

Industrial Plasticizing/Dispersion Aids for Cement Based on Polyflavonoid Tannins

H. R. E. KASPAR¹ and A. PIZZI^{2,*}

¹Department of Chemistry, University of the Witwatersrand, Johannesburg, South Africa; ²ENSTIB, Université de Nancy 1, Epinal, France

SYNOPSIS

Natural and modified polyflavonoid tannin extracts have been shown to behave as superplasticizers of cement and concrete mixes, improving fluidity without any significant retardation of the onset of hardening. This was shown by applied tests, by conduction calorimetry, and by X-ray diffraction analysis. The tannin extracts' behavior was ascribed to the balance of different effects, namely, (1) their increase in molecular mass induced by the presence of the silicate and aluminate component of cement, (2) the decrease first and then stabilization of the molecular mass and improved solubility induced by introduction of sulfonic groups in the structure of the tannin, and (3) the stabilization in the molecular mass induced by urea through its hindrance to tannin autocondensation and its decrease of tannin extract colloidal association in a water solution. © 1996 John Wiley & Sons, Inc.

INTRODUCTION

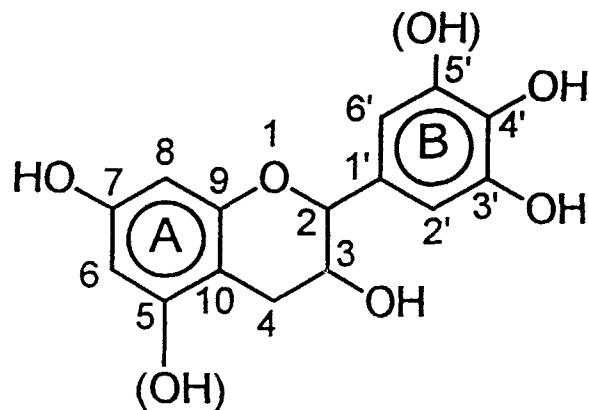
Plasticizers/dispersion agents are additives which are incorporated into concrete to improve its workability, reduce its water content needs, and to improve its strength development. Unfortunately, these properties are usually mutually exclusive. Thus, all plasticizers cause also a retardation in the setting and early strength development of concrete. Superplasticizers instead are comparatively newer products and far more effective in decreasing the viscosity and improving the workability of a fresh concrete mix than are ordinary plasticizers. This improved workability without addition of extra water does not entail a loss of final strength. It is also important that use of such additives does not result in gross retardation of concrete setting or initial low strength.¹ Superplasticizers can turn doughlike mixes into free flowing fluids and are generally based on sulfonated melamine-formaldehyde resins or naphthalene sulfonate-formaldehyde resins and

modified lignosulfonates.¹⁻³ Their remarkable plasticizing action is demonstrated by slumps of 200 mm without increases in water content or by water reductions of up to 30%.²

The mechanism by which superplasticizers produce their effect is by the sulfonic groups being oriented toward water but also adsorbing on the cement grain surface in sufficient number to form a monolayer around the grain. The combination of electrostatic repulsion and large ionic size brings about a rapid dispersion of the individual cement grains. In doing so, water trapped within the original flocs is released and can contribute to the mobility of the cement paste and, hence, to the workability of concrete. Superplasticizers do not cause much reduction in the surface tension of water. The adsorption of the anions on the surface of the cement grain is also less tenacious than in the case of retarders and the course of the hydration reaction is not hindered at normal dosage levels. Hence, for normal superplasticizers, there should not be significant retardation of setting and hardening.³

Polyflavonoid tannins are polymeric materials of natural origin⁴ which are soluble in water. The structures of their monomer units are as follows:

* To whom correspondence should be addressed.



Such structures have the capability of complexing metallic ions such as $\text{Fe}^{2+}/\text{Fe}^{3+}$ and aluminum ions through the *ortho* hydroxy groups of the B-ring of the flavonoid units.⁴ They can also be sulfonated, and often are, to improve their solubility in water, with consequent opening of their heterocyclic pyranic ring and introduction of the sulfonic group at the C2 sites of some of the flavonoid units.⁴ The tannin extracts also contain up to 20% of monomeric and polymeric carbohydrates.

These characteristics should render polyflavonoid tannins, in theory, an interesting material for use as dispersing/plasticizing agents for cements, which are materials mostly composed of silicates and aluminates of Ca and Fe. This article describes the investigation of this application of polyflavonoid tannins with some unexpected and interesting results.

EXPERIMENTAL

Tannin Origin

The tannin extracts used were commercial samples of mimosa (*Acacia mearnsii*) bark tannin extract from South Africa, quebracho (*Schinopsis balansae*, variety chaqueno) wood tannin extract from Argentina, pine (*Pinus radiata*) bark tannin extract from Chile, and pecan (*Carya illinoensis*) nut pith tannin extract from the United States.

Addition of Cold Mixtures of Model Compounds and Tannin Extracts

The additives were added at the level of 0.25% additive as 35–40% water solutions on dry cement powder. Resorcinol, phloroglucinol, and catechol were used as model compounds of the A-rings and B-rings of the flavonoids. Maltose, sucrose, and mo-

lasses were used as model compounds of the carbohydrates in the tannin extracts.

