INVESTIGATION OF IMPREGNANTS FOR LOW-COST BUILDINGS

A Thesis
submitted to the
Victoria University of Technology
for the degree of
Doctor of Philosophy
by
Kebao Ren

Department of Chemistry and Biology
Faculty of Science
March, 1995

ACKNOWLEDGMENTS

I wish to express my sincere gratitude to my supervisor, Dr. Douglas A. Kagi, for his guidance, encouragement, and support in every aspect over the past three years.

Thanks are also extended to Mr. Gary Holliday for his fruitful exchange of ideas and Prof. John Stearne for his sincere guidance. I wish to thank Dr. Andrew Smallridge, Assoc. Prof. Geoffrey Hamilton, Mr. John Doering, Mr. Anthony Caselli and all my colleagues who have contributed to many discussions. Thanks are also extended to Assoc. Prof. Bob Vinen, the Head of Chemistry and Biology Department, for providing the research facilities.

Thanks are also extended to my wife Junqi and daughter Mandy for the great encouragement and support with love during my study in Australia. I am very grateful to my parents, my parents in-law and all my family members for their encouragement and support for my postgraduate degree in Australia.

The opportunity to undertake the research work provided by an AIDAB Scholarship under the Australian Development Co-operation Scholarship Scheme, the Department of Chemistry and Biology, Victoria University of Technology and Tech-Dry Building Protection Systems Pty. Ltd. is gratefully acknowledged.

Kebao Ren

March, 1995.

PREFACE

This project was an industrial research project sponsored by the Australian International Development Assistance Bureau under the Australian Development Co-operation Scholarship Scheme (ADCSS). The scheme is to finance researchers from developing countries and aims to help developing countries in specific areas.

The project was to investigate water-based impregnants for low-cost buildings in developing countries to protect the building material from water penetration by capillary action in order to improve the durability of the buildings. The research area requires interdisciplinary input and the project was of necessity oriented towards academic and commercial research with a possible market outcome. An aim for a market result was a low-cost water-based technology and this limited the selection of raw materials to commercially available materials.

The academic and commercial aims of the project have been achieved. Part of the academic results of the project has been accepted for publication as refereed papers:

i) "Reduction of water absorption in silicate-treated concrete by post-treatment with cationic surfactants", *Building and Environment*, 1994, in press

ii) "Upgrading the durability of mud bricks by impregnation", *Building and Environment*, 1994, in press

iii) "Study of water repellent effect of earth substrates impregnated with water-based silicones", *Journal of Chemical Technology and Biotechnology*, 1995, in press

A novel technology of introducing an organo-silicate into the substrates by reaction of the silicate with a cationic surfactant in masonry capillary pores has been developed in this research. The water penetration of the silicate-treated masonry substrates has been significantly reduced by this treatment. A novel method of enhancing the performance of impregnants on earth substrates by pre-treatment with silicate was also developed. The quality of the earth substrates was significantly improved by the treatment.

The commercial aims have been achieved in the invention and development of two novel water-based impregnants. Part of the commercial basis of the results has been lodged as patent applications:

iv) "Alkali resistant aqueous water repellent compositions", Australian Provisional Patent Application, PM 9537, 1994

v) "Aqueous compositions for the water repellent treatment of masonry", PCT Patent Application, PCT/AU95/00085, 1995

The University of Technology is negotiating with international and Australian interested commercial collaborators for commercialisation of these technologies.

ABSTRACT

Masonry building materials are more or less permeable. Water is the most significant factor in building deterioration by capillary water penetration. Impregnation of masonry with water repellents particularly with silicone impregnants is the most successful method of protection of masonry from capillary water absorption.

Alkylalkoxysilanes, alkylalkoxysiloxanes and silicone resins dissolved in hydrocarbon solvents are suitable silicone water repellent impregnants. However, organic solvent-based silicone impregnants have less practical value particularly in treating low-cost buildings due to the solvents being environmentally unfriendly and expensive.

Metal alkylsiliconates and silicone emulsions are water-based masonry impregnants. However, siliconates suffer problems of either imparting little alkali stability to the treated substrates or forming very unstable solutions after dilution. Silicone emulsions achieve unsatisfactory water repellent performance due to the surfactants in the emulsions as the emulsifiers impart a wetting effect to the treated surfaces. In addition, silicone emulsions have difficulty in the treatment of neutral surfaces as incorporation of catalysts in the base emulsion is problematical.

A novel higher alkylsiliconate was obtained by hydrolysing octyltriethoxysilane in potassium methylsiliconate in the presence of an alkylalcohol ethoxylate nonionic surfactant. This novel siliconate forms stable aqueous solutions after dilution and imparts to masonry substrates good alkali stability after impregnation of the substrates. It was found that the silane hydrolysis was greatly accelerated by the surfactant due to surfactant micellar catalysis. The surfactant in turn stabilises the higher alkylsiliconate solutions when the concentrated hydrolysis product is diluted due to the solubilisation by the surfactant micelles and possible interaction between the siliconate and the surfactant.

A novel silicone emulsion impregnant was obtained by emulsifying a mixture of octyltriethoxysilane and octyl/methyl methoxysiloxane in the presence of acidified alkylamine ethoxylate surfactant. The emulsion imparts to various masonry substrates a satisfactory water repellency without imparting a wetting effect to the substrate surfaces. The alkylamine ethoxylate surfactant imparts a significant stabilisation effect to the emulsion due to the satisfactory surface activity of the modified alkylamine ethoxylates. No wetting effect is imparted by the surfactant to the treated substrates due to the cationic nature of the surfactant. The siloxane may take part in the formation of an interfacial film with the surfactant in the oil/water interface to greatly improve the stability of the emulsion. Stability of the emulsion is also attributed to the positive charge induced by the surfactant.

A successful method to consolidate mud brick and effect water repellency was developed in this research. The consolidation effect is due to the increase in adhesion between the substrate particles by impregnation of the substrates with soluble sodium silicate before the silane/siloxane emulsion impregnation. The silicate also improves the water repellent performance by enhancing the interaction between the substrate and the silicone water repellent. By studying the interaction between the silicone impregnant and the mud brick substrate by various methods, it is understood that the water repellent effect is due to the deposited hydrophobic polysiloxane on the masonry capillary wall surface.

A method of decreasing the water penetration of a silicate-impregnated permeable masonry substrate was discovered where the substrate was impregnated with soluble sodium silicate followed by an alkyl quaternary ammonium cationic surfactant. The water resistant effect is assumed to be developed due to an organo-silicate reaction product between the silicate and the cationic surfactant formed in the masonry capillary which imparts a hydrophobic effect rather than blocking the masonry capillaries. This provides a new way to improve the water resistant effect of silicate-treated masonry substrates.

CONTENTS

1. INTRODUCTION

1.1 Properties of masonry materials

1.1.1 Masonry building materials

Most masonry building materials are made up of clay minerals [1] which contain silica and other elements. The silica may be oriented in various geometric structures composed of SiO_4 tetrahedra (see Figure 1.1). Structurally, silica represents an infinite three-dimensional network which is formed by the sharing of all oxygen atoms of a given tetrahedron with neighbouring groups. The possibility of the linking of the tetrahedron with some corners remaining unshared gives rise to a wide range of structural possibilities, some of which are encountered in the silicates. In structures for which all corners of the tetrahedron are not shared, each unshared oxygen atom contributes to the anionic groups thus forming a formal negative charge, which is satisfied by the presence of other cations in the silicate structure [1, 2].

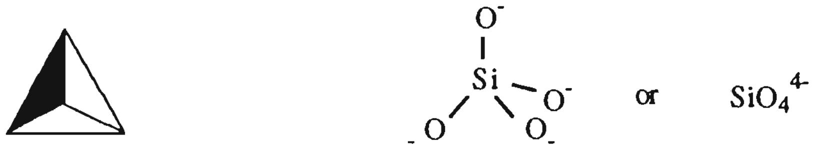


Figure 1.1 Basic silica tetrahedron structure of mineral materials

According to Grim [2], the surface of silica minerals is normally made up of either negatively charged oxygen atoms or hydroxyl groups which make the silica mineral surface hydrophilic (see Figure 1.2). Water may be attracted by the surface through hydrogen bonds to either negatively charged oxygen or to the oxygen of the hydroxyl groups on the surface [2].

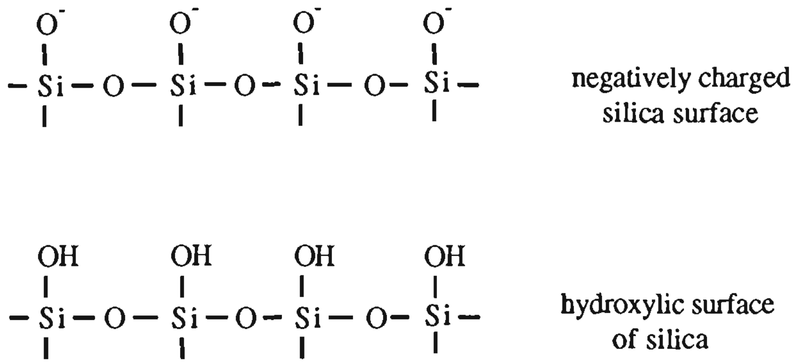
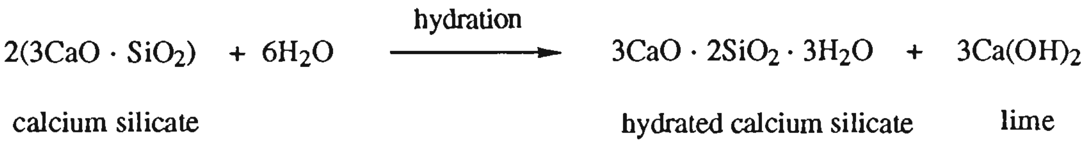


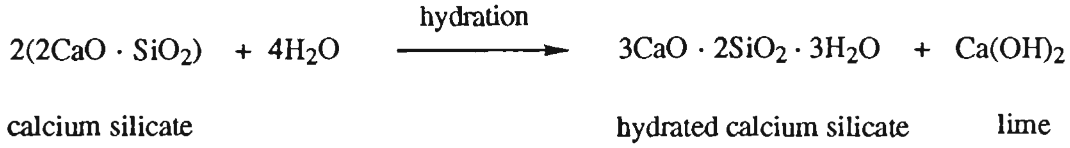
Figure 1.2 Hydrophilic silica surface of mineral materials

Concrete, which is prepared by the mixing of cement, sand, aggregate and water, is the most successful building material of the modern world. Portland cement is made from clay and limestone [1]. Once the cement has been mixed with water, a reaction commences. The chemical reactions are complex but the hydration reaction [3] of cement with water produces insoluble silicate compounds and calcium hydroxide (see Schemes 1.1 and 1.2). The hydration phase is largely complete after 28 days and the concrete is nearly at its final strength.



$$2(3CaO \cdot SiO_2) + 6H_2O \xrightarrow{\text{hydration}} 3CaO \cdot 2SiO_2 \cdot 3H_2O + 3Ca(OH)_2$$

(Scheme 1.1)



$$2(2CaO \cdot SiO_2) + 4H_2O \xrightarrow{\text{hydration}} 3CaO \cdot 2SiO_2 \cdot 3H_2O + Ca(OH)_2$$

(Scheme 1.2)

Carbonation starts simultaneously with hydration [4] (See Scheme 1.3). Carbonation hardens the concrete and helps reduce the permeability of the concrete. However, carbonation reduces the alkalinity of the concrete and it is the alkalinity of the concrete which protects the reinforcing steel in a steel-reinforced concrete structure [4].

$$\underset{\text{calcium hydroxide}}{Ca(OH)_2} + H_2O + CO_2 \xrightarrow{\text{carbonation}} \underset{\text{calcium carbonate}}{CaCO_3} + 2H_2O$$

(Scheme 1.3)

Poor concrete is either concrete which is made with low quality cement or a high water content in water/cement ratio, or concrete with inferior compaction. Poor concrete generally has high capillary porosity, and therefore water can easily penetrate into this low quality concrete to provide water for steel corrosion reaction or carry acids and other pollutants into the concrete structure causing poor durability of the concrete buildings.

Fired bricks are common building materials which are made by firing clay materials at temperatures above 1000°C [5]. The firing of bricks is undertaken to reduce the water content of the clay and to alter the silicate structure to increase the strength [1]. Complete fusion occurs at higher temperatures than 1000°C. Bricks fired at an insufficient temperature have low strength, high porosity and may have high permeability. These low-temperature fired bricks are cheap building materials which are widely used in developing countries. The quality and durability of the buildings built with these bricks may be poor due to their high water absorption by penetrating rainwater.

Earth, mainly composed of clay and sand, is one of the cheapest building materials which has been used in the construction of shelters by mankind for thousands of years. Approximately 30 percent of the world's present population still live in earthen dwellings [6]. Adobe, rammed earth and other forms of earthen structures, are constructed throughout the world. Water is easily absorbed by earth structures due to the hydrophilicity of the clay minerals. The inherent weakness of earth with water makes earth structures an impractical choice due to the subsequent deterioration of the buildings by water.

Many other masonry materials are more or less permeable and hydrophilic, and therefore they all suffer durability and quality problems due to the penetration of water.

1.1.2 Capillary water absorption of masonry materials

Masonry materials are porous and are generally permeable and hydrophilic. As a result of this, water can penetrate the capillaries of masonry. Low-cost building materials may have higher permeability and therefore they usually exhibit high water absorption values. The most important water absorption mechanisms include (as shown in Figure 1.3):

a) capillary water absorption through rain water
b) water absorption through seepage and flooding
c) hygroscopic water absorption
d) water absorption through capillary condensation and surface condensation

In the first two kinds of water absorption, water enters the building materials in liquid form, whilst in the other types it enters in a gaseous form, i.e. as water vapour.

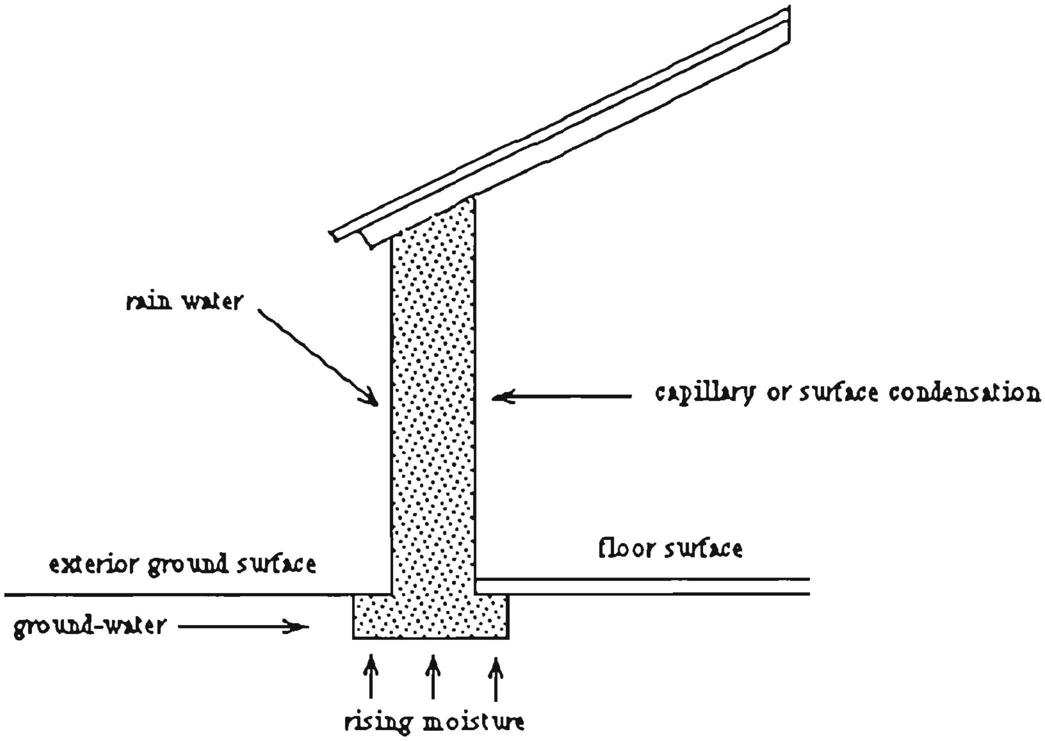


Figure 1.3 Diagram of water absorption mechanisms of masonry materials

Capillary water absorption is the major form of water absorption by masonry material when it comes into direct contact with liquid water [7-9]. It takes place primarily on the facade of a building directly exposed to rain even where there is no pressure differential across the wall [10]. It also occurs in those parts of a building in direct contact with the soil. This capillary water absorption or capillary rise is termed rising damp. The rate of capillary water absorption is high and considerable amounts of water may be taken up by the building materials within a short time. The rate of water absorption essentially depends on the pore or capillary radius. The suction rate during the initial phase is directly dependent on the radius, whilst the height to which the water rises inside the capillary is inversely proportional to the capillary radius. The capillary rise can be expressed as follows [11]:

$$H = \frac{2\gamma}{\rho r g} \cos\theta \qquad (1.1)$$

where H is the height of capillary rise, γ is the surface tension of the liquid, ρ is the density of the liquid, r is the radius of the capillary, g is the acceleration gravity and θ denotes the contact angle of water with the substrate surface. Increasing the contact angle θ reduces the capillary rise H.

