condensed tannins. In some cases strengths also improved, irrespective of the type of tannin. Infra red monitoring of quebracho tannin reacted with metabisulphite and urea showed tannin interflavonoid bond rearrangement from C-4—C-8 to C-4—C-6, resulting in better availability of B-rings for complexing reactions. There is also evidence of urea attaching to a carbocation site, the result of an opened etherocyclic ring and therefore preventing autocondensation with other tannins. The spectra also show signs of some -NH- bonding with the tannin (Section 3.3.5 B). Potassium hydroxide also improved some strengths of Yugoslavian chestnut and quebracho tannins, but also decreased workabilities of the latter. The alkali did not appear important for successful sulphitation and was therefore abandoned.

Even low amounts of formaldehyde (around 10%) have quickly polymerised with condensed tannins making the additive unstable and providing no advantages. Ammonia had a strong precipitating effect on the hydrolysable tannin, without affording any improvements. The condensed tannins were less strongly affected and gave improved workabilities. Both formaldehyde and later ammonia were excluded from further formulations.

Overnight treatment of condensed tannins with alcohol improved solubility and workability but interfered with one day strength. Three days pretreatment resulted in more soluble tannin extracts, but the effect was not extended to storage life. The workability greatly decreased and the alcohol treatment was stopped.

Quebracho tannin best combined good workabilities with good strengths when reacted with metabisulphite and urea. Wattle extract similarly modified also presented good overall results. Yugoslavian chestnut provided the best three day strength results irrespective of modification.

In the following sections various additions for modified tannin extracts are tested to improve on the results obtained so far and to formulate a more effective concrete plasticiser with accelerating ability.

3.4.1 Modified Wattle Extract with Triethanolamine additions

TEA (triethanolamine) has long been used to accelerate or retard the strength development of concrete, depending on the dosage applied[122]. TEA also has some air-entrainment ability. This series was done in order to check whether it would interfere chemically with modified extracts or improve their characteristics.

In the first test a sample was made according to wattle extract : metabisulphite : urea : ammonia : TEA in a mass ratio of 10:2,5:3:1,5:2. The TEA was simply added to the other constituents and together they were heated for one hour at 60°C. At the 0,25% dosage there was hardly any improvement in workability, the first and third day compressive strengths were only a little lower and the seventh day result slightly below the standard (Table 3.4.1 A). It is not clear whether the amount of TEA added was too high or too low to have a greater effect on early strength development, or whether it interfered with the reactions of the other constituents.

Following the above test results, another series was made with a similar mass ratio of constituents 10:2,5:3,5:1:2 wattle extract : metabilsulphide : urea : ammonia : TEA. As can be seen by comparing this and the previous ratio urea was increased a little to ensure good solubility of the extract. Although previously implicated of agglutination with tannin extracts (e.g. Section 3.3.3) ammonia was retained but decreased slightly, because it was thought to also improve the solubility of the wattle extract. To ensure a complete reaction of the first five chemicals they were heated for two hours at 60°C and left to mature for twenty four hours before the TEA was added to the cold solution. With this procedure the TEA could not possibly interfere with the reactions of the other chemicals, even if it was likely.

At a 0,2% dosage of the additive, the fresh mix was made workable, an improvement over the stiff mix of the standard. The one day compressive strength was equal to the control and slightly lower and slightly higher on the third and seventh day respectively. Presumably the TEA had provided an acceleration on the first day and the plasticising additive a higher seven day strength by improving the uniformity of hydration of the cement grains.

At a 0,3% dosage the same additive provided a very workable, though still not flowing mix. This greater improvement over the standard resulted in a little lower one day strength. By the third day the retardation was overcome and on the seventh day the compressive strength was still slightly above the standard.

The main difference between the first and both the second and third additive is that the TEA was added immediately to the other reactants and only twenty four hours later respectively (Table 3.4.1 A). Although there are slight differences in urea and ammonia

content and the dosage tested, there is no indication that TEA behaved chemically different at either stage of its addition. It seems to exert its influence on concrete independent of the other chemicals in additives.

All three additives containing a 10:2 mass ratio of wattle tannin extract: TEA have shown only a marginal improvement in workability. This has not happened before with any other modification of wattle tannin extract, when a moderate to substantial improvement in workability could always be measured. It appears the amount of TEA added was too high and had caused too early setting of the fresh concrete.

It has already been observed that test samples improved within the first couple of days after preparation, hence the minimum twenty four hour maturing period before concrete testing (see Table 3.3.8 B). This lead to the speculation that the reactions were not complete within one hour's heating at 70°C. The next series uses the same original batch with samples taken at hourly (2,3,4,5,6) intervals while maintaining the heat at 70°C. The formulation was 10:3,5:0,5:1 for wattle extract : metabisulphite : urea : TEA, with the last two added later.

Each sample of sulphited wattle tannin was left standing overnight before the small amount urea was added to it. The two hour sample had developed a 5cm thick sediment during this time before urea was added to the cold solution. On the next day the sediment was much lower at 2cm thickness, proving that urea does improve the solubility of the tannin extract so treated. After this procedure each sample was left to stand overnight and then had TEA added to it and was heated for three hours at 70°C.

On testing, the same day, the three hour sample showed the worst and the five hour sample the best flow result (Table 3.4.1 B). The one day strength decreased when the wattle extract was heated with metabisulphite for longer than two hours. This decreasing trend in one day strength and the sediment observed in the two hour sample suggest a degradation of the tannin. This could be the formation of phlobaphenes induced by the sulphite, as proposed in Section 3.3.4 A for the sulphitation of quebracho tannin with subsequent precipitation. The addition of urea reduced the sediment of 5 cm after one day to 2 cm on the next. Since urea is not highly reactive and was mixed in cold, the 3cm redissolved sediment must have been a non-tannin fraction of the quebracho extract. The remaining 2cm precipitate were likely to be phlobaphenes.

The three and seven day results also generally decreased after two hours heating, but gave good improvements over the standard at two, four and six hours heating. The workabilities, which were generally good, did not follow any particular pattern and the three hour sulphited sample gave no flow. As pointed out in the discussion of the above example compared with Section 3.3.4 A the phlobaphene formation does not seem to influence the workability of the fresh concrete, but has a direct detrimental effect on the

strength development, particularly on the first day of curing.

The two hour sulphited sample gave the best all round results with good workability, one day compressive strength equal to the standard and three and seven day strengths considerably higher. The six hour sample was not very far behind and the others roughly similar to one another. An exception is the three hour sample which had no improved workability and together with the five hour sample lower strengths compared to the others, which were closer to or above the standard. In order of all round suitability the summary of hours of sulphitation from best to worst is 2> >6>4>5> >3 (Table 3.4.1 B).

The workability results of the three hour sample have no relation at all to those of the other samples tested. A repeat test of the two and three hour samples (discussed in the next paragraph) shows more credible workability results for the three hour sample. The possible formation of phlobaphenes after two hours sulphitation appears to have a direct detrimental influence on strength development in general and most strongly at one day of curing. The workabilities seem to be unaffected.

On the next day the two and three hours sulphited samples were tested again and compared to a straight addition of TEA. Both flow results were much better, but strengths were lower. This proves the ongoing chemical changes in the freshly prepared additive and the minimum requirement of one days maturing before testing.

The sulphitation reaction is at least partly ionic and therefore fairly fast. An overnight maturing period has previously shown the same effect (particularly on workability) with similarly modified tannin extracts but without the TEA (Table 3.3.8 B). This means the TEA is not noticeably responsible for chemical changes during the maturing. That leaves urea as the common denominator. Urea is slightly basic and is a well known buffer. Unreacted urea probably adjusts to the acidic tannin solution by undergoing on equilibrium to form its own salt during the maturing period.

The TEA only addition provided less flow and only a slightly higher seven day strength compared to the matured two and three low samples. A standard was not made on this day, but it can be assumed to be roughly equal to the previous one.

3.4.2 A Modified Quebracho Extract with TEA Acetate or Formate additions

Having established some beneficial effect of small amounts of triethanolamine (TEA) combined with modified wattle extract it was decided to test TEA acetate and TEA formate accelerators[130] on their own. As with acetates the salts (sodium, calcium ....) of formic acid have also been used as accelerators when chlorides are undesirable.

The TEA salts were prepared cold simply by mixing the constituents and letting the mixture stand overnight. The reactions are of the acid-base type and the heat evolved drives the reaction. The result is a paste of marzipan-like texture and consistency with a slight benzaldehyde-like smell. When stored for several weeks the paste becomes progressively more orange in colour. TEA and acetate were mixed together as 70:30 parts by mass and TEA and formate in a 75:25 mass ratio. Both ratios correspond to a 1:1 molar ratio.

On an equal basis (0,2% addition) the TEA acetate was more effective than the formate equivalent, although it only showed a comparatively small improvement over the standard in one and two days strength (Table 3.4.2 A). The TEA acetate generally had equal or slightly higher compressive strengths than the standard, as did the formate equivalent, but it had a little lower results for three and seven days curing. Since 0,2% is a generally accepted dosage for the salts of these acids, a lower molar mass alkali part of the salt, say sodium, would automatically lead to a higher acid part of the combined mass than TEA and stronger acceleration. At a 0,01% dosage the TEA acetate addition was too low to show any marked beneficial effect and from the third day onward had slightly lower strengths than the standard.

Since TEA acetate is very water soluble, it was thought that its accelerating properties could be combined with the plasticising ability of condensed tannins. To test this 1:1 by mass addition of quebracho extract and TEA acetate was made in a water solution without the application of heat. At a 0,25% dosage there was no improvement in flow or any measurable one day strength. Only the third day strength showed a small improvement over the control, but on the seventh day the result was a little lower.

An interference between the quebracho extract and TEA acetate is indicated by the flash set and non existent one day strength. Both of the components tested separately have shown better results like improved strength and improved flow (see TEA acetate earlier and quebracho extract Table 3.3.1 A respectively). A possible explanation for the interference between quebracho tannin and TEA acetate could be cross-linking. At the mass ratio of 1:1 there are three moles of tannin for every four moles of ester. The TEA acetate may have three possible sites (three ethanol branches) and the tannin three possible sites for cross-linking (see Section 2.6.1 of the literature survey).

In the following test quebracho tannin and TEA acetate were mixed dry in a ratio of 10:1 by mass. There was virtually no improvement in flow, but at least the one day strength was not much lower than that of the standard. Three and seven day compressive strengths were higher and well above respectively than the standard's. It seems the lower TEA acetate content, compared to the previous sample, did not cause any interference with the quebracho tannin which previously resulted in no one day strength.

The TEA acetate appears to only act as an accelerator, some of its performance offset by the tannin. Quebracho tannin on its own tends to slightly retard early strength development, or at the very best give results similar to its control. With the 10:1 quebracho: TEA acetate additive the amount of ester applied to the concrete is about one tenth of the minimum dosage it requires to work as an accelerator on its own. Even at this low content it improved the three day strength and seven day strength by about 20% and 13% respectively over that obtained with quebracho tannin alone (see Table 3.3.1 A). The TEA acetate content was apparently too low to improve the one day strength, but low enough to prevent an interference with the quebracho tannin as observed with the 1:1 ratio additive.

In the another test quebracho extract was modified with metabisulphite and urea in a 10:0,4:0,8 mass ratio. After heating the solution for one hour at 60°C it was mixed cold with TEA acetate in a 5:1 by mass ratio. This mixture tested at a 0,25% addition gave improved workability over the standard and at the same time the one day compressive strength was slightly above the standard and the three and seven day result even higher (Table 3.4.2 B).

At double dosage (0,5%) the workability was much improved over the standard. This was expected, though not a one day strength only a little lower than the standard. At three days the compressive strength was considerably higher and at seven higher than the control. It is interesting to see that although the one day strength development was a little retarded, the strength development significantly increased toward the third day to give a result higher than at the normal dosage.

The same modified quebracho extract was also mixed cold with TEA acetate 4:1 parts by mass. The results obtained at a 0,25% dosage were quite different to the 5:1 mixture discussed above. There was not much improvement in workability, but all compressive strengths from the first day onward, were much higher than the standard. The one and three days results were a third higher and the seven day result a little higher than the control. The slightly higher TEA acetate content in this additive (20% by mass of the final additive vs 16,7% for the previous one) had such a strong effect on the early strength and setting time, that not all of the mix flowed through the funnel. In both cases a better plasticising action is required.

The above results have shown the very good results attainable with a modified quebracho extract and TEA acetate mixture. The content of the latter is fairly high and the following tests were made with 2,5% and 5% by mass TEA acetate part of the additive. For comparison the modified quebracho was also tested on its own and all three additives at 0,25% and 0,5% dosages.

In this follow up series the composition of the basic additive was very similar : 10:0,5:1 parts by mass quebracho extract : metabisulphite : urea. This solution was heated for two hours at 60°C and then mixed cold with TEA acetate 95:5 and 97,5:2,5 parts by mass. Part of reason for the much lower content was the relatively high cost of TEA.

The modified quebracho extract gave only a small improvement in workability, a little lower one and three day strengths and a higher seven day strength at the normal dosage compared to the standard (Table 3.4.2 C). At double dosage (0,5%) workability improved a lot, as expected but the expense of one day strength, which was very low. The second flow test, after fifteen minutes of mixing, gave a much faster result, which is too long a mixing time for practical purposes to obtain high workability and already indicated a retardation in early strength development. The three day result was similar to that of the normal dosage and on the seventh day the strength was slightly higher than the standard.

The same formulation as above, but including 5% TEA acetate, gave less workability at 0,25% dosage than without the addition but still a little better than the standard. One day strength was very similar to the modified extract alone, but subsequent three day considerably higher and seven day result similar. This shows that the additional TEA acetate reduced the flow a little, but also greatly increased three day strength. The latter compares very favourably with the control.

At 0,5% dosage the workabilities were slightly better compared to the additive without the TEA acetate. The exception is that the second flow result is only slightly slower. There was only a slight retardation in early strength for this dosage and the one day result was much higher than that of the modified quebracho alone. Compared to the standard it was still considerably lower. Three and seven day strengths were both considerably higher than the control and the modified quebracho on its own. At this double dosage the TEA acetate with the modified extract offset high early strength retardation and greatly increased subsequent strengths.

The second mixture, containing 2,5% TEA acetate and applied at a 0,25% dosage did not improve the workability as much as the 5% type. With the smaller ester addition the workability results were the same as that of the modified extract alone. The one day strength was also the same, but three and seven days compressive strengths were almost identical to those obtained with 5% TEA acetate, i.e. a great improvement in the three day result compared to the modified quebracho alone.

At 0,5% the 2,5% TEA acetate type improved workability a little compared to the 5% type and this presented a greater improvement over the modified extract alone. Apart from a similar one and seven day strength the three day result was not as high as for the 5% TEA acetate additive, but still much higher than the standard and the modified quebracho on its own.

The smaller addition of TEA acetate (2,5%) to the modified extract improved the workability a little more compared to the 5% ester addition at both dosages. At both TEA acetate contents and 0,25% dosage three day strength was considerably increased over the modified extract and the standard. At 0,5% dosage both additives with the TEA acetate considerably increased three and seven day compressive strengths over both the modified extract and the control. There was also considerably less retardation in early strength development at these high dosages compared to the modified quebracho, coupled with good improvements in workability.

3.4.2. B Investigation into the possibility of a Phenol-TEA Acetate Product

The previous section showed that modified quebracho tannin mixed 5:1 parts by mass with TEA acetate gave the best concrete performance results. To establish, whether there is a reaction between the phenolic tannin and the ester a 5:1 by mass phenol: TEA acetate sample was prepared. This is equivalent to a 11:1 molar ratio.

The pH of the solution was adjusted to a value of ten with potassium hydroxide. This would activate the phenol by converting it to a phenate ion and also represent the conditions of early hydration of cement (See p.16 literature survey). Two tests were carried out, one at room temperature (ca 20°C) to represent the hydration and also the addition of the ester to the modified tannin without heating. The second sample was heated for an hour at 50°C to obtain information on what could happen if the TEA acetate and modified tannin were mixed with the application of heat.

When compared to the Carbon 13 NMR of pure phenol (bibliography) the spectra for the ambient temperature sample (Figure 3.4.2. A) shows some distinct, though small changes. Apart from the peak at 161 ppm, which indicates the C-1 carbon of phenol, the remaining three carbon peaks all show a relative decrease in intensity. The signal at 151 ppm has shifted from 158 ppm. Since its intensity, relative to the other peaks, appears unchanged, this may be due to deprotonation of the hydroxide group in the alkaline solution. The signal at 121 ppm has shifted from 123 ppm, possibly affected by the alkalinity.

It appears that the phenolic anion has formed three types of resonance stabilised structures with the negative charge situated ortho, meta or para to the double bonded oxygen. The centralised nitrogen of the TEA acetate may be electron deficient by inductive effect of the three large groups surrounding it and could be coordinated at the site of the anion. The presence of the negative charge may induce one of the hydroxide groups of TEA acetate to leave. The resulting positive charge could then be carried to the nitrogen which would then bond with the phenate ion. The extent of the reaction is small, the product probably being only present as a few percent of the sample. The smaller signals at below 65 ppm indicate unreacted TEA acetate.

The spectra for the 60°C sample (Figure 3.4.2 B) shows a very similar result with virtually identical shifts. The decrease in intensity of the three signals from 115 to 135 ppm compared to the signal at 161 ppm is greater than that seen for the ambient temperature sample. A phenol-TEA acetate product appears to be present at about twenty percent of the sample. This finding shows that it would not be advisable to mix the ester and modified tannin with the application of heat, since that would most likely reduce the effectiveness of the TEA acetate as an accelerator and the modified tannin as a dispersant.

3.4.3 Comparison of Triacetin and Propylene Carbonate with TEA Acetate as additions to modified Wattle Extracts

In this series wattle extract and conditioned wattle are compared to one another. The latter is also tested with two esters : glycerol triacetate (triacetin) and propylene carbonate, which have been found to have an accelerating effect on the curing of phenol formaldehyde resins under very alkaline conditions[131]. The mechanism by which they react with phenol is known and that of the TEA acetate ester is possibly very similar to the glycerol triacetate.

Both the extracts were prepared in the same way : one hour heating at 60°C, extract : metabisulphite : urea 10:3,5:5 with a small addition potassium hydroxide (Table 3.4.3 A). Comparing the wattle and conditioned wattle based modified extracts mixed cold 4:1 by mass with TEA acetate one finds better flow results for the conditioned wattle type and only slightly lower strengths than the wattle equivalent up to the third day of curing. These results were a great improvement with one and two day strengths around one and a half times that of the control. The three day results were higher than the standard and on the seventh day all compressive strengths were roughly equal.

Both types showed quick stiffening indicated by the second workability test, after fifteen minutes of mixing, when the fresh mix was already so stiff that it did not completely flow through the funnel. This occurred after the first flow test, after five minutes of mixing, when both additives showed a significant improvement in workability over the control.

The wattle extract based additive had a slight all round performance advantage over the conditioned wattle, but its extract is more difficult to dissolve during preparation and forms a precipitate on storage. The most significant result for both additives was their much improved initial workability and much higher one and two day strengths over the standard.

In the next two tests the modified conditioned wattle tannin mixed cold as 4:1 parts by mass with triacetin and propylene carbonate (Table 3.4.3 A). Both additives provided greatly improved workability and gave slightly higher one day strengths. The two and

three day results were higher than the standard. The workabilities of both were virtually the same as for the conditioned wattle TEA acetate mixture, but their one and two day strengths were a little lower. At three days curing the propylene carbonate type had the same and the triacetin a little higher compressive strength then the conditioned wattle TEA acetate type additive. The latter is the only real advantage either has shown over the TEA acetate mixture. At seven days both the triacetin and propylene carbonate showed a little lower strength, also compared to the standard.

A test with the modified conditioned wattle on its own showed much improved flow compared to the standard, slightly lower one and two day strengths, but also three and seven day results well below the standard. Apart from a much smaller improvement in workability the strength development between the second and third day of curing was also much lower than for the modified conditioned wattle ester type additives. These results, which are far less desirable than those obtained with the addition of the esters, show how much they affect the all round performance of the additive.

All the esters added samples showed quick stiffening of the fresh concrete mix in their second flow tests when most of the mix was stagnant. The trend of much improved initial workability and higher compressive strengths over the standard up to the third day, is roughly similar among the ester added samples and may point to a similar mechanism. The TEA acetate, which had the best results of all esters, is made from commercially easily available chemicals and is also the lowest in cost.

All the above samples with esters were also tested at double dosage (0,50%) in Table 3.4.3 B. The workabilities were between good to much better than for the stiff control mix. Apart from the wattle TEA acetate type all other conditioned wattle ester combinations still showed early stiffening. Their strengths generally improved, for the triacetin and propylene carbonate greatly, compared to the standard and their previous 0,25% dosage. The wattle TEA acetate had the only lower strength with a poorer two day result than that for its normal dosage. It gave the least all round improvements at this higher dosage.

One marked difference among the conditioned wattle tannin esters compared to the normal dosage is the lower initial workability of the triacetin and its strengths now virtually identical to the TEA acetate type. The other is the generally much improved strengths of the conditioned wattle propylene carbonate additive at the higher dosage. The conditioned wattle TEA acetate also showed improvements, but not as marked as those for the above mentioned esters. Whether combined with conditioned wattle or wattle tannin the TEA acetate types were the only ones to improve their second workabilities compared to the lower 0,25% dosage at the same time not retarding one day strength. The order of the esters, added to the modified conditioned wattle tannin, according to best all round results remains roughly the same : TEA acetate >> triacetin > propylene carbonate. The

mechanism of the esters is not similar since triacetin showed a much lower workability at the double dosage than at the normal dosage, which is very unusual, compared to the TEA acetate.

These series have proven that a small addition of an ester to a modified conditioned wattle tannin greatly improves its all round performance. Even at double dosage, when other plasticisers and modified tannin extracts generally cause retardation of early strength development, the added esters still showed much improved workability combined with up to twice the one day strength of the standard.

Other tannin extracts : chile pine, pecan nut and chestnut were modified and prepared analogous to the above extracts (10:3,5:5, one hour at 60°C, mixed cold 4:1 parts with TEA acetate, see Table 3.4.3 C). With the chile pine additive workability was considerably improved over the standard and so were one and two day compressive strengths. One and two day results were respectively twice and one and a half times that of the control. Surprisingly the third day strength was identical to that of the second day. This is probably an error since the seven day strength is very similar to the standard. Apart from a slightly better initial workability the results were very similar to the wattle extract based TEA acetate type compared to its standard tested previously at the same 0,25% dosage. This was to be expected since the preparation was identical and the wattle tannin is related to the pine tannin in chemical composition.

The identically formulated and prepared pecan nut tannin TEA acetate mixture performed very poorly at 0,25% dosage. Compared to the standard it showed no improvement in flow or one day strength. Only the two and three day results provided a considerable advantage over the control, being one and a half times higher. The seven day strength was not tested.

Chestnut extract, due to its hydrolysable phenolic structure which is a much smaller molecule than that of the other condensed tannins, was tested at half the normal dosage i.e. 0,125% by cement weight. The Yugoslavian tannin was modified analogous to and mixed in the same ratio as the previous samples with TEA acetate performed very well at this low dosage. Uncharacteristic for any previously modified chestnut extract it improved workability considerably over the standard. The difference between the liquid flow after five minutes of mixing and the stagnant mix after fifteen minutes is very similar to that of the chile pine TEA acetate, wattle extract and conditioned wattle tannin ester mixtures tested at 0,25%. In this case the quick setting did not lead to a higher early strength development. The one day strength was only slightly higher than the standard, but the second day result was over one and a half times higher. The third day strength was one and a half times higher and the seventh day strength not tested. The characteristic high three day strength of the Yugoslavian chestnut is therefore retained.

Apart from practical test results the stability of the extract solutions must be taken into account; they are from best to worst : conditioned wattle > wattle > pine >> quebracho > pecan > chestnut. Quebracho and pecan extracts show a thick sludge-like deposits and chestnut a precipitate of solid extract. This observation is a rule of thumb and varies somewhat according to modification and particularly origin (Italian chestnut poorer than Yugoslavian Section 3.3.4 A) and batch (see quebracho comparisons Section 3.3.5 A).

3.4.4 Modified Yugoslavian Chestnut Extract mixed with TEA Acetate

This series follows the promising results obtained with the modified chestnut TEA acetate 4:1 mix at half dosage (0,125%) in Table 3.4.3C. The chestnut extract was modified in the same way and according to the same procedure : 10:3,5:5 extract : metabisulphite : urea heated with a little potassium hydroxide for one hour at 60°C. It was then mixed cold 2:1 parts by mass with TEA acetate and tested at the normal dosage of 0,25%. The ester content is twice as high as that used with modified condensed tannins (see Table 3.4.3A), which are also more than twice as heavy as the hydrolysable tannin molecules. Condensed tannins therefore are present as less than half the amount of tannin molecules for any given mass compared to the hydrolysable tannins.

The modified chestnut results were very good : improved workability over the control and one and a half times the compressive strength on the first and second day of curing (Table 3.4.4). The three day strength was almost double that of the standard. This presents an improvement in one day strength over the chestnut 4:1 mix type tested at half dosage in Table 3.4.3C. The 4:1 type had a strength advantage at two days curing whereas the 2:1 type tested here had higher one and three day strengths. The increase in early strength took place without greatly affecting the workability of the fresh mix. This can be seen by the same initial flow times, although the 4:1 type had a more stiff standard mix. Therefore the normal (0,25%) dosage used for the 2:1 type did not improve the flow compared to the half dosage (0,125%) dosage of the 4:1 type, probably due to the higher ester content of the former which gave faster early strength development. The seven day strength of the 2:1 was almost the same as the control's.

The modified chestnut extract with TEA acetate was also tested with a small (15:1 by mass) cold addition of furfuryl alcohol and Teepol. Both are known to improve the workability of fresh concrete mixes. Teepol is the brand name for a commercial detergent.

The furfuryl alcohol addition, contrary to expectation, decreased the workability of the chestnut based tannin. The one day strength was slightly lower, but at two days considerably lower than the chestnut based additive. The three day result was also a little

lower and at seven days the same. Therefore furfuryl alcohol provided no advantages as an addition to the modified chestnut extract with TEA acetate. The additive did however give better workability and one and three day strengths than the standard. Two and seven days strengths were only slightly lower compared to the control.

A cold addition of Teepol decreased the flow further to a small extent. Compressive strengths up to the third day were considerably lower than the chestnut TEA acetate to which it was added. At seven days the result was the same. The additional Teepol still provided better workability, but also lower strengths than the standard, apart from the little higher third day result. It was less useful as an addition to the chestnut based sample than the furfuryl alcohol, particularly with the much lower one and three day compressive strengths. Both additions had one characteristic in common : the reduction of the modified chestnut with TEA acetates good two day strength.