Modification of Tannin Extracts

(1) Twenty-five grams of mimosa/quebracho/pine/pecan tannin extract with 7.5 g sodium metabisulfite and 1 g KOH were dissolved in water and heated for 1 h at 70°C. This 40% solution was added at the rate of 0.25% liquid additive on solid cement. (2) Mimosa/quebracho/pine/pecan tannin extracts with the addition of sodium metabisulfite and urea according to the quantities indicated in Table II were heated for 1 h at 60°C. The solution was added at the rate of 0.25% liquid additive on solid cement, except for sample 5, where double the amount of additive was used. Triethanolamine acetate (TEA) is mixed cold, afterward, to the modified tannin.

Concrete Tests

Five concrete cubes were made, each of dimensions 70 × 70 × 70 mm, by mixing 2 kg ordinary Portland cement (Anglo-Alpha) with 1 kg fine river sand (sieved to 0.1–0.3 mm) and 2 kg medium river sand (sieved to 0.75–1.75 mm) to have an aggregate/cement ratio of 1.5. To the dry mix was added 800 g of water to obtain a water/cement ratio of 0.4.

The additive to be tested was mixed into the water added for hydration of the cement. It was added at the rate of 5 g liquid additive of 40% concentration to the above mix. The water for hydration, without any additive in the case of the control, was mixed in for 5 min in a wide dish with a small trowel. The initial workability and fluidity is tested with a standard flow funnel.⁵ 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 procedures are according to the U.S. Corps of Engineers specification 588-78/79.⁵ 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 min of mixing, the flow test is repeated and recorded after a total of 15 min mixing. After this second flow test, the concrete is poured into five cube molds which have been coated in advance with a mold-release oil. The inner part of the machined cast iron molds were of 70 × 70 × 70 mm in size. The wet concrete mix, once in the molds, was tamped with a tamping rod according to SABS 863-1976.⁶ Since the concrete mixes tested presented high workability and were almost self-compacting,

little tamping was required. The surface of the cubes was troweled flush with the top of the mold and reference numbers lightly scratched on the surface when setting had occurred. The cubes were then covered to prevent evaporation at the surface and cured at ambient temperature. Every test series had a control of five cubes and five cubes for each additive combination tested.

After 24 h, all the cube molds are removed and two of the five cubes (of the control and for each additive tested) were tested for compressive strength using a Beckman RIIC Model 00-25 mechanically operated press of up to 50 MPa capacity. The remaining three cubes of each series (including the control series) are cured under water until the next compressive strength test of another two cubes after 3 days. The remaining cube is left under water and tested in the same manner 7 days after preparation.

Conduction Calorimetry Testing

An additive composed of quebracho tannin extract : sodium metabisulfite : urea = 10 : 2.5 : 5 by mass + 5% TEA acetate (40 g tannin extract with 20 g sodium bisulfite and 20 g urea dissolved in 100 mL water and heated for 1 h at 70°C) was used. Twenty-four hours later to 95 g of this modified extract solution was mixed 5 g TEA acetate to form a solution of 44% solids content. The sample was sent to the National Research Council of Canada for conductive calorimetry testing.

Powder X-ray Diffraction of Hydrated Pastes

Forty grams of quebracho tannin extract powder mixed with 12 g sodium bisulfite and 20 g of urea were dissolved in 120 mL of water and heated for 1 h at 70°C to give a tannin extract : metabisulfite : urea mass ratio of 10 : 3 : 5. Two hours later to 90 g of this solution was added 10 g of TEA acetate. A further 24 h later, three pastes were made with a water/cement ratio of 0.4 : 1. Of these pastes, the control was composed of 450 g cement and 180 g water, while to two identical cement/water mixes were added, respectively, 0.125% additive (1 g of the 44% solution) and 0.25% additive (2 g of the 44% solution). Cement cubes were made with identical mixes. Pastes and cubes were cured for 3 days at 18°C in a conditioning cabinet. The cubes were tested for compressive strength while the hardened paste samples were ground in a ball mill and the fractions which passed a 200 mesh sieve were tested in a Phillips PW 1820 X-ray powder diffractometer in the 10°–70° 2θ° range and the X-ray diffraction

patterns recorded.⁷ Cu radiation (2θ° = 1.5405 Å) was used with a nickel filter. The powdered samples were placed on the aluminum sample holder of the camera. The traces were recorded with a detection speed of 2°/min. The different cement phases are discussed in their abbreviated forms: C₃S = 3CaO · SiO₂; C₂S = 2CaO · SiO₂; C₃A = 3CaO · Al₂O₃; and C₄AF = 4CaO · Al₂O₃ · FeO.