1.1.3 Damage to masonry materials induced by water absorption

Water is the most important factor affecting performance and durability of building materials. When building materials absorb water their properties change and, in extreme cases, they may be significantly deteriorated. The most important and the best known types of structural damage are outlined below.

1.1.3.1 Physical destruction

Physical destruction includes everything that leads to the mechanical destruction of building materials. Mud bricks, for example, deteriorate after contact with water due to insufficient adhesion between earth particles [12]. Absorption of water causes the swelling of clay minerals while evaporation of water from the clay gives rise to shrinkage and cracking.

The wetting and drying eventually causes collapse of the earth substrate. Frost damage to masonry materials is another major form of physical destruction. This is caused by water freezing inside the pores and capillaries of the building materials, resulting in a large volume increase. This produces a very high pressure in the pore structure, resulting in destruction or spalling of the top layer of masonry.

1.1.3.2 Biological corrosion

Micro-organisms such as, bacteria, mould, moss, algae and lichens can grow on damp masonry materials. Once an initially dry surface has been attacked in this way, it is kept permanently damp by these micro-organisms. Apart from being unsightly, micro-organism growth can therefore, in severe cases, cause the gradual breakdown of the surface.

1.1.3.3 Loss of thermal insulation caused by damp

Thermal insulation properties are very important in the selection of building materials. Thermal insulation is influenced by the moisture content of the building materials. Wet and damp materials have much poorer insulating properties. The loss of thermal insulation of the materials causes more condensation, resulting in making buildings even more moisture-prone.

1.1.3.4 Chemical corrosion

Chemical corrosion has become a serious matter in the deterioration of masonry materials. Absorption of various salts in masonry can destroy the masonry structure due to expansion of the salts when crystallisation in the pores or the capillaries takes place. Soluble salts, such as sulphates, chlorides, nitrates, and carbonates from the external environment or from within the masonry itself can migrate into building materials through capillary penetration with water. Evaporation of the water causes the salts to be deposited and the concentration of salts gradually increases inside the pores and capillaries. The salts can also be transferred to the surface of the building by capillary water to form white deposits after crystallisation which is termed efflorescence. Damage, often severe, is caused by crystallisation and the formation of hydrates in the capillaries resulting in expansion within the building material.

Another source of chemical corrosion is waste gases from atmospheric pollution. Sulphur oxides (SO_2 or SO_3) and nitrogen oxides (NO or NO_2) can dissolve in surface rain water or form acid rain in the atmosphere which penetrates the masonry materials through capillary absorption. Such chemicals can convert the insoluble binder of stone substrates, e.g. calcium carbonate, into soluble calcium sulphate or gypsum (see Scheme 1.4). The calcium sulphate adheres to the surface of the building material, producing a hard encrustation which finally flakes off with resultant facade deterioration.

$$\underset{\text{calcium carbonate}}{CaCO_3} + H_2O + SO_3 \longrightarrow \underset{\text{calcium sulphate (gypsum)}}{CaSO_4} + H_2CO_3$$

(Scheme 1.4)

In the case of steel-reinforced concrete, carbon dioxide converts calcium hydroxide into calcium carbonate (refer Scheme 1.3). Carbonation reduces the alkalinity of the concrete. The alkalinity in the hydrated cement can form a passive film on the embedded reinforcing steel in concrete to protect it against corrosion under a damp environment with easy oxygen access [13]. Chloride ions can cause serious damage to the reinforcing steel and subsequently the concrete structure. A concentration of chloride ion above 0.2% by weight chloride ion on cement risks steel reinforcement corrosion [4]. Chloride ions dissolved in water can enter the concrete through pores or capillaries. The presence of chloride ions in water, and oxygen expedites the corrosion of the steel. The entrance of chloride ions and oxygen can destroy the passive environment, establish galvanic corrosion cells, and damage the concrete by the expansion caused by steel corrosion products [14]. Corrosion of the reinforcing bars starts as pitting and becomes progressively worse, finally affecting the entire surface. The ultimate result is that the surface of the concrete at the exterior of the steel reinforcing rods spalls. The deterioration of masonry materials caused by chemical corrosion has been the subject of many studies [15-21].

1.2 Building protection

Most deterioration of masonry buildings is caused by water absorbed by the masonry. If, therefore, buildings are to be preserved, water must be prevented from entering the masonry materials by capillary action. Apart from reducing the ingress of water by design and changing the environment, post-treatment of buildings may be useful to stop capillary water absorption. The major methods to post-treat the buildings against water absorption may include coating (or rendering) and impregnation [22]. Treating masonry surfaces with impregnants creates a lining of water repellent on the capillary wall surfaces while coatings (or renderings) can seal the masonry capillaries (Figure 1.4).

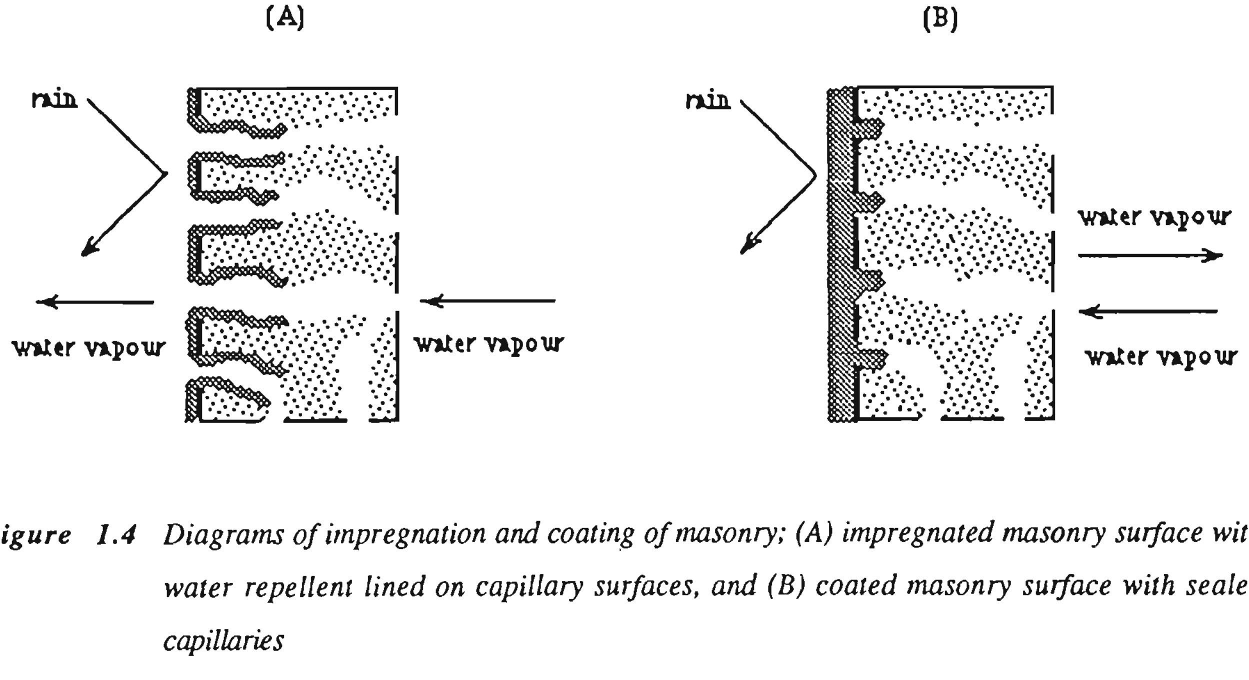


Figure 1.4 Diagrams of impregnation and coating of masonry; (A) impregnated masonry surface with water repellent lined on capillary surfaces, and (B) coated masonry surface with sealed capillaries

1.2.1 Surface coating

The surface of the building may be coated with a specialist surface coating to a certain thickness to interrupt the diffusion of damaging gases and to stop the penetration of liquid water through pores or capillaries. Surface coating may include paints with or without pigments and rendering mortars which may be prepared with various materials. For instance, Swamy and Tanikawa [23] used acrylic (2-ethylhexylacrylate) polymer combined with inorganic filler and pigment to coat concrete with an overall thickness of about 1 mm. This coating satisfies weathering resistance and diffusion resistance to water, air, chloride ions, and water vapour. Organic polymers such as acrylics, epoxies, polyurethanes, and chlorinated rubbers are the most successful organic resins to be used as masonry coating materials [24]. Soluble metal silicates with various additives have been used as coatings for concrete [25]. Khalid and Aslam [26] treated brick walls with a low-cost sodium silicate coating to successfully reduce the water absorption of the substrates.

Browne and Robery [16] tested about 70 coatings which included methacrylate, styrene acrylate, ethylene polymer, vinyl co-polymer, urethane, epoxy, bitumen, chlorinated rubber, alkyd and cementitious coatings for treating steel-reinforced concrete. They demonstrated that most coatings had a high resistance to carbon dioxide and chloride ingress but a poor water vapour transmission rate in comparison to that of silane/siloxane impregnants. In addition, most of the treatments with coatings showed a higher cost than that of silane/siloxane impregnations. Blight [27] studied four waterproofing systems for concrete by impregnating concrete with two different silicone impregnants and coating concrete with a cementitious slurry and a synthetic resin emulsion. After four years, the silicone-treated (by impregnation) concrete showed lower water absorption and a decrease in carbonation compared to the substrates treated with coatings. Bain [20] indicated some disadvantages with surface paints as treatments for concrete to effect water resistance. Surface paints such as epoxy resin paints and urethane resin systems need hardening agents, and such two component systems suffer from the problem of unpredictable workability. Such paints have to be applied as relatively thick coatings to achieve the required durability, and this leads to problems of shrinkage during curing and a comparatively high application cost. Newman [28] recommended that treating masonry with paints may be a commitment to regular maintenance and coating the building with rendering was an expensive remedial method. Impermeable paints may allow water to build up behind the surface coating with the risk of disruption to the coating and the possibility of frost damage.

1.2.2 Impregnation of masonry with water repellents

It is possible to impregnate masonry with a water repellent to protect against water penetration by capillary action. As shown in Figure 1.4, the major difference between impregnation and surface coating is that impregnation only allows the impregnant to penetrate into the masonry to line the capillary wall surface to form a water repellent impregnated zone, whilst surface coating completely seals the capillaries by forming a thick film on the surface. Impregnation and lining of the capillaries can significantly reduce the water absorption by the masonry through capillary depression [11]. By referring to Equation 1.1, the capillary rise H is related to the contact angle θ of water with the substrate surface . If capillaries are treated with a material which induces hydrophobicity and reduces the substance's wettability, the contact angle θ becomes greater than 90^{o}, the capillary height H will become negative since cosine of an angle greater than 90^{o} is negative. Therefore, capillary rise becomes capillary depression, resulting in no water absorption by capillary action (shown in Figure 1.5 and Figure 1.6).

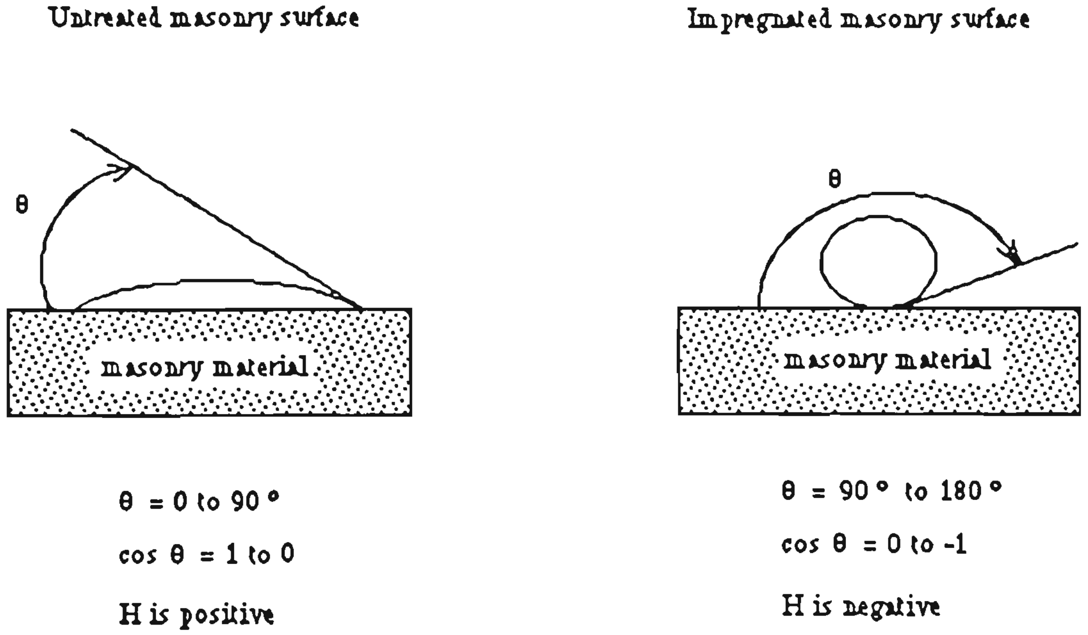


Figure 1.5 Change of water contact angle of masonry surface due to hydrophobisation by impregnation

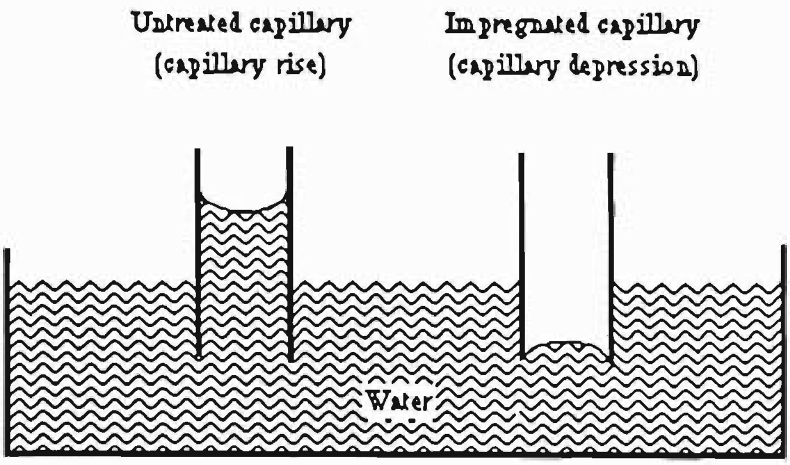


***Figure 1.6** Change of capillary water absorption by impregnation*

There are many advantages of the impregnation of masonry. Reduction of water penetration into masonry through impregnation is significant since the contact angle of masonry capillary surfaces is greatly increased by hydrophobic impregnant [29]. Treating masonry with a water repellent impregnant is an inexpensive but efficient method to protect buildings against deterioration. The lifetime of water repellent treatment for normal clay bricks has been estimated at 10 years [28]. Only a small amount of the impregnant is needed to line masonry capillaries to achieve hydrophobicity. A higher depth of impregnation achieves a longer life time as the very surface impregnated zone may be deteriorated by UV or environmental factors leaving the deeply impregnated zone intact. Water vapour permeability is an essential requirement for building materials [29]. A satisfactory water repellent leaves the treated substrate permeable to water vapour while restricting the passage of liquid water through the capillaries. A natural external finish of masonry buildings may be required for aesthetic purposes [20]. Treatment by impregnation does not change the finish appearance and no yellowing is normally developed during use. Apart from reducing capillary water penetration, impregnation may achieve some consolidation effect for natural masonry materials such as stone and earth structures. Honsinger et al.[30-32] studied consolidation of natural stone by impregnating the stone with polyurethanes, epoxy resins, acrylic resins, silicones, silicate esters, fluoroethylenes and unsaturated polyesters. They found that the impregnants formed a nearly continuous micro-layer covering the mineral pore walls to form a fine supporting structure to impart strength to the substrate and a water repellent effect. Coffman et al.[33], Selwitz et al.[34], Chiari [35] and Helmi [36] treated earth adobe with isocyanate, ethylsilicate and methyltriethoxysilane impregnants to achieve sufficient consolidation and water repellent effect in the earth structures. Huang et al.[37] and Li [38] impregnated earth structures with sodium silicate to successfully achieve a consolidation effect. This consolidation effect is due to the enhancement of the cohesion of the natural material particles by the impregnant/consolidant.

Many materials may be used as masonry impregnants to effect water repellency. Organic resins such as acrylics, polyurethanes, epoxies and polyesters dissolved in suitable solvents or as emulsions have all been used as masonry impregnants. Metal soaps such as aluminium stearates in solvents are relatively cheap water repellents for masonry materials. Solvent-based and water-based silicones such as siliconates, silanes, siloxanes, silicone resins, and silanols are another group of masonry water repellents. The performance of impregnants may by assessed by considering the following properties:

a) molecular size
b) water vapour permeability of the impregnated substrate
c) the contact angle of water with the treated surface induced by the impregnant
d) bonding with the substrate

Molecular size influences the penetration ability of the impregnants. Impregnating masonry materials with organic resins usually suffers from a major deficiency - their relatively large size of molecule cannot penetrate into the fine capillaries [39] of masonry materials. The molecular sizes of various materials are listed in Table 1.1.