3.4.5 Acid and Alkaline modification of Italian Chestnut Extract

The Italian chestnut tannin was heated for two hours at 60°C in an acidified (acetic acid) and alkalised (sodium hydroxide) solution. This was done to see whether non-tannin constitutents could be hydrolysed as in the preparation of conditioned wattle. At the same time they were modified as extract : metabisulphite : urea in a 10:2,5:5 mass ratio. After twenty four hours an additional five parts TEA acetate were mixed cold in each and the solutions left standing another day before testing (Table 3.4.5).

On testing both the acid and alkali treated type gave the same marginal improvement in workability over the standard. The one day strengths were virtually identical compared to one another and the control. At three days curing both modified chestnut types showed a higher strength than the control. At seven days strengths were slightly lower than the standard.

As a comparison the same chestnut extract with the same 10:2,5:5 modification and TEA acetate addition, but without acetic acid or sodium hydroxide was tested. All the results were either very similar or identical to those reported above. This shows that the acid or alkali and TEA acetate treatment of the 10:2,5:5 modified Italian chestnut extract provided no improvements in its characteristics on concrete. This is in contrast to the observations made with the 10:3,5:5 + 0,5g potassium hydroxide modification and TEA acetate addition to Yugoslavian chestnut extract of Section 3.4.4, where good improvements in workability and early strengths were obtained.

Apart from the obvious difference in performance, the Italian chestnut extract is also much lighter in colour and much more difficult to dissolve in water than the tannin obtained from Yugoslavia.

3.4.6 Comparison of modified Conditioned Wattle types 244 and 345 with TEA Acetate additions

Type 244 is used for adhesives where the tannin is used to save on the phenol content. Type 345 is a general wattle extract grade and it is the one used so far and simply denoted as conditioned wattle. Both types were modified in the same way : extract : metabisulphite : urea 10:1:2 by mass, heated for one hour at 60°C. Afterwards the solution was mixed cold with 2,5 parts TEA acetate (Table 3.4.6).

Both additives had amazingly similar test results. The very good improvement in workability over the standard was virtually the same. One day strengths were identical to the standard. At three days curing both additives showed slightly higher strengths and at seven days both had strengths about one and a half times higher than the control. On the seventh day the 345 based type had a slight advantage over the 244 based additive.

A similar sample was made with conditioned wattle type 345 but with a slightly higher tannin extract content, i.e. 12,5:1:2:2,5 including TEA acetate listed in same sequence as above. This resulted in no change in workability compared to the previous type 345 based sample. One day strength was slightly lower and three day compressive strength slightly higher, also compared to the standard. The significant difference came on the seventh day of curing, when the higher tannin content sample had lower strength than the previous type, but still considerably higher than the control. This last result could be due to experimental error.

Since the type 244 based additive did not provide any advantages over that based on the 345 type with this particular modification, it was not used at any later stage. Conditioned wattle 345 had been used extensively before and its characteristics are therefore better known. All three samples had some solid precipitate after three months of storage. Presumably the amount of metabisulphite and urea were too low to keep the tannin extract in solution.

A comparison with test sample nr. 2 of Table 3.4.3A, where the modification was in a mass ratio of 10:3,5:5 including a little potassium hydroxide and mixed with the same amount of TEA acetate (2,5 parts) shows very different results. In this series nr. 2 (10:1:2:2,5 modification) of Table 3.4.6 had a strong improvement in workability over the standard, the same one and three day strengths and a much higher result on the seventh day of curing. By contrast nr. 2 (10:3,5:5:2,5 modification) of Table 3.4.3A had only a strong improvement in initial workability, one and a half times the one day strength, slightly higher three day and the same seven day strength as the standard.

Since the procedure (one hours heating at 60°C), the conditioned wattle 345 extract and the ester content are the same, the difference in performance must be due to the different

metabisulphite and urea contents, which as used here, are roughly a third (10:1:2). The small amount of potassium hydroxide added to the 10:3,5:5 type of Table 3.4.3A presumably only serves to activate the tannin molecule for reaction with the metabisulphite and urea.

The workability tested after fifteen minutes of mixing did not change for the lower modified type (10:1:2) while the early stiffening of the higher type (10:3,5:5) led to accelerated early strength development. The higher modification seems associated with a very good one day strength, whereas the lower amount of metabisulphite and urea seems linked to a much higher seven day strength. It may be assumed that an intermediate amount of chemicals may improve the two or three day strength. The above shows that not only the amount of TEA acetate has a great influence on the additives performance, as has been seen in Table 3.4.2 B.

3.4.7 Conditioned Wattle Tannin with TEA Acetate at various stages of modification

The results of Table 3.4.3 A and 3.4.6 have already shown that the conditioned wattle type extract suitably modified with sodium metabisulphite, urea and mixed with TEA acetate imparts important characteristics on the fresh and hardening concrete. The question arose to whether this extensive modification was really necessary. In this series the conditioned wattle tannin was either mixed cold with the ester or modified successively and separately with metabisulphite and urea in a 10:1:2 ratio respectively. The latter two samples were heated for one hour at 60°C after which they were mixed cold with 2 parts by mass TEA acetate (Table 3.4.7).

All three samples improved initial workability significantly and to the same extent compared to the standard. The second flow test showed marginal improvements over the control and still very similar results. Compressive strengths up to the third day were around one and a half times that of the standard. This can be attributed to the TEA acetate content which all additives had in common. The exception to this trend came on the third day of curing when the conditioned wattle urea TEA acetate sample gave a result almost double that of the standard. The seven day results were all again very similar and only slightly above the control.

Urea, apart from increasing the three day compressive strength here, also improves the solubility of the tannin extract in water. The metabisulphite modification of conditioned wattle grade tannin mixed with the ester seems unnecessary from a performance point of view, but may play a role in stabilisation of the additive on storage. In the case of wattle tannin in Table 3.3.4 the sulphitation greatly improved the workability of the fresh mix, but at that stage no TEA acetate was added. All three samples showed some solid precipitate after three months storage. A full modification of the extract is therefore

necessary.

3.4.8 Triethanolamine Salicylate as an alternative to Triethanolamine Acetate

Salicylic acid has a structure similar to catechol (resonating benzene ring, two neighbouring hydroxide groups). The major difference is that one hydroxide group is attached to the ring via a carbonyl group.

TEA salicylate was made by heating a 1:1 by mole mixture for two hours at 60°C, after which the solution became syrup-like and turned yellow. As expected, it did not affect the workability of the concrete but gave a one day strength slightly below the standard (Table 3.4.8). The three day result was the same and at seven days a little lower than the control. These strength results are in contrast to those obtained with TEA acetate in Table 3.4.2 A, where the strengths were either equal or higher than those of the standard.

TEA salicylate was then added cold to a conditioned wattle urea mixture which had been heated for one hour at 60°C. The mass ratio was 5:10:2 respectively. This gave a slight improvement in workability and very similar strength results to those of TEA salicylate alone. The exception was the seven day compressive strength, this time equal to the control. TEA salicylate and tannin extract together gave no real improvements compared to the constituents tested separately. This is in contrast to the results of nr. 3 Table 3.4.7 where the ratio was 2:10:2 ester : conditioned wattle : urea. There the TEA acetate was used at less than half the amount than the TEA salicylate in this section, but much better results were obtained than for the tannin extract and ester tested on their own in Table 3.3.1 \ and 3.4.2 A respectively.

In the following samples both the tannin extract and urea were omitted. Catechol, which is representative of the B-rings of condensed tannins and on its own improves the workability, as seen in Table 3.1.1 was mixed cold with TEA salicylate on a 1:1 by mass basis. There was only a slight improvement in flow and the one day strength was a little lower than the standard. Three and seven day strengths were similar to the conditioned wattle TEA salicylate and the control. Again there was no benefit in combining the ester with a phenol.

Vanillin has an ether group ortho to the hydroxyl group and an aldehyde group para to the latter. A cold mixture of vanillin and TEA salicylate in the same 1:1 ratio resulted in no changes in workability and a low one day strength. The three day result was a little higher and the seven day strength considerably higher.

A 1:1 by mass cold mixture of TEA acetate with salicylic acid gave a very small improvement in flow, but a little lower one day strength than the standard. Three and

seven day results were slightly higher. Neither the ester itself nor any of the above TEA salicylate combinations provided even equal early strengths to the standard. TEA salicylate was abandoned. The TEA acetate ester on its own has shown slightly higher one and two day strengths compared to the control in Table 3.4.2 A.

3.4.9 Potential additions for modified Tannin Extracts

Acetoacetic ester exists in both in the keto and enol form which are in equilibrium[132]. The proton is either at the carbon atom or the oxygen atom of these structural isomers when they undergo tautomerisation. Acetoacetic ester was tested on concrete to ascertain the effect of a changing bond, i.e. similar to the resonance encountered in the A and B-rings of condensed tannins and the resonance in hydrolysable tannins (Table 3.4.9). The three day strength was not tested due to limited availability of cube moulds at the time. However most of the potential additions were tested again fully with a modified tannin in the next section.

In a cold mixture of 2:1 by mass with TEA acetate it provided a slightly higher one day strength and a much higher seven day strength than the standard. Workabilities were largely unchanged. The tautomerisation could be associated with improved strength development, a three day test would have supported this. The resonating bonds themselves did not appear to improve the workability.

A cold mixture of catechol with TEA acetate 1:1 by mass provided virtually no change in workability, a little higher one day strength and a seven day result slightly lower than the standard. The 1:1 mixture of catechol and TEA acetate seems to have a too high ester content to produce useful results. Presumably it had led to too early setting of the fresh concrete mix.

Similarly a catechol : resorcinol 1:1 component mixed cold with TEA acetate also in a 1:1 by mass ratio also provided no improvement in workability and similar one day strength. At least the seven day result was slightly higher than the standard. The resorcinol component did not improve early compressive strength, as it did on its own in Table 3.1.1. Again the TEA acetate content may have been too high and probably interfered with the phenols action at an early stage in the alkaline environment of concrete. This early setting may have prevented the chemicals from improving the dispersion of cement particles which would have improved the flow of the fresh mix and homogeneity of hydration which provides better strength development.

An additive was made with wattle extract : metabisulphite : urea in a 10:1:2 ratio and heated one hour at 60°C. Two parts TEA acetate were mixed in cold. It was tested on its own before further modification and gave much improved workability over the control

and a little higher one day strength. The seven day compressive strength was considerably higher than the standard. A flow time of over a minute for the second workability test shows very good cohesive properties of the fresh concrete mix.

The same additive was mixed cold with resorcinol and TEA acetate in a 10:2:1 mass ratio. Both chemicals accelerated the setting, the resorcinol as seen in Table 3.1.1. and the ester in Table 3.4.2 A. The result was a much stiffer mix than for the additive alone, but still more workable than the standard. The one day strength was lower than that for the additive, but still equal to the standard. The seven day result was almost identical to the very high figure obtained with the additive alone. All round, the extra TEA acetate and resorcinol did not provide a successful combination with the fully modified wattle extract.

3.4.10 Various 5% additions to a fully modified Wattle Tannin Extract

The modified tannin additive was made in the same way as that of the previous section (3.4.9). On its own it provided a good improvement in workability over the control (Table 3.4.10). Surprisingly, the second flow result was half that of the first. However there was no retardation in early strength development, with one and three day results one and a half times that of the standard. The seven day compressive strength was still a little higher.

The same additive was further modified with various chemicals to see whether improvements were possible at little extra cost. A 5% by mass catechol addition resulted in improved initial workability compared to the modified tannin extract alone. An improvement in flow was already observed with catechol on its own in Table 3.1.1. The second flow result was still quicker than the first. The strengths decreased slightly compared to the additive, but were still higher than the standard, particularly on the third day. On the seventh day the result was equal to the control.

A 5% addition of acetoacetic ester to the modified tannin decreased its initial workability, but was still better than for the standard. The second flow result was similar to the previous two additives tested. Compressive strengths were largely similar to the modified tannin on its own, with a slightly lower result on the third day, but higher result on the seventh day. These compare well with the standard and the seventh day result presents a considerable improvement.

Zinc acetate added 5% by mass decreased the modified tannins initial workability and its compressive strengths slightly. The characteristic faster second flow result, without early strength retardation, was retained. These results were still better than that of the standard. The zinc acetate addition had made the modified tannin, which already contained 13,5% TEA acetate, less suitable as an additive. Therefore not only the anion affects the strength

development to provide accelcration.

The very long initial flow times of both zinc acetate and acetoacetic ester additions are an indication of the good cohesiveness of the fresh mix, which could be attributed to the modified wattle tannin in spite of the stiffening effect of the acetates. Irrespective of the type of chemical added 5% by mass to the modified wattle tannin, the workability test after fifteen minutes showed little variations. It seems an inherent characteristic of the modified extract. A good flow obtained after fifteen minutes of mixing is however impractical.

3.5 The effect of Calcium Oxide and Calcium Hydroxide on modified Wattle Tannin and Sulphonated MF partial condensate

The fully modified wattle tannin (mix 32, nr 1 of the previous section, Table 3.4.10) has given good improvements in workability combined with increased early strengths. Many other related condensed tannins and the hydrolysable tannin of Yugoslavian origin similarly modified and tested at the same dosage have shown improved to much improved workability combined with roughly equal, higher or even significantly higher one day strengths than the standard. An improvement in the flow of the fresh concrete mix without retardation in one day strength development is very unusual (see Section 1.2.3 plasticisers). The additives were made from hydrolysable or condensed tannins reacted with metabisulphite and urea and thereafter an addition of TEA acetate.

In Section 1.1.3 it was pointed out that with the initial hydration of concrete the pH strongly increases in alkalinity with the consumption of water by the cement. At advanced stages of hydration of low water-cement pastes the pH can rise above a value of 13. Saturated lime-water has a pH of 12,4.

To investigate the effect of the alkaline environment of concrete on a wattle based additive a 1:1 by mass mixture of mix 30 and calcium oxide was left standing twenty four hours before testing. This gave a fluid paste which initially warmed up. Mix 30 was made to the following formulation : extract : metabisulphite : urea : TEA acetate 10:1:2:2. The first three chemicals were heated for one hour at 60°C and the ester added cold afterwards (Table 3.5).

A test with the mix 30 additive on its own only showed a small improvement in workability over the standard and the almost same strengths almost throughout the seven days of curing. The one day result obtained with mix 30 was slightly higher than the control.

The 1:1 mix 30 hot lime mixture was tested at a 0,50% dosage so that the mix 30 content

was applied at the same 0,25%; dosage used above. It resulted in no improvement in flow and a little higher one day strength than the standard and the mix 30 additive on its own. Three and seven day compressive strengths were slightly lower and slightly higher respectively than both standard and mix 30.

This shows a degradative effect on the additive in alkaline environment. Partial auto-condensation of tannins has been observed in strongly alkaline conditions, see Section 2.6.4 of the literature survey. That may explain why after a workability improvement the one day strengths of the concrete are close to or higher than that of the control which has much lower workability. Thus after initially improving the workability of the fresh mix the additive becomes ineffective well within the first twenty four hours, thereby causing no retardation in the early strength development of concrete. Partial autocondensation is thought to be due to the reactions of the flavonoids C-4 of the lower terminal units with the C-6 and/or C-8 of flavonoids in other tannin polymers. This alkaline autocondensation is due to the reactivity of the hydroxy-group-carrying C-4.

The same mixture applied at 1%, corresponding to 0,50% of mix 30, gave a slight improvement in workability over the standard but much less compared to mix 30 only. This contradicts the better flow that would have been obtained at the equivalent dose of the additive only. All compressive strengths were a little lower than the standard, though not much. At the 0,50% dosage the additive itself would also have shown retardation in early strength development.

The above retardation of curing may explain why at double dosage the additive itself shows the same effect. Presumably due to double the additive present only part of the additive degrades or the whole amount degrades slower due to relatively only half the alkalinity being present.

The next test was done with mix 32 which was made according to the same formulation and procedure as mix 30. Only 5% by mass calcium hydroxide was added to the additive and a sulphonated melamine formaldehyde condensate (sulphonated MF) and left standing one hour before testing (Table 3.5).

The mix 32 additive on its own gave a great improvement in workability over the standard. One day compressive strength was equal and the three and seven day results significantly higher and higher respectively. The small amount of alkali ($Ca(OH)_2$) added to mix 32 and short maturing time had a remarkable effect on the additive's performance: There was now virtually no improvement in flow compared to the standard. The strengths were hardly affected, with only slightly lower results on the first and seventh day of curing compared to the mix 32 only. Apart from the slightly lower one day strength compared to the control the other results were still higher to considerably higher.

This confirms the observation of the earlier test with a similar additive (mix 30) and calcium oxide. The modified wattle extract is very susceptible to alkalinity. As indicated earlier, partial autocondensation of tannins has been observed in strongly alkaline conditions. Considering the low dosage of calcium hydroxide used and the short maturing time in the second test, the change in performance of the additive is probably also due to the calcium cation being complexed by the tannin. Apart from alkaline autocondensation the complexation of tannins probably also contributes to make the tannin ineffective after its initial influence on fresh concrete. In the hydrating cement environment the physical effect of viscosity reduction of the water-cement suspension (Section 1.1.4 of the literature survey) toward paste formation and hardening should immobilize any remaining 'active' tannins.

The leading plasticiser a German sulphonated MF, a sulphonated melamine formaldehyde partial condensate (see Section 1.2.4 of the literature survey), was tested at its recommended dosage of 1,5% by cement weight. At this relatively high dosage it gave a very small improvement in flow and its one day strength was a little below the standard. The three and seven day results were only slightly lower. The German sulphonated MF also showed changes after being treated with the calcium hydroxide. In this case the workability was hardly affected, being only slightly lower. Its one day strength was now almost half and seven day result considerably lower than the standard, while the three day result increased to the same value.

The German sulphonated melamine formaldehyde condensate and the modified wattle tannin react very differently to either alkalinity or the calcium cation as far as high workability or flow is concerned. The modified wattle tannin changes in its characteristic as a superplasticiser so that it becomes ineffective within an hour and does not interfere with early strength development. The German sulphonated MF acts as a plasticiser, a property which it largely retains in the same environment for a longer period of time, but also causes some retardation in early strength development. However at six times the dosage and therefore over twenty times the cost it is still a less effective concrete plasticiser.

3.6 Comparison of two modified Wattle Tannins with three types of Sulphonated Melamine Formaldehyde partial condensates

One sulphonated MF is the same one discussed in the previous section (3.5) and generally referred to so far in this dissertation. It will now be denoted "German sulphonated MF". An improved version of the same type and made by the same company gives greatly improved workability and workability retention. This new type will here be referred to as "New German sulphonated MF". The third sulphonated MF is similar in chemistry to the New German sulphonated MF, but is manufactured locally. It will be referred to as "SA

sulphonated MF".

The two wattle tannin based additives used for comparison are mix 32 and mix 33. Mix 33 was made according to the same formulation as mix 30 and 32 in the previous section (3.5). Both the MF types were tested at a dosage of 1% by cement weight whereas both "mix" additives were tested at the usual 0,25% (Table 3.6).

The New German sulphonated MF 40% by mass solution gave a great improvement in workability and still the same one day strength as the standard. Three day compressive strength was higher, but the seven day result lower by an equal measure. The SA sulphonated MF 40% solution improved initial flow almost as well and the second flow result was equal to that of the New German type. The SA type gave a slightly higher one day strength than the New German equivalent and the standard. The three and seven day results were the same as for the New German type.

The mix 32 36% solids solution also improved flow greatly over the control, although not quite to the same extent as the sulphonated MF additives. Its one day strength was equal to that of the SA sulphonated MF and therefore also slightly higher than the standard. Three day compressive strength was better than those of both sulphonated MF condensates and the seven day result considerably better. All results with mix 32 were an improvement over the standard.

Considering all the test results the mix 32 modified wattle tannin additive performed better at a quarter of the dosage at which both sulphonated MF types were tested. The sulphonated MF additives lower strength at seven days of curing would present considerable drawbacks when high strengths are required at later stages of curing.

The next series was done with a older type, ie. German sulphonated MF tested as a 31% solution at a 1,5% dosage. It is the same one used in Table 3.5 and performs much poorer than the New German sulphonated MF discussed above, which entered the market while this project was already underway. Mix 33 has the same composition as mix 32 and as a 36% solids solution was tested at a 0,25% dosage.

The German sulphonated MF gave hardly any improvement in workability and its one and three day strengths were a little lower than the standard. The seven day compressive result was equal to the control. These results are very close to those obtained with the same additive used as a 30% solution at the same 1,5% dosage and compared to its standard in Table 3.5.

Mix 33 showed the customary high improvement in workability and a slightly higher one day strength than the standard. Compressive strengths on the third and seventh day of curing were higher and equal respectively compared to the control.

Comparing the above two tests one comes to the same conclusion as in Section 3.5 : the modified wattle tannin applied at a sixth of the dosage and therefore at about 3,5% of the cost-in-use of the German sulphonated MF, is still more effective. With the New German sulphonated MF, tested at the beginning of this section, the difference is less dramatic : at four times the dosage and about fifteen times the cost-in-use it still performs poorer than the modified wattle extract additive. The major drawback of the New German sulphonated MF is that its addition to concrete results in a lower seven day strength than the standard. The advantage of the newer over the older type are the greatly improved flow results (see Tables 3.5 and 3.6). The local SA sulphonated MF additive performed very similar to the New German sulphonated MF. The modified wattle tannins (see mix 30 and 32 Table 3.5 and mix 32 and 33 Table 3.6) have always improved workability considerably and given compressive strengths, at all stages of curing, equal or higher than their respective standards.

3.7 Compressive Strength Test by an Outside Laboratory

A sample made with quebracho : metabisulphite : urea in a 10 : 2,5 : 4 mass ratio was heated one hour at 70°C. No TEA acetate was added. The additive was sent to an independent concrete testing laboratory "Structest". The results are shown in Table 3.7, which is a photocopy of their report. Structest laboratories used two types of mixes with different cement contents and tested only compressive strengths at 1, 2, 3, 7 and 28 days of curing.

They found that at 400 kg/m^3 cement content (kg cement/m^3 of concrete) the additive performed almost as well as the control after one day. The workability of the fresh mix was not tested, but would have shown a considerable advantage for the additive mix. This can be inferred from the ten to twenty percent higher strengths over the control from the second day onward to the 28th day. The increase in strength, particularly after three days, is most likely due to the better self compacting ability of high workability mixes. The improved compaction results in a better interlocking network of crystals formed during the hydration of cement. The highest rate of strength development took place between the third and seventh day. The best strength result over the control was achieved at seven days, an improvement of almost twenty percent.

At 300 kg/m^3 cement content Structest recorded a one day strength of just below seventy percent of that of the control. This results appears somewhat low compared to the strengths following it or the corresponding result of the richer (400kg/m^3) mix. It could be due to a testing error, since an improvement toward 108 percent over the control on the second day within a day seems unlikely. However, at three and seven days curing the additive gave more than twenty percent improvement. As with the higher cement content, the rate of strength development decreases rapidly towards twenty eight days to give a

roughly ten percent higher result than the control. The greatest strength development for the 300kg/m^3 mix appears to have occurred between the second and third day. The best strength over the control was at seven days, with an improvement of almost twenty five percent.

On a basis of percentage increase over their control, the seven and twenty eight day strengths of the 400kg/m^3 mix compare favourably with those of a normal plasticiser (column No. 2 of Table 7, p. 38) and accelerating plasticiser (second column of Table 10, p. 40). The corresponding 300kg/m^3 mix Structest results compare similarly and are only a few (1-5) percent lower. This shows that the additive sent to Structest, is more than equal to a normal plasticiser and can qualify as an accelerating plasticiser.

The concrete tests done in this dissertation were carried out on a mix with 500 kg/m3 cement content. Although the cement type and brand, aggregates and water/cement ratio used by Structest Laboratories are likely to be quite different, their tests results show a roughly similar tendency to those of this dissertation. This shows that the additive performs well with most types of mixes and is suited for a wide range of applications.

3.8 Hydration of an Additive Modified Cement Monitored by Heat Evolution

An additive was made in a mass ratio of 10 : 2,5 : 5 quebracho : metabisulphite : urea and heated one hour at 70°C. The following day TEA acetate was added cold active five percent by mass. The sample was sent to the National Research Council of Canada (NRC). The NRC tested the additive's effectiveness using a conduction calorimeter.

The reaction of portland cement and its components with water is an exothermic process. Isothermal conduction calorimetry is used to measure the rate of heat and total heat evolved during hydration as a function of time. Most of the heat is released during the first seventy two hours of hydration (See p. 14, literature survey).

The sample was tested with cement for three days and run concurrently with a control, a standard plasticiser and a standard superplasticiser. Two plots were made, one representing heat evolved versus time (Figure 3.8 A), the other total heat evolved versus time (Figure 3.8 B).

The first plot shows that the additive (2) modified sample closely follows the heat released or degree of hydration of the control (1). The more clearly defined second peak of the additive paste (arrow) may show that in its presence a certain phase of cement is hydrated more strongly after the faster phase has. Taking the current literature into account (See Figure 5, p. 14) the first peak could represent the C_4AF and the second enhanced peak the C_3A phase.

The additive of this project, which has shown its good plasticising ability, clearly interferes less with the initial hydration than a standard plasticiser (3). This means there is a much shorter dormant period for the additive (about five versus fourteen hours) in the initial hydration, which is only about two hours longer than for the control.

Compared to a standard superplasticiser (4) the additive provides an even greater advantage. The approximately twenty four hour setting advantage could be reduced by applying the additive at twice its normal dosage to obtain close to superplasticiser characteristics.

The plot of accumulated heat (Figure 3.8 B) gives an even better representation of how little the additive retards the onset of hydration compared to the control. It also shows that in just under forty eight hours the hydration has proceeded to the same extent and consequently the strengths should almost be the same. At this stage the standard plasticiser, with about the same plastification, would have a considerably lower strength. Application of the superplasticiser would result in very much lower strength. It is interesting to see that after forty eight hours the additive overtakes the control in hydration by only a small margin.

This means the Canadian cement used responds less in strength development to the additive from around one day to three days curing than the South African cement used throughout this project, where at three days considerable strength advantages were obtained. Therefore the composition of the cement appears very important in its response to the additive.

3.9 X-Ray Diffraction of a Hydrated Cement Paste

Powder XRD is a widely used method for identifying the components of mixtures containing many crystal phases, as well as determining structure-property relationships. It is the main well established method for the quantitative determination of crystal phases in cement.[134]

As can be seen from the literature survey pp. 12-14, the major phases in the clinker of cement are C_3S, ß-C_2S, C_3A and C_4AF. Of these, C_3S and ß-C_2S are clearly identifiable crystal phases, as is C_3A, although some of it may be amorphous. C_4AF is a poor crystalline solid solution, of which ninety percent hydrates within one day (see Figure 5, p.14). It is therefore difficult to detect in hydrated pastes.

