

Laboratory Optimisation of a Urea-Formaldehyde Soil Stabiliser

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Synopsis

The Indirect Tensile Strength (ITS) was used to characterise the soil stabilising properties of a urea-formaldehyde (UF) resin. The test soil was brown shale gravel. Synergistic strength improvements were obtained when combining the resin with anionic bitumen emulsion and dosing both at 2%. Performance levelled off above these concentrations. For full strength development, the soil moisture content must be reduced to below 3%. Optimum indirect tensile strength is obtained at formaldehyde to urea molar ratio of 2:1. Soil strength increases as the reaction pH is lowered but the need for adequate application times restricts it to pH > 4,5. The experimental results also suggest that the presence of appropriate organic matter is critical for effective soil stabilisation with UF resin.

KEYWORDS: soil, stabilisation, urea formaldehyde resin, strength

Sinopsis – Laboratorium Optimisasie van 'n Urea-Formaldehyd

Grondstabiliseerder. Die Indirekte Treksterkte (ITS) is gebruik om die grondstabilisasie-eienskappe van 'n urea-formaldehyd hars (UF) te kwantifiseer. Die toetsgrond was 'n bruin skaliegruis. Kombinasie van die hars met 'n anioniese bitumen emulsie toon sinergistiese sterkteverbetering wanneer beide doseer word op die 2% vlak. Werkverrigting plat af bokant hierdie konsentrasies. Vir volle sterkte-ontwikkeling moet die grondvogtigheid verlaag word tot onder 3%. Optimale indirekte treksterktes word behaal met 'n formaldehyd-tot-urea molverhouding van 2:1. Grondsterkte neem ook toe soos die reaksie pH verlaag word maar vir pH < 4,5 word die beskikbare aanwendings tyd ontoereikend. Die eksperimentele resultate dui ook daarop dat die teenwoordigheid van 'n geskikte organiese fraksie in die grond krities is vir effektiewe stabilisasie met UF hars.

SLEUTELWOORDE: grond, stabilisasie, urea-formaldehyd hars, sterkte

1. INTRODUCTION

Its low cost and ready availability should make soil an ideal material for road construction. Unfortunately, soil usually has a low wet strength and exhibits poor volume stability with respect to moisture content. The usual high water permeability further exacerbates these undesirable properties. Soil stabilisation is the process whereby the existing engineering properties are modified to such an extent that the soil becomes a useful material of construction. Ideally the stabilised road material must be able to offer sustained resistance to deformation under repeated loads in both wet and dry conditions (Ballantine and Rossouw, 1989). Desired soil property improvements include increased workability during construction, as well as higher strength, durability and dimensional stability in the end-use application. Cement, lime, bitumen and tar are well-established soil stabilisers with proven track records (Road Research Laboratory, 1952).

The soil volume stability refers to its ability to resist swelling and shrinkage with changes in moisture content. Swelling, in particular, is a problem associated with clayey soils. It can cause disintegration of road surfaces and cracking of buildings. Several strategies are employed to prevent, or at least reduce, shrinkage and swelling. One approach aims to reduce the intrinsic tendency of the clay component to swell. This can sometimes be achieved by the simple addition of lime to the soil. Another approach seeks to prevent water ingress, e.g. by sealing soil pores with hydrophobic additives such as bitumen. Converting the soil into a granular mass can reduce the effect of moisture. Binding the soil particles together by a cementation process can also improve soil stability (Ballantine & Rossouw, 1989).

Resins based on formaldehyde condensation products are widely used as binders in industry (Diem and Matthias, 1986). Owing to their low cost, these polymers could provide commercially viable alternatives to traditional soil stabilisers (Ebdon *et al.*, 1990). In a previous paper (Germishuizen *et al.*, 2002) we have reported on the application of a proprietary urea-formaldehyde (UF) resin as a soil stabiliser. Excellent wet and dry strengths were obtained when the UF resin was used in combination with either Portland cement or bitumen emulsion. Surprisingly, strength development levelled off above very low resin additions (ca. 2%). This paper describes the laboratory optimisation of this UF resin based stabiliser system. The indirect tensile strength (ITS) was used as a measure of soil stabilisation efficacy. The effects of cure pH; reactant stoichiometry; the type of bitumen emulsion used; and the importance of organic soil components on stabilisation performance were investigated. The influence of soil moisture content and stabiliser dosage level was also evaluated.

2. EXPERIMENTAL

Unless otherwise stated, all experiments were carried out at a constant temperature of 23°C.

Reagents. Technical grade formaldehyde solution (37% stabilised with 7% methanol) and fertiliser grade urea (46% N) were obtained from commercial sources. Chemically pure citric acid, calcium hydroxide and sodium hydroxide were obtained

from Chemical Supplies and used as is. Anionic bitumen emulsion (Grade SS60) and cationic bitumen emulsions (Grades KRS60 and KMS60) were obtained from Tosas.