Silicones such as silanes and siloxanes are relatively small and therefore can achieve, all other things being equal, a deeper penetration depth in the substrate pores or capillaries. Long-term water repellent effectiveness of water repellents depends on high penetration depth which is required to be greater than the depth of surface microcracks. The surface microcracks may extend into untreated substrate zone and therefore the masonry is treated ineffectively if impregnation depth is not sufficient (see Figure 1.7). In addition, a higher depth of penetration increases the effective UV-resistance since the thin water repellent layer on the surface of the substrate is easily decomposed by UV weathering. However, the deep impregnated zone remains intact. Similarly, physical damage such as abrasion of the masonry surface may wear off the surface but with deep impregnation the impregnated zone beneath the surface remains as a water repellent zone. Organic polymers and metal soaps show only very poor penetration ability [21]. Therefore, it is not surprising that these products do not show high durability.

Table 1.1 Molecular size of various materials

Materials	Diameter (nm)
Chloride ion	0.2
Water	0.5-0.7
Isobutylsilane	0.5-1.0
Acid rain	0.8-1.5
Isooctylsilane	1.5-2.0
Siloxanes	3.5-4.5
Polysiloxanes	15-20
Smallest acrylics	30-35
Epoxies	50

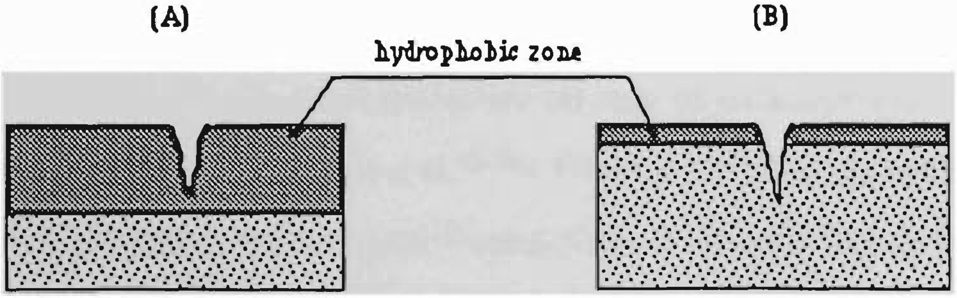


Figure 1.7 *Effectiveness of impregnation influenced by penetration depth; (A) impregnation effective, and (B) impregnation ineffective*

Metal soaps are good water repellent agents for masonry but decrease the water vapour permeability due to a blocking of the masonry capillaries [21]. Organic polymers may form a film covering the masonry surface, resulting in some blocking of the masonry pores and this results in an effect on the water vapour permeability of the substrate. Silicones are well-known impregnants which usually achieve a significant water repellent effect but do not significantly affect the water vapour transmission of the masonry [16, 20, 29].

Surface free energy modifying effects of the impregnants greatly affects water repellency of the treated masonry. Impregnation can alter the critical surface tension of a substrate by lowering surface free energies. A low critical surface tension of the substrate corresponds to a high contact angle of water to the substrate surface, resulting in higher capillary depression or good water repellency. Many organic resins are intrinsically less hydrophobic [21] than certain other materials by virtue of their relatively polar functionality and high critical surface tension values averaging 30-40 dynes/cm. Critical surface tensions of various materials according to Arkles [40] are shown in Table 1.2. With the exception of aminosilane and phenylsilane treated surfaces, silane treated surfaces show relatively lower critical surface tension than those of organic resins and therefore the silanes can impart a better water repellent effect in masonry treatment.

Permanent bonding between masonry capillaries and impregnants results in long term durability. Most organic polymers and metal soaps are considered to physically adsorb on masonry with little chemical bonding due to the absence of functional groups within the molecules. However, silicones such as alkylalkoxysilanes are well-known coupling agents of mineral materials [41, 42]. Chemical interaction between alkylalkoxysilanes and mineral surfaces have been studied by Leyden et al.[43-46], Miller et al.[47], Dubois and Zegarski [48], Ishida et al.[49-52] and Gilpin and Gangoda [53] using NMR, FTIR and other methods. When reactions occur between alkylalkoxysilanes and the masonry substrates it is assumed that the silanes can bond with the hydroxyls of the masonry substrate through siloxane bonding (Scheme 1.5).

Table 1.2 Critical surface tensions of various materials according to Arkles [40]

Materials	Critical surface tension * (dynes/cm)
Polytetrafluoroethylene	18.5
Methyltrimethoxysilane	22.5
Paraffin wax	25.5
Ethyltrimethoxysilane	27.0
Propyltrimethoxysilane	28.5
Polypropylene	31.0
Polyethylene	33.0
Polystyrene	34.0
Aminopropyltriethoxysilane	35.0
Polyvinylchloride	39.0
Phenyltrimethoxysilane	40.0
Polyethyleneterephthalate	43.0
Aluminium (dry)	45.0
Water	72.8
Silica (fused)	78.0
Titanium dioxide	91.0

* Critical surface tensions for silanes refer to the silane treated surfaces and for water refers to the normal surface tension.

$$\underset{\text{silane}}{RSi(OR')_3} + \underset{\text{substrate}}{HO-Si\equiv} \xrightarrow{\text{condensation}} \underset{\text{siloxane bonded on substrate}}{RSi(OR')_2-O-Si\equiv + R'OH}$$

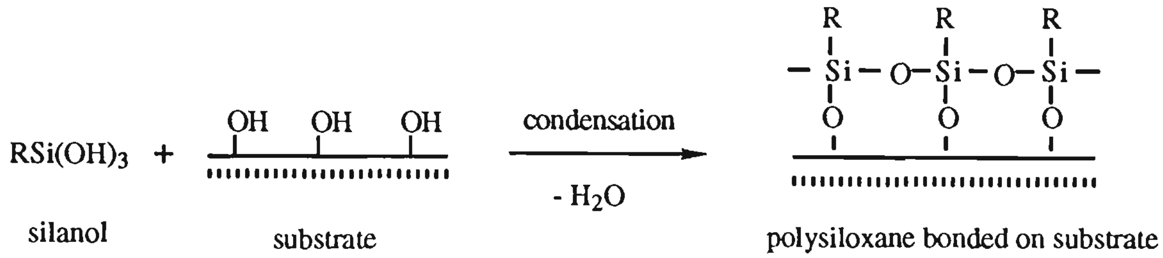
(Scheme 1.5)

In most cases, moisture which is always present in the substrates, accelerates the interaction between the silicone and the substrate by first hydrolysing the silane to reactive silanol intermediates (Scheme 1.6).

$$\underset{\text{silane}}{RSi(OR')_3} + 3H_2O \xrightarrow{\text{hydrolysis}} \underset{\text{silanol}}{RSi(OH)_3} + 3R'OH$$

(Scheme 1.6)

Condensation and crosslinking of the silanol with the mineral surfaces proceeds to form a hydrophobic polysiloxane covering on the substrate surface (see Scheme 1.7). The silicone group of materials have been found to be the most useful impregnants for general masonry water repellent treatment [21].



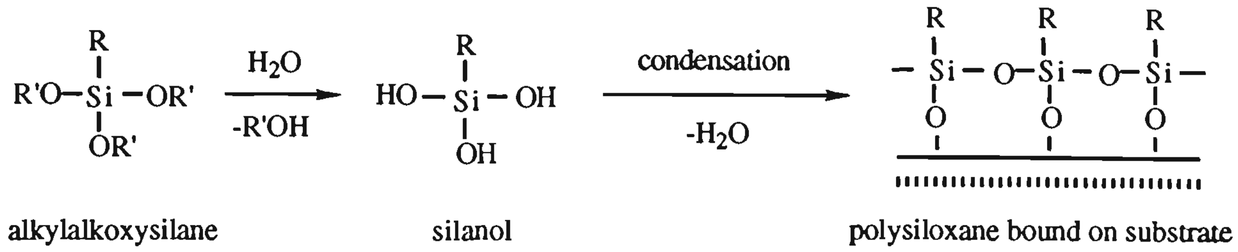
(Scheme 1.7)

1.2.3 Review of silicone impregnants

Silicone masonry impregnants may include solvent-based and water-based materials. Solvent-based silicone impregnants are solutions of silanes, siloxanes or silicone resins dissolved in organic solvents. Water-based silicone water repellents may include, soluble metal silicates, silanols or silane hydrolysis products, metal alkylsiliconates, and silicone emulsions such as silane, siloxane and silicone resin emulsions or their microemulsions.

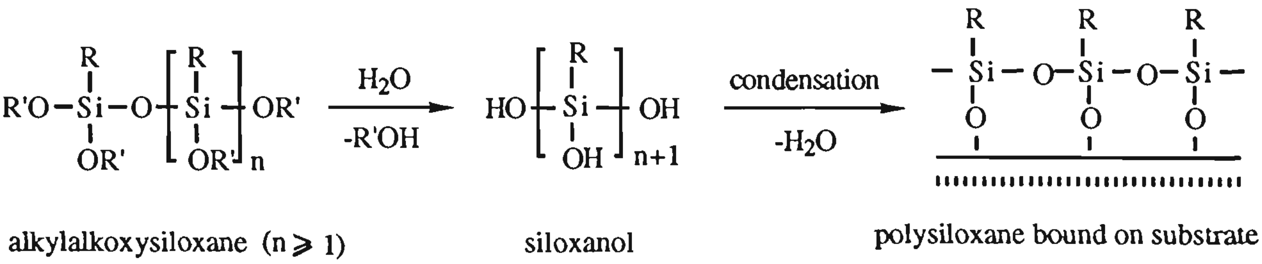
1.2.3.1 Organic solvent-based silicone impregnants

Silanes, siloxanes or silicone resins dissolved in organic solvents are well-known masonry water repellents. In most cases, alkylalkoxysilanes delivered to masonry in organic solvent are first hydrolysed to silanols by the presence of moisture. The silanols then chemically bond to the masonry via siloxane bonding with surface hydroxyl groups and condense with other reactive silicone intermediates to form hydrophobic silicone resin in the capillaries to achieve a water repellent effect (see scheme 1.8). The silanols may also react to form a polysiloxane in the capillary not bonded to the substrate surface.



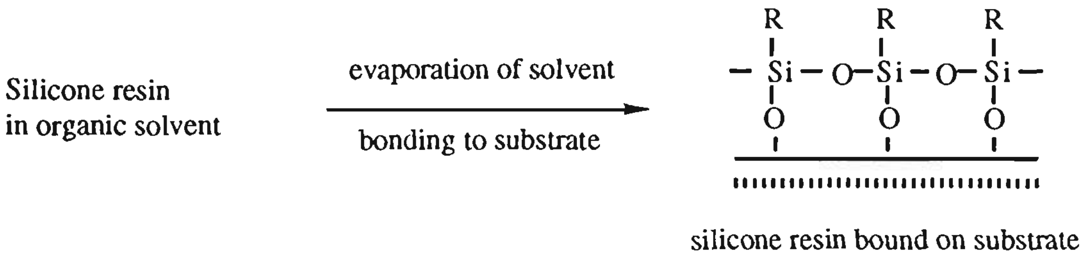
(Scheme 1.8)

A water repellent effect induced by alkylalkoxysiloxanes is similar to that of the silanes (see Scheme 1.9). In this case also the polysiloxane may remain in the capillary not bonded to the substrate surface.



(Scheme 1.9)

Silicone resin in organic solvent may directly impart a water repellent effect to the substrate after evaporation of solvent. Silanol groups (SiOH) still present will react with the hydroxyl groups on the masonry surface and the silicone resin itself to further increase the silicone resin molecular size (see Scheme 1.10) ^{54}. The advantage of silicone resins are their early water repellent and film-forming effects, resulting in excellent surface water repellency properties in the treated masonry. However, the relatively large molecular size of silicone resins results in a limited impregnation depth.



(Scheme 1.10)

Robinson [15] investigated the impregnation of concrete with various silanes, siloxanes or their mixtures in white spirit and concluded that silanes produce impregnated surfaces which offer good chloride ion diffusion resistance due to a higher impregnation depth, whilst siloxane impregnation produces superior water repellency of the concrete due to the good film-forming effect. The siloxane impregnation also induced some carbon dioxide diffusion resistance in the concrete surface due to the formation of a film. Schamberg and Fritsch [55] have successfully treated isolated bricks in a test method for rising damp with a 6.5% by weight solution of ethoxy-functional polysiloxane in white spirit with the addition of crosslinking additives. Janning et al.[56] impregnated a variety of natural stones to make them water repellent with various solvent-based silanes, siloxanes and silicone resins. Sodium chloride (NaCl) penetration resistance of concrete was greatly increased by impregnating the concrete with silanes as disclosed by Brown and Stout [57].

Fey et al.[58, 59] claimed that an alkylalkoxysilane in alcohol, mineral spirit or the mixed solvent, together with beading agents such as fluorosilicones and catalysts such as tetraisopropyltitanate can achieve both deep penetration and good film-forming effect on masonry materials. Fritsch et al.[60] claimed that an alkylalkoxysiloxane in a water-immiscible solvent together with a tin catalyst was able to impart sufficient alkali stability for masonry substrates with a deep penetration depth and a good surface effectiveness. Nestler et al.[61] found that 35% butyltrimethoxysilane in ethanol solution with addition of 5% γ-aminopropyltriethoxysilane imparted better water repellency for masonry than that of the impregnant without the aminosilane. Nestler and Plankl [62] also realised that 40% butyltrimethoxysilane in ethanol solution with addition of 2% $Ca(OH)_2$ can achieve significant reduction in the water absorption of concrete.

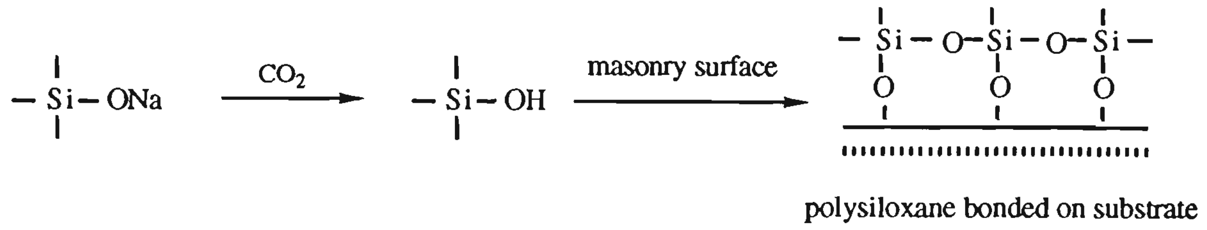
Hydroxyl-substituted polyorganosiloxane in a mixed solvent of aromatic, chlorinated, and aliphatic solvents was found to achieve satisfactory penetration for concrete. The impregnated concrete was resistant to water, metal ions and chloride ions as disclosed by Hodson [63]. However, pure silanes such as propyl- and isobutyltrialkoxysilanes without use of any solvent carrier has been claimed by Rödder [64] to be able to achieve deeper penetration depth in substrates over the depth achieved by use of the same silane in solvents. On the other hand, Roth [65] recommended that isooctyltrimethoxysilanes in solvents such as white spirit can have better penetration ability to the substrates which were wet by water before impregnation due to a phenomenon termed the "aquaplane effect". Applying silane solutions in solvent to wet masonry substrate has also been disclosed by Seiler [66].

Organic solvent-based silicone impregnants have been successfully used to render masonry materials water repellent for many years. If an alkali stable impregnant is selected, the quality and durability of the water repellency is excellent. However, the solvents used to carry the active materials to the substrate are generally flammable and have become increasingly expensive. In addition, the odour, environmental effects and the physiological effects of organic solvents are important factors against the use of organic solvent-based products. In various countries, there is now legislation in place limiting the use of organic solvents in the coating and impregnant industries [67]. Therefore, there is an increasing demand for water repellent materials which may be delivered to the substrate in water and where the penetration into the substrate and performance of the treated substrate is similar to that achieved with organic solvent-based materials.

1.2.3.2 Water-based silicone masonry impregnants

a) Soluble metal silicate

After application to building materials, soluble metal silicate such as sodium silicate can form silanols in the presence of atmospheric carbon dioxide or when the pH of the solution is reduced. Then the silicate silanol can condense to inorganic polysiloxane and at the same time can bond to the masonry substrate [25] in the masonry capillaries. The soluble sodium silicate reactions are shown in Scheme 1.11.