Both C_3S and ß-C_2S hydrate to give an amorphous calcium silicate hydrate gel (C-S-H gel) which is difficult to identify on the diffractogram. One byproduct of this hydration is coarsely crystalline $Ca(OH)_2$ (portlandite) which can be clearly seen on the diffractogram.

In order to study the effect of the additive on cement, one was made with quebracho : metabisulphite : urea in a 10:3:5 mass ratio, heated one hour at 70°C and ten percent by mass TEA acetate added cold. After a twenty four hour maturing period pastes were made with a water/cement ratio of 0,4. Three samples were made : a control, the second with a 0,125% dosage and the third with a 0,25% dosage of the additive. After three days curing the paste samples were broken with a pestle and mortar, sieved and ground in a ball mill. No internal standard, like CeO_2, was included in the grinding process. An interpretation of the diffractograms can therefore not be done quantitatively, only qualitatively. The powders were then XRD scanned in the 10° - 70° 2-theta range.

At the same time concrete cubes were made to test compressive strengths corresponding to the three pastes. The cubes and pastes were cured at approximately 18°C. The strength results for the control, 0,125% and 0,25% dosage were twenty nine, thirty and thirty four Mpa respectively. The half dosage application therefore had virtually no influence on early strength development. The generally higher strengths obtained, compared to any of the tables, were due to the higher curing temperature.

Comparing the progress of hydration of the 0,125% dosage additive sample (Figure 3.9 B) with the control (Figure 3.9 A), the $Ca(OH)_2$ peak at 18°C appears considerably lower than for the control. This would imply a much stronger hydration toward crystal formation for the control, which is not realistic since the corresponding cube strength tests have shown that the control was marginally below that of the 0,125% applied additive. However $Ca(OH)_2$ can grow in the form of hexagonal plates in the cement paste. This would lead to a preferential orientation of a $Ca(OH)_2$ when the powder was packed into the sample holder of the XRD, which could explain the disproportionately large peak for the control (Figure 3.9 A). The $Ca(OH)_2$ peaks are therefore unsuitable for quantitative following of the hydration reactions.

There are some small changes in peaks corresponding to both ß-C_2S and C_3S phases, but at 34° the double peak has a shorter left arm and longer right arm than for the control. This indicates a preference for the hydration of one of the silicate phases, which appears to be the ß-C_2S phase, since a peak at 52° characteristic of C_3S is higher for the additives sample (Figure 3.9 B). The preference is not great, since the compressive strengths of the hydration products are virtually the same for the control and additive applied at 0,125%. Together the strengths and the XRD diffractograms show that the additive is largely ineffective at half its normal dosage.

The results are quite different when comparing the additive applied at the normal 0,25% dosage (Figure 3.9 C) with the control (Figure 3.9 A). Peaks characteristic of ß-C_2S and C_3S phases again show some small changes. A small peak at 31° denoting ß-C_2S has decreased a little. This is unusual since that phase is the slowest to hydrate (Figure 4, p.14), but lends support to the observation made for the diffractogram of the 0,125%

additive.

More noticeable is a decrease of peak at 33° which indicates the C_3A phase, which is the second fastest first to hydrate. It is known that C_3A requires much more water for hydration than the silicate phases (p.13). The tannin based additives have shown their ability as water reduces by improving workability, the result of freed water and improved wetting action (p.33). This means more available water for hydration of the cement particles. Since the pastes were made with the same water/cement ratio as the control, more water was available for hydration of the 'thirsty' C_3A phase. Two new peaks, at 38° and a large one at 45° could not be identified and may be due to an impurity in the ball mill.

All samples were ground in separate equipment. Also new is the appearance of a large peak at 65° which indicates $Ca(OH)_2$. There is an increase in the level of background, compared to the other ractograms, in the 25° to 30° region indicating amorphous material : C-S-H gel. Since ß-C_2S and notably C_3S hydrate to produce $Ca(OH)_2$ and C-S-H gel (p.13), the peak and the region (Figure 3.9 C) show a greater degree of hydration of the cement paste with the additive. Together with the diminished C_3A peak this correlates well with the higher pressive strengths obtained for the additives cube.

Further tests, at different stages of curing with a suitable internal standard, slower scanning and aimed at the 28° - 34° region (with many of the characteristic peaks) could provide a clearer picture and quantitative following of the additives influence on the hydration of the cements composite crystal phases. The tests done indicate that at normal 0,25% dosage the additive somewhat improves the hydration of the ß-C_2S phase, more noticeably the C_3A phase and the overall hydration of cement.

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CONCLUSION

This project has demonstrated that tannins are suitable raw materials for concrete additives. Of the condensed tannins quebracho and wattle extracts were better than pine and much better than pecan extract. This is i.t.o handling, all round concrete performance and storage life. However, a newer batch of quebracho extract showed very different characteristics, highlighting the importance of an extraction process which yields a consistent product. In the case of pine extract the much higher molecular mass tannins appeared to be less water soluble than quebracho and wattle extracts, which hindered its effectiveness and stability on storage.

Of the two hydrolysable tannins the one of Yugoslavian origin was superior to the Italian type w.r.t. strengths and storage life. The former also gave the greatest improvement in three day strengths of this project. This appeared to be due to complexation of adjacent hydroxide groups resulting in deflocculation of cement particles and improving their hydration.

Condensed tannins required modification with metabisulphite and urea to improve the solubility of the extracts and the stability of their solutions. This was shown to be due to interflavonoid bond cleavage and opening of the etherocyclic ring by the sulphitation. Urea prevented precipitation of these tannins by blocking the carbocation formed at the site of the opened ring. Both urea and metabisulphite may also have improved the solubility of non-tannins contained in the extracts. They have already shown this effect with an established molasses based superplasticiser.

A bonus of the above-mentioned modifications were much improved concrete characteristics i.t.o workability and strengths. The better performance can be ascribed to the improved solubility of the condensed tannins and an observed recyclation of the C-4—C-8 interflavonoid bond to C-4—C-6 links. The new link would make a catecholic B-ring more available for complexation with cement agglomerations. This may cause the breaking up of agglomerations leading to a lower viscosity of the fresh mix, more homogenous hydration of cement particles resulting in improved strengths. Complexations of adjacent hydroxide groups with metals are well known and the proposed mechanism arises from test results obtained with catechol on its own as a model compound.

Hydrolysable tannins have shown a very different interaction with metabisulphite and urea. They largely retained their characteristics, whether modified or not. It was observed in the model compound studies that metabisulphite and urea did not affect the phenolic ring. However both chemicals appeared to be necessary to stabilise the non-tannin constituents of the extracts. Even with the same modifications Yugoslavian chestnut extract was generally still less stable than quebracho and wattle extracts. Neither of the hydrolysable

tannins gave the same improvements in workabilities as the condensed tannins. This was the main reason for the preference of quebracho and wattle tannins over the Yugoslavian chestnut.

Small additions of a TEA acetate accelerator mixed cold with modified condensed and hydrolysable tannins produced further improvements of one and three day strengths. A test simulating the early high pH conditions of hydrating cement indicated that the modified tannins and the accelerator act independently on concrete. A variety of other accelerators could probably be used, provided they do not react with the modified tannins before each have been able to have their desired effect on concrete.

Another test representing the early high pH conditions indicated that a modified wattle based additive with TEA acetate is very sensitive towards alkalinity and/or calcium ions. Any improvements in workabilities by the additive were quickly lost and some strengths slightly affected. That may have been due to partial autocondensation of the tannin, but after a second test with only a small amount of calcium hydroxide, appeared more likely due to a tannin-calcium ion complex being formed which may be insoluble.

A wattle based additive, formulated as above, gave equivalent performance i.t.o. workability and up to third day strengths in a comparison with the latest sulphonated melamine formaldehyde plasticisers, which are market leaders. There was also a considerable advantage for the tannin based plasticisers: a somewhat higher seven day strength. These results were obtained at a quarter of the dosage and an even smaller fraction of the cost-in-use of the leading non-retarding plasticisers.

A similarly formulated wattle based additive was quickly accepted by block and precast manufacturers although the market underwent a recession. In these field tests, excellent results were obtained with very dry concrete mixes (bricks, etc) where other products failed. The additive also demonstrated its good dispersing ability by improving the colour and brightness of pigments in paving bricks and roof tiles.

An independent concrete testing laboratory, Structest, confirmed the trends in concrete compressive strengths observed in this project with modified quebracho tannins. A conduction calorimetry test by the National Research Council of Canada illustrated by heat of hydration measurement that which had largely been observed from the compressive strength tests: the quebracho based additive with TEA acetate only slightly interferes with the early hydration of cement. That is compared to the control. In relation to a standard plasticiser or superplasticiser this retardation is much lower.

Powder X-ray diffraction indicated, while not quantitatively , that the overall hydration of a cement with the additive, as described above, is improved. This correlated well with the compressive strengths of a concurrent concrete test. The technique also suggested a

preferential hydration of particularly the C_3A phase and ß-C_2S phase. The former is ordinarily the second fastest to hydrate and appears partly responsible for higher three day strengths. The ß-C_2S phase, ordinarily the second slowest phase, may be partly responsible for improved seven day strengths. At that stage the better compaction of high workability mixes could also play a role.

The best heating time and temperature for modifications of both hydrolysable and condensed tannins were one hour and 60-70°C. The amounts of chemicals used depended on the origin and type of tannin used. Variations between batches of extracts required variations in processing. Wattle and quebracho extracts have been successfully modified and formulated into concrete plasticisers which do not retard early strength development. The wattle based additive made mostly from local raw materials, is effective and economic in use and established itself well in a competitive market.

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EXPERIMENTAL

5.1 MATERIALS

5.1.1 Tannins

Natural pine tannin

Bark extract of pinus radiata D.Don Chile, supplied by DITECO LTD., Concepcion, Chile.

Chemical Analysis:

tannin	73.9%	non-tannin	..6%
moisture content	4.5%	tannin/non-tannin	3.4
sulphite added	2.0%	pH	4.1

Wattle tannins

Commercial tannin extract and conditioned types 244 and 345 from acacia mearnsii (black wattle), supplied by BISON BOARD LTD, South Africa.

Quebracho tannin

Both batches of straight extract and sulphited and semi-sulphited extract supplied by P. Battaglia, Induno SA, Buenos Aires, Argentina.

Chestnut tannins

Italian: Dr V. Bottari. Silva, Industria Chimica Leguno S.P.A., San Michelle, Mordovi (CN), Italy.

Yugoslavian: sample sent to Prof. Pizzi.

Pecan nut shell tannin

Sample sent to Prof. Pizzi.

5.1.2 Benzene derivatives

Phloroglucinol (1,3,5 - Trihydroxybenzene)

MW 126.15, colourless solid, plate crystals

mp = 218°C; bp = sublimes; density = 1.46 g/ml, AR, BDH.

Resorcinol (1,3 benzenediol)
MW 110, 11, colourless crystals
mp = 110°C; bp = 276,5°C; density 1,285 g/ml, AR, Merck.

Catechol (Brenzcatechin) (1,2 benzenediol)
MW 110, 11, colourless crystals
mp = 105°C; bp = 240°C; density = 1,37 g/ml, AR, Merck.

5.1.3 Solvents

Benzene (C_6H_6)
MW 78.11, colourless liquid
bp = 80.1°C; density = 0.88 g/ml, CP, Mikrochem.

Ethylacetate ($CH_3CO_2CH_2CH_3$)
MW 88.11, colourless liquid
bp = 77.1°C; density = 0.90 g/ml, AR, SAARChem.

Methanol (CH_3OH)
MW 32.04, colourless liquid
bp = 65.2°C; density = 0.79 g/ml, AR, BDH.

5.1.4 Miscellaneous Reagents

Ammonia (NH_3)
MW 17.03, colourless liquid, solubility 89.9g gas per 100ml water (25°C), 25% → 13,5M, AR, ACE. Diluted to 2M by mixing 74ml 13,5 M with 426ml distilled water to obtain 500ml 2M ammonia.

Urea (H_2NCONH_2)
MW 60.06, white solid, tetragonal prisms
mp = 135°C; bp - decomposes, density = 1.32g/ml, CP. BDH.

Iodine (I_2)
MW 253.81, violet black solid, rhombic crystals
mp = 113.5°C; bp = 184.4°C; density = 4.93g/ml, Merck.

Paraformaldehyde ((HCHO)n)
MW 30.03, white solid, on dissolving in water, depolymerisation and hydration result in the formation of formaldehyde solution, CP, Unilab, SAARChem.

Sodium metabisulphite ($Na_2S_2O_5$)
MW 190.10, white solid, powder
mp - decomposes above 150°C; density = 1.4g/ml, water solubility = 54g/100ml (20°C) and 81.7g/100ml (100°C), CP, BDH.

Glycerol (1,2,3 propandiol)
MW 92.09, colourless liquid
mp = 17.9°C; bp = 290°C, density = 1.26g/ml, AR, SAARChem.

Ethanediol (Ethylene glycol)
MW 62.07, colourless liquid
mp = -17,4 - 12°C; bp = 198 - 200°C, density = 1.116g/ml, CP, ACE.

Diethyl Ether (Ethoxyethane)
MW 74.12, colourless liquid
mp = -116 - 123°C; bp = 34.6°C, density = 0.71g/ml, CP, ACE.

Tetrahydrofurane (THF) (Tetramethylene oxide)
MW 72.10, colourless liquid, supplied by Wits stores.

Maltose ($C_{12}H_{22}O_{11}.H_2O$)
MW 360.31, colourless crystals
mp = 102,5°C (decomposes); density = 1,54g/ml, reducing (Fehling sol.) supplied by Wits stores.

Sucrose ($C_{12}H_{22}O_{11}$)
MW 342.30, colourless crystals
mp = 186°C (decomposes); density = 1,59g/ml, non-reducing (Fehling sol.) supplied by Wits stores.

Triethanolamine (TEA) ($N(CH_2CH_2OH)_3$)
MW 149.19, viscous colourless liquid
mp = 21.2°C; bp = 277°C; density = 1.124 g/ml, CP, supplied by Protea Chemicals.

Acetic Acid (CH_3COOH)
MW 60.05, colourless liquid
mp = 16.6°C; bp = 118.1°C; density = 1.05 g/ml, BP, supplied by Protea Chemicals.

Ethyl acetoacetate ($CH_3COCH_2CO_2C_2H_5$)
MW 130.14, colourless combustible liquid
mp = -43°C; bp = 181°C, density = 1.02g/ml. AR, Aldrich.

Formic Acid (HCOOH)
MW 46,03, colourless liquid
mp = 8,4°C; bp = 100,7°C; density = 1,226g/ml, CP, supplied by Protea Chemicals.

Phenol (Hydroxybenzene) (C_6H_5OH)
MW 94,11, colourless crystals
mp = 41°C; [illegible] 182°C; density = 1,07g/ml, AR, BDH.

Glycerol Triacetate (Triacetin) ($C_9H_{14}O_6$)
MW 218,21, colourless liquid
mp = -78°C; bp = 263-266°C; density = 1,158g/ml, AR, Fluka.

Polypylene Carbonate ($C_4H_6O_3$)
MW 102,09, colourless liquid
mp = -55°C; bp = 240°C; density = 1,189g/ml, AR, Aldrich.

Furfuryl Alcohol ($C_4H_3O.CH_2OH$)
MW 98,10, yellow liquid
mp = n/a; bp = 171°C; density = 1,13g/ml, supplied by Wits stores.

Teepol
Commercial detergent supplied by [illegible]hell.

Vanillin ($CH_3O(OH)C_6H_3COOH$)
MW 152,14, colourless liquid
mp = 81-82°C; bp = 285°C; density = 1,47g/ml, AR, SAARchem.

Salicylic Acid (OHC_6H_4COOH)
MW 138,12, colourless crystals
mp = 159°C; bp = sublimes; density = 1,443g/ml, AR, Merck.

Zinc Acetate ($Zn(C_2H_3O_3)_2$)
MW 183,47, crystals
mp = 242°C; bp = sublimes; density = 1,84g/ml, CP, BDH.

Sodium Hydroxide (NaOH)
MW 40,1, white flakes
mp = 318,4°C; bp = 1390; density = 2,13g/ml, AR, Merck.

Potassium Hydroxide (KOH)
MW 56,10, white pellets
mp = 360,4°C; bp = 13[illegible]4°C; density = 2,04g/ml, CP, SAARchem.

Sulphited Melamine Formaldhyde (Germ., New Germ, and SA origin)
Partial condensate, concrete grade, supplied by KLS Chemicals.

Calcium Oxide (CaO)
MW 56,08, colourless crystals
mp = 2580°C; bp = 2850°C; density = 3,346g/ml, supplied by Wits stores.

Calcium Hydroxide ($Ca(OH)_2$)
MW 74,10, colourless crystals
mp = loss of water, 580°C; bp = decomposes; density = 2,343g/ml, supplied by Wits stores.

5.2 EXPERIMENTAL METHODS

5.2.1 Concrete Tests

Cement:	Anglo Alpha Ordinary Portland Cement
Aggregates:	Fine river sand sieved to 0,1-0,3mm
	Medium river sand sieved to 0,75-1,75mm

Concrete mix for five cubes:
2kg cement, 1kg fine sand and 2kg medium sand mixed dry in a wide dish with a trowel until uniform, aggregate/cement ratio 1,5.
800g water, therefore water/cement ratio of 0,4.

The additive to be tested was mixed into this water for hydration of the cement. In the following sections the amount of additive used is referred to as "addition of". The amount is based on the solid content of a 40% (m/m) solid content concrete additive applied at a dosage of 0,25% (m/m) based on the cement weight.
For example: one set of tests of five cubes containing 2kg cement requires 5g of a 40% (m/m) solid content additive, or 2g of a solid to be tested. The additions referred to in section 5.2.2 - 5.2.6 relate to the 0,25% dosage unless otherwise stated.

The water for hydration, not containing any additive for the control, is mixed with the dry premixed cement and sand in a wide dish with a small trowel. The mixing continues for 5 minutes with the round dish turned in the opposite direction to the scoop of the trowel. Then the "initial" workability is tested with a flow funnel. The funnel is closed at the bottom and tapped while filling to the prescribed mark to ensure that no air bubbles are entrapped. A stopwatch is used to measure the time taken for the wet concrete mix to flow through the funnel. Testing and procedure are according to US Corporation of

Engineers specification 588-78/79. If part of the mix stagnates in the funnel the initial flowing time is taken at that point and the stoppage noted.

After another 10 minutes of mixing the flow test is repeated and recorded for the workability after a total of 15 minutes of mixing. After this second flow test, the concrete is filled into five cube moulds, which have previously been coated with a mould releasing oil. The machined cast iron moulds are 70 x 70 x 70 mm in size.

The wet concrete mix is poured into these moulds and tamped with a tamping rod according to SABS 863-1976. Since the concretes tested are of a high workability and therefore almost self compacting little tamping is required.

The surface of the cubes is trowelled flush with the top of the mould and reference numbers lightly scratched on the surface when setting has occurred. The cubes are then covered to prevent evaporation at the surface and cured at ambient temperatures. Every test series has a control of five cubes and five cubes for each additive tested.

After 24 hours all the cube moulds are removed and two of the five cubes (of the control and additive test) are tested for compressive strength using a hand operated press. The cubes are centred between top and bottom platens with the reference number upright and facing forward. The press is a Beckman/RIIC model 00-25 with up to 50 Mpa capacity. The remaining three cubes of each lot are cured under water until the next compressive strength test, mostly after three days. Two further cubes are broken and after seven days one.

5.2.2 Straight Additions and Cold Mixtures of Model Compounds and Tannin Extracts

Table 3.1.1
Resorcinol, Catechol, Phloroglucinol
2g addition corresponding to 0,25% dosage.

Phloroglucinol: Catechol 1:1 by mass
2g addition of a solid mixture of 1g each, mixed cold by hand.

Superplasticiser
5g addition of a 40% by mass solution

Superplasticiser : Catechol 9:1 by mass
5g addition of a mixture of 9g (40% by mass) liquid and 1g solid respectively, hand stirred cold.

Table 3.2 / Table 3.3.1 A/B
2g addition of all straight additions of solid and liquid chemicals and powder tannin extracts corresponding to 0,25% dosage.
4g addition quebracho extract corresponding to 0,50% dosage.

Table 3.3.1 B
Pine extract : Catechol 9:1 by mass
2g addition of a solid mixture of 9g and 1g respectively, mixed cold by hand.

Quebracho extract : Superplasticiser 9:1 by mass
2g addition of a mixture of 9g solid and 1g (40% by mass) liquid respectively, hand stirred cold.

5.2.3 General Procedures for Modifications

All chemical reactions were done in two necked flasks, one neck for the reflux, the other for the thermometer dipped into the solution. After all the chemicals had been dissolved, often with some warmth applied, the flasks were clamped into a hot oil bath on a magnetic stirrer with the thermostat set for the appropriate temperature.

Where applicable, pH readings were taken when the chemicals were dissolved and without the magnetic bean in the flasks. If warmed or heated, the solutions were cooled to room temperature before pH measurements were made, with a Metrohm 691 pH meter.

5.2.4 Modifications of Model Compounds

Table 3.1.2 A (all heated 1 hour at 70°C)
Catechol : Ammonia 1:1 molar
5,5g catechol dissolved in 50ml water and 3,7 ml
13,5M ammonia added.

Catechol : Paraformaldehyde : Ammonia 1:1:1 molar
As type 1:1 above with 1,5g paraformaldehyde added afterwards.

2:1:2 molar, listed as above
As type 1:1:1 above but with 0,75g paraformaldehyde.

4:1:4 molar, listed as type 1:1:1 molar
As type 1:1:1 but with 0,38 g paraformaldehyde.

Phloroglucinol : Ammonia 1:1 molar
6,3g phloroglucinol dissolved in 50ml water and 3,7 ml 13,5M ammonia added.

18g addition of these ca 11% (m/m) solutions, corresponding to 0,25% dosage.

Table 3.1.3 A (All heated 1 hour at 70°C)
Catechol : Metabisulphite 1:1 molar
5,5g catechol and 9,5g sodium metabisulphite dissolved in 50ml warm water.

Phloroglucinol : Metabisulphite : Ammonia 1:1:2 molar
6,3g phloroglucinol dissolved in 50ml warm water with 7,4ml 13,5M ammonia added. In that warmed solution 9,5g sodium metabisulphite dissolved.

9g addition of the above ca 22% (m/m) solutions.

Catechol : Urea 1:1 molar
5,5g catechol and 3g urea dissolved in 50ml warm water.

Phloroglucinol : Urea : Ammonia 1:1:1 molar
6,3g phloroglucinol and 3g urea dissolved in 50ml warm water and 3,7ml 13,5M ammonia added.

13,5 addition of the above 15% (m/m) solutions.

5.2.5 Modifications of Tannin Extracts

Most modifications of tannin extracts required warming up of solutions and some stirring to ensure complete dissolution before the timed heating.

Table 3.3.2 (First stage heated 1 hour at 70°C)
Sulphited/semi-sulphited quebracho : urea 10:5 by mass
20g of each extract and 10g of urea dissolved in 50ml water and heated 1 hour at 70°C. After heating each of the above samples was split in half. To each 40g of the still warm solutions 1g paraformaldehyde (thus 10:5:1 by mass) was added and a pellet of potassium hydroxide, stirring continued 1 hour at room temperature.
5g addition of the above 38% (m/m) solutions.

Table 3.3.3 A (Both heated 1 hour 70°C)
Yugoslavian chestnut : Ammonia 1:1 by mass
6g extract dissolved in 60ml water and 6g 13,5M ammonia added.
24g addition of this 8% (m/m) solution.

Quebracho : Ammonia 3:1 by mass
20g extract dissolved in 40ml water and 6g 13,5M ammonia added.
6,5g addition of this 30% (m/m) solution.

Table 3.3.3 B (First two heated 1 hour at 70°C)
Wattle/Pine : Ammonia 10 : 0,25 by mass
40g of each extract dissolved in 80ml water and 1 g 13,5M ammonia added to each.
6g addition of these 33% (m/m) solutions.

1 part (Pine:Ammonia) 10 : 0,25 by mass + 2 parts catechol
2g of above pine additive solution mixed cold with 4g catechol.
2,5g addition of this 77% (m/m) paste.

Table 3.3.4 (All heated 1 hour at 70°C)
Wattle/Pine : Metabisulphite 10 : 3,3 by mass
25g each extract, 7,5g sodium metabisulphite and 1g potassium hydroxide dissolved in 50ml water.
5g addition of these 40% (m/m) solutions.

Italian chestnut : Metabisulphite 10:2 by mass
6g extract and 1,2g sodium metabisulphite and 0,2g potassium hydroxide pellet dissolved in 60ml water.
22g addition of these 9% (m/m) solutions.

Plain Yugoslavian Chestnut
2g addition of extract

Yugoslavian chestnut : Metabisulphite 10:2,5 / 10:5 by mass
6g extract and 1,5g/3g sodium metabisulphite dissolved in 60ml water.
17g addition of these ca 12% (m/m) solutions.

Pecan/Quebracho : Metabisulphite 10:3 by mass
20g of each extract, 0,8g potassium hydroxide and 6,7g sodium metabisulphite dissolved in 120ml water.
10,5g addition of these 19% (m/m) solutions.

Table 3.3.5
(First two lots 1 hour at 60°C, last additive 2 hours at 60°C)
Wattle/Quebracho/New Quebracho : Metabisulphite 10 : 1,5 by mass
50g each extract, 7,5g sodium metabisulphite and 0,5g potassium hydroxide dissolved in 100ml water.

Wattle/Quebracho/New Quebracho : Metabisulphite : Urea 10:1,5:1,5 by mass
As above, but 7,5g urea added to warmed extract solution.

New Quebracho : Metabisulphite : Urea 10:1,5:3 by mass
As above, but with 15g urea.

5g addition of the above 37-42% (m/m) solutions.

Table 3.3.6
Pine/Wattle : Metabisulphite : Urea : paraformaldehyde 10:3,5:5:0,5 by mass
20g of each extract and 7g sodium metabisulphite dissolved in 50ml water and heated 1 hour at 70°C. To each warm solution 10g urea was added, stirring continued without heat for 1 hour. Then 1 g paraformaldehyde and 0,6g potassium hydroxide were added and stirring continued another hour at room temperature.
4,5g addition of these 44% (m/m) solutions.

Table 3.3.7 A
Numbers 1-4 prepared individually according to the weights given in Table 3.3.7 A.
Numbers 2-4 heated 1 hour at 60°C.
Numbers 1-4, 8g additions of 25% (m/m) solutions based on extract content only.
Numbers 5 and 6, 2g and 1g addition of plain Yugoslavian chestnut corresponding respectively to the solid content and to half the solid content of the extract in numbers 1-4 as applied.