Resin sample preparation. Resin mixtures were prepared by dissolving the appropriate amount of solid urea in (diluted) formaldehyde solution. The pH was then adjusted to the required value by adding either citric acid or sodium hydroxide. Where necessary, the required quantity of bitumen emulsion was added. The effects of pH and reactant stoichiometry on resin gel-time were determined on 10 ml samples. For the temperature effect 200 ml samples, placed in a water bath, were used. The pH was varied from 3 to 8 and temperature from 13°C to 34°C. Viscosity changes during the cure reaction were followed with a Brookfield viscometer.

Synthesis of formose. The formose solution was prepared by condensing a formaldehyde solution in an alkaline medium (Weiss and Socha, 1980). 100 g water was added to 100 g of a 37 % formaldehyde solution and heated to boiling point. 1 g of $\text{Ca}(\text{OH})_2$ was added to the boiling mixture every 15 to 20 minutes until a total of 9 g was added. The reaction mixture turned dark brown after 2,5 hours. After 6 hours the mixture was allowed to cool to room temperature.

Test soil. The properties of the brown shale used in this study are presented in Appendix A. The soil was classified as a G7 material in terms of TRH 14 (1985). The moisture content of the soil was maintained by storing it in a sealed plastic bag.

The effect of organic matter on soil stabilisation was also investigated. For this purpose the organic component of the soil was removed by heating it at 500°C for 30 minutes followed by thorough washing with water.

Preparation of stabilised soil samples. The formaldehyde solution was diluted with water before dissolving the urea. The amount of water used was chosen such that the final soil mixture would be at its optimum moisture content (OMC) of 9,5%. The OMC is the moisture content at which the maximum density for a specific material is obtained for a specified compactive effort.

Optimised sample preparation methods were previously reported (Germishuizen *et al.*, 2002). In a typical procedure, the liquid stabiliser solution was added to approximately 1 kg of the soil and thoroughly mixed to ensure good dispersion in the soil phase. Cylindrical test briquettes were prepared using the Marshall compaction apparatus according to Method 2C, TMH1 (CSRA, 1989). Standard moulds (ID = 101.6 mm) were used and compaction was achieved using 50 blows on each side of the sample. The compacted samples were air-dried for a specified number of days. The Indirect Tensile Strength (ITS) was determined using a standard ITS machine. Unless stated otherwise, the ITS dry strengths were determined using samples that were air-dried for either 7 or 21 days. Wet strengths were determined after soaking the air-dried samples in water for 24 hours.

3. RESULTS AND DISCUSSION

3.1 Neat Resin Properties

Formaldehyde:urea molar ratios between 1:1 and 2:1 were studied, as this is the range applicable for resins used as adhesives and binders (Duvenhage, 1992). During the curing stage, the resins were observed to turn milky before gelling. This is attributed to a phase separation effect: As the cure reaction proceeds, the reaction products become progressively more hydrophobic and less water-soluble (Ebdon *et al.*, 1990, Duvenhage, 1992, Diem and Matthias, 1986) Above pH = 6,3 only a white precipitate formed in the solution and it failed to gel. The resinous reaction products formed below this pH were homogeneous, hard and brittle. With addition of bitumen the products obtained at pH = 4 or 5 were generally softer and remained homogeneous.

The pot life is defined in terms of the time available for application of the resin. It corresponds to the reaction time available up to the point where the resin gels. The gel point corresponds to a system-specific degree of conversion where a macroscopic network has just formed and where the resin changes from a free flowing liquid into a crosslinked solid. At this point the viscosity becomes infinite and the resin loses its workability.

It is conventional to assume that a resin cure reaction can be modelled using the following empirical rate equation (Addabo and Williams, 1982):

$$\frac{dx}{dt} = k_o e^{-E/RT} (1-x)^n \quad (1)$$

Here x is the degree of conversion, n is the reaction order and k_o and E are Arrhenius constants. The latter are expected to vary with pH as the cure reaction is acid catalyzed.

For an isothermal cure the gel time can be obtained by integrating equation (1) to yield:

$$t_{gel} = \frac{I}{k_o} e^{E/RT} \quad (2)$$

with

$$I = \int_0^{x_{gel}} \frac{dx}{(1-x)^n} \quad (3)$$

The degree of conversion (x_{gel}) at the gel point only depends on the reagent stoichiometry. This implies that the integral in equation (3) will vary with the formaldehyde:urea mol ratio but that it should be independent of pH and temperature.

The proper application of soil stabilisers requires a pot life of at least one hour. The above analysis shows that pot life is affected by the reaction pH and temperature as well as by the formaldehyde:urea mol ratio. For reasons of convenience it was decided to measure the gel time for the neat resin (i.e. in the absence of bitumen) as this was expected to provide conservative estimates.