(Scheme 1.11)

Generally speaking, soluble sodium silicates cannot impart water repellent effects to the substrate by impregnation because there are no organic hydrophobic groups introduced to the masonry substrate. However, it is still claimed by previous workers [25, 68, 69] that the impregnation of masonry materials achieves water resistance with soluble sodium silicate solution. The improved water resistance of masonry substrates is only due to the reduced permeability of the substrate by the silicate polymer in the capillaries and not due to any hydrophobic effect. In the case of treating concrete, a significant reduction in the permeability of substrates due to silicate solution impregnation may be achieved if the concrete is very fresh and repeated impregnations are carried out to give a filling of all the masonry capillaries [68, 69]. According to Vail [68], it is sufficient to seal the capillaries by saturating the concrete with the silicate solution on three successive days. If the concrete is fresh enough to contain some free calcium hydroxide, a satisfactory reaction may be obtained with a 10% solution of sodium silicate.

Various curing agents such as calcium chloride ($CaCl_2$), sodium aluminate ($NaAlO_2$), magnesium silicofluoride ($MgSiO_2F$), hydrogen chloride (HCl), sodium bicarbonate ($NaHCO_3$), glyoxal (HCOCHO), and monoethylene glycol diacetate (MEGDA, $CH_3CO_2CH_2CH_2O_2CCH_3$) have been used by previous workers [26, 70, 71, 72, 73] to improve the water resistant effect of either silicate coatings or impregnants.

Another important effect induced by sodium silicate impregnation is consolidation of masonry materials. The sodium silicate can increase the strength of the building materials, particularly natural masonry materials such as sandstones and mud bricks, through reaction with the substrate [25, 68, 69]. Huang et al.[37] and Li [38] impregnated earth structures with sodium silicate to successfully achieve a consolidation effect. The consolidation of earth is assumed to be due to the improvement of the cohesion of the natural material particles by the silicate polymer. O'Connor et al.[74] reported the use of soluble sodium silicate as chemical grout to stabilise soil due to a consolidation effect. In addition, silicate treatment of concrete gives it a greatly increased resistance to abrasion according to Vail [68]. The applications of soluble silicates as binders, adhesives or consolidation agents for masonry are numerous and have been reported in the literature [25].

It is clear that masonry substrates may be consolidated by soluble sodium silicate. However, a water repellent effect is not obtained by impregnating masonry substrates with soluble sodium silicate. Instead, some water resistant effect may be imparted to the substrate due to the reduced permeability of the substrate capillaries. However, this reduction of permeability to water is not marked and is not equivalent to the reduction achieved by impregnation with, for instance, organic silicone water repellents. This is due to the hydrophilic property of the silicate structure. Significant water resistance may be achieved by a complete filling of all the masonry capillaries, but this destroys the water vapour permeability of the masonry substrate.

b) Silanols or silane hydrolysis products

Silanol solutions or aqueous hydrolysis products of alkylalkoxysilanes may be used directly as water repellent impregnants for masonry materials. Alkylalkoxysilanes can be hydrolysed at a suitable pH in water to form a clear aqueous solution [75] which can be used as masonry water repellent impregnant. Condensation of silanol in the solution may start immediately to form polysiloxanols and eventually silicone resin. However, by carefully controlling the pH of the solution or by adding stabilising agents, the silanol solution (strictly a mixture of silanol monomers, oligomers and polysiloxanols) may be kept stable in the pot for a certain period [76]. This silanol solution may be used as a masonry water repellent impregnant.

Schamberg [77] has impregnated concrete with silanol solutions prepared from a mixture of alkyltriethoxysilane and alkyltriethoxysiloxane. Schmidt [78] disclosed a silanol masonry impregnant by hydrolysing propyltrimethoxysilane in the presence of hydrochloric acid and claimed that a low concentration of such silanol solution is more effective in treating masonry to effect water repellency than that of a high concentration of the same silane solution in organic solvent. Deubzer and Wilhelm [79] recommended a method for preparing silanols by hydrolysing silanes in the presence of polyvinyl alcohol or water-soluble cellulose under acidic conditions.

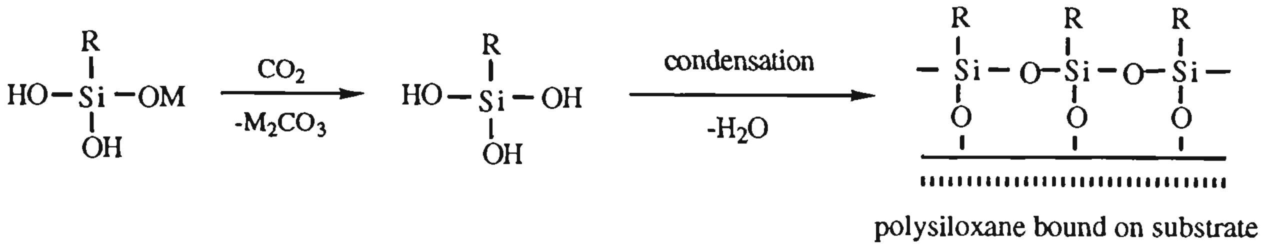
In order to overcome the problem of a short pot-life of silanol solutions, a method to continuously prepare silanol solutions by hydrolysing alkylalkoxysilane in the presence of organic acids was disclosed by Giesing et al.[80]. The silanol solution prepared was used directly to effect the water repellent treatment of masonry on site. Stout and Brunken [81] invented another method to continuously prepare silane or siloxane aqueous dispersions as masonry water repellents.

Hydrolysis products of silanes together with aminosilanes were considered as ideal water-based masonry impregnants by Stark et al.[67]. Cuthbert and Plueddemann [82] disclosed an aqueous silane solution produced by hydrolysing alkylalkoxysilanes together with aminoalkylalkoxysilanes for use as a masonry water repellent treatment. Hydrolysis products of silanes together with aminosilanes was also disclosed by Bank et al.[83]. They found that such silane hydrolysis products can be blended with various other materials (e.g. urea-formaldehyde resins) to render masonry surfaces water repellent. Price [84] claimed a stable silane hydrolysis product by hydrolysing octamethylcyclotetrasiloxane together with N-(2-aminoethyl)-3-aminopropyl dimethoxymethylsilane and tetramethylammonium silanolate. This hydrolysis product, after dilution with a water miscible solvent and then further dilution with water to 4%, can impart a satisfactory water repellent effect to masonry materials. A long shelf-life silanol solution was obtained by keeping the silanol solution in a solvent of a mixture of ethanol and water [85].

Silanol solutions or aqueous hydrolysis product of silanes, although soluble in water, are not ideal products as masonry water repellent impregnants. They are water soluble but they are dynamically unstable in solution resulting in a limited pot-life. Continuously making silanol on site may be inconvenient and a hazardous gas such as methanol may be evolved if the alkoxysilane is a methoxysilane. Further, the silanols of higher alkyltriethoxysilanes are difficult to obtain by hydrolysis without the addition of a water-miscible solvent. Using an aminosilane hydrolysis product as a stabilisation agent for the silanol solution may increase the cost of the impregnant as a large quantity of aminosilane is needed. Further, aminosilicones may affect the water repellency of the masonry as aminoalkylsilane treated surfaces have higher critical surface tension than alkylsilanes according to Arkles [40] and therefore are not ideal hydrophobic agents. Using mixed water-miscible solvent to stabilise the silanol solution still involves the problem of using organic solvents.

c) Metal alkylsiliconates

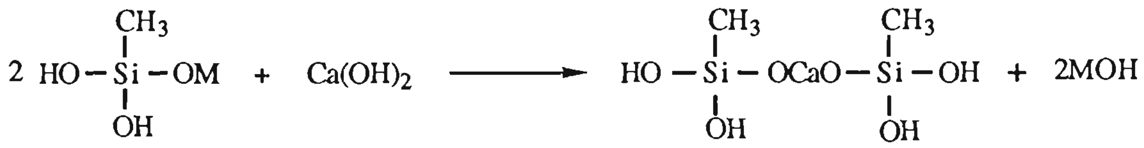
Siliconates are highly alkaline aqueous solutions. When applied to masonry, they react with carbon dioxide to form alkali metal carbonates and reactive silanol intermediates which then chemically bond with masonry substrates and condense with similar intermediates to form silicone resin in the substrate capillaries (shown in Scheme 1.12). Sodium methylsiliconate is a typical metal alkylsiliconate and probably the cheapest silicone water repellent impregnant. It has been used to impregnate masonry materials such as stone, brick and concrete to make them water repellent for many years since disclosure by Elliott and Krieble [86], and Kather and Torkelson [87]. The application of sodium methylsiliconate solutions to highway surfaces to render the highway surface water repellent was disclosed by Spalding and Mackey [88]. Kitagawa et al.[89] used a mixture of sodium or potassium methylsiliconate and nitrite to protect concrete against steel-reinforcement corrosion. Potassium methylsiliconate is the preferred material over sodium methylsiliconate since potassium carbonate is less voluminous and therefore less visible than sodium carbonate after application [54].



$$HO-\underset{OH}{\overset{R}{Si}}-OM \xrightarrow[-M_2CO_3]{CO_2} HO-\underset{OH}{\overset{R}{Si}}-OH \xrightarrow[-H_2O]{\text{condensation}} -\underset{O}{\overset{R}{Si}}-O-\underset{O}{\overset{R}{Si}}-O-\underset{O}{\overset{R}{Si}}-$$

(Scheme 1.12)

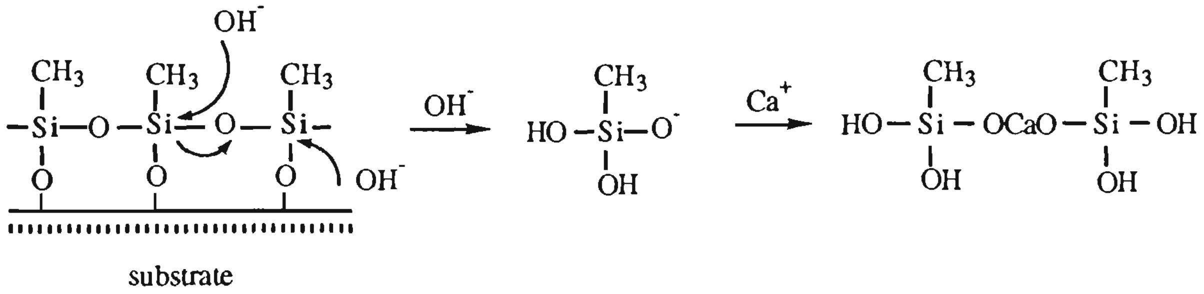
It is known that methylsiliconates are not suitable for substrates which contain free lime (calcium hydroxide) such as fresh concrete. The methylsiliconate reacts with calcium hydroxide [29, 90] to form calcium methylsiliconate which precipitates. The calcium methylsiliconate is somewhat soluble and not very hydrophobic and can be washed out by rain water from the treated surface [29] (see Scheme 1.13).



$$2\ HO-\underset{OH}{\overset{CH_3}{Si}}-OM + Ca(OH)_2 \longrightarrow HO-\underset{OH}{\overset{CH_3}{Si}}-OCaO-\underset{OH}{\overset{CH_3}{Si}}-OH + 2MOH$$

(Scheme 1.13)

In addition, the methylpolysiloxanes formed in the substrate after methylsiliconate impregnation may be hydrolysed by alkali in the presence of water to become methylsiliconate monomer and then calcium siliconate [29] (see Scheme 1.14).

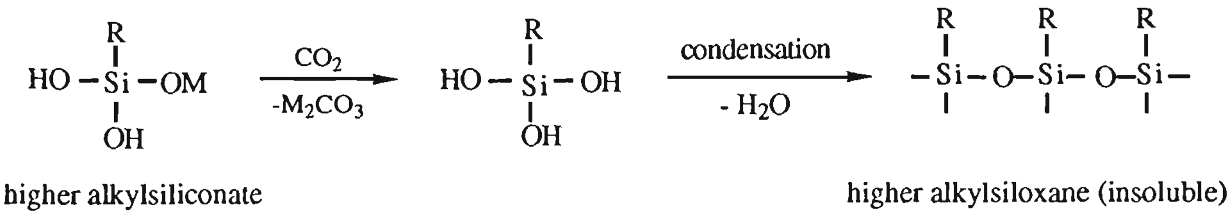


$$HO-\underset{OH}{\overset{CH_3}{Si}}-O^- \xrightarrow{Ca^+} HO-\underset{OH}{\overset{CH_3}{Si}}-OCaO-\underset{OH}{\overset{CH_3}{Si}}-OH$$

(Scheme 1.14)

To overcome the alkali stability problem of methylsiliconates, Nitzsche et al.[91] disclosed a method of either pre-treating the alkaline substrate with a solution of ammonium carbonate or bicarbonate or mixing the solution with the impregnant. The solution neutralises the surface alkalinity of the substrate and accelerates the siliconate condensation in the substrate without the necessity of carbon dioxide access after impregnation. However, this requires an expensive pre-treatment of the substrate such that the impregnation process becomes a two-step process. Bosch et al.[92, 93] disclosed a water repellent composition of metal alkylsiliconate for alkaline masonry substrates. These compositions contained alkali metal higher alkylsiliconates particularly propylsiliconates and an aqueous miscible alcohol and/or ketone solvents to attain solubility. Larger alkyl groups attached to the silicone atom provided higher resistance to hydrolysis of silicone resin by alkali due to steric hindrance [21]. In addition, precipitation of higher alkylsiliconate by calcium ions may occur but the calcium higher alkylsiliconate is less soluble and more hydrophobic than calcium methylsiliconate and therefore satisfactory water repellency of the masonry substrates is achieved [94].

Unfortunately, siliconate solutions suffer a stability problem when higher alkyl siliconates are used. When a concentrated solution of a higher alkyl siliconate is diluted, the pH of the solution decreases and the siliconate then absorbs carbon dioxide from the solution to form silanol. Condensation then occurs to form an insoluble polysiloxane which precipitates from the solution if the alkyl group is larger than methyl (shown in Scheme 1.15). Bosch et al.[92] used aqueous alcohols and/or ketone solvents or an organic water-soluble complex or chelating agent to stabilise higher alkyl siliconate solutions.



(Scheme 1.15)

Traver and Schryer [95] disclosed aqueous siliconate containing water repellent compositions which were obtained from hydrolysing mixtures of aminoorgano-functional alkylsilane and various alkyltrimethoxysilanes in potassium hydroxide. This potassium amino-functional siliconate and alkylsiliconate mixture was used as a water repellent for concrete. These authors suggested using water-miscible solvents or nonionic surfactants to stabilise these solutions of potassium aminofunctional siliconate and alkylsiliconate mixture.

As discussed above, treating alkaline substrates with metal methylsiliconate is not successful. Pre-impregnation of the substrates with carbonate or bicarbonate solution according to Nitzsche et al.[91] involves an expensive and time-consuming pre-treatment. The carbonate or bicarbonate salts could be added to the impregnating solution to overcome the alkali stability problem, or lack of exposure to the atmosphere after impregnation, but this addition deteriorated the stability of the impregnant solution according to these workers [91]. Further, decreasing the alkalinity of the concrete risks establishing conditions suitable for corrosion of the embedded steel bar [13] if reinforced concrete is impregnated. Using higher alkyl siliconates according to Bosch et al.[92, 93] can increase the alkali stability but a water-miscible solvent had to be added to improve the stability of the diluted siliconate solution. Further, the commercial price of higher alkylsiliconates (e.g. a commercial product of potassium propylsiliconate known as Wacker BS 20) is considerably higher than that of potassium methylsiliconate. The mixtures of aminosiliconates and alkylsiliconates disclosed by Traver and Schryer [95] cannot achieve better alkali stability than that of methylsiliconate according to their test results.

d) Silicone emulsions and microemulsions

Emulsions or microemulsions of silanes, siloxanes and silicone resins are another group of water-based impregnants recently developed for effecting water repellency for various masonry substrates. Generally they are more stable than silanol solutions. They can achieve sufficient water repellency to highly alkaline substrates without the stability problems of higher alkylsiliconate solutions. Further, particular properties of the silicone emulsion may be obtained by carefully choosing the initial raw silicone material.

According to DePasquale and Wilson [96], a silane emulsion can be obtained by emulsifying an alkyltriethoxysilane with a nonionic surfactant such as a sorbitan fatty acid ester. The emulsion can be applied to either dry or damp concrete substrates to impart water repellency. Suzuki [97] disclosed a silane emulsion as a masonry water repellent by emulsifying an alkyltriethoxysilane with a mixture of nonionic and anionic surfactants. According to Suzuki, a mixture of nonionic and anionic surfactants is the best emulsifier for production of a silane emulsion. This surfactant mixture was preferred to a nonionic surfactant alone or a mixture with a cationic surfactant. However, Koerner et al.[98] disclosed a stable polysiloxane emulsion with either a mixture of nonionic surfactant and anionic surfactant or a mixture of nonionic surfactant and cationic surfactant. Grape et al.[99] found that a silicone resin emulsion made by emulsifying a methylmethoxy silicone resin with mixed nonionic surfactants achieves good water repellency if a tin catalyst such as dioctyl tin maleate is used. Göbel et al.[100] disclosed a silane emulsion with a nonionic silicone surfactant for water repelling building materials.