Table 3.3.7 B
As Table 3.3.7 A, amounts of chemicals used given in Table 3.3.7 B and dissolved in 120ml water. Numbers 1-4 heated 1 hour at 60°C.
6,5g addition of numbers 1-4, 13g addition of number 5 (double dosage)
Additions based on 29% (m/m) extract content.

Table 3.3.8 A (All 1 hour at 60°C).
Extract alcohol treatment: 100g each of wattle and quebracho extract mixed cold with 5g

of a commercial alcohol mixture (70% ethanol and 30% methanol by mass) and left standing overnight in a closed container before being used.

Quebracho : Metabisulphite : Urea 10:1,5:3 by mass
20g alcohol treated extract, 3g sodium metabisulphite and 6g urea dissolved in 50ml water.

Chemicals as listed above 10:2:4 by mass.
20g alcohol treated extract, 4g sodium metabisulphite and 8g urea dissolved in 50ml water.

5g addition of the above two 37/40% (m/m) solutions.

Wattle : Metabisulphite : Urea : Sugar 10:3:2:5 by mass
20g alcohol treated extract, 6g sodium metabisulphite and 4g urea and 10g sugar dissolved in 50ml water.

Chemicals as listed above 10:3:0:5 by mass.
As above but without urea.

10g addition of the above two 39/41% (m/m) solutions for double (0,5%) dosage.

Table 3.3.8 B (2,5 hours at 70°C)
Extract alcohol (5% by mass) treatment as for Table 3.3.8 A.

Wattle : Metabisulphite 10:1,5 by mass
50g alcohol treated extract, 7,5g sodium metabisulphite and 0,5g potassium hydroxide dissolved in 100ml water.

Wattle : Metabisulphite : Urea 10:1,5:1,5 by mass
As above, but no alkali and 7,5g urea added.

Each additive tested fresh after preparation and again after twenty four hours.

5g addition of above 37-39% (m/m) solutions.

Table 3.3.9 (All 1 hour at 70°C)
Extract alcohol (5% by mass) treatment as for Table 3.3.8 A.

Quebracho : Metabisulphite : Urea (by mass)

First Type 10:3,5:5
20g untreated extract, 7g sodium metabisulphite and 10g urea dissolved in 50ml water.

First Type 10:2:5
20g untreated extract, 4g sodium metabisulphite and 10g urea dissolved in 50ml water.

Second Types 10:3,5:5/10:2:5
As first types of corresponding ratio, but with extract alcohol treated for three days and then used for additive preparation.

Type 10:2:2,5
20g overnight alcohol treated extract, 4g sodium metabisulphite and 5g urea dissolved in 50ml water.

Type 10:1:5
20g overnight alcohol treated extract, 2g sodium metabisulphite and 10g urea dissolved in 50ml water.

5g addition of above 37-42% (m/m) solutions.

Table 3.3.10 (All 1 hour at 70°C)
Quebracho: Metabisulphite : Urea (by mass)

Type 10:3,5:5
20g new batch extract, 7g sodium metabisulphite and 10g urea dissolved in 50ml water.

First Type 10:2,5:5
20g extract, 5g sodium metabisulphite and 10g urea dissolved in 50ml water.

Second Type 10:2,5:5
As above, but sodium metabisulphite dissolved in water first, then urea and then extract respectively added to the solution.

Type 10:5:3,5
20g extract, 10g sodium metabisulphite and 7g urea dissolved in 50ml water.

Type 10:2,5:2,5
Weights corresponding to chemicals as listed above: 20g, 5g, 5g, 50ml water.

5g addition of the above 37-42% (m/m) solutions, 10g addition for double (0.5%) dosage.

Type 10:0.5:1
20g, 1g, 2g, respectively in 50ml water.
6g addition of this 32% (m/m) solution
12g addition for double (0.5%) dosage.

5.2.6 Modified tannin extracts with various additions

Table 3.4.1 A
Wattle: Metabisulphite : Urea : Ammonia : TEA (by mass)

Type 10:2,5:3:1,5:2
50g extract, 12,5g sodium metabisulphite and 15g urea dissolved in 100ml water.
7,5g 13,5M ammonia and 10g TEA added to that solution and heated 1 hour at 60°C.
4,5g addition of this 45% (m/m) solution.

Type 10:2,5:3,5:1:2
50g extract and 12,5g sodium metabisulphite and 17,5g urea dissolved in 100ml water.
5g 13,5M ammonia added to that solution and heated 2 hours at 60°C. 24 hours later, 10g TEA mixed in cold.
3,5g addition of this 47% (m/m) solution for 0,2% dosage, 5g addition for 0,3% dosage.

Table 3.4.1 B
Wattle: Metabisulphite : Urea : TEA 10:3,5:0,5:1 by mass
200g extract and 70g sodium metabisulphite dissolved in 400ml water and heated 6 hours at 70°C.
Five samples of 100g each were taken from 2-6 hours heating at hourly intervals and left standing 24 hours.
Then 1,5g urea was mixed cold with each sample. Another 24 hours later 3g TEA was added to each solution and heated 3 hours at 70°C.
All samples were tested fresh after the last heating. The 2 and 3 hour samples were tested again 24 hours later.
5g addition of these 42% (m/m) solutions.

Table 3.4.2 A
TEA : Acetate 70:30 by mass
70g TEA mixed cold with 30g acetic acid
(TEA acetate used in the following tables made in the same way)
TEA : Formate 75:25 by mass
75g TEA mixed cold with 25g formic acid.

4g ddition of the resultant pastes for 0,2% dosage, 0,2g addition for 0,01% dosage.

Quebracho : TEA acetate (by mass)
Type 1:1
10g extract mixed cold with 10g TEA dissolved in 30ml water.
5g addition of this 40% (m/m) solution.

Type 10:1
10g extract mixed with 1g TEA acetate.
2g addition of resultant paste for 0,1% dosage corresponding to 0,25% dosage of a 40% (m/m) solution.

Table 3.4.2 B
Quebracho : Metabisulphite : Urea 10:0,4:0,8 by mass
25g extract, 1g sodium metabisulphite and 2g urea dissolved in 50ml water and heated 1 hour at 60°C. Then mixed cold with TEA acetate (70:30 by mass, see Table 3.4.2 A) in ratios:
5:1 by mass : 30g modified extract solution and 6g TEA acetate.
4:1 by mass : 30g modified extract solution and 7,5g TEA acetate.
4,5 g addition of these 47% (m/m) solutions for 0,25% dosage, 9g addition for double (0,5%) dosage of 5:1 mixture.

Table 3.4.2 C
Quebracho : Metabisulphite : Urea 10:0,5:1 by mass
80g extract, 4g sodium metabisulphite and 8g urea dissolved in 160ml water and heated 2 hours at 60°C (mix). Then part of solution tested on its own and remaining solution mixed cold with TEA acetate in ratios:
95:5 : 95g mix and 5g TEA acetate.
97,5:2,5 : 97,5g mix and 2,5g TEA acetate.
5 g addition of these 37-40% (m/m) solutions for 0,25% dosage, 10g addition for double (0,5%) dosage.

Table 3.4.3 A/B
Extract : Metabisulphite : Urea 10:3,5:5 by mass + 0,5g KOH
20g wattle, 7g sodium metabisulphite, 10g urea and 0,5g potassium hydroxide dissolved in 50ml water and heated 1 hour at 60°C. This solution then mixed cold with esters as 20g and 5g respectively. Since propylene carbonate and triacetin are poorly soluble in water the mixtures were diluted with 75ml water.

For conditioned wattle modification, twice the amounts used i.e. 40g, 14g, 20g and 1g in 100ml and also heated 1 hour at 60°C.
A 20g modified extract solution was diluted with 80ml water (Table 3.4.3 A Nr.5 only) to compensate for the dilution of the above mixed esters solution. The ester mixtures were made as above i.e. 20g and 5g respectively.

15 g addition of the above in 13% (m/m) solutions for 0,25% dosage (Table 3.4.3 A), 30g addition for double (0,5%) dosage (Table 3.4.3 B).

Table 3.4.3 C

Extract : Metabisulphite : Urea 10:3,5:5 by mass + 0,5g KOH
Pine, pecan and Yugoslavian chestnut modifications with the same amount of chemicals as for the wattle type in Table 3.4.3 A/B, but in 80ml because of chestnut's lower solubility. Heating also 1 hour at 60°C. To compensate for the lower solid content 27g of the solutions instead of 20g were mixed cold with 5g TEA acetate for the 20:5 mixture and diluted with 68ml water.
15g addition of the above ca 13% (m/m) pine and pecan solutions for 0,25% dosage, 7,5g addition of chestnut type for 0,125%

Table 3.4.4

Yugoslavian Chestnut : Metabisulphite : Urea 10:3,5:5 by mass + 0,5g KOH
Extract modified with same amount of chemicals in same amoutn of water and same heating as in Table 3.4.3 C and mixed cold with additions in amounts as stated in Table 3.4.4.
3,5g additions of the above ca 54% (m/m) solutions.

Table 3.4.5

Modified Italian chestnut : Metabisulphite : Urea 10:2,5:5 by mass
25g extract mixed into 0,75g acetic acid or sodium hydroxide dissolved in 75ml water. In 40g of each solution 2,5g sodium metabisulphite and 5g urea dissolved and 50ml water added due to the poor solubility of the extract. This solution was heated 2 hours at 60°C and after 24 hours 5g TEA acetate mixed in cold.

10g unmodified dry extract (corresponding to 40g of modified solutions above) treated with the same amount of chemicals as above, but 80ml water used instead of 50ml, heating and TEA acetate addition as above.

10g addition of the above 20% (m/m) solutions.

Table 3.4.5

Conditioned Wattle 244 or 345 : Metabisulphite : Urea 10:1:2 by mass
Three solutions: 20g either extract, 2g sodium metabisulphite and 4g urea dissolved in 50ml water and heated 1 hour at 60°C. Then each mixed cold with 5g TEA acetate.

Chemicals as listed above [1]2,5:1:2 by mass
25g type 345 modified with the same amounts of chemicals, heated and mixed with TEA acetate as above.

5g addition of these 38-42% (m/m) solutions.

Table 3.4.7

Conditioned Wattle : TEA acetate 10:2 by mass with various additions.

Nr.1: 20g extract dissolved in 50ml water and mixed cold with 4g TEA acetate.

Nr.2: As Nr.1, with 2g sodium metabisulphite in extract solution, heated 1 hour at 60°C, then 4g TEA acetate added cold.

Nr.3: As Nr.2, with 4g urea instead of metabisulphite, heating and TEA acetate the same.

6g addition of the above 32-36% (m/m) solutions.

Table 3.4.8

Nr.1: 20g TEA and 20g salicylic acid heated 2 hours at 60°C.

Nr.2: 20g conditioned wattle, 4g urea dissolved in 50ml water and heated 1 hour at 60°C. Then 37g of this solution (containing solids of 10g conditioned wattle and 2g urea) mixed cold with 5g TEA salicylate.
6,5g addition of this 31% (m/m) solution.

Nr.3-5: Chemicals mixed cold in amounts as stated in Table 3.4.8.

Nrs. 1, 3, 4, 5: 2g additions of the pastes.

Table 3.4.9

Nrs 1-3: Chemicals mixed cold in amounts as stated in the table.
2g additions of these pastes.

Nr.4: 'Mix 30' stock solution for further tests.
Wattle : Metabisulphite : Urea 10:1:2 by mass
80g extract, 8g sodium metabisulphite and 16g urea dissolved in 200ml water and heated 1 hour at 60°C. Then mixed cold with 8g TEA acetate.
5,5g of this 36% (m/m) solution.

Nr.5: 10g resorcinol and 5g TEA acetate mixed with 50g of 'mix 30'. The constituents, now 64% (m/m) had to be dissolved in the mixing water for the concrete - an addition of 3g was used.

Table 3.4.10

Nr.1: Mix 32: composition as mix 30 of Table 3.4.9. Stock solution for further tests. Chemicals as for mix 30, but double the amounts in 160g, 16g, 32g respectively in 400ml. heating also 1 hour at 60°C and cold mixing with 16g TEA acetate.

Nrs. 2-4: Chemicals mixed cold in amounts as stated in the Table i.e. 95g and 5g respectively.

5,4g additons of the above 36-39% (m/m) solutions.

Table 3.5

Mix 30, mix 32 from stock solutions made and described earlier.

Mix 30: CaO 50:50, cold mixture of 50g each, left standing 24 hours before testing.

10g addition of this mixture with half content of additive for 0,50% dosage, i.e. effective 0,25% for mix 30 content.

20g addition for 1% dosage, i.e. effective 0,50% for mix 30 content.

Mix 30 : $Ca(OH)_2$ 95:5, cold mixture of 95g and 5g respectively, left standing 1 hour before testing.

5,5g addition of this 36% (m/m) solution based on mix 30 content.

Sulph.M.F.: 30g powder dissolved in 70ml water.

30g addition of this 30% (m/m) solution for 1,5% dosage.

Sulph. M.F. : $Ca(OH)_2$ 95:5, cold mixture of 95g and 5g respectively, left standing 1 hour before testing.

30g addition of this 30% (m/m) solution based on sulph. MF content.

Table 3.6

New Germ. Sulph. MF / SA Sulph. MF : 40g of each poweder dissolved in 60ml water.

20g addition of these 40% (m/m) solutions for 1% dosage.

Mix 32: 5,5g addition of 36% (m/m) stock solution of Table 3.4.10.

Germ. Sulph. MF: 31g powder dissolved in 69ml water.
30g addition of this 31% (m/m) solution for 1,5% dosage.

Mix 33: formulation as mix 30, (10:1:2 by mass Table 3.4.9) and mix 32, but smaller amounts of chemicals used. 20g wattle, 2g sodium metabisulphite and 4g urea dissolved in 50ml water and heated 1 hour at 60°C. Then mixed cold with 2g TEA acetate.

5,5g addition of this 36% (m/m) solution.

Table 3.7
Additive sent to Structest for concrete testing
Quebracho : Metabisulphite : Urea 10:2,5:4 by mass
40g extract, 10g sodium metabisulphite and 16g urea dissolved in 100ml water and heated 1 hour at 70°C.
Solution containing 40% (m/m) solids tested at Structest laboratories at recommended 0,25% dosage.

5.2.7 Structural and General Investigations

Thin layer chromatography (TLC)
Kieselgel 60 F254 silica gel thin layer chromatography plates were used, layer thickness 0,2mm, Merck.
The liquid sample was spotted onto a plate with a micropipette and let dry. The bottom of the plate was immersed in the eluting solvent in a sealed chamber. After separation, the plate was exposed to iodine vapour. This resulted in the formation of a dark coloured spot in the presence of any organic component. Alternatively, the plate was observed under UV light. The Rf value was calculated as the distance travelled by the sample divided by the distance travelled by the solvent front, and expressed as a fraction.
Eluent: Benzene, ethyl acetate, methanol 3:2:1 (V/V). Made by mixing 300ml, 200ml and 100ml respectively.

Section 3.1.2 B
NMR of Catechol : Ammonia 2:1 molar
1,106g catechol dissolved in 50ml distilled water and 2,5ml 2M ammonia added. Heated 3 hours at 70°C.
Samples for TLC tests were taken from ½ hour after the heating started to 2 hours later. Using a micropipette three small spots were made on three individual strips 8cm in length. The final samples were taken after the 3 hours heating and five individual spots were made on a broad plate.

24 hours later a ca 10ml sample concentrated in rotary evaporator and then freeze dried for carbon 13 and proton NMR. This and the following samples were all analysed in D_2O on a Bruker nuclear magnetic resonanee machine.

Section 3.1.3 B

NMR of Catechol : Urea 1:1 molar

1,103g catechol and 0,302g urea dissolved in 50ml distilled water. Heating, TLC tests, concentration and drying for carbon 13 and proton NMR as for Section 3.1.2 B.

Section 3.3.4 B

NMR of Yugoslavian Chestnut : Metabisulphite 10:1 molar (based on dimers of gallic acid)

25g extract and 2,5g sodium metabisulphite dissolved in 100ml distilled water and heated 2 hours at 70°C. Concentration and drying for carbon 13 NMR as for Section 3.1.2 B.

Section 3.3.5 B

IR of Quebracho : Metabisulphite : Urea 3:1:6 molar (based on monomer unit)

20g extract and 5g sodium metabisulphite and 10g urea dissolved in 50ml distilled water and heated 1 hour at 70°C.

Then first sample taken for immediate infra red testing using KBr salt plates.

After 1 hour heating second sample. 24 hours later last sample taken and each tested immediately using KBr plates on a Pye Unicam Infra red spectrophotometer.

Chemicals as listed above 3:1,3:6 molar (based on monomer unit)

As above, but with 6,7g sodium metabisulphite. Heating and samples for infra red taken at the same stages and following the same procedures as above, with one additional sample taken 1 hour after heating.

Section 3.4.2 B

NMR of Phenol : TEA acetate 1:1 molar

Two lots of 2g phenol and 0,4g TEA acetate (70:30 m/m) were dissolved in 20ml distilled water. Potassium hydroxide was added to each until the pH of the solution was 10. One sample in a small flask was stirred on the magnetic stirrer at room temperature, the other at 60°C, both 1 hour. Then the samples were immediately freeze dried for carbon 13 NMR analysis.

Section 3.8

Additive sent to NRC for conduction calorimetry testing.

Quebracho : Metabisulphite : Urea 10:2,5:5 by mass + 5% TEA acetate

40g extract and 10g sodium metabisulphite and 20g urea dissolved in 100ml water and heated 1 hour at 70°C.

24 hours later 95g of modified extract mixed cold with 5g TEA acetate. Solution containing 44% (m/m) solids sent to National Research Council, Canada.

Section 3.9

Powder X-ray diffraction of hydrated pastes.

Quebracho : Metabisulphite : Urea 10:3:5 by mass +10% TEA acetate

40g extract, 12g sodium metabisulphite and 20g urea dissolved in 120ml water and heated 1 hour at 70°C.

24 hours later 90g of modified extract mixed cold with 10g TEA acetate.

Another 24 hours later 3 pastes were made with a water/cement ratio of 0,4:

Control: 450g cement + 180g water.

Additive 0,125%: as above with 1g of 44% (m/m) additive

Additive 0,25% : as above but 2g of the additive

At the same time concrete cubes were made as described in section 5.2.1. Additions were 4,6g and 2,3g for 0,25% and 0,125% dosage respectively.

The pastes and cubes were cured for three days at ca 18°C in a curing cupboard. The cubes were tested for compressive strength (results in text). The paste samples were broken down with a pestle and mortar and sieved to 1,5mm. These fractions were then ground in a ball mill and the fractions which passed a 200 mesh sieve were XRD tested in a Philips PW 1820 powder diffractometer in the 10° - 70° 2-theta range.

GUIDE TO TABLES

Workabilities are measured using the flow funnel test. The values stated are the time taken, measured in seconds, for the fresh concrete mix to flow through the funnel. Where the fresh mix did not flow through completely, the time of flowing until stagnation is taken and marked with an "s" for stop. The first test was done after five minutes of mixing and the second, where applicable, after fifteen minutes of mixing hence the 5/15 annotation.

The compressive strengths measured in Mpa were carried out on hardened concrete cubes. The column or row is marked "Mpa" with subdivisions of "1, 3, 7" to indicate the days of curing. Some samples have also been tested after two days of curing, they have an additional "2" marking next to the "Mpa".

Both the flow funnel and compressive strength test were outlined in Section 1.1.5 of the literature survey.

3.1.1 Model Compounds

Dosage corresponding to 0,25% by cement weight

COMPOSITION	MASS RATIO	FLOW	Mpa		
		5	1	3	7
Resorcinol		2s	8	24	30
Catechol		19	5	17	30
Phloroglucinol		30	3	15	24
Phlorogluc. + Catechol	1:1	-	-	12	26
Superplasticiser (SPC)		12	-	10	34
Superplas. + Catechol	9:1	28	2	13	29
Standard		30	5	16	29

s: stop of flow after initial movement for x amount of seconds

3.1.2 A **Model Compounds reacted with Paraformaldehyde and Ammonia**

Catechol : paraformaldehyde : ammonia

1 hour at 70°C

Dosage 0,25% by cement weight

MOLAR RATIO	FLOW	Mpa			COMMENT
	5	1	3	7	
1:0:1	18	6	18	30	
1:0:1	16	5	16	32	Double Dose: 0,5%
1:1:1	20	7	17	34	
2:1:2	19	9	17	34	
4:1:4	20	8	16	28	
Standard	29	5	16	29	
1:0:1	22	5	15	28	Phloroglucinol instead of Catechol

3.1.2 B **Catechol : Ammonia 2:1**

Heated at 70°C for 3 hours

Developer ; benzene : ethyl acetate : methanol 3:2:1 (V/V)

Rf catecnol : 0,67 Ammonia : 0,15

TIME (hr)	Rf (TLC)		
½	0,84	0,85	0,86
1	0,78	0,79	0,80
1½	0,78	0,79	0,81
2	0,815	0,82	0,83
3	0,83	2x(0.84)	2x(0.86)

3.1.3 A **Model Compounds reacted with Metabisulphite, Urea and Ammonia**

1 hour at 70°C

Dosage 0,25 % by cement weight

COMPOSITION	MOLAR RATIO	FLOW	Mpa		
		5	1	3	7
Catechol : Metabisulphite	1:1	19	5	20	32
Phlorogluc. : Metabis : Ammonia	1:1:2	19	5	15	30
Catechol : Urea	1:1	-	8	19	26
Phlorogluc. : Urea : Ammonia	1:1:1	-*	8	17	25
Standard	-	29	5	16	30

* better than Catechol : Urea 1:1

3.1.3 B **Catechol : Urea 1:1**

Heated at 70°C for 3 hours

Developer ; benzene : ethyl acetate : methanol 3:2:1 (V/V)

Rf catechol : 0,67 urea 0,20

TIME (hr)	Rf (TLC)		
½	2 (0,855)		0,86
1	0,89	0,90	0,924
1½	0,915	0,92	0,925
2	0,90	0,91	0,915
3	0,88 2(0,89)	0,885 0,90	

3.2 Sugars, Polyalcohols and Ethers

Dosage corresponding to 0,25% by cement weight

COMPOSITION	FLOW	Mpa		
	5/15	1	3	7
Maltose	18/16	-	18	34
Sucrose	20/19	-	12	30
Molasses	36/36	-	20	36
Glycerol	3s/-	8	19	30
Ethanediol	4s/-	7	20	29
THF	5s/-	7	21	27
Diethylether	4s/-	6	19	32
Standard	-/-	5	16	29

s : stop of flow after initial movement

3.3.1 A **Tannin Extracts as Additives**

COMPOSITION	FLOW	Mpa				DOSAGE
	5/15	1	2	3	7	
Wattle	10s/-	7		20	29	
Standard	-/-	9		24	30	
Conditioned Wattle	30/-	4	12	14	24	
Standard	29s/-	5	13	20	31	
Quebracho	35/40	10		20	35	0,25%
Quebracho	20/25	8		19	36	0,50%
Standard	-/-	10		19	32	

Most dosages corresponding to 0,25% by cement weight

3.3.1 B **Tannin Extracts as Additives**

Dosage corresponding to 0,25%

COMPOSITION	MASS RATIO	FLOW	Mpa		
		5/15	1	3	7
Yogusl. Chestnut		8s/-	8	20	29
Standard		-/-	8	14	28
Pine + Catechol *	9:1	15/-	9	18	31
Quebracho + Superplasticiser *	9:1	-/-	-	20	26
Standard		30/-	10	16	29

* : mixed cold

s : stop of flow after initial movement

3.3.2 Sulphited and Semi-Sulphited grade Quebracho Extracts reacted with Urea and Paraformaldehyde

Quebracho : urea : paraformaldehyde (last one added cold after one hour at 70°C)

Test sand : not graded, high clay content - therefore higher water/cement ratio and slower strength development

Dosage 0,25%

EXTRACT	MASS RATIO	FLOW	Mpa		
		5/15	1	3	7
Sulphited	10:5	-/-	5	9	14
Semi	10:5	-/ 1)	5	9	13
Sulphited	10:5:1	-/-	6	8	15
Semi	10:5:1	-/ 2)	5	8	14
	Standard	-/-	5	11	14

1) Worse than Sulphited

2) Better than Sulphited

3.3 3 A **Tannin Extracts modified with Ammonia**

One hour at 70°C

Dosage 0,25%

COMPOSITION	MASS RATIO	FLOW	Mpa		
		5/15	1	3	7
Yugosl. Chestnut + Ammonia	1:1	7s/-	6	16	27
Quebracho + Ammonia	3:1	20/22	5	21	36
Standard	-	29/-	6	18	30

s : stop of flow after initial movement

3.3.3 B **Tannin Extracts modified with Ammonia**

One hour at 70°C

Dosage 0,25 %

COMPOSITION	MASS RATIO	1	2	3	STD
Wattle + Ammonia	10:0,25	0,75	-	-	-
Pine + Ammonia	10:0,25	-	0,75	0,25	-
Catechol	-	-	-	0,50	-
Flow 5/		18	18	15	29
Mpa 1		6	5	4	5
3		18	17	18	16
7		34	31	31	34

3.3.4 A <u>Various Tannin Extracts Sulphited</u>

Extract : metabisulphite + small addition of KOH; 1 hour at 70°C, Dosage 0,25%

EXTRACT	MASS RATIO	FLOW 5/15	Mpa 1	3	7	COMMENT
Wattle	10:3,3	18	6	19	34	+ 1g KOH
Pine	10:3,3	18	5	17	31	+ 1g KOH
Standard	-	30	5	16	29	
Ital. Chestnut	10:2	8s/-	8	18	30	+ 0,2g KOH
Standard	-	-/-	6	18	30	
Yugosl. Chestnut	-	8s/-	8	20	29	
Yugosl. Chestnut	10:2,5	8s/-	7	22	30	
Yugosl. Chestnut	10:5	5s/-	8	20	28	
Standard	-	-/-	8	14	28	
Quebracho	10:3	15/15	3	20	32	+ 0,8g KOH
Standard	-	29/-	6	18	30	
Pecan	10:3	-/-	8	21	32	+ 0,8g KOH
Standard	-	-/-	6	25	34	

3.3.5 Quebracho and Wattle Tannin Extracts Sulphited and Treated with Urea

Extract : metabisulphite : urea + 0,5g KOH 1 hour at 60°C
* heated 2 hours at 60°C, Dosage 0,25%