DISCUSSION

Strength and Fluidification of Cement by Tannins and Models

In Table I are shown the results of the development of the strength of concrete cubes after 1, 3, and 7 days from their preparation and the flow characteristics of the concrete mixes 5 and 15 min after addition of 0.25% plasticizer (by mass on dry cement powder). The results obtained with different model compounds of the phenolic nuclei of flavonoid tannins indicate that all phenolic nuclei appear to contribute to the fluidification of the cement mix. The first result of interest with the model compounds is that catechol (*ortho*-dihydroxybenzene), which can form *o*-diphenol complexes with Fe and Al, does not appear to work as a better dispersant than does resorcinol (1,3-dihydroxybenzene), which does not present complexation capabilities, or worse than does phloroglucinol (1,3,5-trihydroxybenzene). This indicates that both A- and B-rings of the flavonoids contribute, although to a different extent, to the dispersion effect and that the dispersion effect is due very little or not at all to any *o*-diphenol complexation effect of the cement constituents by part of the B-ring.⁷

A study of the effect of monomeric carbohydrates on cement setting was also necessary as commercial tannin extracts contain between 4 and 20% of monomeric and polymeric carbohydrates. In Table I, the results show that the effect of the carbohydrates is what was expected and already reported by other authors.^{3,8} The carbohydrates are powerful retarders of cement setting (note strength after 1 day), causing very low or no "green" strength but leaving undisturbed the strength of concrete after 7 days. They also have a noticeable fluidification effect on the mix. They are then at the same time powerful retarders and plasticizers. Comparison of the two profisetinidin/prorobinetinidin tannin extracts (mimosa and quebracho) show clearly that the overall effect obtained by using a raw tannin extract is somewhat an effect of compromise between the characteristics

Table I Results of Funnel Flow Test and Compressive Strength Results for Different Concrete Mixes

	Flow at		Compressive Strength		
	5 min (s)	15 min (s)	1 Day (Mpa)	3 Days (Mpa)	7 Days (Mpa)
Resorcinol	2	—	8	24	30
Catechol	19	—	5	17	30
Phloroglucinol	30	—	3	15	24
Control (no additives)	30	—	5	16	29
Maltose	18	16	0	18	34
Sucrose	20	19	0	12	30
Molasses	36	36	0	20	36
Control (no additives)	Does not flow		5	16	29
Mimosa tannin extract	10	No flow	7	20	29
Quebracho tannin extract 0.25%	35	40	10	20	35
Quebracho tannin extract 0.5%	20	25	8	19	36
Control (no additives)	Does not flow		10	19	32
Mimosa + 30% metabisulfite	18	18	6	18	34
Pine + 30% metabisulfite	18	18	5	17	31
Quebracho + 30% metabisulfite	15	15	3	20	32
Pecan + 30% metabisulfite	Does not flow		8	21	32
Control (no additives)	Does not flow		6	19	34
Mimosa + S ₂ O ₅ ²⁻ + urea + TEA	22	15	9	24	29
Pine + S ₂ O ₅ ²⁻ + urea + TEA	17	4	10	22	29
Pecan + S ₂ O ₅ ²⁻ + urea + TEA	21	No flow	4	31	32
Control (no additives)	Does not flow		5	18	28
Sulfited MF control	19	12	9	21	26

of the phenolic component of the extract (the tannin) and its carbohydrate component. Thus, they noticeably fluidify the cement, they appear to maintain the mix fluidity over some time (15 min at least), and, most important, they do not decrease much, if at all, the green strength of the concrete. The final strength is also unaffected. This is an excellent result as it means that these materials present inherent superplasticizer behavior (fluidification + no retard of setting + good green strength + good final strength).

In the case of the raw tannins, it can also be seen that increase in dosage from 0.25 to 0.5% further improves fluidification, but starts to affect somewhat the green strength after 1 day, but still to an extent which is acceptable. It is interesting to note that the tannin extract which hardly contains any carbohydrates, namely, pecan tannin (3–4% of only monomeric carbohydrates), does not show a fluidifying, plasticizing behavior. This indicates that the carbohydrate fraction is an important component for obtaining the wanted effect. Thus, sulfonation of

the tannin contributes to fluidification, but sulfonation of monomeric and polymeric carbohydrates is also a definite contributor to fluidification (but not to green strength) as has already been shown by the commercial use as plasticizers of sulfonated molasses.⁸

Other tannin modifiers can contribute to further improve the superplasticizer behavior of the tannin extracts. In Table II, it is possible to see that addition of urea⁹ and of triethanolamine acetate⁸ also improve the balance of effects in the tannin-based superplasticizer. Two of these formulations (nos. 5 and 6) have now been commercial for 2 years.

Molecular Level Flavonoid Tannin Rearrangements

It is interesting to understand why tannin extracts as such, or modified, can behave as cement superplasticizers. The first characteristic of the tannin-based superplasticizers is not just the fluidification effect, but, mainly, the maintenance of excellent

Table II Tannin Extracts at Different Levels of Modification

	Control	1	2	3	4	5	6	7	8
Quebracho	—	50	50	50	50	50	—	—	—
Mimosa	—	—	—	—	—	—	50	50	50
KOH	—	0.5	0.5	0.5	0.5	0.5	0.5	0.5	0.5
TEA acetate	—	—	—	—	—	—	10	10	10
Na ₂ S ₂ O ₅	—	—	—	5	5	5	—	5	—
Urea	—	—	—	—	10	10	—	—	10
Flow 5/15 (s)	-/-	69/-	39s/-	75/-	24s/-	23/25	25/5s	25/8s	25/12s
Compression strength (MPa)									
After 1 day	9	7.5	7	7	9.5	8	6	6	7
After 3 days	20	18	22	20	20	26	20	20	25
After 7 days	26	26	29	26	29	31	31	31	32

5 = double dosage of 4, i.e., 0.50% on dry cement weight. s = stop of flow after initial movement.