Schamberg et al.[101] disclosed a silicone emulsion with mixed anionic surfactants being secondary alkanesulfonates. They found that the emulsion made by using a mixture of octyltriethoxysilane and methylpolysiloxane imparts a better depth of impregnation and water repellent effect than those of emulsions made with either a silane or polysiloxane alone. Raleigh [102] disclosed a polysiloxane emulsion with an anionic surfactant consisting of an ammonium salt of an aliphatic carboxylic acid for the water repellent treatment of perlite. The carboxylic acid salt was decomposed by a subsequent heating process.

Heaton [103] disclosed aqueous silane emulsion compositions comprising hydrolysable silanes, thickening agents, buffering agents, biocides and hydrophobic fumed silica as masonry water repellents. Kaijou [104] invented a water repellent emulsion comprising essentially colloidal silica treated with a silylating agent, a nonpolar organic solvent, cationic surfactants, fluorine or silicone-containing surfactant and water as a water repellent for masonry materials.

Microemulsions are a clear or translucent solutions which have very fine particle sizes and are dynamically stable [105]. Once an impregnant is applied to the masonry surface, normal silicone emulsions may break on the substrate surface but a microemulsion is stable and claimed to be able to penetrate deeply into the substrates [106]. Mayer et al.[107] successfully developed a silicone microemulsion with an aminofunctional silane, acetic acid and an organopolysiloxane to render masonry material water repellent. Huhn et al.[108] disclosed a microemulsion comprising aminofunctional polysiloxanes, nonionic surfactants and water. In a study to establish suitable water repellents for clayrich sandstone, Snethlage and Wendler [109] found that, by mixing an aqueous solution of protonated aminoalkylsilane with an ethanolic solution of alkylsilanes in an exactly defined ratio, an almost clear solution was obtained. The solution was believed to be a silicone microemulsion which can be used as water repellent impregnant. Merrifield et al.[110] disclosed a microemulsion with an amino functional polysiloxane, mixed nonionic surfactants, water and acetic acid.

Most alkylalkoxysilanes and alkylalkoxysiloxanes are sensitive to water particularly in either acidic or basic conditions and hydrolyse and condense to form polysiloxanes according to Osterholtz and Pohl [75]. Silicone contact with water is unavoidable when preparing silicone emulsions, and therefore silicone hydrolysis may more or less occur resulting in reduction of the stability of the emulsion or a decrease in the water repellent performance. In order to minimise the hydrolysis of the silane in the emulsion, Wilson [111] and Heaton [103] disclosed that a buffering agent such as sodium bicarbonate could be added into the octyltriethoxysilane emulsion to keep the pH at 7.5 to obtain a non-hydrolysable emulsion. The buffering agent may keep the pH of the silane emulsion at a required pH to limit the silane hydrolysis during storage of the emulsion. Grape et al.[99] suggested using an amine to adjust the pH to 7.5-9 in the final siloxane emulsion to keep the emulsion stable. However, DePasquale and Wilson [96] believed that polyhydroxy type nonionic surfactants such as the Spans (the sorbitan esters) and the Tweens (the ethoxylated sorbitan esters) may act as inhibitors of hydrolysis of the silane in the absence of an acid or alkaline medium.

In a comparison with organic solvent-based silicone water repellent impregnants, the performance of the previously discussed silicone emulsions is not as good in terms of stability, penetration depth, and water repellent effect of the treated substrates. The surface water beading effect is particularly poor. In particular, the use of surfactants may result in a poor water repellent effect, possibly due to the adsorbed surfactant at the substrate surface causing a net hydrophilic effect termed as a "wetting effect" on re-exposure to water. After impregnation with silicone emulsion, the silicone may form a permanent bond with the substrate with the hydrocarbon groups facing upwards from the surface. However, surfactants are inert to the substrate and they may orient themselves on the hydrophobic substrate surface by surfactant adsorption [112-115] leaving their hydrophilic group facing upwards (see Figure 1.8). Any surface excess concentrations may decrease the contact angle θ (see Equation 1.1) and result in a hydrophilic surface of the treated masonry substrate.

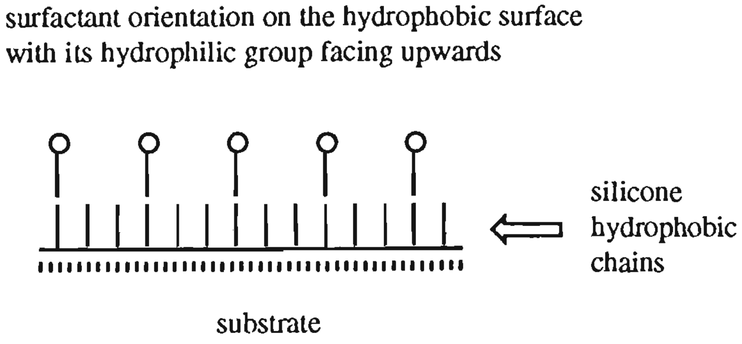


Figure 1.8 *Hydrophilic surface with surfactant on the surface*

From the test results of Pühringer [116], the water repellent effect of a substrate treated with an emulsion without surfactant was much better than that of an emulsion with an anionic surfactant. According to Suzuki [97], the quality of the water repellent effect of the substrate treated with a silicone emulsion was decreased with increase in concentration of either nonionic or anionic surfactants in the emulsion. The effect of the surfactant on the masonry surface deteriorates the water repellent effect on the treated surface since the surfactant causes a wetting of the very surface of the substrate and therefore would not be acceptable in freezing climatic conditions. In addition pollutive substances could be carried into the substrate via this wetted layer.

A large quantity of surfactants is needed for formulating microemulsions [105]. Silicone microemulsions for water repellent treatment are usually composed of aminofunctional silicones as emulsifiers. Normal surfactants may also be needed to formulate silicone microemulsion impregnants. A large quantity of aminofunctional silicones [107, 108, 110] in the emulsion actives may be required for formulating a stable microemulsion. The aminosilicone may reduce the water repellency of the treated substrate as an aminosilicone treated surface has a higher critical surface tension according to Arkles [40] and is therefore less hydrophobic than an alkylsilicone impregnated surface. In addition, using such a large quantity of the aminosilicone as surface active material results in a high production cost for the microemulsions.

1.3 Research design

The organic solvent-based silanes, siloxanes and silicone resins are not suitable in the long term due to their use of environmentally unfriendly, physiologically unsafe, and expensive solvents. Silanols or silane hydrolysis products are dynamically unstable and are therefore of less practical value for treating buildings. Metal alkylsiliconates such as potassium methylsiliconate are not suitable for substrates which contain free lime. Potassium propylsiliconate may be used for alkaline substrates but dilution with water miscible organic solvents is necessary and this is undesirable. Most silicone emulsions involve various surfactants or their mixtures which may cause wetting of the treated surfaces of the substrates. Silicone microemulsions are expensive and inefficient due to the inclusion of a large quantity of amino functional silanes which are not good hydrophobic agents.

Moreover, silicone microemulsions may also contain significant amounts of normal surfactants which may affect the water repellency of the impregnant. Therefore, it is desirable to develop alternative aqueous silicone water repellents without organic solvent additions. These repellents should be stable, capable of effectively impregnating alkaline substrates, achieve a good water repellent effect and be suitable for various materials particularly for low-cost buildings.

Siliconates such as potassium methylsiliconate may be the basis for effective water-based water repellent impregnants for low-cost buildings if a process could induce good alkali stability with sufficient stability in aqueous solution. In addition, silicone emulsions may also be ideal impregnants for low-cost buildings if sufficient water repellency at low concentration of active material could be achieved without the surfactant wetting effect. These properties of water-based water repellent impregnants have not been achieved by the prior art. The aim of this project is to better understand the interface between surface and solution, in particular, building material and organosilicone species stabilised with surfactants such that more effective solutions can be invented and more efficient delivery systems of the liquids to the treatment of the pores be conceived. The main objects of the research therefore become:

a) to develop a novel low-cost siliconate which is suitable for treating alkaline substrates but has sufficient stability in aqueous solution without solvent addition, and

b) to develop a novel silicone emulsion impregnant which can effectively render low-cost masonry substrates water repellent at a low concentration of active materials but does not induce surfactant wetting in the substrate, and

c) to develop methods to apply the novel impregnants onto the masonry substrates to impart sufficient water repellency, to examine the impregnated properties and performance of the treated substrates and to understand the impregnation mechanism by studying the interaction between the impregnants and the substrate.

2. MATERIALS AND METHODS

2.1 Materials

Materials included chemicals and masonry building materials. As the project was an industrial research project, most chemicals such as silicones, surfactants and solvents were either industrial grade reagents or commercial products. Masonry building materials were either real building materials or substrates prepared in the laboratory according to practical standards.

2.1.1 Chemicals

2.1.1.1 Potassium alkylsiliconates

Potassium methylsiliconate (PMS) with a formula of $CH_3Si(OH)_2OK$, was an industrial grade product of trade name Rhodorsil 51T purchased from Rhone-Poulenc Chimie. Analysis according to British Chemical Dampcourse Association [117] showed that Rhodorsil 51T contained 44.33% solids and 24.46% active silicone (the calculation was based on $CH_3SiO_{1.5}$). These results accorded with the data sheets supplied by the manufacturers.

Pure potassium propylsiliconate, with a basic formula of $CH_3(CH_2)_2Si(OH)_2OK$, was not commercially available. An industrial grade potassium propylsiliconate containing some methylsiliconate with the trade name of Wacker BS20 was purchased from Wacker-Chemie GmbH. This potassium propyl and methyl siliconate (PPMS) contained 41% solids and 20.5% total active silicone ($RSiO_{1.5}$) with a propyl/methyl siliconate ratio of 7/3 according to the manufacturer.

All of the siliconates were used as they were without further purification. All siliconate concentrations used herein are active silicone by weight based on $RSiO_{1.5}$ unless otherwise stated.

2.1.1.2 Soluble sodium silicate

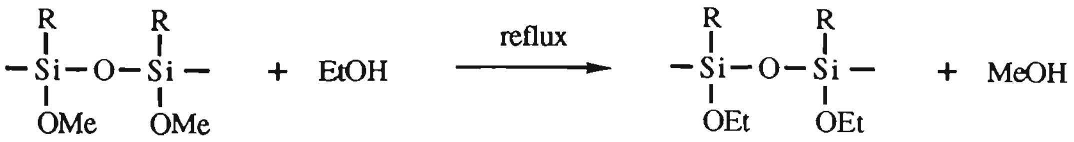
Soluble sodium silicate was an industrial grade product with a trade name Vitrosol N42 purchased from ICI Australia and was used without further purification. It contained 395g/litre solid with a SiO_2/Na_2O ratio of 3.2.

2.1.1.3 Silanes and siloxanes

Isobutyltrimethoxysilane (BTMS), isobutyltriethoxysilane (BTES) and octyltriethoxysilane (OTES) were industrial grade products with a concentration of more than 98% of the active silane purchased from Hüls AG and were used without further purification. Methyltrimethoxysilane (MTMS) and octyltrimethoxysilane (OTMS) were laboratory grade with a concentration of 96% of the active silane purchased from Aldrich Chemical Company and were used without further purification.

Octyl/methyl methoxysiloxane with a tin catalyst (OMMS-Sn) was a commercial water repellent product with a trade name of Wacker 290 purchased from Wacker-Chemie GmbH. It contained octyl/methyl methoxy co-oligomeric siloxane and dibutyltin dilaurate catalyst according to the manufacturer. The octyl/methyl ratio of the siloxane was found to be approximately 3/7 according to the ^1H NMR spectrum. The same oligomeric siloxane without tin catalyst (OMMS) was purchased from Wacker-Chemie GmbH. The siloxane has the trade name Wacker VP 1268. Both octyl/methyl methoxysiloxanes with or without tin catalyst were used without further purification unless otherwise stated.

The octyl/methyl ethoxysiloxane (OMES) was obtained by alcoholysis of OMMS using the transetherification procedure of Voronkov et al.[118]. The alcoholysis was carried out by refluxing Wacker VP1268 in excess ethanol (1 part of Wacker VP1268 with 10 parts of dry ethanol by volume) for 8 hours (shown in Scheme 2.1). The alcoholysis product after distillation of methanol and excess ethanol was quantitatively analysed by ^1H NMR. The final product was found to contain at least 95% of OMES. Both ^1H NMR spectra of initial OMMS and the OMES product of alcoholysis with ethanol are shown in Figure 2.1.



$$-\overset{\displaystyle R}{\underset{\displaystyle OMe}{Si}}-O-\overset{\displaystyle R}{\underset{\displaystyle OMe}{Si}}- \;+\; EtOH \xrightarrow{\text{reflux}} -\overset{\displaystyle R}{\underset{\displaystyle OEt}{Si}}-O-\overset{\displaystyle R}{\underset{\displaystyle OEt}{Si}}- \;+\; MeOH$$

(Scheme 2.1)

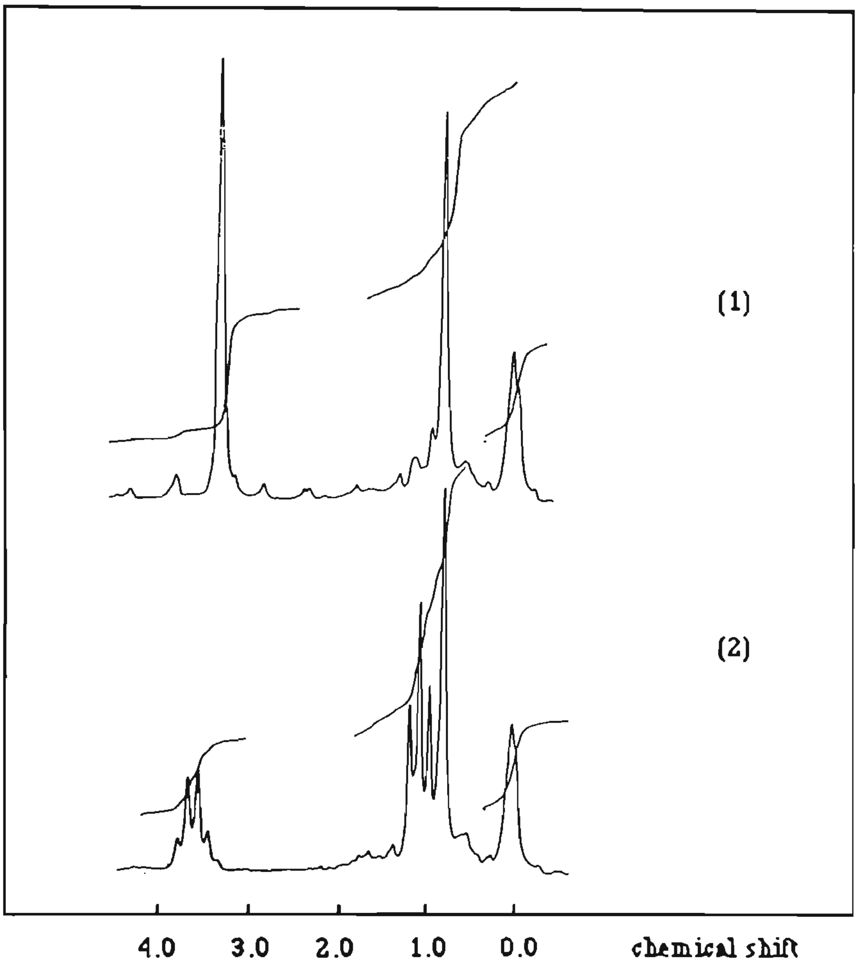


Figure 2.1 ^1H NMR spectra of; 1) initial OMMS, 2) final OMES after alcoholysis with ethanol (the spectra were recorded at 60 MHz with a Perkin-Elmer spectrometer R-24R)

2.1.1.4 Surfactants

All surfactants including, the nonionics, the anionics and the cationics were industrial grade and were used without further purification unless otherwise stated.

Nonionic surfactants included (fatty) alkylalcohol ethoxylates (trade names Teric GmAn) with chemical formulas of $R_m(OCH_2CH_2)_nOH$ (m = 9-17, n =2-25), (fatty) alkylamine ethoxylates (trade names Teric 16Mm) with chemical formulas of $R_{16}N[(OCH_2CH_2)_{\bar{n}}OH]_2$ (m = $2\bar{n}$ = 2-15), nonylphenol ethoxylates (trade names Teric GN n) with chemical formulas of $R_9C_6H_5(OCH_2CH_2)_nOH$ (n = 8-30), and ethoxylated sorbitan fatty acid esters (trade names Tween n with n = 20-85). All of these surfactants were purchased from ICI Australia.