EXTRACT	MASS RATIO	FLOW	Mpa		
		5/15	1	3	7
Quebracho	10:1,5	36s/34	8	20	40
Quebracho	10:1,5:1,5	70/68	10	19	36
Wattle	10:1,5	65/62	13	24	30
Wattle	10:1,5:1,5	60/65s	12	22	32
Standard	-	-/-	9	24	30
New Quebracho	10:1,5	42s/41s	5	23	34
New Quebracho	10:1,5:1,5	26s/35s	5,5	22	36
New Quebracho	10:1,5:3 *	60/-	8	24	34
Standard	-	29/-	6	18	30

s : stop of flow after initial movement

3.3.6 Pine and Wattle Tannin Extracts reacted with Metabisulphite, Urea and Paraformaldehyde

Extract : metabisulphite : urea : paraformaldehyde

Sulphitation 1 hour 70°C, then urea added

1 hour later added paraformaldehyde and KOH (0,6g)

Dosage 0,25%

EXTRACT	MASS RATIO	FLOW	Mpa		
		5/15	1	3	7
Wattle	10:3,5:5:0,5	23/25	6,5	22	28
Pine	10:3,5:5:0,5	23/33	6,5	20	32
Standard	-	-/-	6	18	30

3.3.7 A **Yugoslavian Chestnut Tannin Extract at Various Stages of Modification**

Nrs 2 - 4 : 1 hour 60°C
Dosage 0,25%

COMPOSITION	STD	1	2	3	4	5	6
Chestnut	-	25	25	25	25	2	1
KOH	-	-	0,25	0,25	0,25	-	-
Metabisulphite	-	-	-	2,5	2,5	-	-
Urea	-	-	-	-	5	-	-
Water	75	75	75	75	75	-	-
Flow 5/15	-/-	5s/-	1s/-	5s/-	-/-	5s/-	3s/-
Mpa 1	8	8	8,5	7	8	6	7,5
3	14	22	24	23	24	22	20
7	28	28	30	27	32	30	28

5 and 6 : added as dry powder to the mixing water, corresponding to 0,25% and 0,125% dosage respectively
s : stop of flow after initial movement

3.3.7 B **Quebracho Tannin Extract at Various Stages of Modification**

Nrs 2 - 4 : 1 hour 60°C

COMPOSITION		STD	1	2	3	4	5
Quebracho		-	50		50	50	50
KOH		-	-	0,5	0,5	0,5	0,5
Metabisulphite		-	-	-	5	5	5
Urea		-	-	-	-	10	10
Flow 5/15		-/-	69/-	39s/-	75/-	24s/-	23/25
Mpa	1	9	7,5	7	7	9,5	8
	3	20	18	22	20	20	26
	7	26	26	29	26	29	31

1-4: normal dosage 0,25%

5 : double dosage of 4, i.e. 0,50% by cement weight

s : stop of flow after initial movement

3.3.8 A **Improving the solubilities of Wattle and Quebracho Tannin Extract with small amounts of Alcohol**

Extract treated with 5% alcohol mixture by extract weight, left to mature overnight
1 hour 60°C

COMPOSITION	STD	1	2	3	4
Quebracho	-	10	10	-	-
Wattle	-	-	-	10	10
Metabisulphite	-	1,5	2	3	3
Urea	-	3	4	2	-
Sugar	-	-	-	5	5
Flow 5/15	-/-	16/15	18/16	18/17	18/17
Mpz. 1	6	2	1	-	-
3	25	20	17	19	16
7	34	36	30	25	35

1 and 2 : normal dosage 0,25%
3 and 4 : added at double dosage i.e. 0,5%

3.3.8 B **Improving the solubilities of Wattle Tannin Extract with small amounts of Alcohol**

Wattle extract treated with 5% by mass alcohol mixture overnight
Wattle : metabisulphite : urea
2,5 hours at 70°C
Dosage 0,25%
First lot tested fresh after preparation
Second lot tested after 24 hours maturing

MASS RATIO	FLOW	M_1 a			COMMENT
	5/15	1	3	7	
10:1,5	-/-	5	22	32	+ 0,5g KOH
10:1,5:1,5	-/- [1)]	6	22	32	
Standard	-/-	6	25	34	
10:1,5	-/-	10	28	32	+ 0,5g KOH
10:1,5:1,5	-/-	9	28	34	
Standard	-/-	9	24	30	

1) better than above

3.3.9 Quebracho Tannin Extract at various stages of Alcohol treatment

Quebracho : metabisulphite : urea
1 hour 70°C
1) Treated with alcohol mixture 5% by mass of extract for three days
2) Treated with alcohol mixture 5% by mass of extract overnight
Dosage 0,25%

MASS RATIO	FLOW	Mpa		
	5/15	1	3	7
10:3,5:5	18/38	5	22	34
10:2:5	23/42s	5	24	34
10:3,5:5 1)	36/-	5	24	34
10:2:5 1)	-/-	4,5	22	29
10:2:2,5 2)	16/14	2	24	29
10:1:5 2)	14/14	1,5	18	33
Standard	-/-	6	18	30

s : stop of flow after initial movement

3.3.10 **Quebracho Extract modified with various dosages of Metabisulphite and Urea**

Quebracho : metabisulphite : urea

1 hour at 70°C, Dosage generally 0,25%

MASS RATIO	FLOW	Mpa			COMMENT
	5/15	1	3	7	
10:3,5:5	-/-	8	21	33	New quebracho
10:2,5:5	-/-	6	21	32	Powders mixed before adding water
10:2,5:5	22/24	9	26	28	Above, double dosage i.e. 0,5%
10:2,5:5	-/-	6	20	26	Quebracho added last to solution
10:5:3,5	20s/-	7	22	28	
Standard	-/-	9	24	30	
10:2,5:2,5	24/34	4	16	36	
Standard	-/-	6	18	30	
10:0,5:1	53s/-	6,5	18	30	
10:0,5:1	39/22	1,5	17	28	Double dosage, i.e. 0,5%
Standard	-/-	5	16	28	

s : stop of flow after initial movement

3.4.1 A **Modified Wattle Extract with Triethanolamine additions**

Wattle : metabisulphite : urea : ammonia : TEA

1) 1 hour at 60°C

2) 2 hours 60°C, TEA cold added 24 hours later

EXTRACT	MASS RATIO	FLOW	Mpa			DOSAGE
		5/15	1	3	7	
Wattle[1)]	10:2,5:3:1,5:2	6s/-	7,5	20	28	0,25%
Standard	-	-/-	9	24	30	
Wattle[2)]	10:2,5:3,5:1:2	Workable	8	24	32	0,2%
Wattle[2)]	10:2,5:3,5:1:2	Very work	6	27	32	0,3%
Standard	-	Stiff	8	26	30	

s: stop of flow after initial movement for x amount of seconds

3.4.1 B **Modified Wattle Extract with Triethanolamine additions**

Wattle : metabisulphite : urea : TEA 10:3 5:0,5:1
2 - 6 hours at 70°C
urea added cold next day
TEA added day after, heated 3 hours at 70°C
Dosage 0,25%

COMMENTS	FLOW	FRESH Mpa			FLOW	24 HOURS LATER		
	5/15	1	3	7	5/15	1	3	7
2 hours	32/32	6	23	40	18/16	2	19	26
3 hours	-/-	3	18	32	16/15	3	19	28
4 hours	30/26	4	21	35	-	-	-	-
5 hours	21/24	4	18	32	-	-	-	-
6 hours	26/29	4	25	35	-	-	-	-
TEA only	-	-	-	-	27/20	2	20	31
Standard	-/-	6	18	30	-	-	-	-

3.4.2 A **Quebracho Extract with TEA Acetate or Formate additions**

All mixed cold

COMPOSITION	MASS RATIO	FLOW	Mpa				
		5/15	1	2	3	7	DOSAGE
TEA Acetate	70:30*	-/-	5	14	18	29	0,2%
TEA Formate	75:25*	-/-	4	13,5	16	26	0,2%
TEA Acetate	70:30*	-/-	5	12	16	27	0,01%
Standard	-	-/-	4	12	18	28	
Quebracho + TEA Acetate	1:1	-/-	-		20	26	0,25%
Standard	-	-/-	6		18	30	
Quebracho + TEA Acetate	10:1	2s/	7		24	32	0,25%
Standard	-	-/-	9		20	26	

s: stop of flow after initial movement for x amount of seconds

*Correspond to 1:1 molar ratio

3.4.2 B **Modified Quebracho Extract with TEA Acetate**

Quebracho : metabisulphite : urea
10:0,4:0,8
1 hour at 60°C
mixed cold with TEA : Acetate (70:30)
5:1 and 4:1 parts by mass

MASS RATIO	FLOW	Mpa			DOSAGE
	5/15	1	3	7	
5:1	60/-	9,5	24	31	0.25%
5:1	30/39	7,5	27	30	0,5%
4:1	33s/-	12	27	32	0,25%
Standard	-/-	9	20	26	

3.4.2 C **Modified Quebracho Extract with TEA Acetate**

Quebracho : metabisulphite : urea (Mix)
10:0,5:1
2 hours 60°C
mixed cold with TEA : Acetate (70:30)

MASS RATIO	FLOW	Mpa			
	5/15	1	3	7	DOSAGE
Mix	53s/-	6,5	18	30	0,25%
Mix	39/22	1,5	17	28	0,50%
95:5	85s/-	7	26	29	0,25%
95:5	34/30	5	32	37	0,50%
97,5:2,5	50s/-	6,5	26	30	0,25%
97,5:2,5	30/25	4	28	36	0,50%
Standard	-/-	9	20	26	

3.4.3 A **Comparison of Triacetin and Propylene Carbonate with TEA Acetate as additions to modified Wattle Extracts**

Extract : metabisulphite : urea
10:3,5:5 +0,5g KOH, 1 hour 60°C
Mixed cold with esters
Dosage 0,25% (normal)

COMPOSITION	STD	1	2		4	5
Wattle type	-	20	-	-	-	-
Conditioned Wattle type	-	-	20	20	20	20
TEA acetate	-	5	5	-	-	-
Glycerol triacetate	-	-	-	5	-	-
Propylene carbonate	-	-	-	-	5	-
Flow 5/15	29s/-	20/6s	16/8s	17/3s	15/-	30/-
Mpa 1	5	9	8	6	6	4
2	13	19	18	16	15	12
3	20	26	23	26	22	14
7	31	30	32	28	28	24

3.4.3 B **Comparison of Triacetin and Propylene Carbonate with TEA Acetate as additions to modified Wattle Extracts**

Extract : metabisulphite : urea
10:3,5:5 +0,5g KOH, 1 hour 60°C
Mixed cold with esters
Dosages 0,50% (double)

COMPOSITION	STD	1	2	3	4
Wattle type	-	20	-	-	-
Conditioned Wattle type	-	-	20	20	20
TEA acetate	-	5	5	-	-
Glycerol triacetate	-	-	-	5	-
Propylene carbonate	-	-	-	-	5
Flow 5/15	-/-	35/30	25/3s	42/5s	29/7s
Mpa 1	5	9	10	10	8
2	15	17	20	20	20
3	18	24	24	24	22
7	28	29	30	32	30

3.4.3 C **Modified Extracts with TEA Acetate as addition**

Extract : metabisulphite : urea
10:3,5:5 +0,5g KOH, 1 hour 60°C
Combined cold with TEA acetate (70:30) 'mix'

COMPOSITION	MASS RATIO	FLOW	Mpa				DOSAGE
		5/15	1	2	3	7	
Chile Pine : mix	20:5	17/4s	10	22	22	29	0,25%
Standard	-	-/-	5	15	18	28	
Pecan : mix	20:5	-/-	4	18	31	-	0,25%
Yugosl. Chestnut : mix	20:5	21/-	5	20	30	-	0,125%
Standard	-	-/-	4	12	19	30	

3.4.4 Modified Yugoslavian Chestnut Extract mixed with TEA Acetate

Extract : metabisulphite : urea
10:3,5:5 +0,5g KOH; 1 hour at 60°C
Additions mixed in cold
Dosage 0,25%

COMPOSITION	STD	1	2	3
Chestnut	-	10	10	10
TEA Acetate	-	5	5	5
Furfuryl Alcohol	-	-	1	-
Teepol	-	-	-	1
Flow 5/15	40/-	20/3s	27/2s	31/-
Mpa 1	4	6	5	3
2	11	16	10	10
3	14	26	24	16
7	29	28	28	28

3.4.5 Acid and Alkaline modification of Italian Chestnut Extract

Chestnut A; chestnut : NaOH 10:0,3 by mass
Chestnut B; chestnut : CH_3 COOH 10:0,3 by mass
Extract : metabisulphite : urea
10:2,5:5 ; 2 hours 60°C
Mixed cold with 5 parts TEA acetate
Dosage 0,25%

COMPOSITION	STD	1	2	3
Chestnut	-	-	-	10
Chestnut A	-	40	-	-
Chestnut B	-	-	40	-
Flow 5/15	-/-	5s/-	5s/-	3s/-
Mpa 1	8	7	8	8
3	16	20	19	18
7	31	28	30	30

Nr 3) 10g dry extract correspond to 40g modified solution of A or B

3.4.6 Comparison of modified Conditioned Wattle types 244 and 345 with TEA Acetate additions

Extract : metabisulphite : urea , 1 hour 60°C
10:1:2 (nr. 1 and 2) 12,5:1:2 (nr. 3)
Mixed cold with 2,5 parts TEA acetate
Dosage 0,25%

COMPOSITION		STD	1	2	3
Conditioned Wattle 244		-	20	-	-
Conditioned Wattle 345		-	-	20	25
Flow 5/15		-/-	17/17	18/18	17/18
Mpa	1	11	11	11	10
	3	31	33	32	34
	7	32	45	48	40

3.4.7 Conditioned Wattle Tannin with TEA Acetate at various stages of modification

Nr 2 and 3 : 1 hour 60°C, ester added cold
Dosage 0,25%

COMPOSITION	STD	1	2	3
Conditioned Wattle	-	10	10	10
TEA Acetate	-	2	2	2
Metabisulphite	-	-	1	-
Urea	-	-	-	2
Flow 5/15	40/-	25/5s	25/8s	25/12s
Mpa 1	4	6	6	7
2	11	17	15	16
3	14	20	20	25
7	29	31	31	32

3.4.8 Triethanolamine Salicylate as an alternative to Triethanolamine Acetate

Nr 1 : 2 hours 60°C
Nr 2 : 1 hour 60°C
Esters added cold Dosage 0,25%

COMPOSITION	STD	1	2	3	4	5
Conditioned Wattle	-	-	10	-	-	-
Catechol	-	-	-	5	-	-
Vanillin	-	-	-	-	5	-
Salicylic acid	-	-	-	-	-	5
TEA Salicylate	-	10	5	5	5	-
TEA Acetate	-	-	-	-	-	5
Urea	-	-	2	-	-	-
Flow 5/15	-/-	-/-	7s/-	11s/-	-/-	9s/-
Mpa 1	8	7	6	6	5	6
3	16	16	17	16	18	18
7	31	27	31	32	36	32

3.4.9 Potential additions for modified Tannin Extracts

Mix 30 : Wattle extract : metabisulphite : urea
10:1:2 ; 1 hour 60°C
Mixed cold with 2 parts TEA Acetate
Nrs 1 - 3 made cold, Dosage 0,25%

COMPOSITION	STD	1	2	3	4	5
Acetoacetate	-	10	-	-	-	-
TEA Acetate	-	5	5	5	-	5
Catechol	-	-	5	2,5	-	-
Resorcinol	-	-	-	2,5	-	10
Mix 30	-	-	-	-	100	50
Flow 5/15	-/-	-/- *	1s/-	-/-	35/80	10s/5s
Mpa 1	10	11	12	12	12	10
3	-	-	-	-	-	-
7	28	35	25	30	34	33

* Better than the standard

3.4.10 **Various 5% additions to a fully modified Wattle Tannin Extract**

Mix 32 : as in table 3.4.9, but different batch
Dosage 0,25 %

COMPOSITION	STD	1	2	3	4
Mix 32	-	100	95	95	95
Catechol	-	-	5	-	-
Acetoacetate	-	-	-	5	-
Zn acetate	-	-	-	-	5
Flow 5/15	7s/-	54/25	40/27	78/30	82/28
Mpa 1	4	6	5	6	5
3	13	21	19	19	18
7	26	29	26	34	27

3.5 The effect of Calcium Oxide and Calcium Hydroxide on modified Wattle Tannin and a Sulphonated MF partial condensate

Mix 30, mix 32 : same formulation as in table 3.4.9

1) left standing 24 hours

2) left standing 1 hour

COMPOSITION	MASS RATIO	FLOW	Mpa			DOSAGE
		5/15	1	3	7	
Mix 30	-	61/-	10	24	30	0,25%
Mix 30 : Ca 0 [1)]	50:50	-/-	12	23	32	0,50%
Mix 30 : Ca 0 [1)]	50:50	6s/-	7	20	26	1,0%
Standard		-/-	9	24	30	
Mix 32	-	22/27	7	27	34	0,25%
Mix 32 : $Ca(OH)_2$ [2)]	95:5	4s/-	6	27	33	0,25%
Sulph. MF*	-	7s/-	5	20	28	1,5%
Sulph. MF* : $Ca(OH)_2$ [2)]	95:5	4s/-	4	22	26	1,5%
Standard	-	-/-	7	22	31	

* 30% by mass solution

3.6 **Compari of two modified Wattle Tannins with three types of Sulphonated MF partial condensates**

Sulph. MF : Sulphonated melamine formaldehyde condensate
Mix 32, mix 33 : same as in table 3.4.9

COMPOSITION	FLOW	[illegible]			
	5/15	1	3	7	DOSAGE
New Germ. Sulph. MF 40% soln	16/12	4	19	24	1,0%
S.A. Sulph. MF 40% soln	19/12	5	19	24	1,0%
Mix 32 36% soln	22/15	5	21,5	30	0,25%
Standard	23s/-	4	15	28	-
Germ. Sulph. MF 31% soln	5s/-	4,5	20	31	1,5%
Mix 33 36% soln	27/25	7	26	31	0,25%
Standard	-/-	6	22	31	-

3.7 Compressive Strength Test by an Outside Laboratory

We carried out two sets of trial mixes of nominal cement contents 300 and 400 kg/m3.

A control test was carried out at each cement content, together with an admixtured concrete dosed at 300mL/100kg of cement.

The following results were obtained:

Cement Content	300kg/m3		400kg/m3	
	Control	Admix.	Control	Admix.
Compressive Strength @ various ages.				
24 hours	9,4	6,5 (69,1)	14,7	14,2 (96,6)
48 hours	15,4	16,6(107,8)	23,6	26,4(111,9)
3 days	18,9	23,1(122,2)	30,3	34,1(112,5)
7 days	26,1	32,6(124,9)	41,0	48,8(119,0)
28 days	41,5	45.5(109,6)	58,2	65,6(112,7)

Figures in parentheses give test mix strengths as percentage of control.

We trust you will find this of interest.