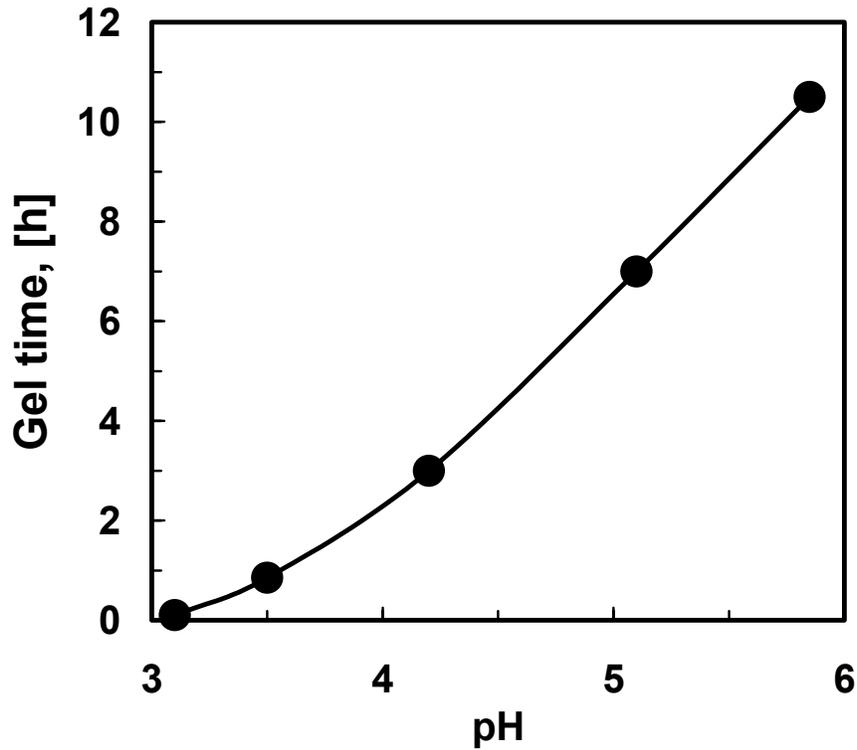


Figure 1: The effect initial resin pH on geltime at 25°C for a resin with a formaldehyde:urea molar ratio of 1,25:1.

Figure 1 shows that the gel times increased with cure pH. Figure 2 suggest a linear decrease in gel time with the molar ratio at a constant cure pH of 3,9. The temperature dependence followed the expected Arrhenius temperature dependence (Duvenhage, 1992, Diem and Matthias, 1986) predicted by equation (2). For a cure pH of 4,0 at a formaldehyde:urea molar ratio of 1,25:1 the data correlates according to:

$$t_{gel} = 2,89 \cdot 10^{-5} \exp\left(\frac{47640}{T}\right)$$

Where t_{gel} is the gel time in seconds, T the temperature in Kelvin and R is the gas constant (8,314 J/(mol.K)).

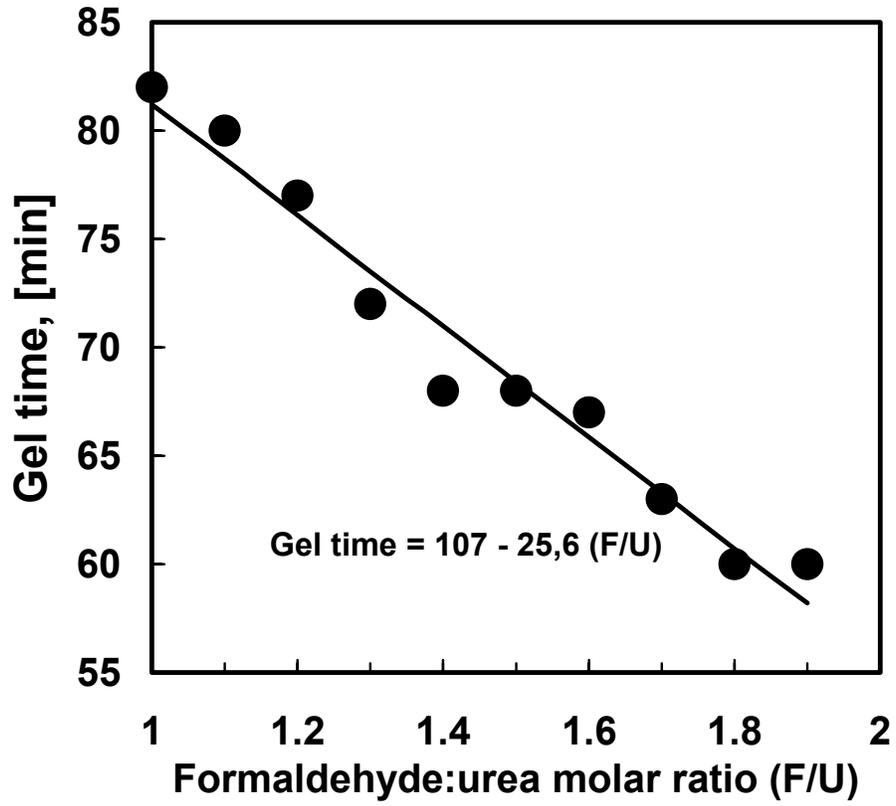


Figure 2: The influence of the formaldehyde:urea molar ratio on the resin gel time at a temperature of 25°C and pH =3,9.