green strength after cement setting. The mechanism by which superplasticizers produce their effect is very similar to that of normal plasticizers: The main difference is that the former consists of much larger molecules forming charged colloidal solutions.^{3,10} Polyflavonoid tannins have a number-average degree of polymerization (DP_n) varying between 4.9 (mimosa)^{11,12} and 6.7 (quebracho),^{11,12} already at the lower end of the superplasticizer range.³ Sulfonation, while improving their surfactant behavior, also tends to decrease their average DP_n and number-average molecular mass (M_n).^{11,12} Recently, however, it has been shown that silica can function under alkaline conditions as a powerful catalyst of the autocondensation reaction of tannins.⁷ Traces of small amounts of weak Lewis acids such as silica, silicic acid, and silicates and aluminum trichloride induce rapid autocondensation of the tannin solutions under alkaline conditions to polymers of higher molecular weight and even to hardening.⁷ The reactive C2 site on the flavonoid structure so-formed condenses then with the A-ring of a flavonoid unit of another chain. This leads to noticeable increases in molecular weight of the tannin and, under particular conditions, even to networking and hardening. Cement contains approximately 17–25% hydrated silica in the form of calcium silicate and 3–8% alumina in the form of aluminates. As it is also the hydration of such cement components which leads to cement setting and hardening, the existence of the silica-induced and -catalyzed autocondensation of the tannin contributes (1) to move the molecular mass of the tannin at first well into the superplasticizers range, with similar effects, and (2) by tannin net-

working and hardening to contribute to the initial green strength of cement.

Tannin sulfonation limits the extent of autocondensation, as already demonstrated,^{4,7} and this limits the extent and rate of hardening by partly blocking in advance some of the C2 reactive site: The first effect becomes then the most important one. Urea has both the same effect of reacting at the C2 site,⁹ hindering autocondensation,^{9,14} but also diminishing the interaction between colloidal particles of the tannin,^{13,14} allowing better dispersion of and better results from the material. It is the tension between these two effects, the silica-induced tannin autocondensation and the extent of its prereaction with metabisulfite and urea, which is the parameter affecting the performance of a tannin as a superplasticizer.

Hydration of an Additive-modified Cement by Heat Evolution

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 cement hydration as a function of time. Most of the heat is released during the first 72 h of hydration. This technique was also used to compare the behavior of a tannin additive with that of established superplasticizers. A tannin additive of a mass ratio of quebracho tannin extract : sodium metabisulfite : urea = 10 : 2.5 : 5 and heated for 1 h at 70°C and with the addition at ambient temperature, 24 h later, of TEA acetate 5% by mass was used. The sample

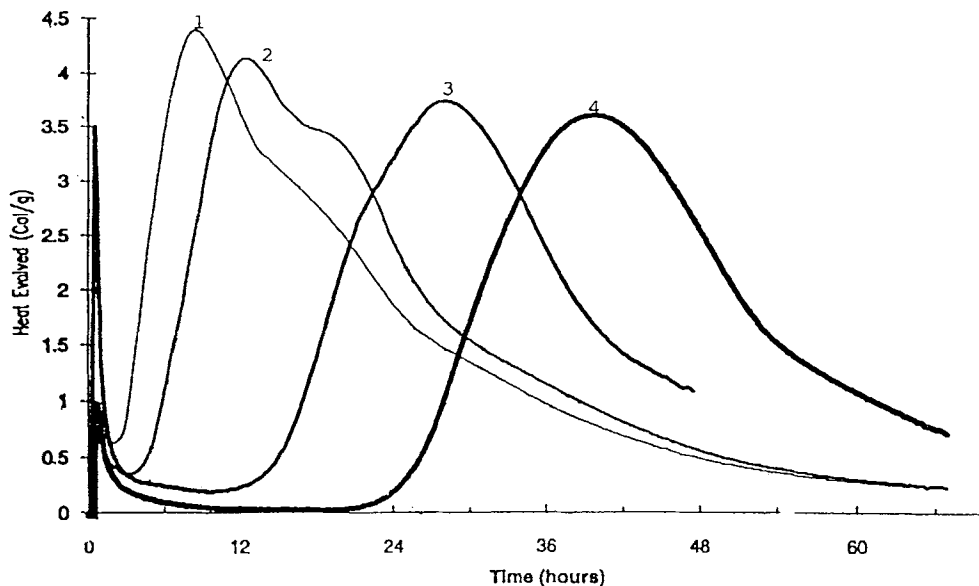


Figure 1 Heat-evolution curves as a function of time for the hydration of additive-modified cement mixes: (1) control; (2) tannin additive; (3) standard plasticizer; (4) standard superplasticizer.

was tested with cement for 72 h and run concurrently with a control mix, a mix with a standard commercial plasticizer, and a mix with a standard commercial superplasticizer. Two plots of the data were made: one representing heat evolved as a function of time (Fig. 1); the other representing total (cumulative) heat evolved in function of time (Fig. 2).