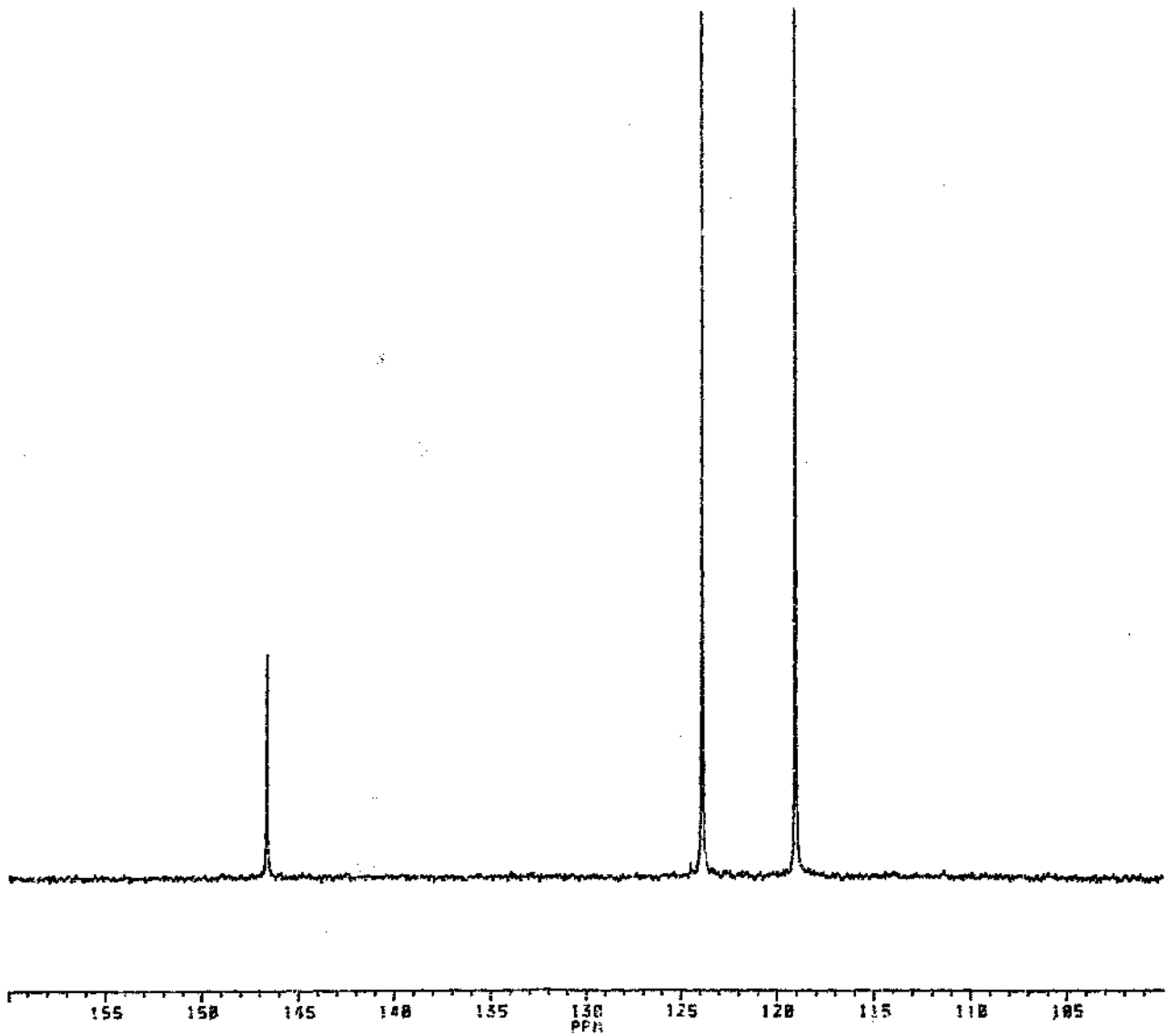


Figure 3.1.2 B **Carbon 13 NMR of Catechol : Ammonia 2:1 D_20**

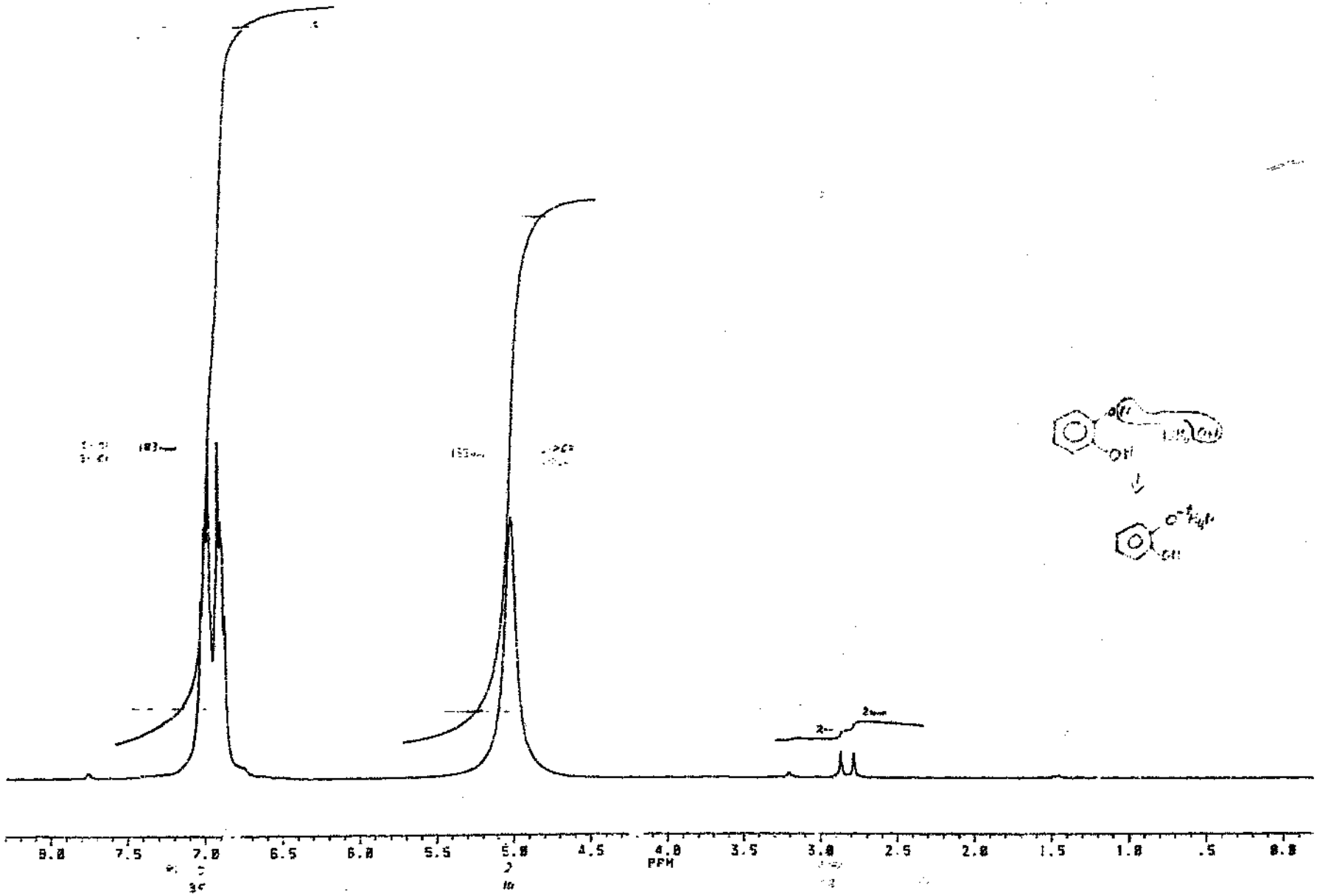


Figure 3.1.2 C **Proton NMR of Catechol : Ammonia 2:1 D_20**

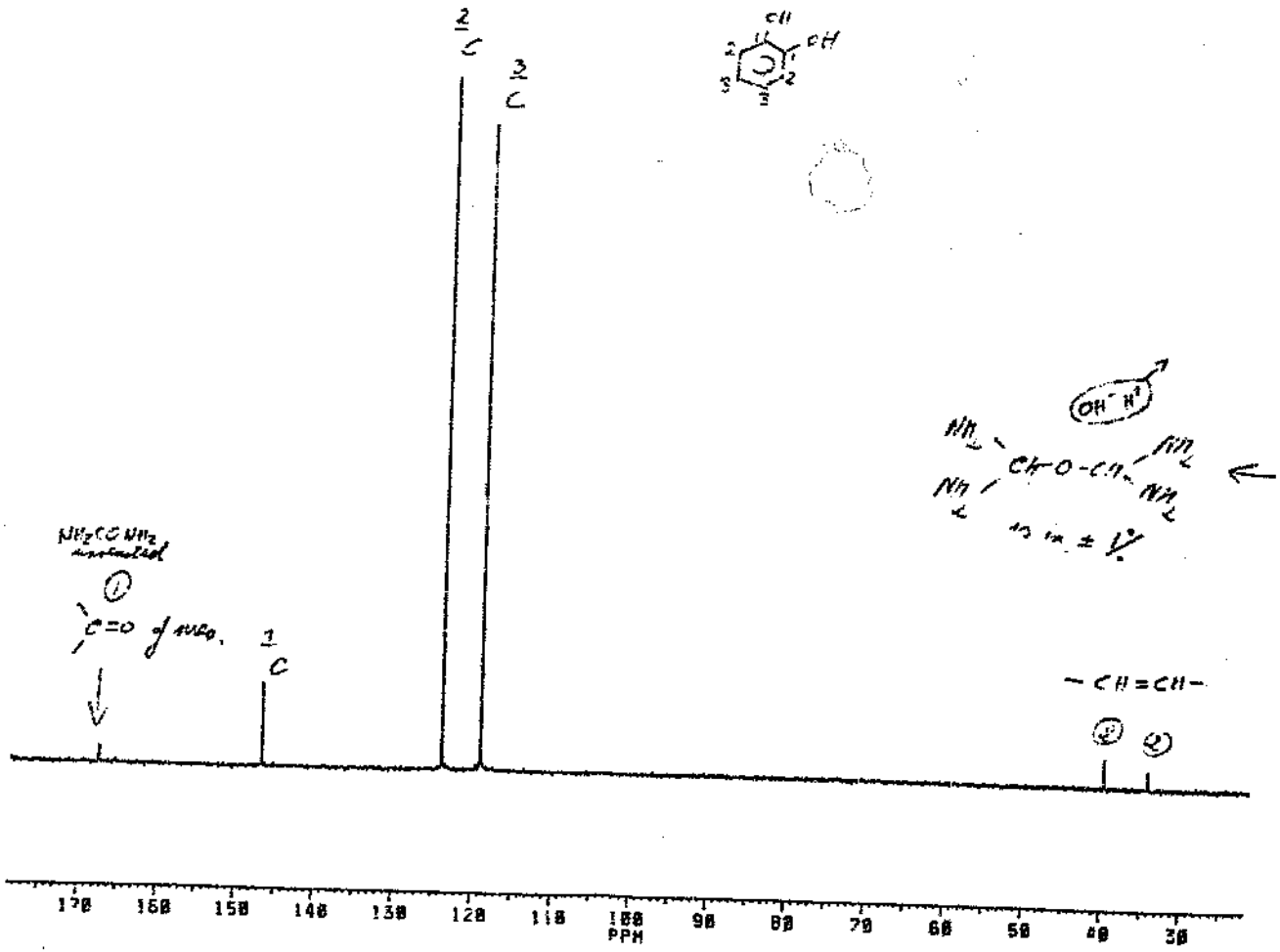


Figure 3.1.3 B Carbon 13 NMR of Catechol : Urea 1:1 D_2O

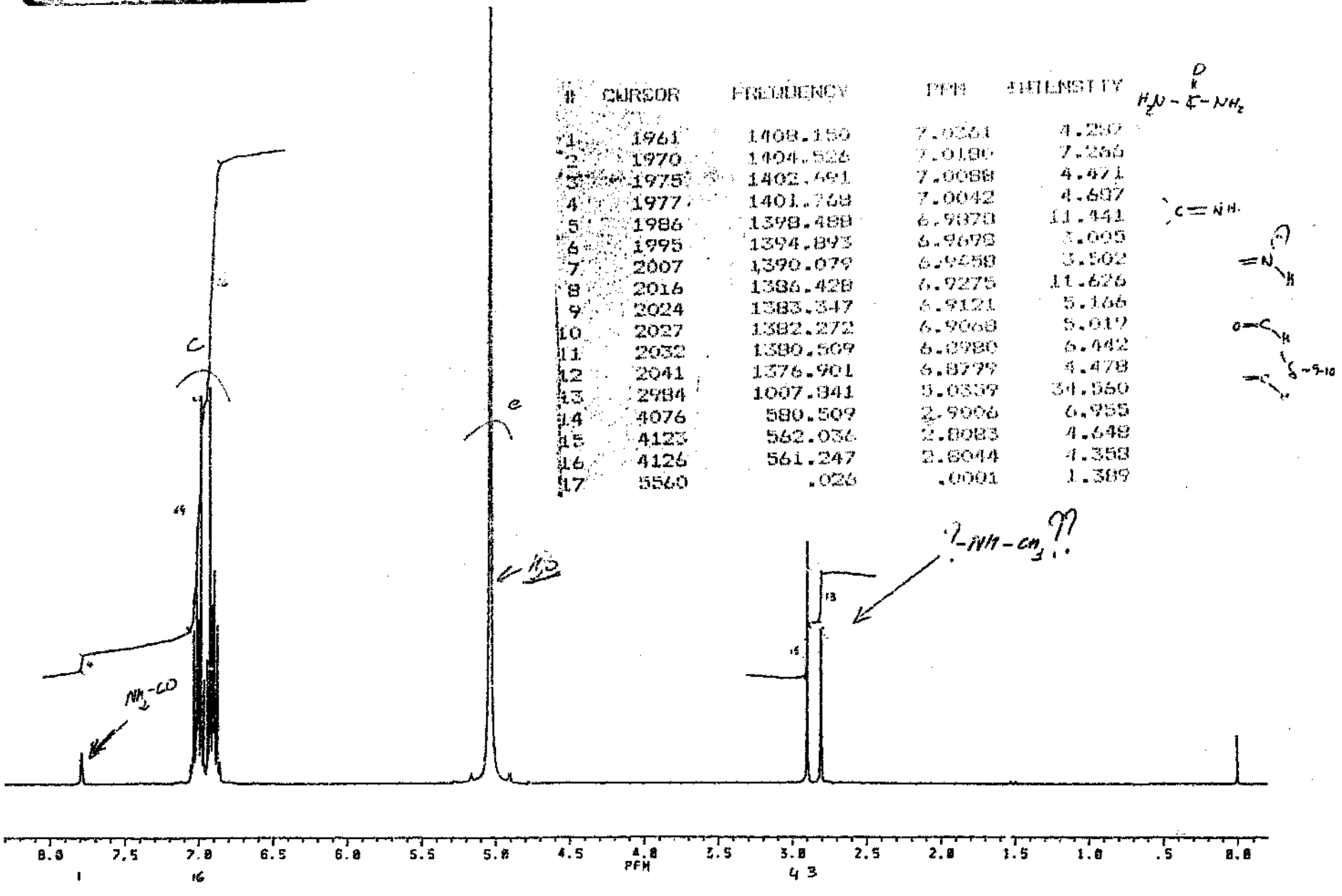


Figure 3.1.3 C **Proton NMR of Catechol : Urea 1:1 D_2O**

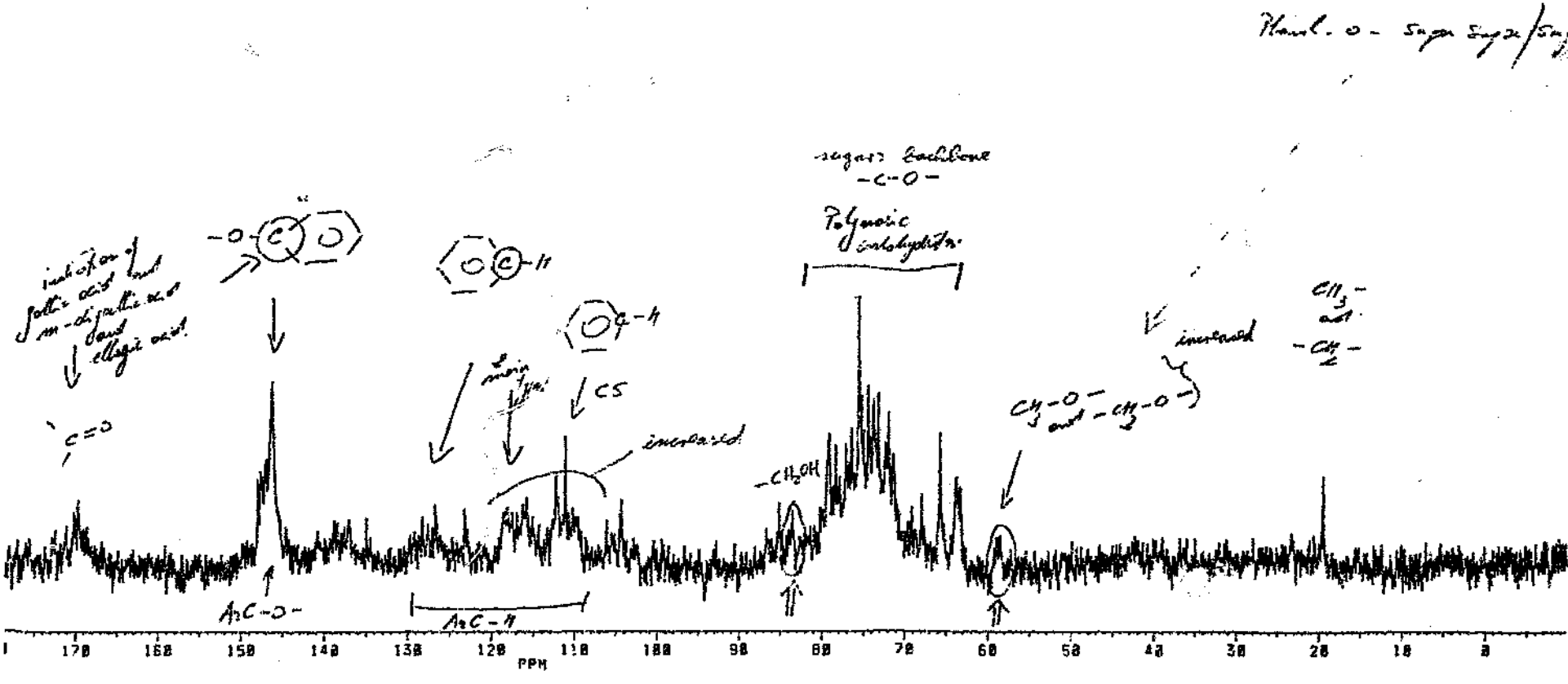


Figure 3.3.4 B **Carbon 13 NMR of Chestnut : Metabisulphite 10:1 D_2O**

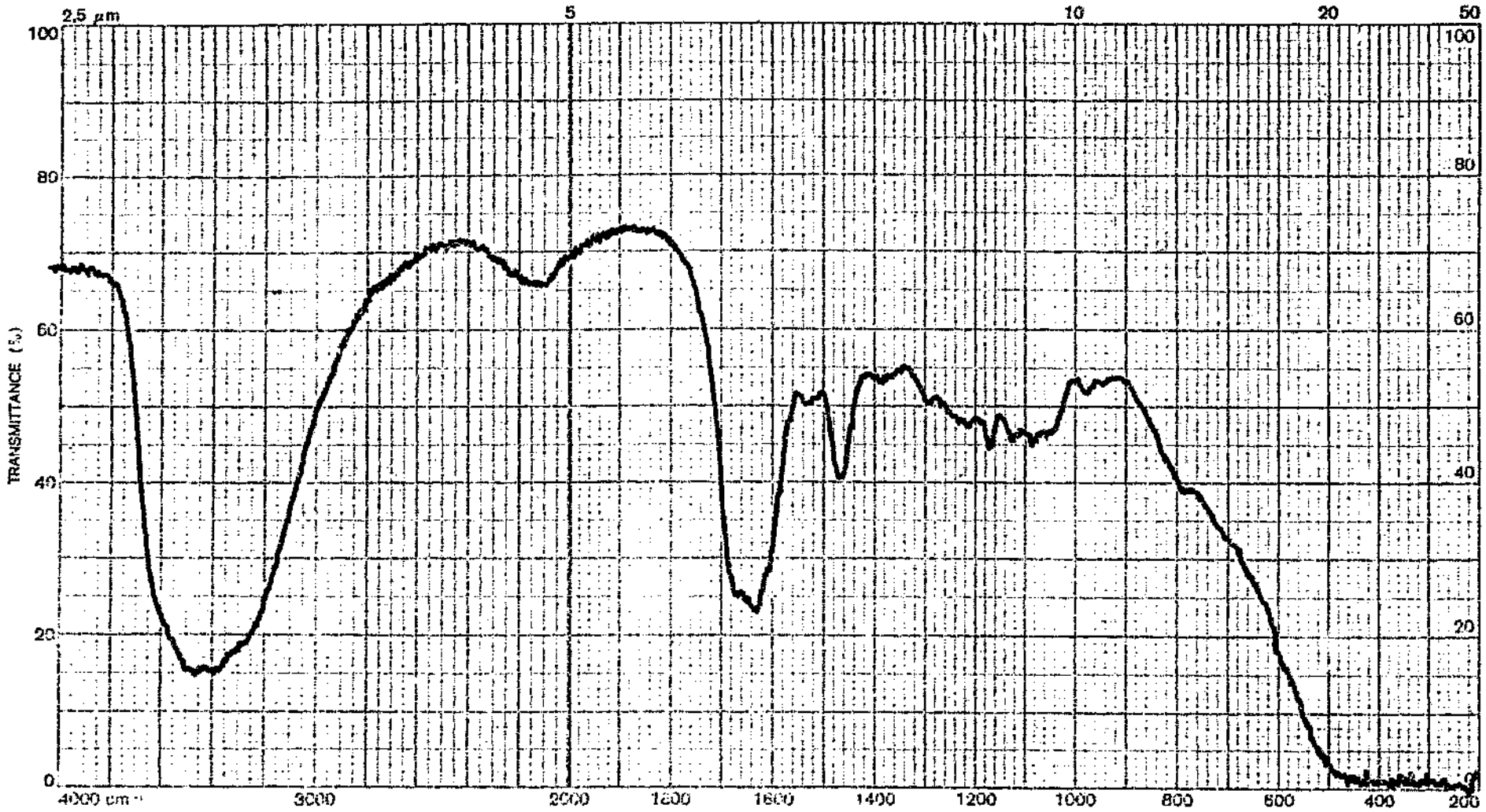


Figure 3.3.5 A **Infra Red of Quebracho : Metabisulphite : Urea 3:1:6 before heating**

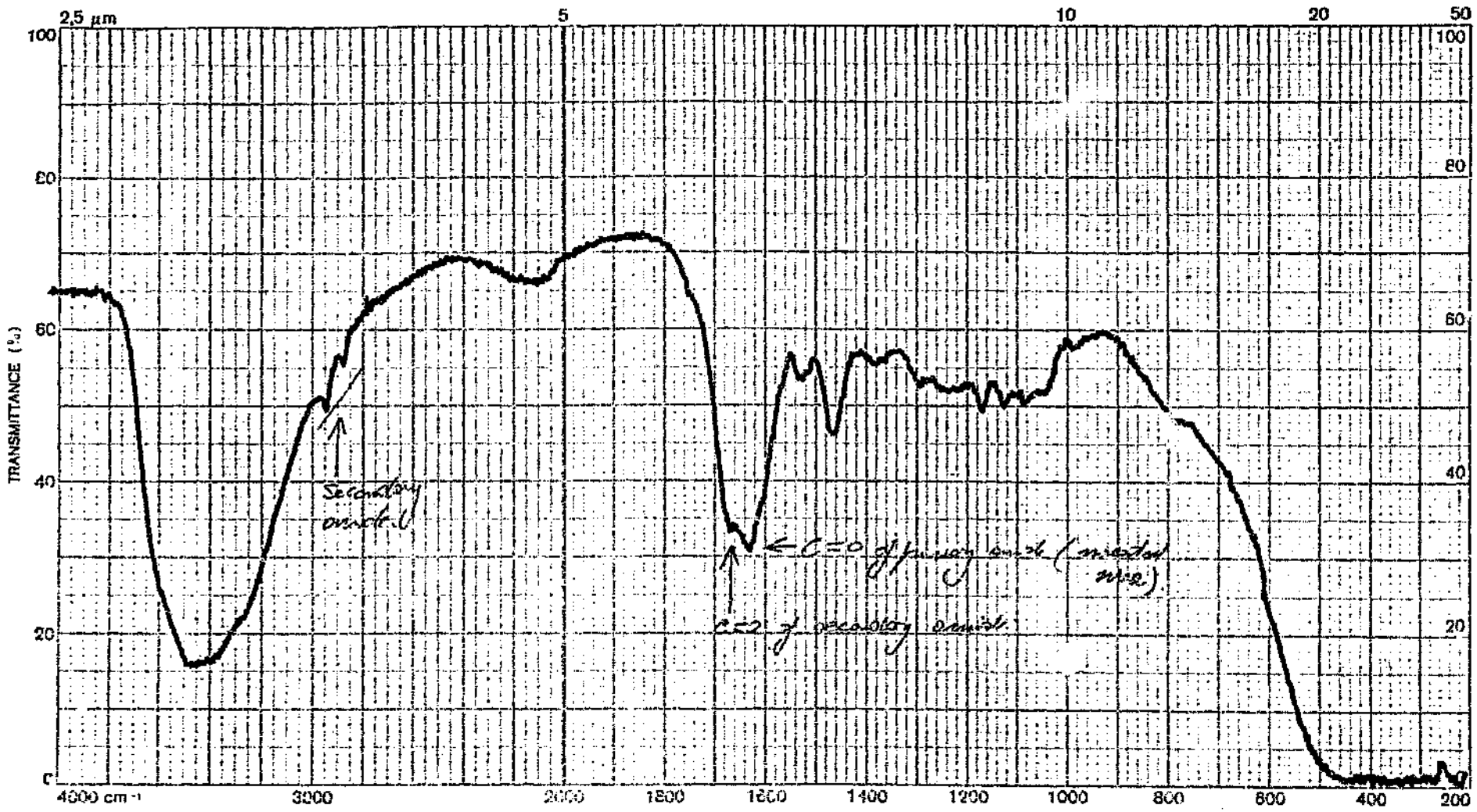


Figure 3.3.5 B Infra ed of Quebracho : Metabisulphite : Urea 3:1:6 after heating

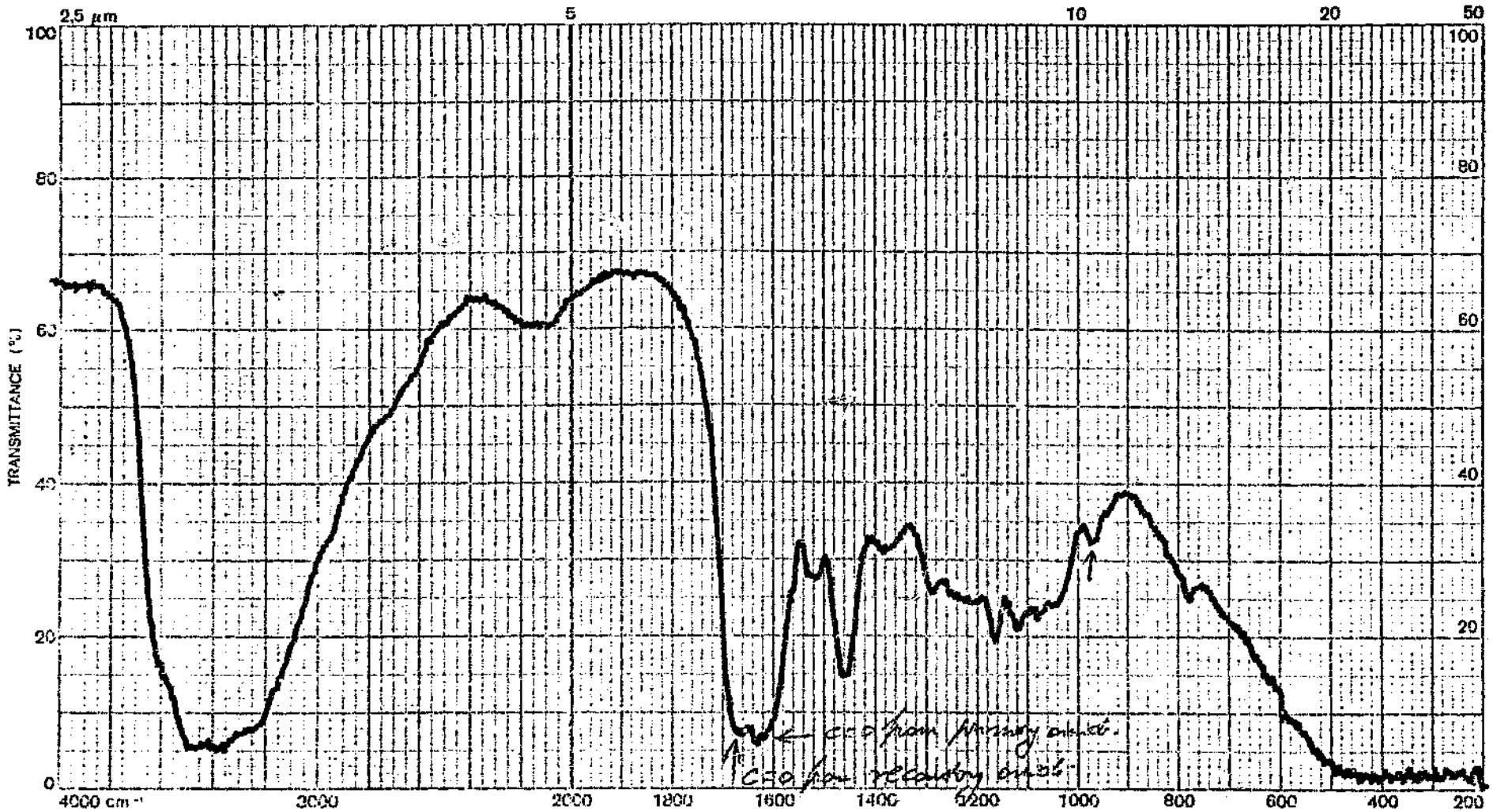


Figure 3.3.5 C **Infra Red of Quebracho : Metabisulphite : Urea 3:1:6 24 hours later**

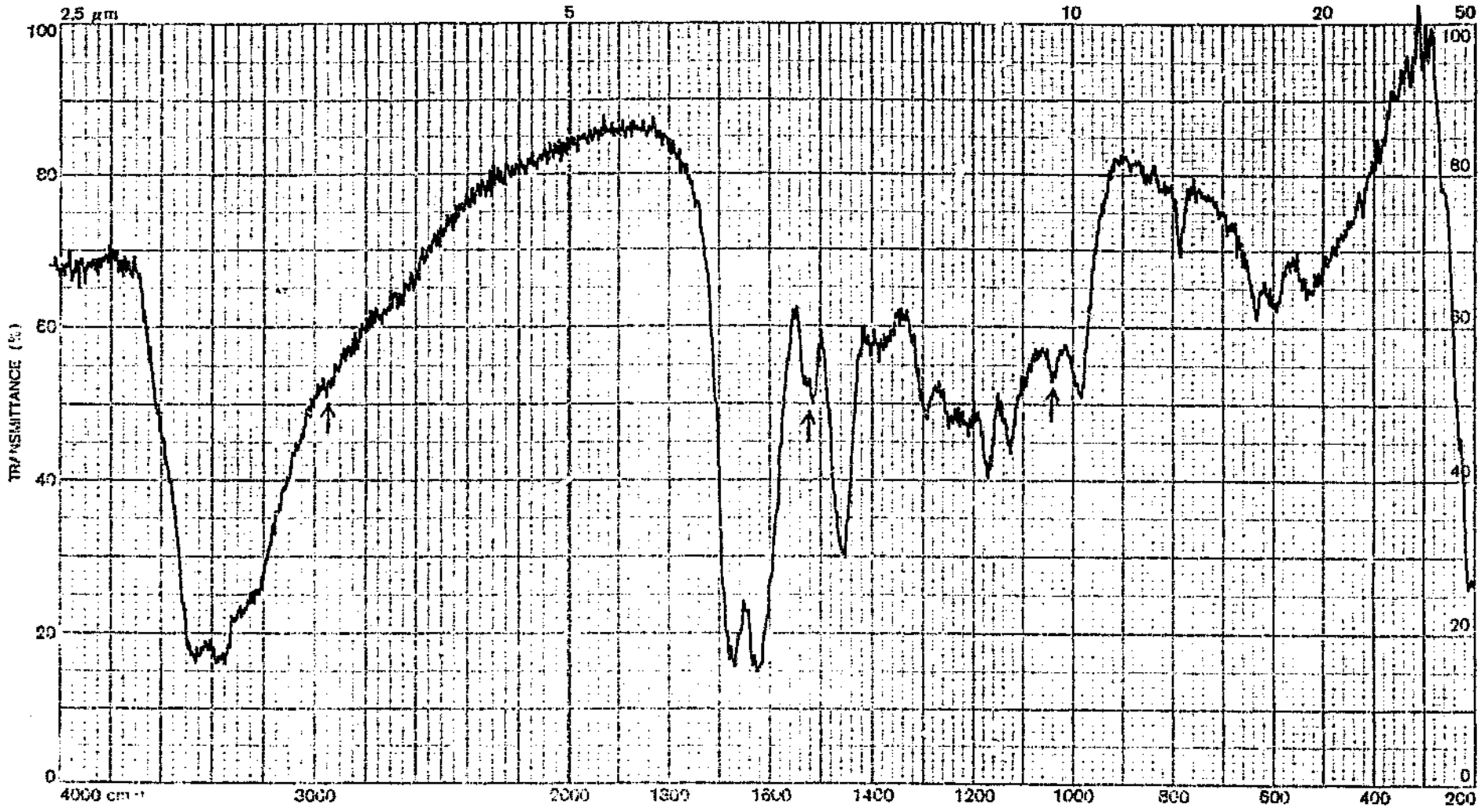


Figure 3.3.5 D **Infra Red of Quebracho : Metabisulphite : Urea 3:1,3:6 before heating**