Modified alkylamine ethoxylates for silane/siloxane emulsion preparation were obtained by the addition of an acetic acid into the alkylamine ethoxylate nonionic surfactant solution. To a conical flask, 6 parts of water was mixed with 1 part of the surfactant (w/w) with stirring. 10% acetic acid (HAc) solution was added dropwise into the surfactant/water mixture until the pH of the mixture became approximately 7 as measured with pH paper (the pH measurement of the surfactants and the emulsions will be discussed in §2.3.9). The mixture was then stirred for 1-2 hours or more until the suspension became clear or became homogeneous. The concentration of the final surfactant solution was adjusted to 10% by the addition of distilled water based on the alkylamine ethoxylates in the solution or suspension. The properties of the acidified alkylamine ethoxylate surfactant of Teric 16M2 $[R_{16}N(OCH_2CH_2OH)_2]$ used in this project are listed in Table 2.1.

Table 2.1 *The properties of the acidified alkylamine ethoxylates of Teric 16M2*

Surfactant code names	Ratio of HAc/16M2	pH of the surfactant	Solubility in water
Teric 16M2*	0	9	dispersion
Teric 16M2-1	0.05/1	8	dispersion
Teric 16M2-2	0.08/1	7.5-8	dispersion
Teric 16M2-3	0.10/1	7.5	soluble
Teric 16M2-4	0.12/1	7-7.5	soluble
Teric 16M2-5	0.14/1	7	soluble
Teric 16M2-6	0.17/1	7	soluble
Teric 16M2-7	0.20/1	6.5-7	soluble
Teric 16M2-8	0.24/1	6.5	soluble

* Teric 16M2 is the untreated alkylamine ethoxylate nonionic surfactant.

Anionic surfactants used included linear alkylbenzene sulphonic acid (LABSA), sodium fatty acid isethionate (trade name Hostapon KA), sodium alkane sulphonate (trade name Hostapur SAS60) and isopropylamine alkylbenzene sulphonate (trade name Gardilene IPA/94). The first three surfactants were purchased from Hoechst and the last was purchased from Albright & Wilson (Australia) Ltd.

Cationic surfactants included, myristyltrimethyl ammonium bromide (trade name of Vantoc N40), cetyltrimethyl ammonium chloride (trade name of Vantoc CC30), benzyllauryldimethyl ammonium chloride (trade name of Vantoc CL80). All were purchased from ICI Australia.

Table 2.2 lists some properties of most surfactants used according to McCutcheon [119] or the manufacturer.

2.1.1.5 Other chemicals

Ethanol for alcoholysis, GC and FTIR analysis was GLC grade (> 99.9% ethanol) provided by BDH Chemicals Ltd. It was further distilled from magnesium turnings and the distillate was stored with the addition of molecular sieves to obtain dry ethanol.

n-Propanol as an internal standard for Head Space Gas Chromatography (HSGC) was GLC grade reagent (> 99.9% n-propanol) provided by BDH Chemicals Ltd. The purity of the n-propanol for HSGC analysis was such that further purification was not necessary.

Distilled water was always used if dilution of water-based materials was needed. To prepare samples for NMR of water-based siliconates, deuterium oxide (D_2O) provided by SIC Stohler Isotope Chemicals was used, which contained 99.8% D and was used without further purification.

Table 2.2 *Some properties of surfactants used*

Surfactant names	Chemical structures [c]	Contents %	HLB or Solubility
Nonionic [a]:			
Teric G9A2	$R_{9-11}(OCH_2CH_2)_2OH$	99.5-100	8.7
Teric G9A4	$R_{9-11}(OCH_2CH_2)_4OH$	99.5-100	about 10
Teric G9A6	$R_{9-11}(OCH_2CH_2)_6OH$	99.5-100	12.4
Teric G9A8	$R_{9-11}(OCH_2CH_2)_8OH$	99.5-100	13.7
Teric G9A12	$R_{9-11}(OCH_2CH_2)_{12}OH$	99.5-100	15.4
Teric G12A3	$R_{12-15}(OCH_2CH_2)_3OH$	99.5-100	7.1
Teric G12A4	$R_{12-15}(OCH_2CH_2)_4OH$	99.5-100	9.8
Teric G12A6	$R_{12-15}(OCH_2CH_2)_6OH$	99.5-100	11.2
Teric G12A8	$R_{12-15}(OCH_2CH_2)_8OH$	99.5-100	12.6
Teric G12A9	$R_{12-15}(OCH_2CH_2)_9OH$	99.5-100	13.6
Teric G12A12	$R_{12-15}(OCH_2CH_2)_{12}OH$	99.5-100	14.4
Teric G12A23	$R_{12-15}(OCH_2CH_2)_{23}OH$	99.5-100	16.6
Teric G17A2	$R_{16-18}(OCH_2CH_2)_2OH$	99.5-100	6.0
Teric G17A6	$R_{16-18}(OCH_2CH_2)_6OH$	99.5-100	10.2
Teric G17A8	$R_{16-18}(OCH_2CH_2)_8OH$	99.5-100	11.6
Teric G17A10	$R_{16-18}(OCH_2CH_2)_{10}OH$	99.5-100	12.7
Teric G17A25	$R_{16-18}(OCH_2CH_2)_{25}OH$	99.5-100	16.2
Teric 16M2	$R_{16-18}N(OCH_2CH_2OH)_2$	99.5-100	9.5
Teric 16M5	$R_{16-18}N[(OCH_2CH_2)_{\bar{n}}OH]_2$ ($\bar{n}$ = 2.5)	99.5-100	10.5
Teric 16M15	$R_{16-18}N[(OCH_2CH_2)_{\bar{n}}OH]_2$ ($\bar{n}$ = 7.5)	99.5-100	13.8
Teric GN30	$R_9C_6H_5(OCH_2CH_2)_{30}OH$	99.5-100	17.2
Tween 80	sorbitan monooleate + 20 EO	99.5-100	15.0
Anionic [a, b]:			
LABSA	linear alkylbenzene sulphonic acid	94	soluble
Hostapon KA	sodium fatty acid isethionate	80 (powder)	soluble
Hostapour SAS60	sodium alkane sulphonate	60	soluble
Gardilene IPA/94	isopropylamine alkylbenzene sulphonate	94	insoluble
Cationic [a]:			
Vantoc N40	myristyltrimethyl ammonium bromide	40 (w/v)	soluble
Vantoc CC30	cetyltrimethyl ammonium chloride	30.5 (w/v)	soluble
Vantoc CL80	benzyllauryltrimethyl ammonium chloride	80 (w/v)	soluble

a) Data from the manufacturer, b) Data from McCutcheon [119], c) R_n represents surfactant hydrocarbon chain

Organic solvents used to dilute solvent-based impregnants or additives for emulsions were a mixture of petroleum hydrocarbons (mostly isoparaffins) with the trade name Isopar G and a mixture of n-paraffins/iso-paraffins and naphthenes with the trade name Exxsol D60, both provided by Exxon Chemicals. Both of the solvents were industrial grade products and were used without further purification.

All other chemicals used in the research were laboratory grade reagents and were used without further purification unless otherwise stated.

All concentrations of the chemicals used herein are calculated as a percentage by weight unless otherwise stated.

2.1.2 Masonry substrates

2.1.2.1 Cement mortar substrates

Cement mortar substrates were made according to either Australian Standard AS 3700 M3 (sand/cement/water: 6/1/1) or German Standard DIN 1164 (sand/cement/water: 3/1/0.5). The cement was GP type of Australian Standard AS 3972 and the sand was general concrete sand with a particle size distribution as shown in Figure 2.2. The cement and sand were first mixed with a FESTO Concrete Mixer (WR-140R provided by FESTO Pty. Ltd.) at the lowest speed for 5 minutes before water was added. Then the cement, sand and water were mixed at the highest speed for 5 minutes before moulding in plastic rings or rectangular moulds. The mortar substrates were de-moulded from the moulds after 3 hours and cured at ambient conditions for 1 to 8 weeks or more depending on the test. The final size of the mortar substrates was d=75 mm and h=30 mm for discs and 75x105x30 mm for rectangular blocks. Before tests the surface of the mortar substrate was brushed with a wire brush, washed with tap water and dried in an oven at 105^{o}C for 24 hours.

Permeable commercial concrete pavers purchased from a paver supplier were also used for some tests. They were analysed for cement content as described by British Standard [120].

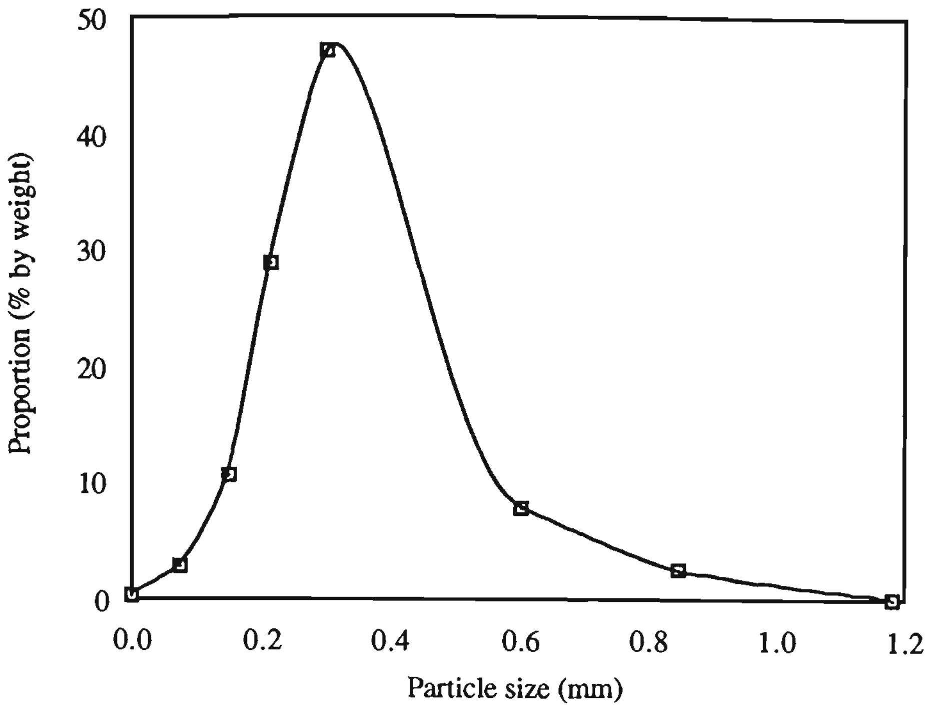


Figure 2.2 *Particle size distribution of the concrete sand used*

The carbonation depth of cement mortar substrates was checked by use of a 1% phenolphthalein solution in a mixed solvent of alcohol and water (1/1 by volume). By wetting the fresh broken surface of the mortar substrate with the phenolphthalein solution and observing the colour change of the phenolphthalein on the substrate, the carbonation depth of the substrate can be determined by measuring the colourless layer near the surface of the substrate according to the pH change [121] of the indicator shown in Table 2.3.

Table 2.3 *Carbonation of the cement mortar or concrete substrate*

Change of colour	pH range	Carbonation
dark pink	>10	uncarbonated
colourless to light pink	8.2-10	almost carbonated
colourless	<8.2	carbonated

2.1.2.2 Low temperature fired bricks

Low temperature fired bricks were not obtainable in Australia. Indian bricks which had high porosity , high permeability and low strength were used as the brick substrates.

Bricks were cut using a masonry saw into small blocks with a size of either 50x50x30 mm or 75x105x30 mm depending on the test. The cut surfaces of brick substrates were brushed with a wire brush and washed with tap water and dried in an oven at 105°C for 24 hours before tests were undertaken. The cut surface of the bricks was used for tests.

2.1.2.3 Mud brick substrates

The mud brick substrates were made from Kalimantan (Indonesia) soil. The soil contained 0.7% gravel (>2.36 mm), 62.5% sand (0.06-2.36 mm), 9.4% silt (0.002-0.06 mm) and 27.4% clay (<0.002 mm) based on an analysis carried out according to Clifton and Brown [122]. In order to reduce the proportion of clay and silt in the soil to minimise the shrinking and cracking on drying [123], concrete sand (as used in mortar substrate preparation) was mixed with the soil to adjust the clay and silt proportion to about 30%. The mud brick substrates were prepared by mixing 1 part of water with 6 parts of the soil/sand mixture with a FESTO Concrete Mixer at the highest speed for 5 minutes in a similar way as that of making mortar. The substrates were dried at ambient conditions for at least 28 days. The final size of the mud bricks was d=70 mm and h=30 mm for the disc substrates and 75x105x30 mm for the rectangular substrates.

Some properties of the above substrates as determined according to British Standard [120] and Clifton and Brown [122] are listed in Table 2.4.

Table 2.4 Properties of masonry substrates used

Substrate	Bulk density (kg/m^3)	Capillary porosity (%)	pH
Cement mortar AS3700 M3	1920	14.3	>10*
Cement mortar DIN 1164	2062	10.6	>10*
Permeable concrete paver **	2187	8.4	8.2-10
Indian fired bricks	1721	22.1	6.5
Mud brick substrates	1767	19.1	5.3

* The pH of cement mortar substrates depends on the curing time of the substrate. The pH of fresh cement mortar substrate of 8 weeks old or less is usually more than 10. ** The pavers contained 8.2% cement.

2.2 Preparation of novel water-based impregnants

2.2.1 Preparation of potassium octyl/methyl siliconate

A conical flask equipped with a thermometer and a magnetic stirring bar was placed in a water bath which was placed on a heater/stirrer. PMS was mixed with a surfactant (melted first in a microwave if necessary) in the flask to form a homogeneous pre-reaction mixture. Silane was then added dropwise into the mixture with continuous stirring to form a homogeneous suspension at room temperature. The exothermic hydrolysis commenced once the silane was added. The reaction was carried out either at a specific temperature from room temperature up to 60°C and maintained at this temperature for from a few minutes, to 24 hours, depending on the reaction conditions. The mixture turned from a cloudy suspension to a clear "solution" at the end of the procedure. The hydrolysis end point was determined as that time when the hydrolysis mixture was further dilutable with a volume of 10 times of distilled water to form a clear siliconate solution (this end point was further confirmed by FTIR and HSGC). The final active siliconate ingredient can be calculated as the total $CH_3SiO_{1.5}$ from the initial methylsiliconate and the $RSiO_{1.5}$ from the silane.

2.2.2 Solubilisation of potassium higher alkylsiliconate solutions

Investigation of the solubilisation of metal higher alkylsiliconate solution was undertaken with a commercial potassium propylsiliconate (PPMS) solution. The solubilisation was carried out in a conical flask. The flask was equipped with a thermometer and a magnetic stirrer bar and was placed in a water bath which was placed on a heater/stirrer. Under constant stirring, solubilised PPMS was made by either adding surfactant into the concentrated PPMS solution which was then diluted with distilled water or by adding PPMS into distilled water which contained a surfactant. Potassium octyl/methyl siliconate (POMS) developed by this research already contained a surfactant before hydrolysis and therefore it was not necessary to add surfactant into the diluted POMS solution. Solubilised POMS solution was spontaneously formed upon dilution with distilled water.

2.2.3 Preparation of silane/siloxane emulsions

A cylindrical flask of internal size (d=30 mm and h=175 mm) was equipped with an Ultra-Turrax T25 shear mixer (provided by Janke & Kunkel GmbH & Co. KG IKA Laboratory Technology). The flask was placed in a water bath or a water jacket with running tap water (about 20°C) (shown in Figure 2.3). Acidified alkylamine ethoxylate surfactant was first mixed with distilled water in a cylindrical flask as the aqueous phase. The silane and siloxane or other oil soluble additives were pre-mixed in a beaker as the oil phase and then added dropwise into the aqueous phase in the flask with shear at a speed of 13,500 rpm. Unless otherwise stated, the emulsion was then mixed at the same speed for a further 10 minutes. For the preparation of emulsions with emulsifiers other than acidified alkylamine ethoxylates, emulsifiers were either mixed with the aqueous or the organic phase depending on their solubility in the phases. If two surfactants were used where one was oil-soluble and the other was aqueous-soluble, the oil-soluble surfactant was dissolved in the organic phase whilst the other was dissolved in the aqueous phase. The emulsions were then prepared in the same manner as stated above.