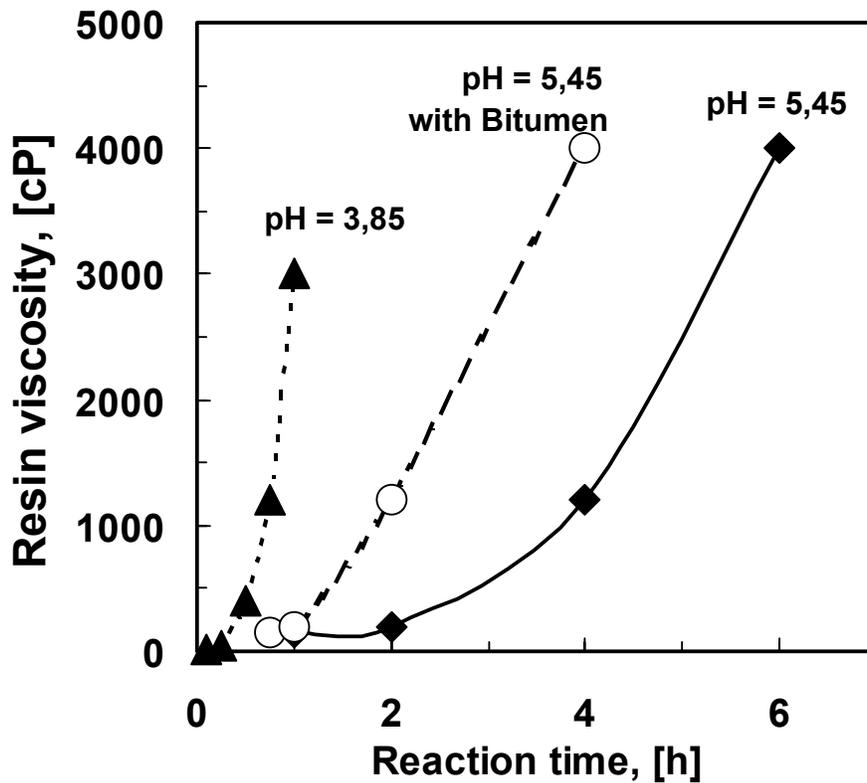


Figure 3: The influence of pH and anionic bitumen addition on the viscosity of the resin during curing at a temperature of 25°C. The formaldehyde:urea molar ratio was 1,23:1. The bitumen emulsion was SS60 added at a 1:1 mass ratio.

Figure 3 shows the effect of pH and addition of the anionic bitumen emulsion on the change in resin viscosity. It is clear that bitumen emulsion had an accelerating action on the cure rate.

3.2 Factors Influencing Soil Stabilisation

It was anticipated that the cure reactions would be modified in the presence of the soil. It was therefore decided to investigate the influence of the reaction parameters indirectly by evaluating their effect on the soil stabilisation efficiency. Unless a parameter was varied in the experiment, the following conditions were kept: 2% each of resin and anionic bitumen emulsion; initial resin pH = 4,5; formaldehyde:urea molar ratio = 1,5 and an air-drying time of 21 days.