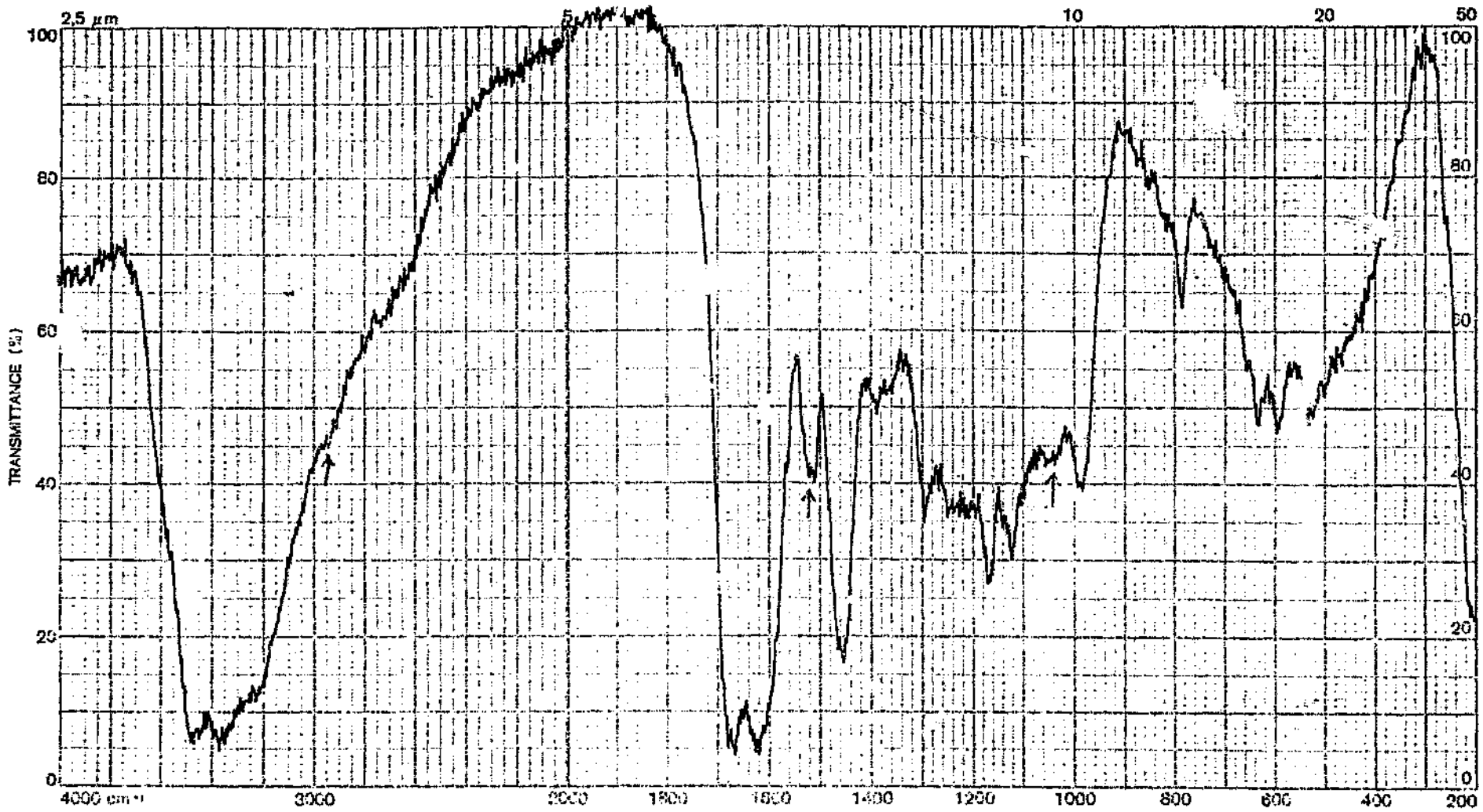


Figure 3.3.5 E Infra Red of Quebracho : Metabisulphite : Urea 3:1,3:6 after heating

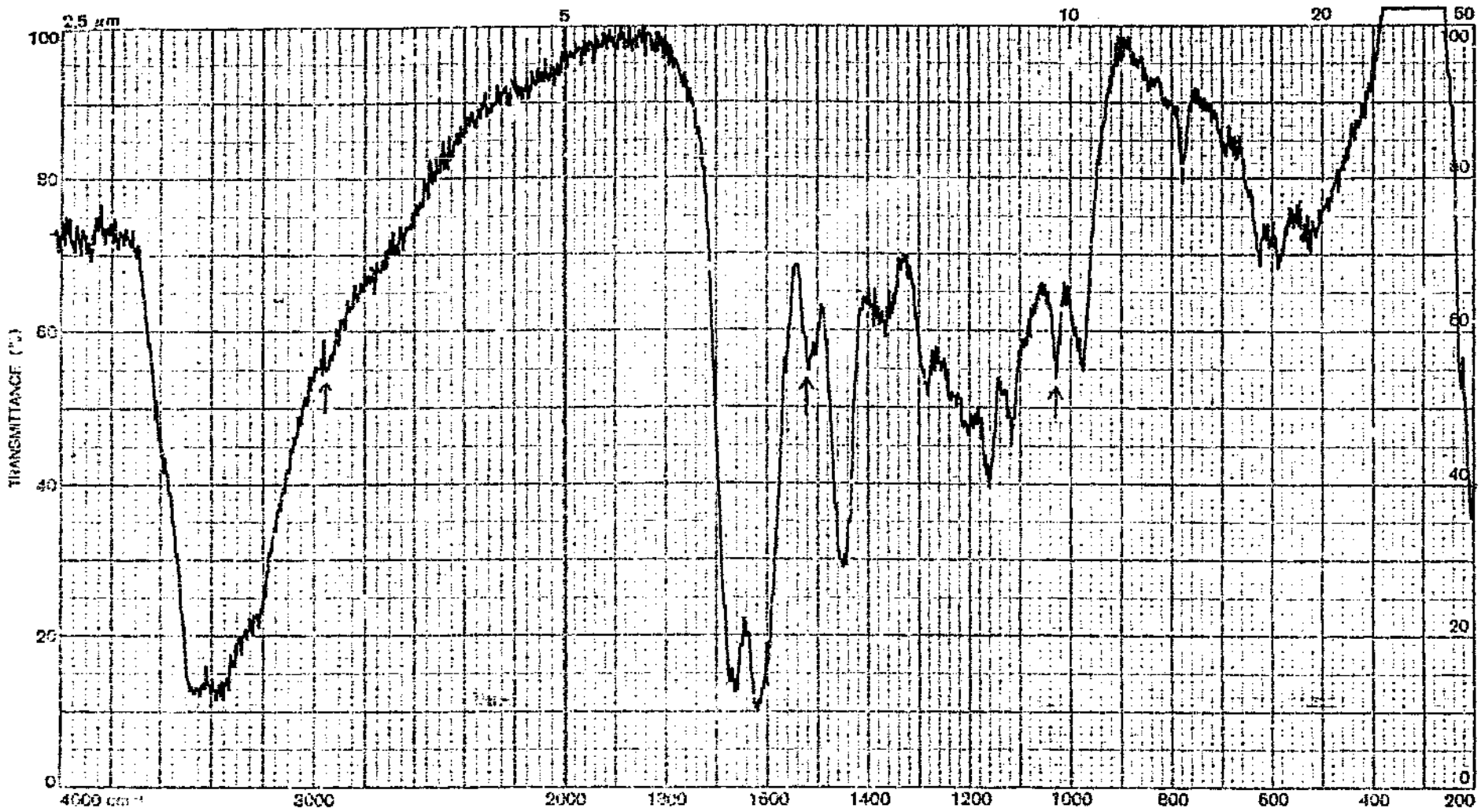


Figure 3.5 F **Infra Red of Quebracho : Metabisulphite : Urea 3:1,3:6 1 hour after heating**

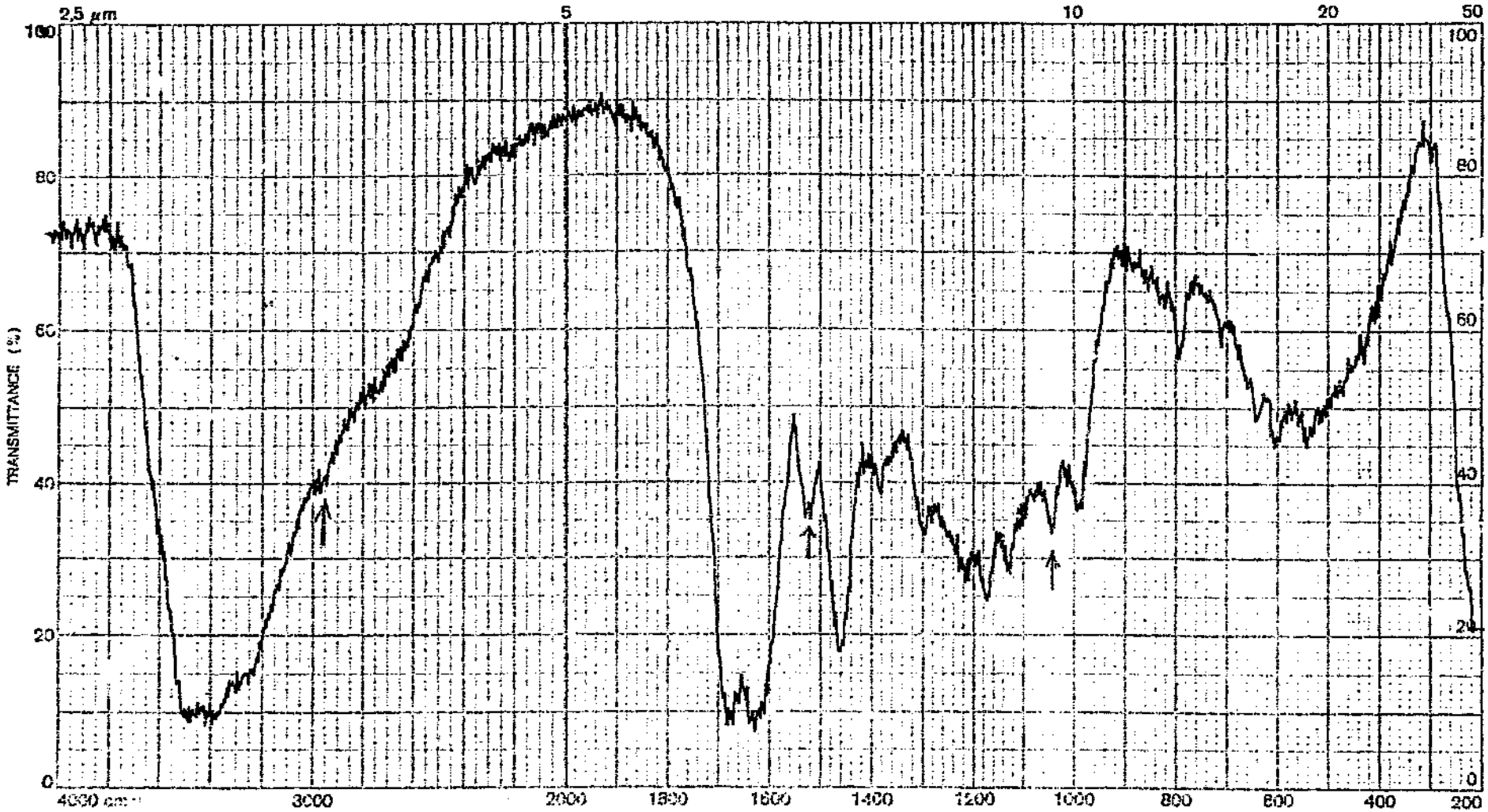


Figure 3.3.5 G **Infra Red of Quebracho : Metabisulphite : Urea 3:1,3:6 24 hours later**

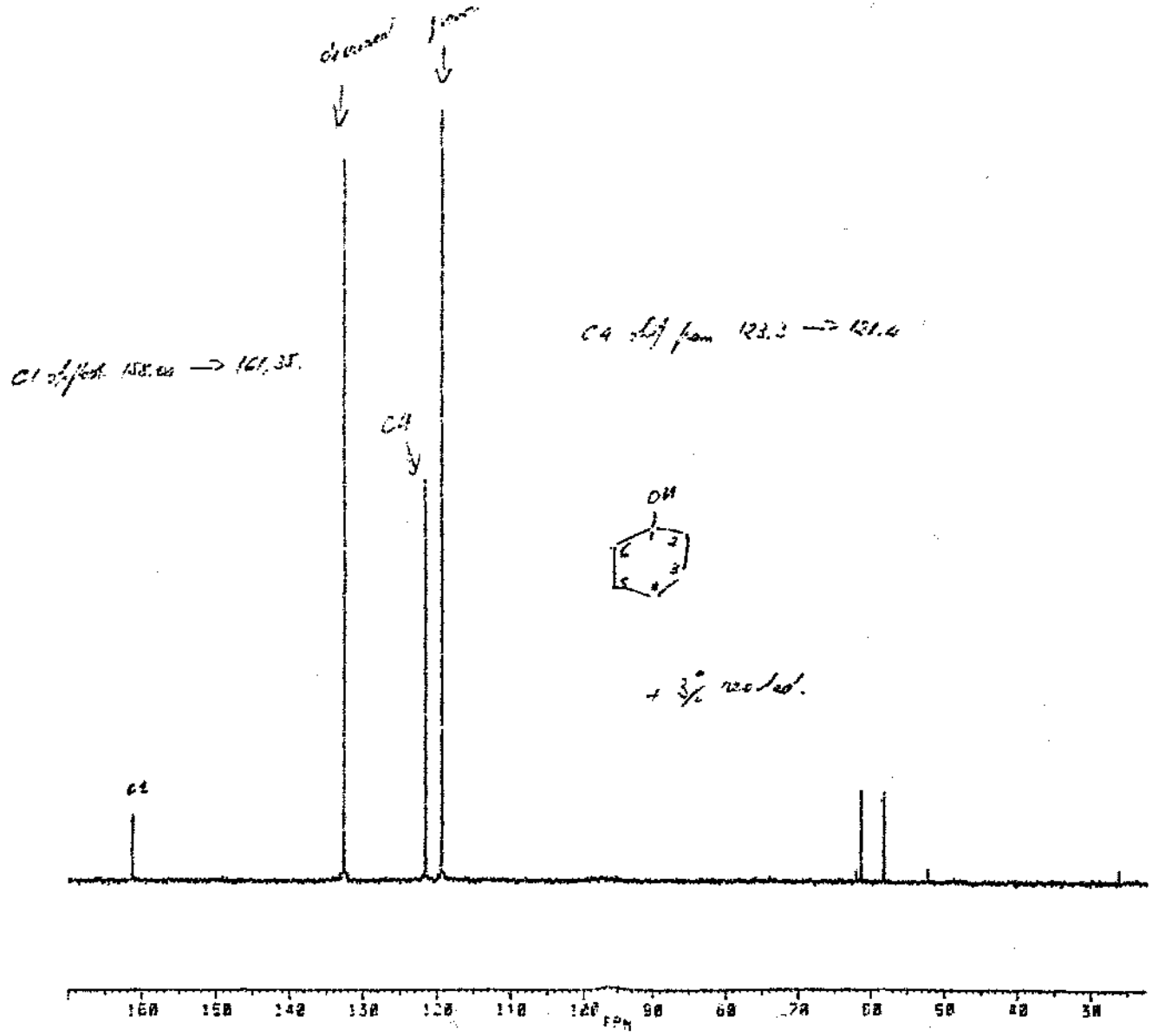


Figure 3.4.2 A **Carbon 13 NMR of Phenol : TEA Acetate 11:1 D_2O 20°C**

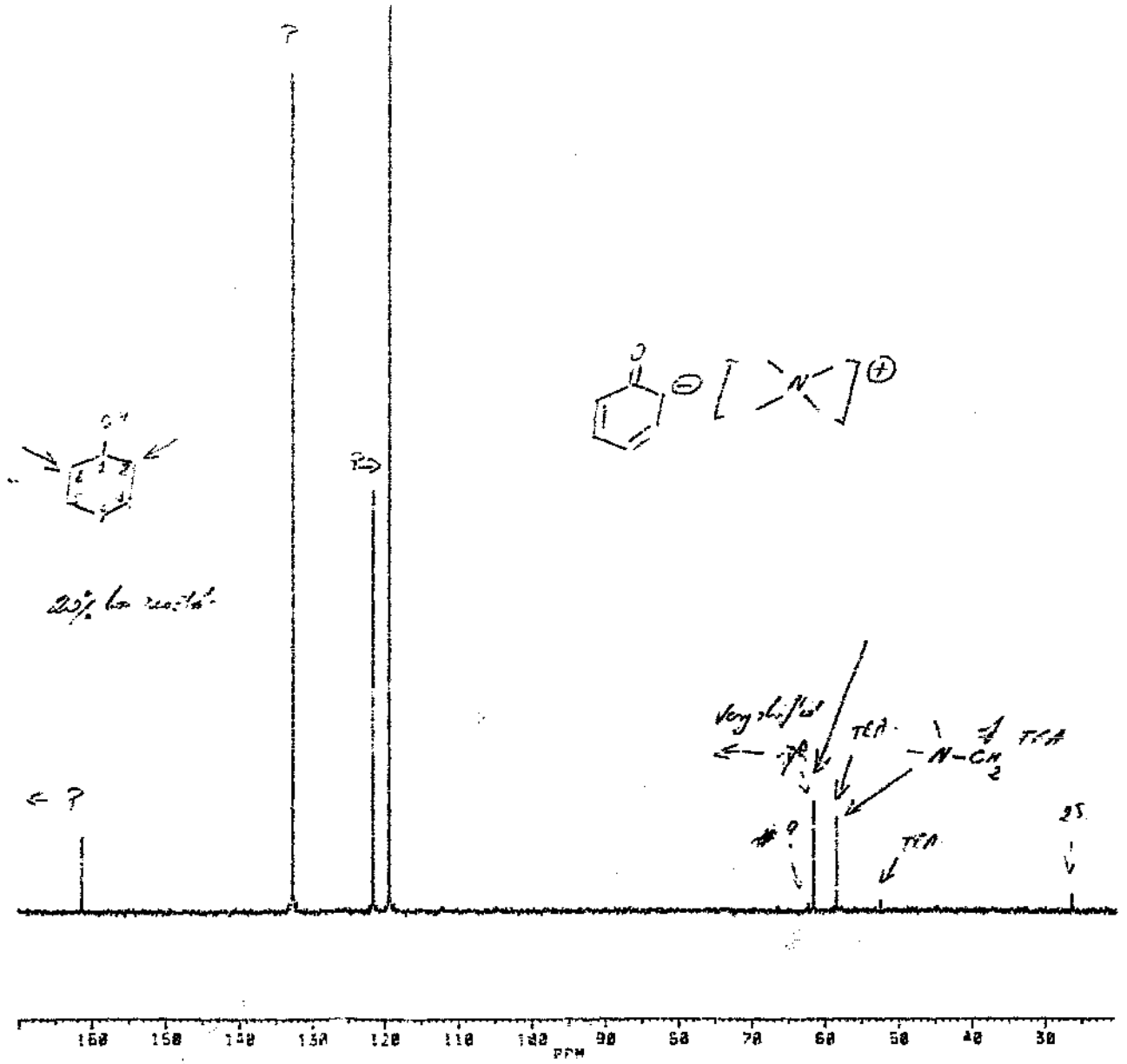


Figure 3.4.2 B **Carbon 13 NMR of Phenol : TEA Acetate 11:1 D_2O 60°C**

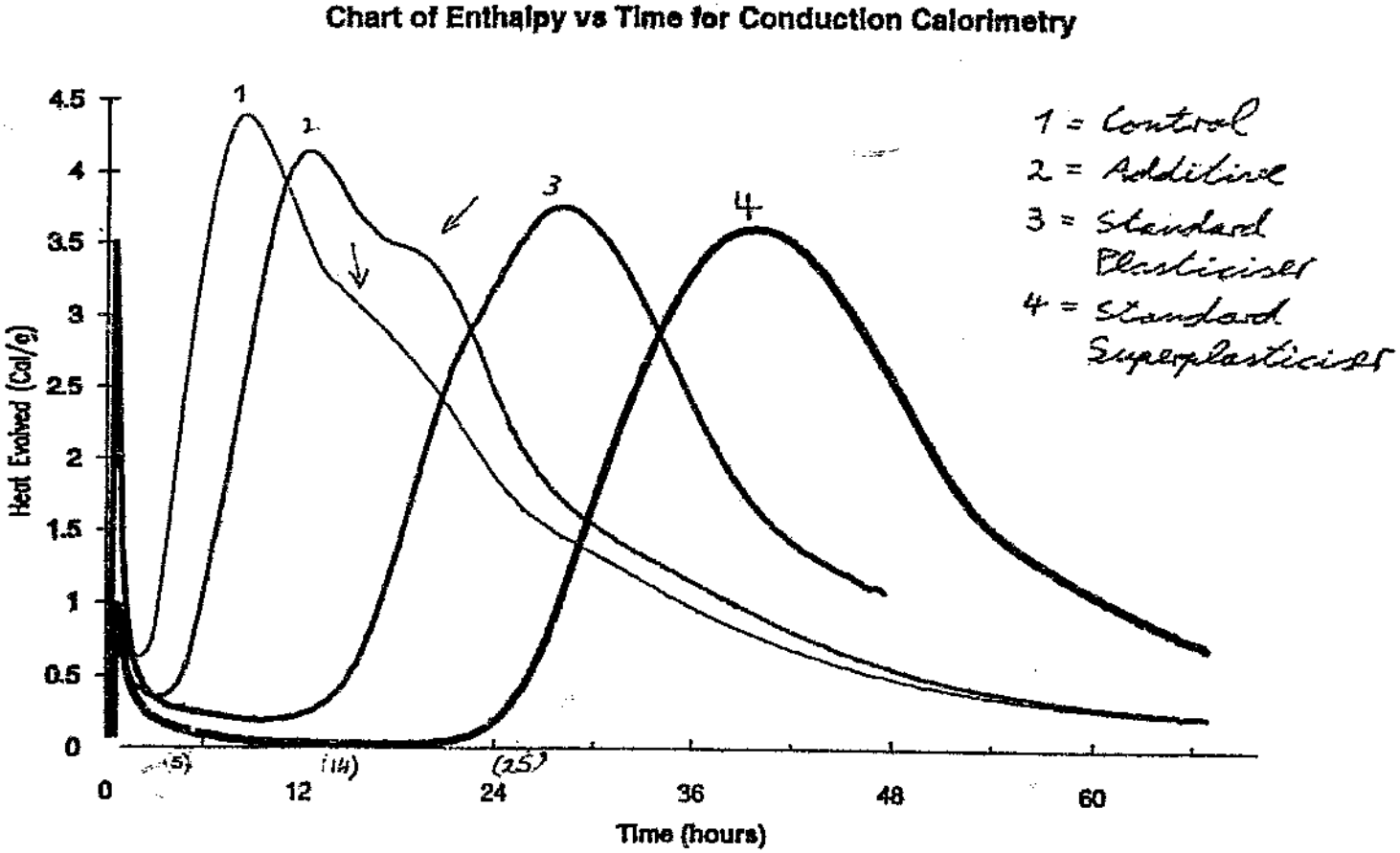


Figure 3.8 A **Hydration of an Additive Modified Cement monitored by Heat Evolution**

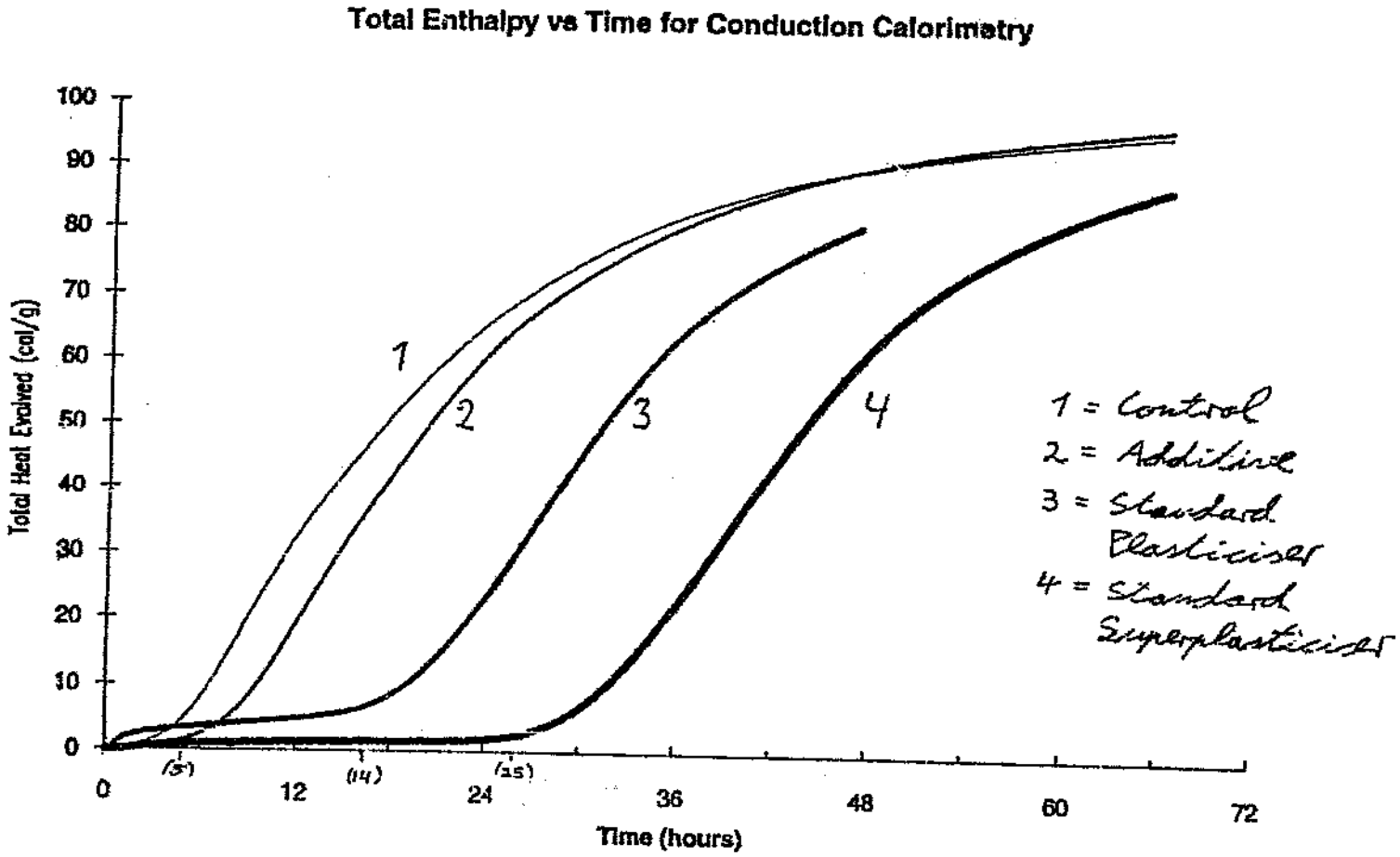


Figure 3.8 B Hydration of an Additive Modified Cement monitored by Heat Evolution (Accumulative)