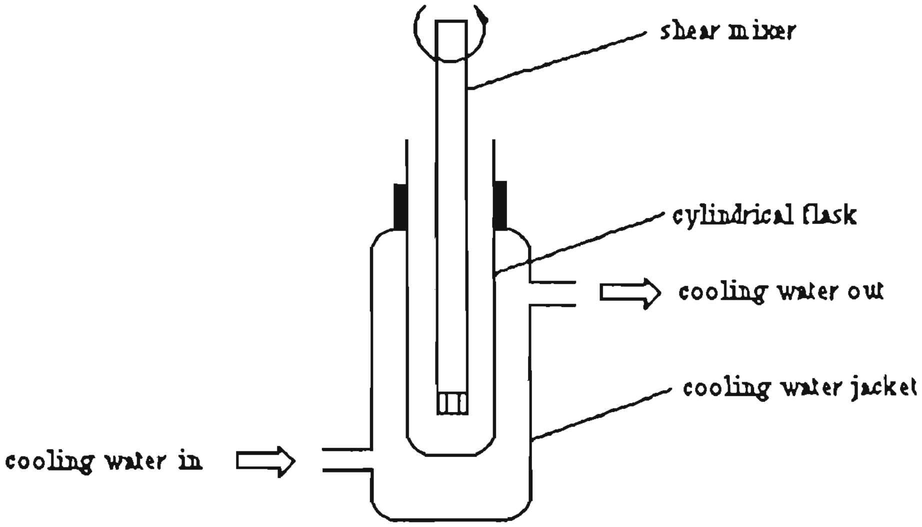


Figure 2.3 Device for making a silicone emulsion

2.3 Analysis of materials and impregnants

Due to both novel siliconates and silicone emulsions being water-based and complex products, analysis of such products is difficult, particularly for the hydrolysis of silane in the highly alkaline PMS system. Peace et al.[124] and Brinker et al.[125] employed Gas Chromatography (GC) to investigate the hydrolysis of tetraethoxysilane. However, injecting siliconate solutions into the GC column is generally not possible as siliconate is not volatile and may react with the column materials spontaneously after injection. Savard et al.[126] studied the hydrolysis of γ-methacryloxy propyltrimethoxysilane by ^{1}H NMR. It is difficult to monitor ethoxysilane hydrolysis by proton NMR as the spectrum of the hydrolysis system is complex and the chemical shift of $-OCH_2-$ protons in ethoxysilane, ethanol (hydrolysis product) and the ethoxylate chains of the surfactant are quite similar. McNeil et al.[127] investigated tris(2-methoxyethoxy)phenysilane by using a UV spectrometer. However, the alkylalkoxysilane is not detectable by UV as is the phenysilane. Ishida and Koenig [128] studied vinyltrimethoxysilane hydrolysis with a Fourier Transform Infrared (FTIR) spectral technique but Leyden et al.[129] stated that the analysis of ethoxysilanes is not amenable to this technique due to their complex spectra in the region 1300-800 cm^{-1}. Miller and Ishida [130] combined size-exclusion chromatography (SEC) and FTIR to study phenytrialkoxysilanes and γ-methacryloxy propyltrimethoxysilanes. The analysis of alkylalkoxysilanes by this method is not suitable due to their low UV sensitivity. Nishiyama and Horie [131] studied silane hydrolysis and condensation employing ^{13}C and ^{29}Si NMR. However, none of these methods can provide enough information for the complex hydrolysis system of octyltriethoxysilane in potassium methylsiliconate with surfactant present.

In the present research, sufficient information has been obtained to study either the novel siliconate products or the novel silicone emulsions by using a combination of Head Space Gas Chromatography (HSGC), FTIR, ^{1}H and ^{29}Si NMR and various other analytical methods.

2.3.1 Fourier Transform Infrared spectrometry (FTIR)

FTIR spectra were recorded using a Perkin-Elmer 1640 Spectrometer equipped with DGTS detector. The spectra were obtained at a resolution of 4 cm^{-1} by 16 scans at room temperature in absorbance mode. All the spectra were stored and subsequently processed with Perkin-Elmer IRDM software. General spectra recorded refer to thin films of liquids. Spectra of silane hydrolysis products were collected as outlined below.

The sample from the reaction mixture as described in §.2.2.1 was placed into a semi-sealed cell with two AgBr windows and scanned during the hydrolysis. The thickness of the cell was controlled with a 25 μm teflon spacer so that quantitative analysis was possible and the intensity of the most interesting bands were strong enough but less than 1.5 absorbance in order to minimise deviations from the Beer-Lambert Law caused by a reflectance of the infrared beam. The cell and the windows were completely cleaned with chloroform followed by washing with distilled water and drying after every experiment. The same mixture with addition of dry ethanol rather than silane (the amount of ethanol was calculated as the theoretical production of ethanol from hydrolysis of the silane) was recorded as the background spectrum in the same conditions unless otherwise stated. The neat hydrolysis product spectrum was obtained by digitally subtracting the spectrum of the reaction mixture from that of background using the Si-CH_3 band of methylsiliconate at 1260 cm^{-1} as an internal thickness band [132] as shown in Figure 2.4.

2.3.2 ^1H and ^{29}Si NMR spectrometry

Proton nuclear magnetic resonance (^1H NMR) spectra were recorded at 60 MHz with a Perkin-Elmer Spectrometer R-24R or at 300 MHz with a Bruker AM 300 Spectrometer. Silicone nuclear magnetic resonance (^{29}Si NMR) spectra were recorded using a Bruker AM 250 Spectrometer operating at 49.694 MHz. The chemical shift reference used was tetramethylsilane (chemical shift δ 0.00 ppm). The deuterium signal of D_2O or $CDCl_3$ was employed for field/frequency locking for high field NMR unless otherwise stated. Samples for NMR spectra were prepared as usual [133]. Unless otherwise stated, the organic sample was diluted with $CDCl_3$ and the siliconate samples including the silane hydrolysis product were diluted with D_2O before NMR analysis.

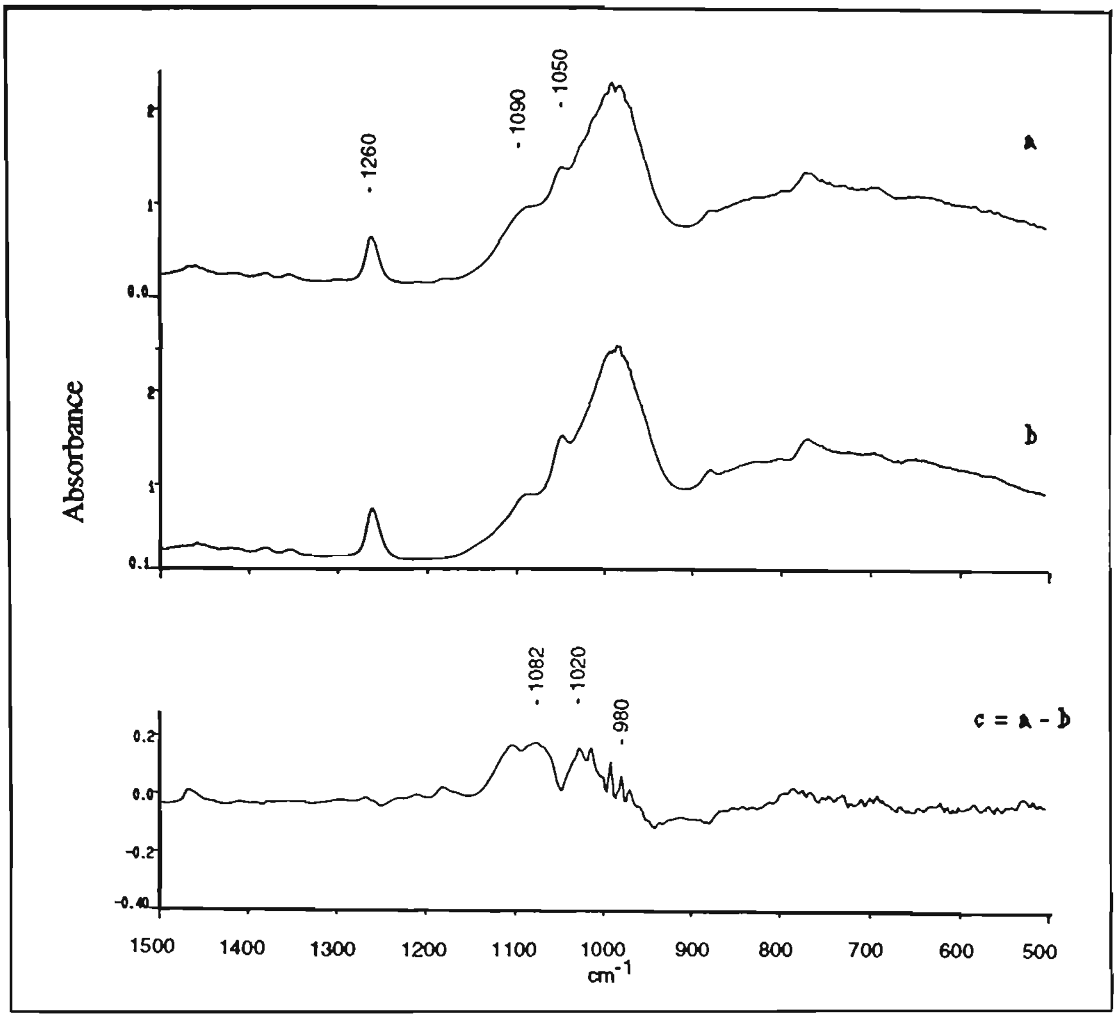


Figure 2.4 FTIR spectra of silane hydrolysis; a) spectrum of the hydrolysis reaction mixture, b) background spectrum, and c) subtracted spectrum of the neat silane hydrolysis products

2.3.3 Head space gas chromatography (HSGC)

HSGC is a suitable technique to analyse volatile compositions such as methanol or ethanol in aqueous solutions [134, 135]. By monitoring the ethanol cleavage through GC, it was possible to study the rate of the silane hydrolysis [124, 125]. It is also the most suitable and the simplest way to monitor the methanol or ethanol cleavage from the silane/siloxane emulsion to indirectly study the hydrolysis of the silane and the siloxane if this occurs in the emulsions. HSGC was employed for monitoring the methanol or ethanol cleavage from the silane hydrolysis in PMS or from the silane/siloxane emulsion. The GC spectra were recorded using a Shimadzu 8A Gas Chromatograph equipped with a flame ionisation detector combined with a Shimadzu Integrator C-R6A. The column was a DB-Wax 0.53 Megabore capillary column. The operation conditions were the injection port temperature at 250°C, a detector temperature of 300°C and a constant oven temperature of 60°C.

n-Propanol was found to be the most suitable internal standard for HSGC monitoring of ethanol in the reaction system. It was dilutable with both initial reagents and final products and gave a peak with sufficient separation from that of ethanol in the spectrum under the GC operating conditions. The addition of n-propanol was controlled at the ratio of 0.10 to 1.75 (by weight) of n-propanol to the silane in order to minimise the possible alcoholysis (as discussed by Voronkov et al. in a different system [118]) of the silane by n-propanol. The pre-reaction mixture of surfactant and methylsiliconate prepared as described in §.2.2.1 with an internal standard n-propanol, was added into in a 20 ml HSGC vial (total reactant volume was controlled to about 10 ml). Then the silane was added and the vial was sealed immediately with a rubber septum and aluminium crimp. The vial was placed in a constant temperature water bath with occasionally shaking. 10 µl of vapour sample from the vial was manually injected in the GC column to monitor both ethanol and n-propanol at about 5 minute (or more) intervals which was found to be sufficient for the formation of the liquid-vapour equilibrium in the vial. The ethanol production from the hydrolysis can be then clearly monitored by GC (shown in Figure 2.5).

The ratio of peak area of ethanol/n-propanol can be calculated from the GC spectra. The calibration curve was obtained by adding various amounts of pure ethanol into the pre-reaction mixture without the silane addition and running HSGC at the same conditions. The relationship between the peak area ratio of ethanol/n-propanol and ethanol concentration in the reaction mixture was almost a straight line (as shown in Figure 2.6) so that it was possible to use the peak area ratio of ethanol/n-propanol to indirectly monitor the ethanol concentration in the hydrolysis system to study effects of various reaction conditions on the rate of silane hydrolysis.

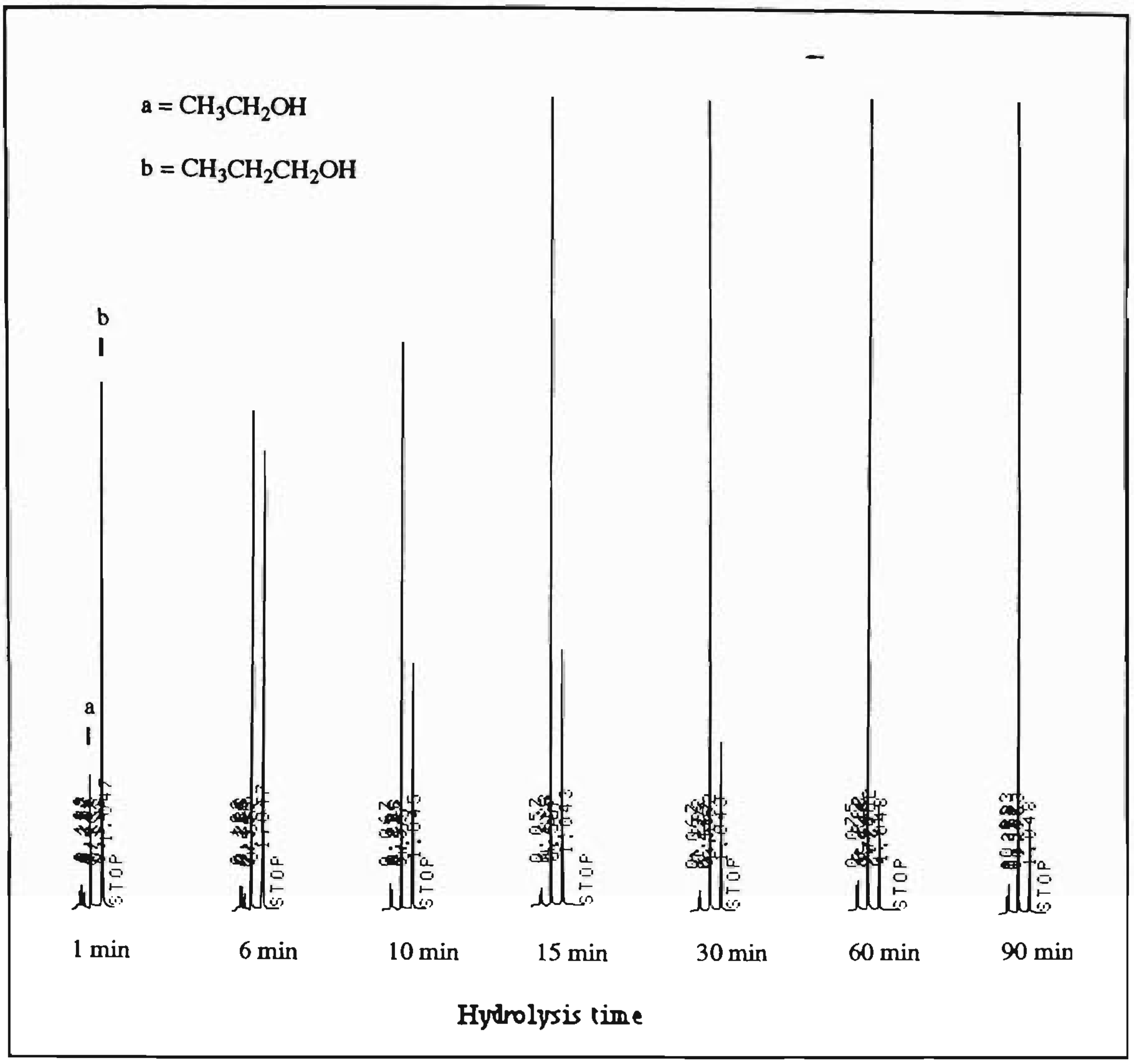


Figure 2.5 HSGC spectra of ethanol and n-propanol from the silane hydrolysis system during the hydrolysis reaction

In monitoring the methanol and ethanol concentration in silane/siloxane emulsions, n-propanol was also used as internal standard. 5 Gram of silane/siloxane emulsion was diluted with 5 ml of distilled water which contained 1% n-propanol by weight as the internal standard in a 20 ml head space vial which was placed in a water bath at 25°C. The vial was maintained in the bath with occasional shaking for at least 10 minutes before sample injection onto the GC column. Calibration curves were obtained by injecting various concentrations of standard methanol and ethanol solutions. The relationship between the GC peak area ratio of the methanol or ethanol to n-propanol and the methanol and ethanol concentration in the standard samples was linear (shown in Figure 2.7), which was sufficient to quantitatively determine the methanol and ethanol concentration in the emulsion.