Figure 1 shows that the experimental tannin additive follows closely the heat released and, hence, the degree of hydration of the control. The clearly defined second peak of the tannin additive curve indicates that in the presence of the tannin additive a certain cement-phase hydration is stronger after the faster hydration phase. Taking current literature

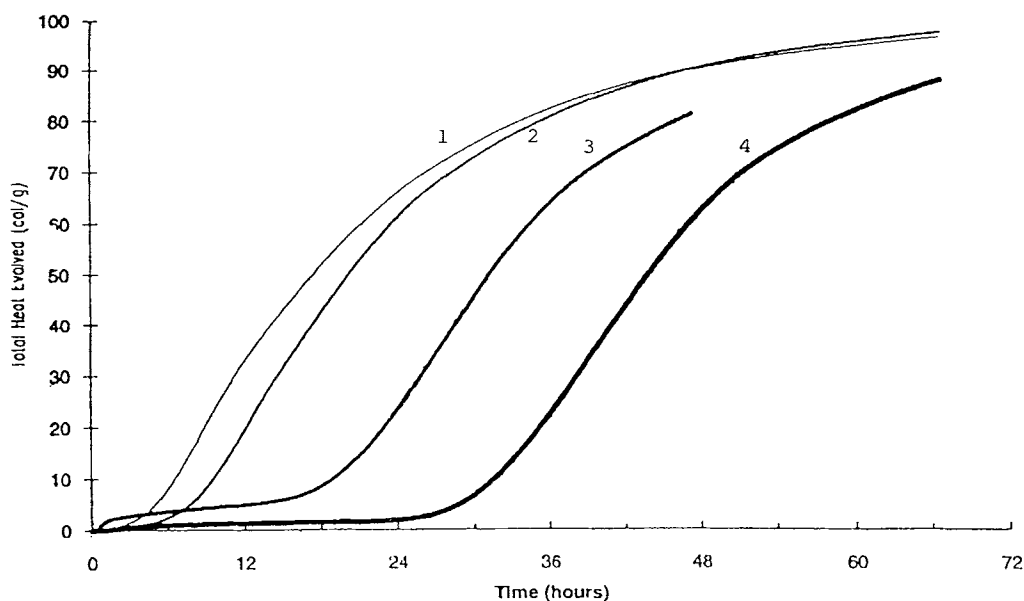


Figure 2 Cumulative heat-evolution curves as a function of time for the hydration of additive-modified cement mixes: (1) control; (2) tannin additive; (3) standard plasticizer; (4) standard superplasticizer.

into account,¹⁵ the first hydration peak could well represent the C_4AF phase and, the second, the enhanced peak of the C_3A phase. From the curves in Figures 1 and 2, it appears then that the experimental tannin additive, which has already shown its plasticizing ability in the more applied tests, interferes less with the initial hydration of cement than does a standard plasticizer. This means that there is a much shorter dormant period for the tannin additive (about 5 vs. 14 h) for the initial hydration, which is only approximately 2 h longer than for the control.

In this respect, compared to a standard superplasticizer (Figs. 1 and 2), the experimental tannin additive provides an even greater advantage. The approximately 24 h setting advantage can be reduced, if and when needed, by using the tannin additive at twice its normal dosage to obtain characteristics closer to the commercial superplasticizer. The curves of cumulative heat vs. time (Fig. 2) give 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 48 h hydration has proceeded to the same extent and, consequently, the compressive strengths of the concrete should be almost the same. At this stage, the standard plasticizer, at about the same level of a given plasticization, would have considerably lower strength; this is the reason why higher amounts would need to be used. It is also interesting to note that after 48 h the additive overtakes the control in hydration by only a small margin. It also means that the Canadian cement used for conductive calorimetry responds less in strength development to the additive, from around 1 to 3 days curing, than the South African cement used for the more applied part of this study, with which after 3 days considerable strength advantages were obtained. Therefore, also the composition of the cement used appears to be of importance in its response to the additive: a fact also well known for other types of additives.

X-ray Diffraction of Hydrated Cement Pastes

Powder X-ray diffraction is a widely used method for identifying the components of mixtures containing many crystal phases, as well as establishing structure-property relationships for such materials. It is the main well-established method for the quantitative determination of crystal phases in cement.¹⁶

As can be seen from the literature,¹⁷⁻²⁵ the major phases in cement clinker are C_3S , β - C_2S , C_3A , and C_4AF . Of these, C_3S and β - 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 90% hydrates within 1 day. It is therefore difficult to detect in hydrated pastes. Both C_3S and β - C_2S hydrate to give an amorphous calcium silicate hydrate gel (C—S—H gel) which is difficult to identify on diffractograms. One byproduct of this hydration is coarsely crystalline $Ca(OH)_2$ (portlandite) which can, instead, be clearly seen on the diffractogram.

The diffractograms in Figures 3-5 show the results obtained for a cement control hardened without any additives and the same mix hardened with 0.125 and 0.25% of the tannin additive, respectively. Compression cubes were also made at the same time with the three mixes and the strength results after 3 days were of 29, 30, and 34 MPa for the control and the 0.125 and the 0.25% additive mixes, respectively. The half-dosage application therefore had virtually no influence on early strength development.

Comparing the progress of hydration of the control (Fig. 3) with the 0.125% additive case (Fig. 4), the $Ca(OH)_2$ peak¹⁵ appears considerably higher in the control. This implies a much stronger hydration toward crystal formation for the control, which is not realistic since the corresponding cube strength tests show that the control presented strength slightly below that of the 0.125% additive mix. However, $Ca(OH)_2$ can grow in the form of hexagonal plates¹⁵ in the cement paste. This would lead to preferential orientation of $Ca(OH)_2$ when the hardened cement powder is packed in the X-ray diffraction sample holder, which could explain the disproportionately intense peak of $Ca(OH)_2$ for the control. The $Ca(OH)_2$ peaks are therefore unsuitable to follow realistically the hydration reactions.