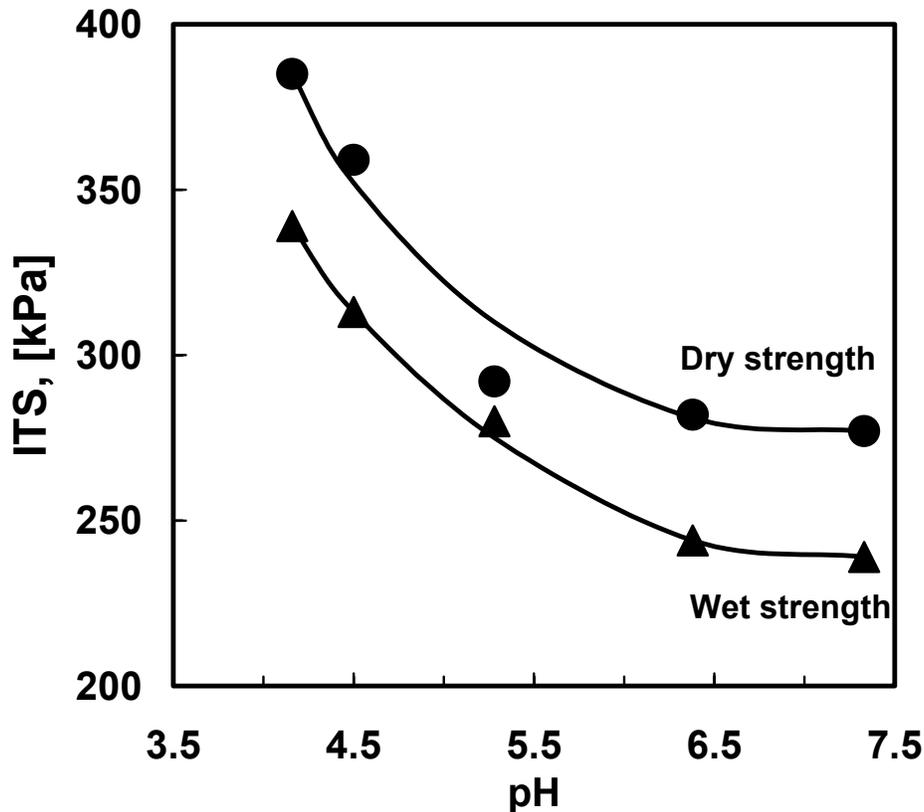


Figure 4: The effect initial resin pH on the 7-day strength of soil stabilised with 2% UF resin and 2% anionic bitumen emulsion. The initial soil moisture content was set at 10%.

3.2.1 Stoichiometry and initial resin pH

Figure 4 shows that the dry soil strength increased with decreasing initial resin pH. Since one hour is a reasonable time for the proper application of soil stabilisers, pH = 4,5 was chosen as the lowest viable value. Figure 5 shows the highest strengths were obtained at formaldehyde to urea molar ratio of 2:1. However, high free formaldehyde content is not desirable from an application point of view. It was therefore decided to maintain the 1,5:1 ratio for practical purposes.

3.2.2 Stabiliser dosage level and the type of bitumen emulsion

The effect of the type of bitumen was determined using 2% dosage together with 2% resin. Only the anionic bitumen emulsion showed an improvement in both dry and wet strength. While the improvement in dry strength was marginal, it was significant for the wet strength. The cationic bitumen emulsions caused a slight loss in dry strength and a complete loss in wet strength in comparison with the resin used alone. These effects are not currently understood but could be due to the nature of the surfactants used in the respective bitumen emulsions.

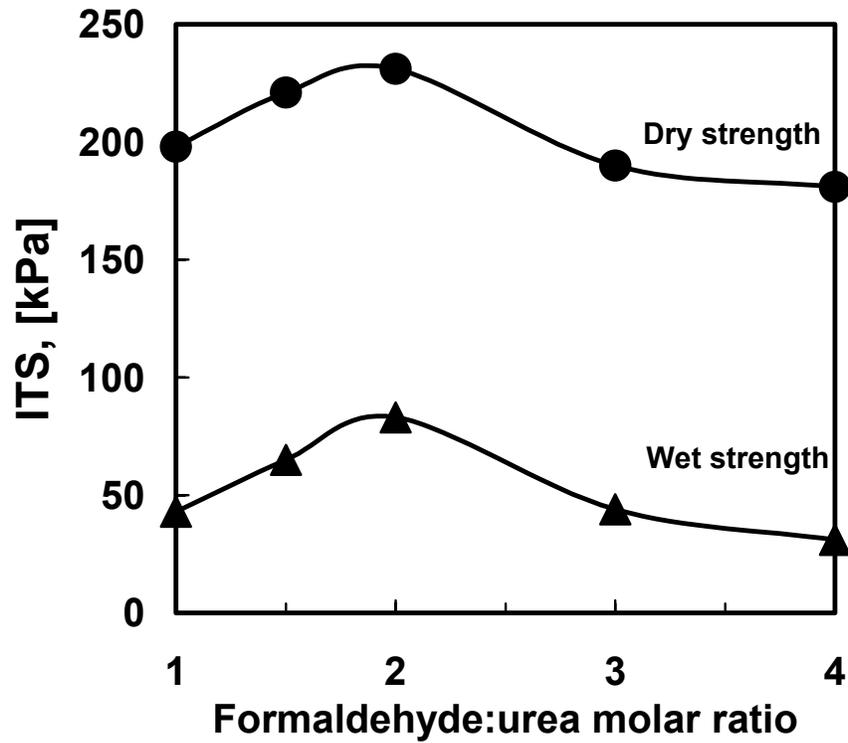


Figure 5: The effect the reactant stoichiometry on the 7-day strengths of soil stabilised with 2% UF resin and 2% anionic bitumen emulsion. The soil moisture content was set at 10% and the resin pH adjusted to pH = 4,5.