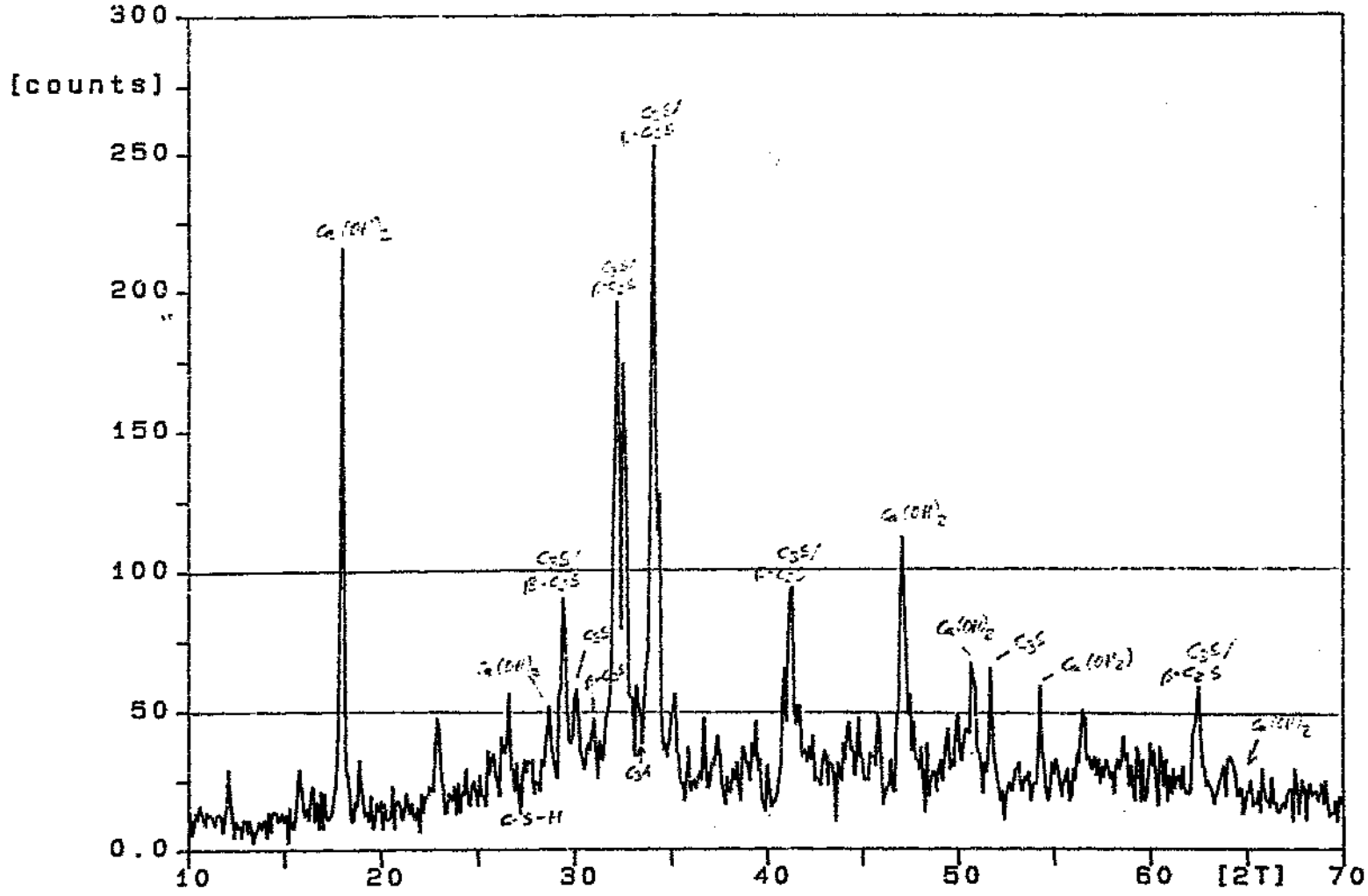


Figure 3.9 A **X-Ray Diffraction of a Hydrated Cement Paste : Control**

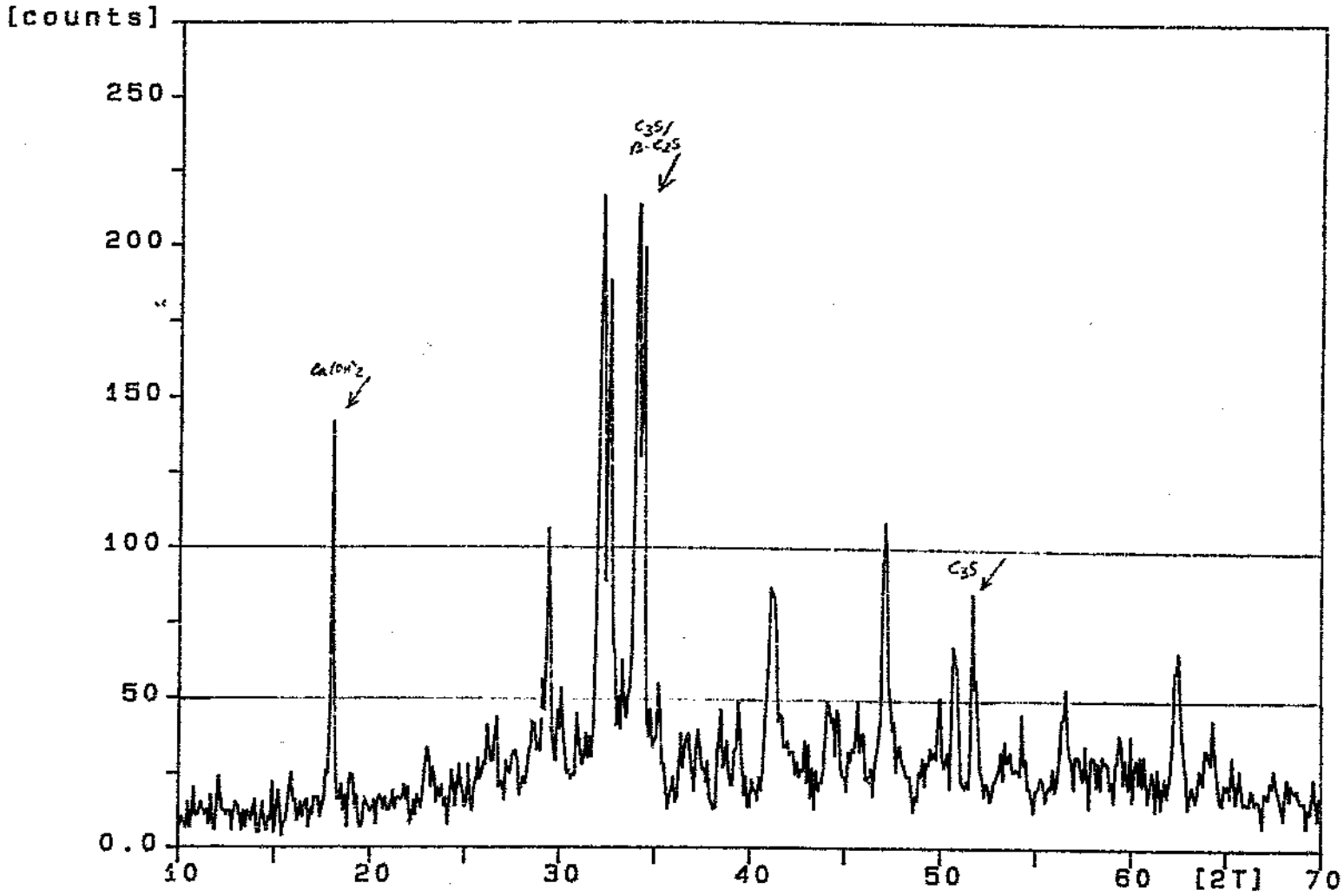


Figure 3.9 B **X-Ray Diffraction of a Hydrated Cement Paste : 0,125% dosage of Additive**

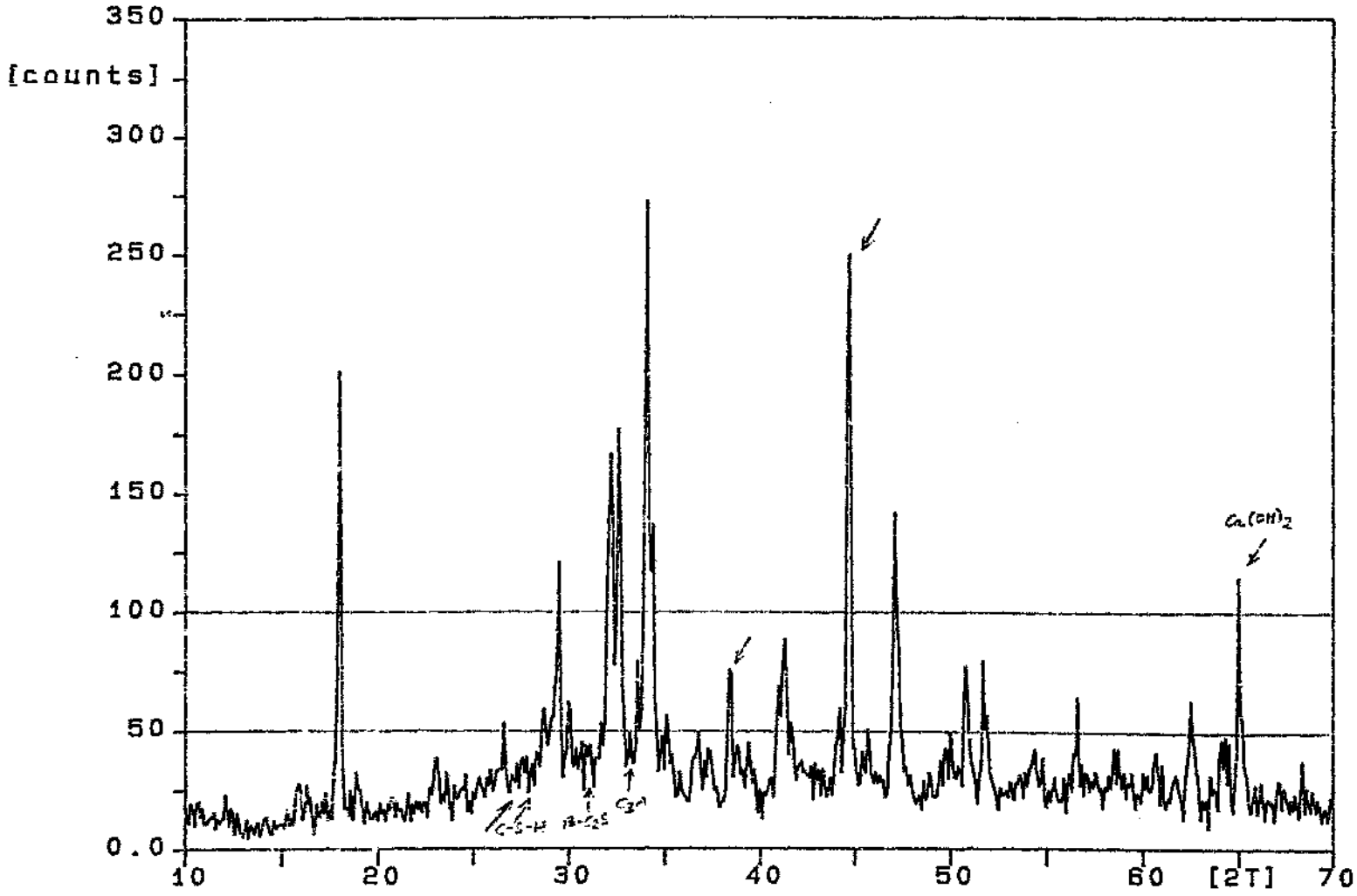
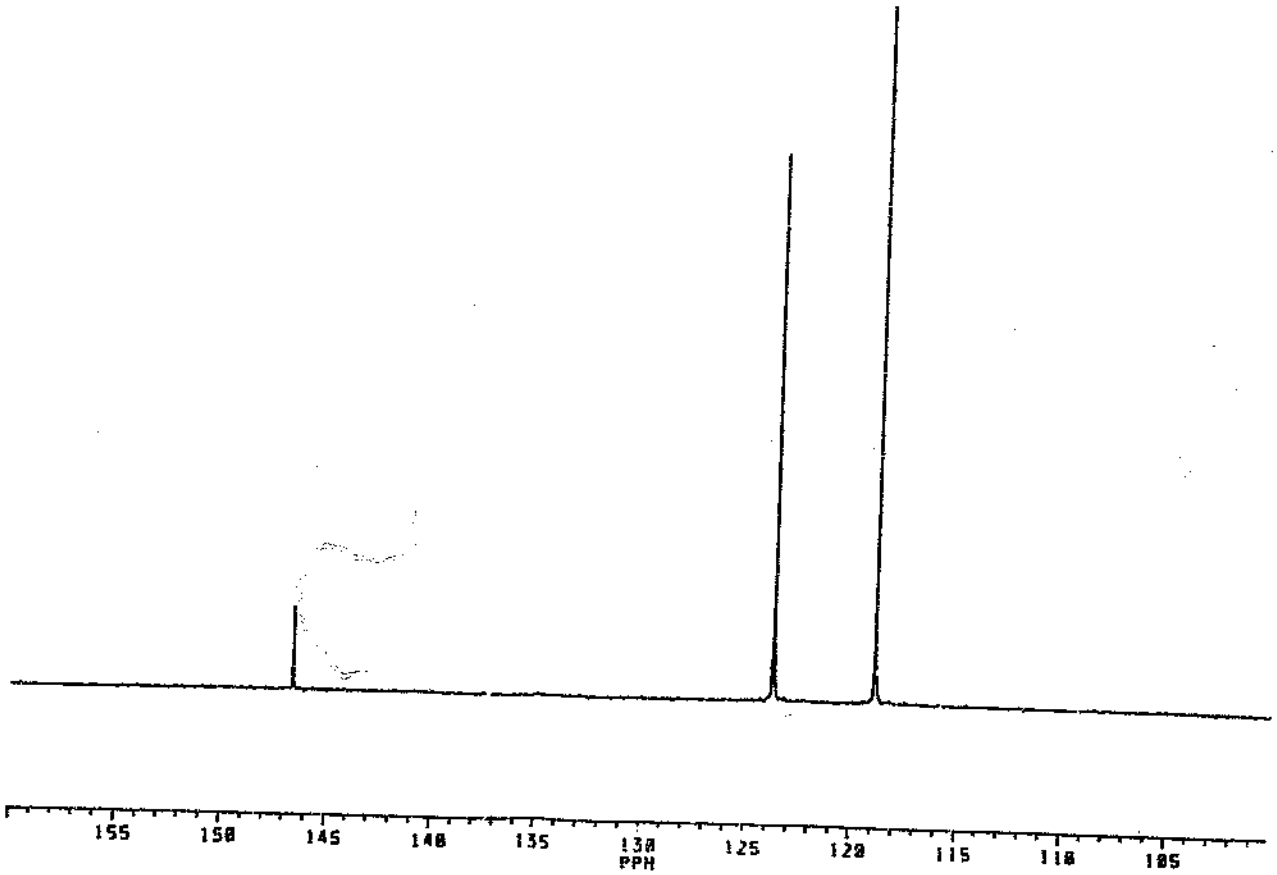


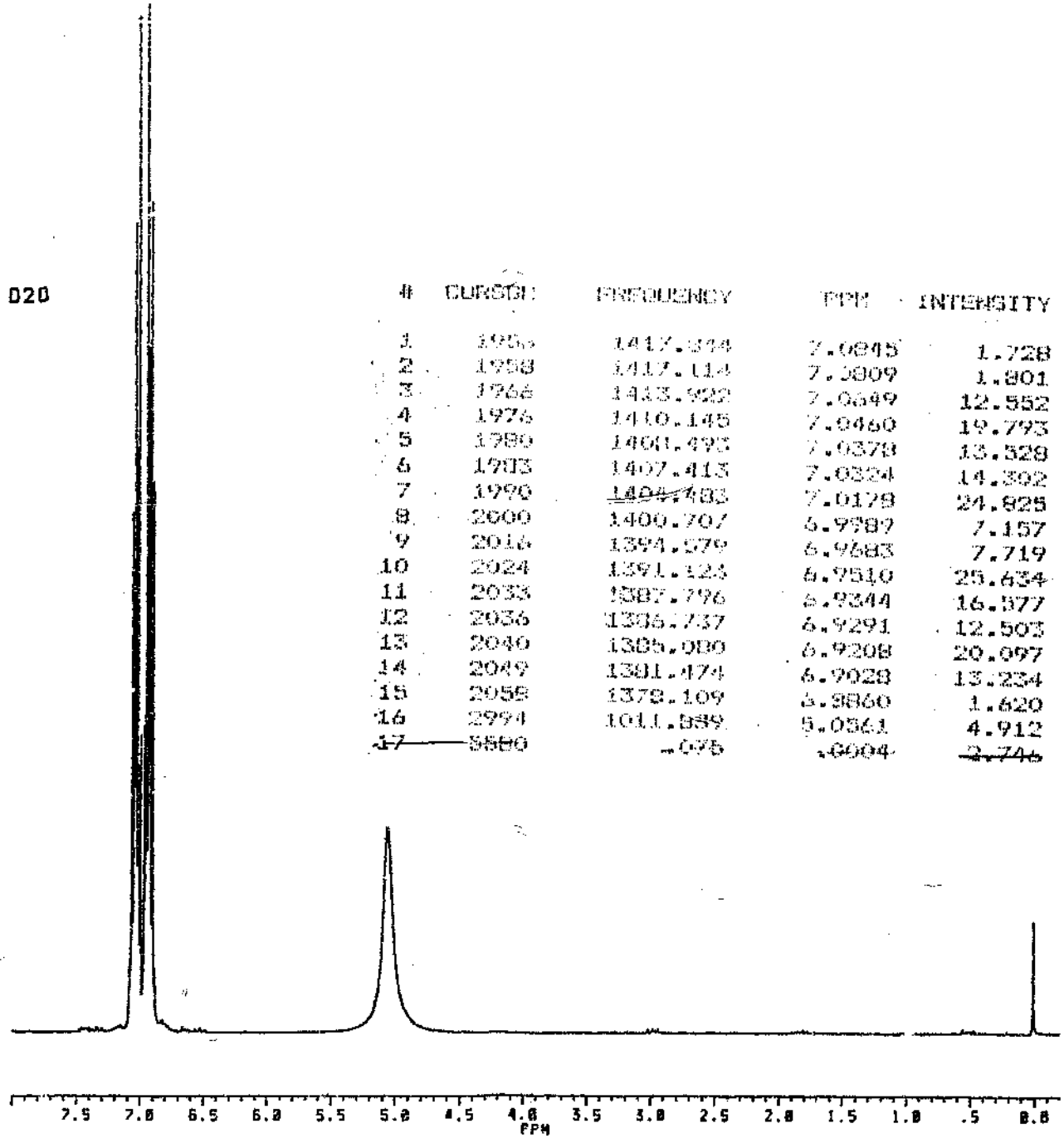
Figure 3.9 C **X-Ray Diffraction of a Hydrated Cement Paste : 0,25% dosage of Additive**

CATECHOL / D2O

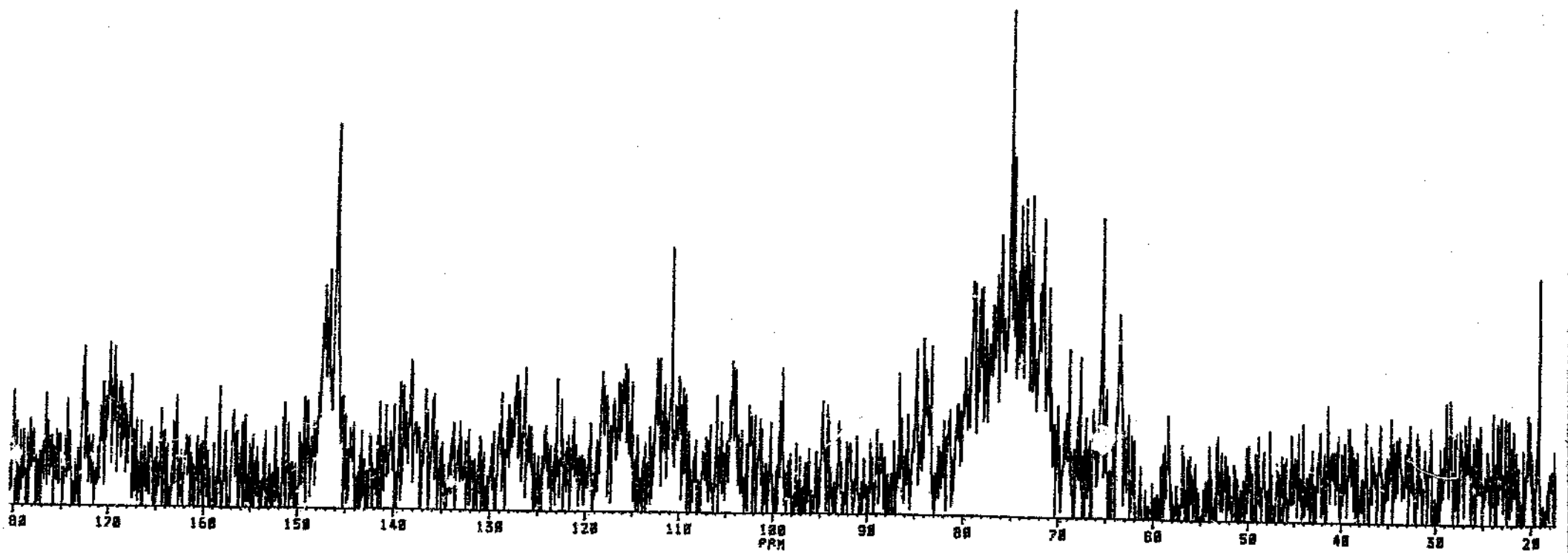


CATECHOL / D2O

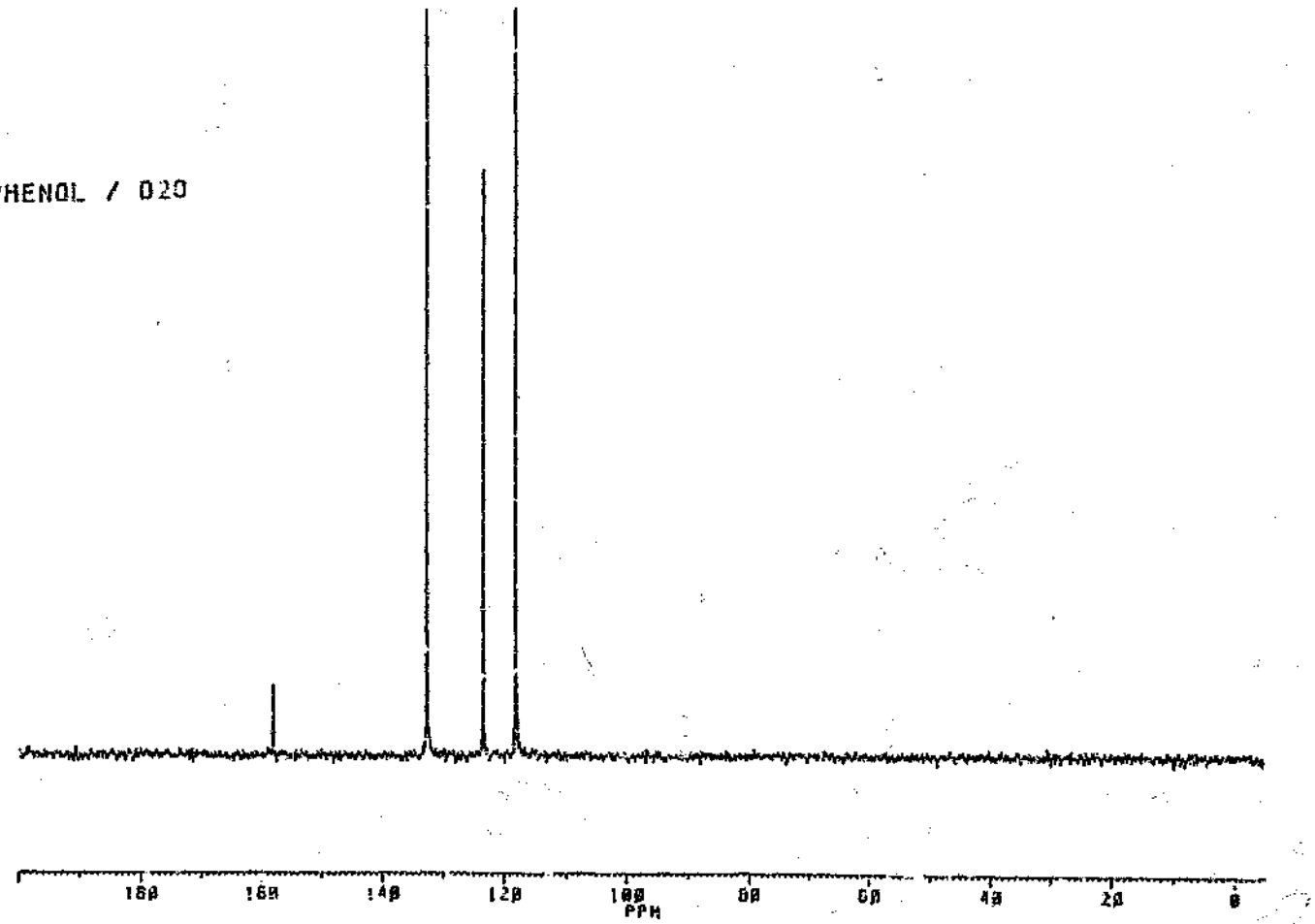
#	CURSOR	FREQUENCY	PPM	INTENSITY
1	1956	1417.334	7.0045	1.728
2	1958	1417.114	7.0009	1.801
3	1966	1413.922	7.0649	12.552
4	1976	1410.145	7.0460	19.793
5	1980	1408.493	7.0378	13.528
6	1983	1407.413	7.0324	14.392
7	1990	1404.483	7.0179	24.825
8	2000	1400.707	6.9987	7.157
9	2016	1394.579	6.9683	7.719
10	2024	1391.124	6.9510	25.634
11	2033	1387.796	6.9344	16.377
12	2036	1386.737	6.9291	12.503
13	2040	1385.080	6.9208	20.097
14	2049	1381.474	6.9028	13.234
15	2058	1378.109	6.8860	1.620
16	2994	1011.589	5.0561	4.912
17	5580	-.095	-.0004	2.746



CHESTNUT EXTRACT



PHENOL / D2O



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