There are some small changes in intensity in the peaks corresponding to both the β - C_2S and C_3S phases: The doublet at $34^\circ\theta$ has a shorter left peak and a longer right peak than for the control (Figs. 3 and 4). This indicates preferential hydration of one of the silicate phases, which appears to be the β - C_2S phase, since a peak at $52^\circ\theta$ characteristic of C_3S is higher for the additive sample (Fig. 4). The preference is not great, since the compressive strengths are virtually the same for the control and for the 0.125% additive sample. Together, the compressive strength and the X-ray 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 0.25% level (Fig. 5) with the control (Fig. 3). Peaks characteristic of the β - C_2S and C_3S phases again show some small but sig-

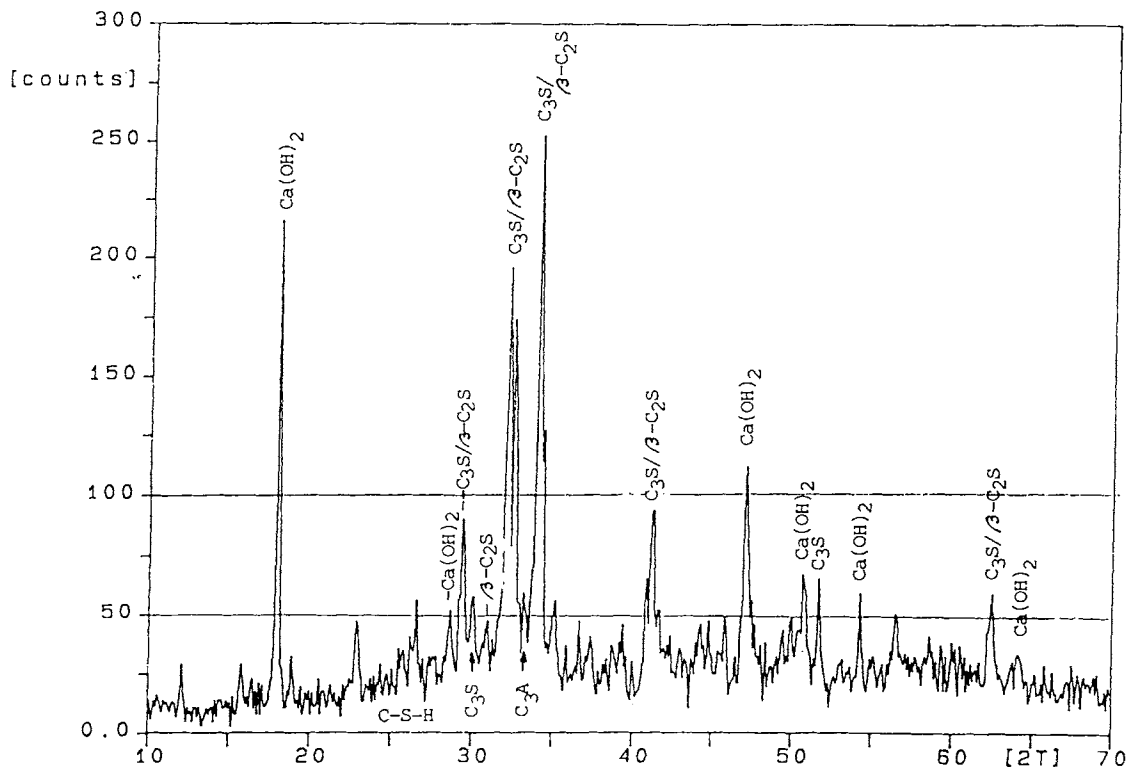


Figure 3 X-ray diffraction pattern of hydrated cement paste: control.