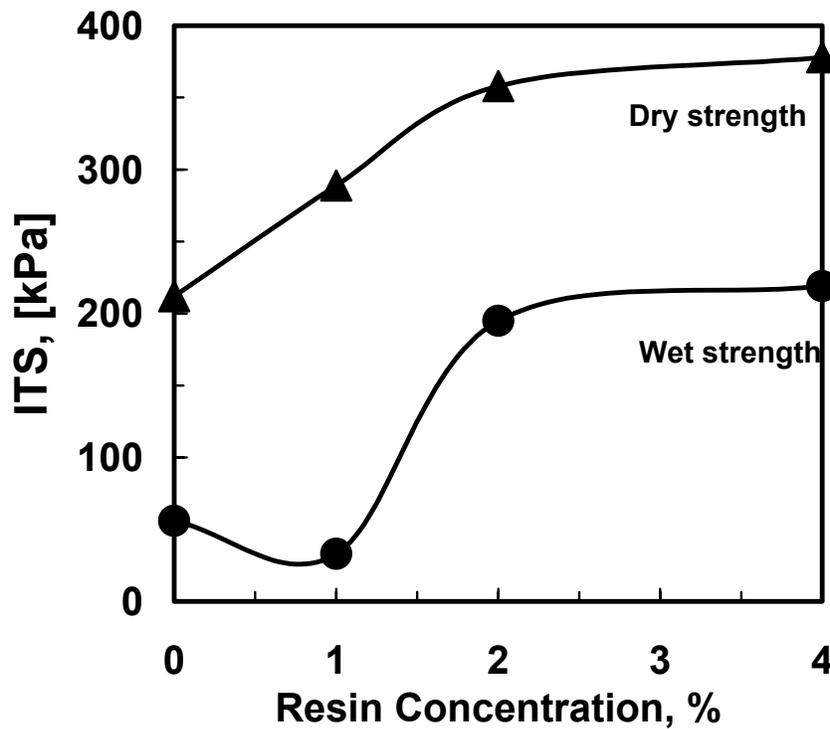


Figure 6: Effect of resin concentration on the dry- and wet strengths of a soil containing 2% anionic bitumen emulsion. Resin pH was adjusted to pH = 4,5 and soil moisture content to 10%. Samples were dried in air for 21 days before being subjected to dry and wet strength testing.

Figures 6 and 7 show the effect of stabiliser composition on soil stabilisation. In Figure 6 the bitumen emulsion dosage was kept constant at 2% and the resin level varied. At low resin dosage levels wet strength was reduced. With further resin addition, the ITS recovers and reaches a plateau level above a resin level of 2%. Results obtained for varying the bitumen content with the resin concentration fixed at 2% show that the main effect of bitumen is to increase the wet strength of the stabilised soil (Figure 7).

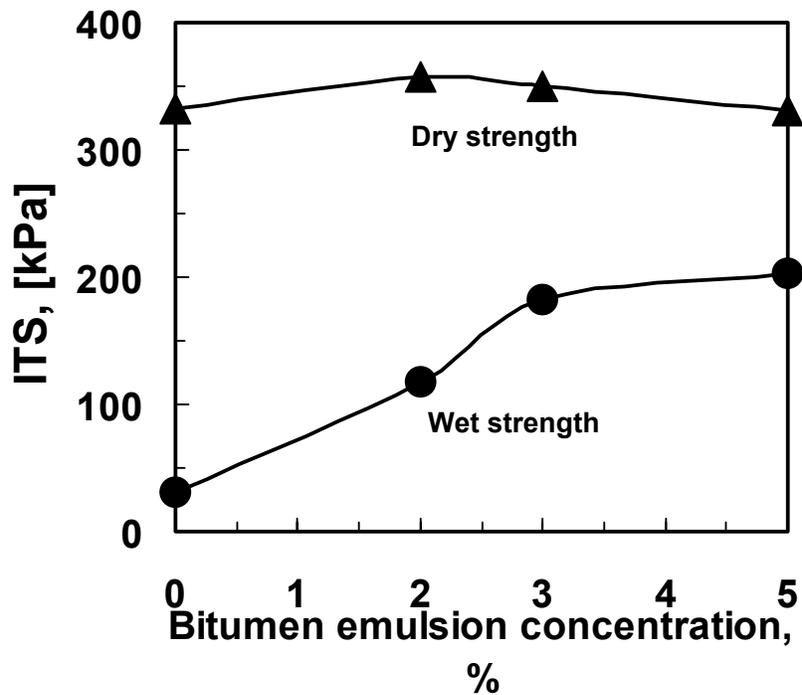


Figure 7: Effect of anionic bitumen emulsion concentration on the dry- and wet strengths of the soil containing 2% resin. Resin pH was adjusted to pH = 4,5 and soil moisture content to 10%. Samples were dried in air for 21 days before testing.

3.2.3 Soil moisture content

The effect of moisture content on soil strength was studied by varying either drying time or water soak time. Three different series of experiments were conducted with drying time varied up to sixty days and soak time for up to two days. In all cases the soil was stabilised by adding 2% UF resin and 2% bitumen emulsion. One set of the samples was simply allowed to air-dry. For another set, sealing the samples in thin polyethylene bags reduced the rate of moisture loss. In a final series of experiments, fully dried samples were soaked in water for up to 48 hours.