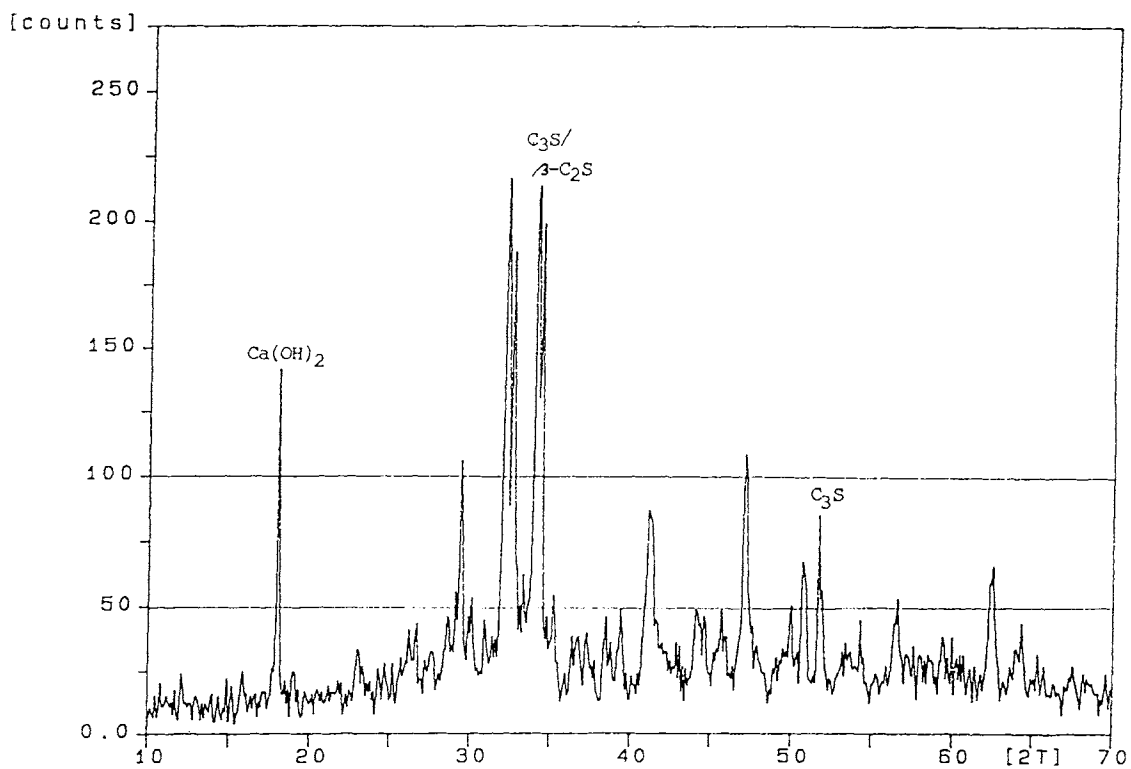


Figure 4 X-ray diffraction pattern of hydrated cement paste: 0.125% dosage of tannin additive.

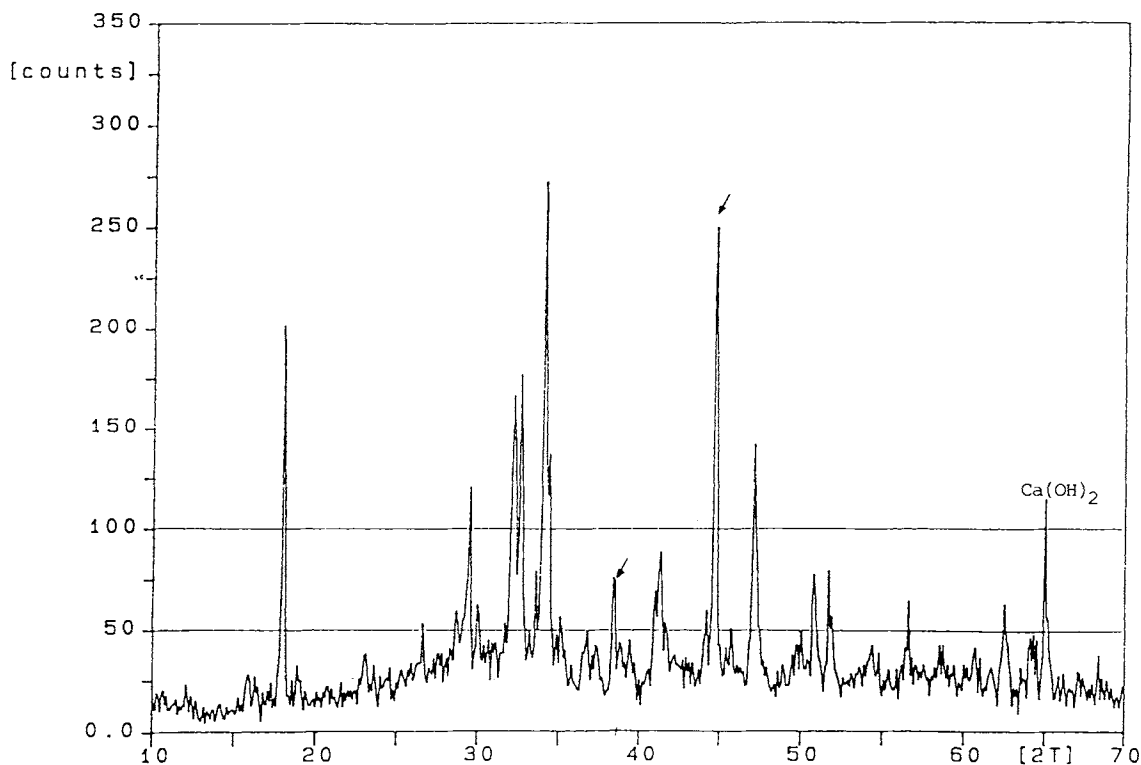


Figure 5 X-ray diffraction pattern of hydrated cement paste: 0.25% dosage of tannin additive.

nificant changes. A small peak at $31^\circ\theta$ denotes that β - C_2S has slightly decreased. This is unusual since this phase is the slowest one to hydrate,¹⁷ but lends support to the observation made from the diffractogram of the 0.125% sample.

More noticeable is a decrease of the peak at $33^\circ\theta$ corresponding to the C_3A phase, which is the one known to be the second most rapid one to hydrate. It is known that C_3A requires much more water to hydrate than do the silicate phases. The tannin-based additives have shown their ability as water reducers by improving workability and mix fluidity, this being the result of freed water and improved wetting action.^{1,26} This means more available water for hydration of the cement particles. Since the pastes were made with the same water/cement ratio as that of the control, more water was available for hydration of the "thirsty" C_3A phase. Two new peaks, at $39^\circ\theta$ and an intense one at $45^\circ\theta$, are the peaks belonging to the intermediate reaction compound formed between silica and tannin⁷ during tannin autocondensation. This confirms previous results that the presence of the tannin decreases somewhat the silica crystallinity (not much), but mainly that the original silica and silicate crystalline network has been considerably distorted.⁷ This con-

firms previous ²⁹Si-NMR results indicating the change of coordination number of Si and introduction of another atom (an O from the tannin) in the $Si(O_{1/2})_4$ network. This confirms that part of the $Si(O_{1/2})_4$ is linked to the tannin,⁷ as found by ²⁹Si-NMR,⁷ this being partly a transitory phase in the autopolymerization of the tannin and partly a stable situation in a hardened network.⁷

Also new is the appearance of an intense peak at $65^\circ\theta$ which indicates a different phase of $Ca(OH)_2$, in line with the variation of orientation of its hexagonal plates suggested earlier. There is an increase in the background level, compared to the other two diffractograms in the 25° to $30^\circ\theta$ range, indicating an amorphous material: the C—S—H gel. Since β - C_2S and notably C_3S hydrate to produce $Ca(OH)_2$ and C—S—H gel, this peak and this region 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 compressive strengths obtained for the additive mix.

In conclusion, the tests done indicate that at a 0.25% dosage the tannin-based additive is effective as a superplasticizer mainly by improving the hydration of the β - C_2S phase and, more noticeably, of the C_3A phase and, thus, the overall hydration

of cement. This sheds some more light also on the mechanism of silica-induced⁷ and aluminum-induced⁷ autocondensation of tannins and the linkage between the two materials.

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REFERENCES

1. P. C. Hewitt, *Cement Admixtures: Uses and Applications*, 2nd ed., Longman Scientific and Technical, The Bath Press, London, 1988, Chap. 1.
2. S. M. Khalil, *Cement Concrete Res.*, **3**, 677 (1973).
3. P. C. Hewitt, *Cement Admixtures: Uses and Applications*, 2nd ed., Longman Scientific and Technical, The Bath Press, London, 1988, Chap. 7.
4. A. Pizzi, in *Wood Adhesives Chemistry and Technology*, A. Pizzi, Ed., Marcel Dekker, New York, 1983, Vol. 1, Chap. 4.
5. U.S. Corps of Engineers, Specification 588-78/79 (1979).
6. South African Bureau of Standards, specification SABS 863-1976 (1976).
7. N. Meikleham, A. Pizzi, and A. Stephanou, *J. Appl. Polym. Sci.*, **54**, 1827 (1994).
8. H. R. E. Kaspar, MSc Thesis, University of the Witwatersrand, Johannesburg, South Africa, 1994.
9. V. J. Sealy-Fisher and A. Pizzi, *Holz Roh Werkstoff*, **50**, 212 (1992).
10. P. C. Kreijgler, in *Proceedings International Congress on Admixtures*, London, April 1980, C180.
11. D. Thompson and A. Pizzi, *J. Appl. Polym. Sci.*, **55**, 107 (1995).
12. M. Fechtal and B. Riedl, *Holzforschung*, **47**, 349 (1993).
13. S. Kim, D. Saratchandra, and D. E. Mainwaring, *J. Appl. Polym. Sci.*, **56**, 905 (1995); **56**, 915 (1995).
14. A. Pizzi and A. Stephanou, *Holzforsch. Holzverwert.*, **45**(2), 30 (1993).
15. L. E. Copeland and R. H. Bragg, *Portland Cement Association Report*, Chicago, May 14, 1953.
16. G. C. Bye, *Portland Cement: Composition, Production and Properties*, Materials Engineering Practice Series, Chaps. 5, 7, and 8, Pergamon Press, London, 1983.
17. A. M. Neville, *Properties of Concrete*, 2nd ed., Pitman, London, 1975, Chap. 1.
18. E. P. Flint and L. S. Wells, *J. Res. Natl. Bur. Stand.*, **12**(687), 751 (1934).
19. S. Brunauer, *Portland Cement Assoc. Res. and Dev. Bull.*, No. 138, 1962.
20. H. H. Steinour, *Portland Cement Assoc. Res. Bull.*, No. 98, Nov. 1958.
21. G. Malquori and V. Cirilli, in *Proceedings of the 3rd International Symposium on the Chemistry of Cement*, London, 1954.
22. F. S. Fulton, *Concrete Technology*, 4th ed., Portland Cement Inst., Cape Town, 1969, Chap. 1.
23. L. S. Brown and R. W. Carlson, *ASTM Proceedings* **36**, Part 2, 1956, pp. 332-350.
24. L. E. Copeland, *J. Am. Concrete Inst.*, **52**, 863 (1956).
25. L. E. Copeland, D. L. Kantro, and G. Verbeck, in *Proceedings of the 4th International Symposium on the Chemistry of Cement*, Washington, DC, 1960, pp. 429-465.
26. M. E. Prior and A. B. Adams, *ASTM Spec. Techn. Pub.*, No. 266, 1960, pp. 170-179.

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