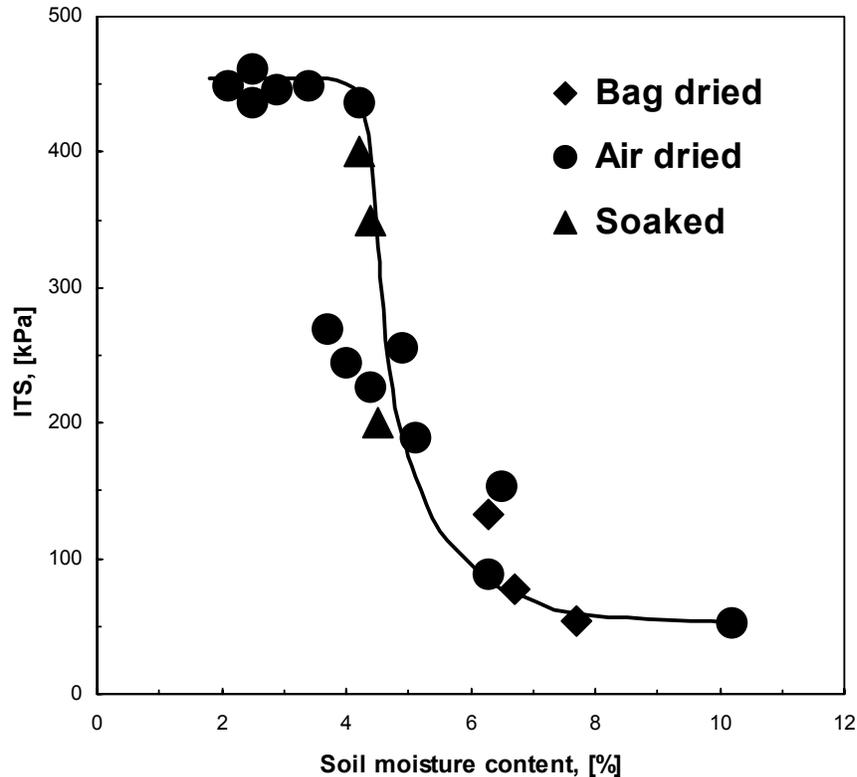


Figure 8: The effect of the final moisture content on the strength of soil stabilised with 2% UF resin and 2% anionic bitumen emulsion. The formaldehyde:urea molar ratio was 1,5:1 and the resin pH = 4,5. Samples were either dried in air or cured covered in polyethylene bags.

Figure 8 shows that the data for all experiments fall on the same curve when plotted against the moisture content of the soil. It shows that full strength development requires a reduction of soil moisture content to below ca. 3%. It also implies a reversible variation in soil strength with moisture content. It is therefore likely that the soil stabilisation mechanism involves physical adsorption rather than the formation of chemical bonds with the soil particles.

3.2.4. Organic soil components

The organic matter present in natural soils is largely composed of humus, a mixture of substances that has a degree of resistance to further degradation (Gieseck, 1975). Humus is formed from organic debris via chemical and microbial transformations, known collectively as the humification process. Humic substances play an important role in soil chemistry. They help retain water; are effective acid-base buffers; they bind molecules, ions and other biopolymers and they are also redox active. Humic acids also tend to adsorb strongly on clays and other mineral surfaces and this implies that their presence could affect soil binder performance.

Pompe *et al.* (1998) suggested formose-like compounds as model substances for soil humic acids. Weiss and Socha (1980) describe a convenient procedure for the synthesis of such synthetic humic acid analogues starting from formaldehyde solution.

With the naturally occurring organic substances present, addition of the synthetic organic substances offered no further strength improvement. Figure 9 shows the effect of adding formose to washed soil and sand stabilised with UF resin. When the soil was stripped of its natural organic content it also lost its natural cohesion. In addition, urea-formaldehyde resin without added organic content had no stabilising effect on the clean soil. However, when formose was added, the stabilising efficiency of the resin improved dramatically. The formose itself had some stabilising qualities, but only at higher concentrations.

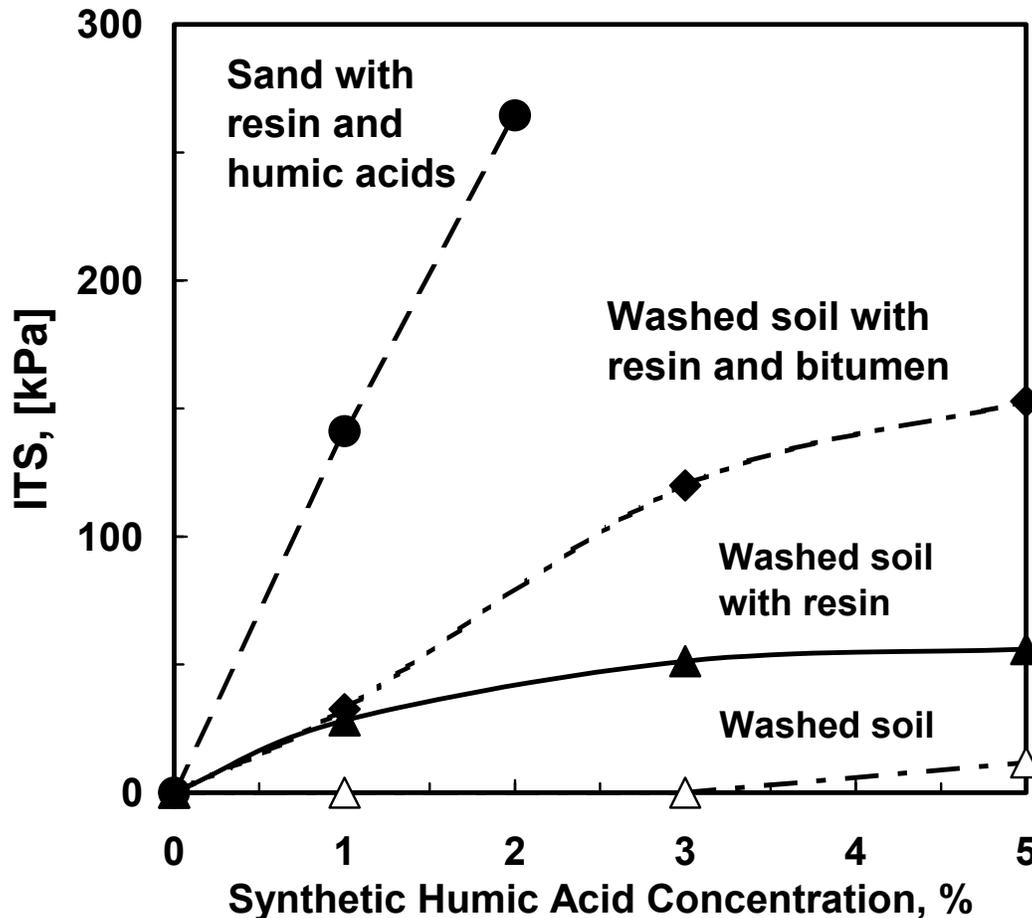


Figure 9: Effect of synthetic fulvic acid addition on 7-day dry strength of soils devoid of natural organic substances. Where indicated, UF resin and/or anionic bitumen was added at the 2% level.

3.3. Comments

Bitumen emulsion is widely used in road construction and maintenance as a binding and waterproofing agent. It is therefore not surprising that it provided a degree of soil stabilisation by itself. However, the large, positive interaction between the resin and

the bitumen was not anticipated. It is not clear what gives rise to this synergistic interaction. We speculate that it could be related to improved wetting of soil particles, reactions between the resin and bitumen components or even a plasticizing effect of the bitumen on the resin.

It is generally accepted that different soil stabilisation methods are more appropriate for certain types of soil (Ingles and Metcalf, 1972). Care should therefore be taken when attempting to extrapolate the results presented here to other soil conditions.

4. CONCLUSIONS

Indirect tensile strength measurements were used to determine the soil stabilisation efficiency of a urea-formaldehyde resin in brown shale gravel. It was found that a combination of urea-formaldehyde resin with an anionic bitumen emulsion improved soil strength by up to a factor of 3. Various system parameters were varied and the following is concluded with respect to soil strength development:

- An optimum value is reached at formaldehyde to urea molar ratio of 2:1. However, owing to the problems posed by free formaldehyde during stabiliser application, a lower value is recommended;
- Strength increases with decreasing cure pH but it is impractical to use a pH below 4,5 as the time available to work the soil becomes too short;
- At 2% bitumen emulsion dosage, strength development levels off above 2% resin addition;
- At 2% urea-formaldehyde resin dosage level, wet strength levels off above 3% bitumen emulsion;
- Strength appears to vary reversibly with soil moisture content and must be controlled below 3% for effective stabilisation. This suggests that the urea-formaldehyde-bitumen stabilisation system is fundamentally unstable in the presence of water. It implies that the UF resin system would only be expected to be suitable for soil stabilisation in very dry climates.
- The soil organic content is a very important parameter in determining the stabilisation efficiency of the urea-formaldehyde resin. Formose can be used with benefit if the soil is deficient in natural organics.

It is concluded that urea-formaldehyde resins may hold promise as soil stabilisers in very dry climates provided application conditions are optimised with respect to the soil to be treated.

Acknowledgement

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APPENDIX: Properties of the Test Soil

The test soil was a dark brown shale with a quantity of sand stone and fine gravel

1. Constants:	Units					
Liquid limit	19					
Plasticity index	5					
Linear Shrinkage	1,5 (%)					
2. Screen analysis:						
Screen aperture (mm)	19.0	13.2	4.75	2.0	0.425	0.075
% pass	100	95	61	60	49	13
3. CBR / UCS Values						
% Mod AASHTO	100	98	97	95		
UCS Value	59	46	40	31		
4. MOD. AASHTO	Units					
Max dry density	1985 (kg/m ³)					
Optimum moisture content	9,6 (%)					
5. Classification:						
Classification System:	TRB	TRH14	Unified			
Classification:	A-1-b(0)	G7	GM, GC			