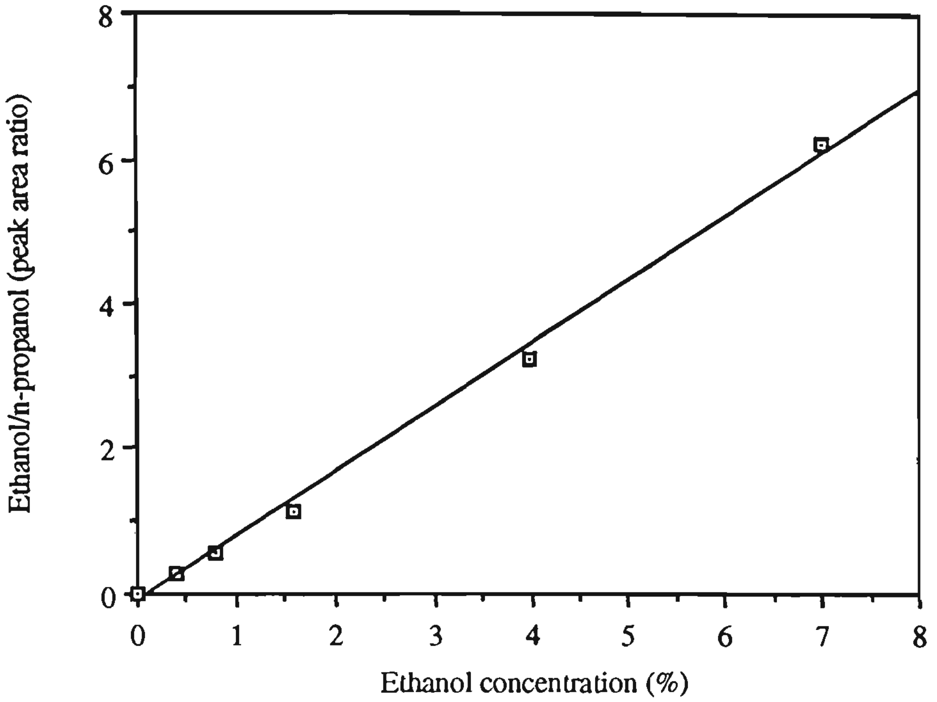


***Figure 2.6** Relationship between peak area ratio of ethanol/n-propanol and the ethanol concentration in pre-reaction mixture at 25^{o}C*

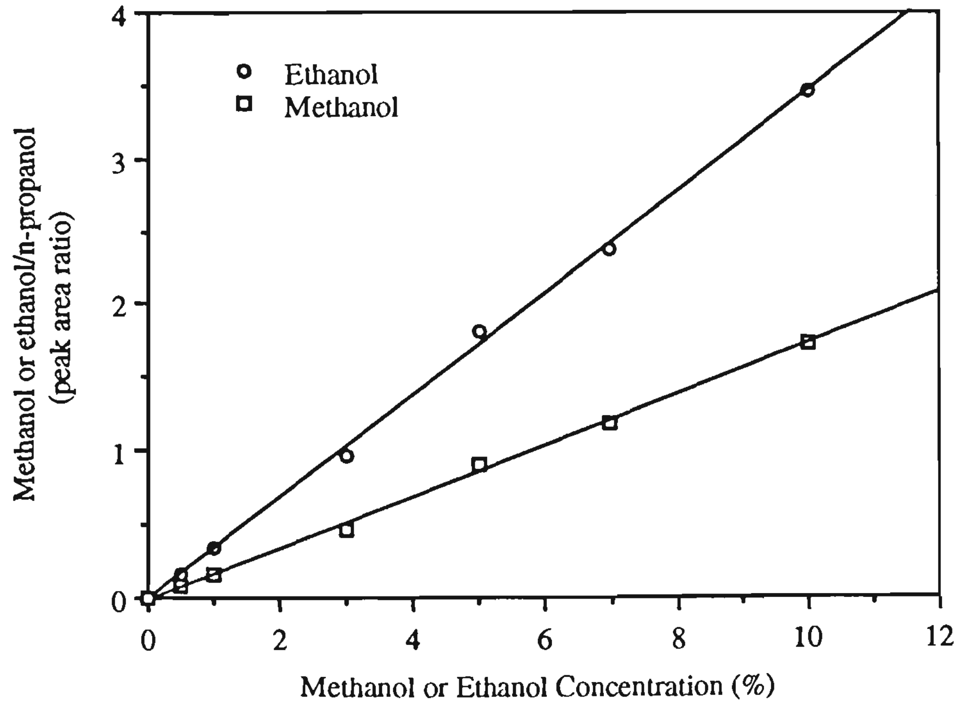


***Figure 2.7** Standard curves of methanol and ethanol concentration*

2.3.4 Viscosity measurement

Viscosity was recorded using a Brookfield Digital Viscometer (Model DV-I+ Version 2.0). The sample was placed in a cylindrical flask of internal size (d=30 mm and h=100 mm) in a water bath at 25°C without a spindle frame. The viscosity of siliconates were recorded with a LV1 spindle at a speed of 6 r.p.m. The viscosity of emulsions were recorded with a LV2 spindle at a speed of 12 r.p.m. Both viscosities were represented as centipoises (cps). The values were based on the average of 3 measurements.

2.3.5 Cloud point (T_c) of solubilised siliconate or surfactant solutions

Cloud points (T_c) of solubilised siliconate solutions and nonionic surfactant solutions were determined by placing 50 ml of the solution in a 100 ml beaker fitted with a thermometer and a magnetic stirrer bar in a water bath on a hot plate. The T_c was determined as described by El-Khordagui [136]. The beaker was heated at a rate of 2°C/min with stirring until the solution became cloudy. The temperature at which the solution (which had been heated above the clouding temperature) lost its last trace of turbidity on subsequent cooling, was recorded as the cloud point T_c. The data presented were the average of at least three determinations.

2.3.6 Particle size and zeta potential measurements

The particle sizes of the solubilised siliconate solutions were recorded using a Malvern Photon Correlation Spectrometer (Zetasizer 4). The analysis was conducted at an angle of 90° at 25°C. The mean particle sizes and the size distributions by number or intensity were obtained by processing the data with Malvern Zetasizer software.

The particle sizes of emulsions were recorded using a Laser Diffraction Particle Sizer (Malvern Mastersizer MS20). The operation conditions included using distilled water as the medium and controlling the sample size automatically by computer. The various mean particle sizes and the size distributions were obtained by processing the data with Malvern particle size analyser software. The particle sizes of the emulsion (especially for particles

>1 μm) were also directly examined with an optical microscope. In addition, the particle size may be estimated by looking at the reflected and transmitted light from the sample in a glass vial with the naked eye according to the Tyndall effect [137]. The guidelines for visual estimation of the particles in liquid is given in Table 2.5 according to Holliday [138].

Table 2.5 Tyndall effect and the relationship with particle size

Particle size (μm)	Scattered light colour	Transmitted light colour	Appearance or opacity of the liquid
0.5-0.3	weak blue	smoky yellow	opaque
0.3-0.2	weak blue	weak red	opaque
0.2-0.1	intense blue	intense red	opaque
0.1-0.01	weak blue	weak red	translucent
<0.01	no colour	no colour	translucent-clear

The zeta potential of the silane/siloxane emulsion was recorded using a Malvern Photon Correlation Spectrometer (Zetasizer 4). The emulsion was diluted with a surfactant solution as a dilution agent which contained the same concentration of the same surfactant as used in the emulsion. Approximately 0.1 ml of emulsion was diluted in 40 ml of the dilution agent. Zeta potential was measured at 25°C. The results were based on the average of at least 5 measurements and were represented as millivolts (mV).

2.3.7 Surface tension and interfacial tension measurements

The surface tension of the diluted siliconate solution was measured using a DÜ NOÜY ring type tensiometer at room temperature (23°C). The platinum ring was cleaned between measurements by a cleaning mixture (made by adding a moderately strong solution of dichromate to a strong solution of sulphuric acid), washed and rinsed with distilled water and followed by flaming until red hot. The results presented were the average of six tension determinations and were represented as dyne/centimetre (dyne/cm).

The interfacial tension between the organic and aqueous phase of the emulsion was measured also using a DÜ NOÜY ring type tensiometer in the same manner as surface tension measurement. Absolute interfacial tension obtained by using a DÜ NOÜY ring type tensiometer may not be obtained [139]. However, relative results with fairly reproducible readings can be used to study the same emulsion system. The platinum ring was applied from the top of the organic phase down to the bottom of the aqueous phase during the interfacial tension measurement. The surfactant was dissolved or suspended in the aqueous phase.

2.3.8 Stability of the emulsions

An emulsion is a thermodynamically unstable system and it ultimately separates into two phases. The physical stability of the emulsion was examined by placing the emulsion in long cylindrical vials and assessing the extent of particle size changes, creaming, sedimentation or phase separation during storage at room temperature or 40°C as described elsewhere for other systems [140-142]. The chemical stability of the emulsion was examined by monitoring the change of the viscosity and the methanol or ethanol production in the emulsion during the storage. This is due to the silane or the siloxane hydrolysis and condensation resulting in producing the methanol or ethanol and changing the viscosity during storage.

2.3.9 pH of emulsions and surfactant solutions

The pH of emulsions and surfactant solutions (or suspensions) were recorded with a pH meter (Orion Research Microprocessor Ionalyzer Model 901 with an Orion RX combination pH electrode) by measuring 1% of either emulsions or surfactant solutions (or suspensions) at room temperature. The pH was also measured by using pH papers (Merck Art. 9560 pH 0.5-5.0, Art. 9564 pH 5.5-9.0 and Art. 9562 pH 9.5-13 paper) particularly for acidified alkylamine ethoxylate or cationic surfactants. The pH values of the emulsions or surfactant solutions measured with both pH meter and the pH paper were quite consistent except for the acidified alkylamine ethoxylate surfactants or other cationic surfactants or emulsions made with those surfactants. When measuring the pH of the those surfactants or emulsions, the pH meter gave much lower pH results than those of the pH paper measurement. This may be attributed to the acidified amine ethoxylate surfactants or cationic surfactants affecting the electrode by strong adsorption of the surfactant through positively charged nitrogen of the surfactant and negatively charged electrode glass membrane surface to give incorrect readings. However, pH paper may give less precise but more reliable pH readings since it only responds to chemical reactions in measuring the pH whereas the pH meter responds to the potential across the glass membrane which may be affected by adsorbed surfactants on the membrane. Therefore, in the case of alkylamine ethoxylate surfactants, cationic surfactants and the emulsions stabilised with those surfactants, the pH was recorded by using pH papers unless otherwise stated. The pH papers were also pre-checked by known pH buffer solutions and compared with values obtained by pH meter. Some examples of pH measurement of 1% surfactant solutions (or suspensions) by both the pH meter and the pH papers are listed in Table 2.6.

Table 2.6 Comparison pH values of some surfactant solutions or suspensions

1% surfactant solutions or suspensions	pH (meter value)	pH (paper value)
Hostapur SAS 60 (anionic)	6.21	6
Gardilene IPA/94 (anionic)	5.74	5.5-6
Teric G16A16 (nonionic)	5.20	5.5
Teric G17A25 (nonionic)	3.36	3-3.5
Teric 16M2 (alkylamine ethoxylates)	9.33	9
Teric 16M2-3 (acidified amine ethoxylates)	4.91	7.5*
Vantoc N40 (cationic)	4.16	7.5*
Vantoc CC30 (cationic)	6.58	7.5-8*

* inconsistent readings when measuring acidified amine ethoxylate or cationic surfactants

2.4 Application of impregnants to masonry materials

The impregnation of masonry substrates was carried out by immersing one surface of the substrate in an impregnant liquid bath at a depth of 3 mm for 60 seconds unless otherwise stated. A metal wire (d=1 mm) of a U shape was placed between the treated surface of the substrate and the bath to avoid close contact of the substrate surface with the flat bottom of the impregnation bath to allow sufficient absorption of the impregnant by the substrate (shown in Figure 2.8). The substrate was then removed and the liquid remaining on the surface was drained off. The substrate was then left with the treated surface face up on a bench and dried at ambient conditions for 7 days. For the treatment of mud brick substrates, they may first be impregnated with soluble sodium silicate and then with water repellent liquid after 24 hours. The first impregnation with sodium silicate was applied by flooding the impregnant onto the horizontal surface of the substrate for 1 minute in order to avoid deterioration of the mud brick by immersion in the aqueous liquid.

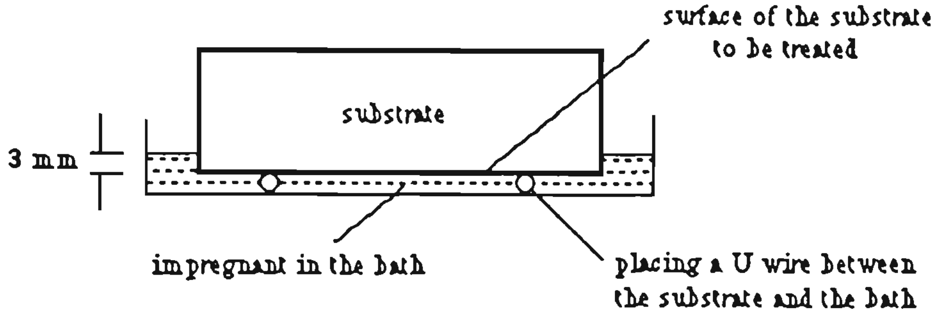


Figure 2.8 Diagram of impregnation of masonry substrate by immersion

2.5 Examination of the treated substrates

The impregnants were novel and the properties of treated substrates with novel impregnants is unknown. Therefore it is necessary to examine the impregnation performance of the treated substrates by various tests.

For all tests, samples treated with 5% by weight of commercial octyl/methyl methoxysiloxane with tin catalyst (OMMS-Sn) in Isopar G solvent were used for comparison. Untreated samples were also examined in every test as controls. All siliconate solution impregnants were 2% by weight active silicone contents, based on

$RSiO_{1.5}$ and all other impregnants were 5% by weight silane or siloxane content unless otherwise stated. Each test result was based on the average of at least three test results.

2.5.1 Beading effect

The beading effect is the simplest and the quickest way to examine the water repellent effect of the substrate treated with the impregnants. The beading effect was checked by placing from a pipette a large droplet of water (about 0.1 ml) on the treated substrate surface. After 10 minutes water was removed and the surface beading effect was assessed according to the following standard as described by Schamberg et al.[101]:

1 = excellent	no wetting of the contact area.
2 = good	50% of the contact area is wetted.
3 = fair	100% of the contact area is wetted.
4 = poor	water partly absorbed by the surface (less than 50%).
5 = bad	water partly absorbed (more than 50%).
6 = very bad	water droplet absorbed completely within 10 minutes
7 = no beading effect	

2.5.2 Water absorption and alkali stability tests

Water absorption is the major method to quantitatively measure the water repellent effect of the substrates treated with the impregnants. The water absorption value was investigated by laying the treated surface of the substrates on a saturated polyurethane sponge in a water bath according to DIN 52617E for a certain period depending on the test as shown in Figure 2.9.

The water absorption value was determined as weight increase over the area of the treated surface of the substrate at different intervals:

$$\text{Water absorption (kg/m}^2\text{)} = \frac{Wt - Wo}{A} \qquad (2.1)$$

where W_0 was the initial weight of the substrate and W_t was the weight of substrate at time t. A is the area of treated surface of the substrate. The water absorption results (kg/m^2) may be then plotted against the test time.

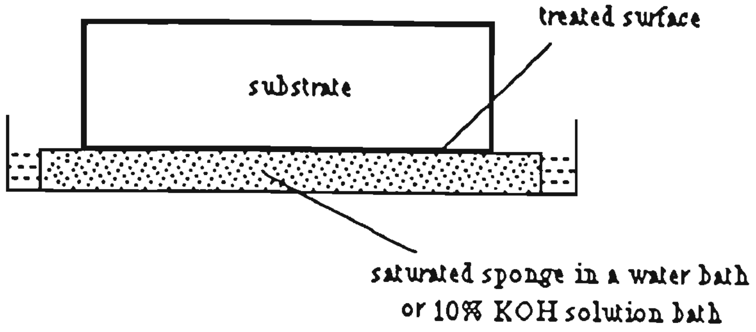


Figure 2.9 Sponge water absorption test

The alkali stability tests were carried out in the same manner as the water absorption tests. Instead of water, 10% KOH solution was used in the bath. Another method for investigating the alkali stability of an impregnant is by the use of a water absorption test where impregnation is carried out with the test liquid on very fresh cement mortar substrate cured for only 1 week. This was found to be equivalent to the alkali stability test with 10% KOH solution. Table 2.7 shows the test results for 10% KOH solution absorption of cement mortar substrates (4 weeks old) and water absorption of cement mortar substrates (1 week old). Both of the substrates were treated with 2.5% PMS solution and the samples failed the test within 2 days.

Table 2.7 Comparative test results for water absorption and 10% KOH solution absorption on different aged mortar substrates

	Absorption values (kg/m^2)			
	8 hours	24 hours	48 hours	72 hours
10% KOH solution	0.22	2.36	4.23*	4.49
water	0.14	1.09	4.32*	4.44

* Water rose through the substrate and the substrate failed the test.

2.5.3 Depth of impregnation and consolidation

The depth of impregnation was examined by breaking the treated substrate and wetting the broken surface with water containing a water soluble red or blue dye. The thickness of the un-wetted, and therefore colourless layer near the treated surface of the substrate was then taken as the depth of impregnation. For mud brick substrates treated with consolidants, the depth of consolidation may need to be determined. The depth of consolidation was examined by completely dipping the treated substrates into a water bath, where the unconsolidated part of the substrate was soon deteriorated by water. The thickness of the remaining consolidated portion of the treated substrate was measured as the depth of consolidation.

2.5.4 Water vapour permeability test

The permeability of the treated substrates was examined through a water vapour transmission test. The untreated side of the substrate was first dipped for 4 hours in a water bath at a depth of about 25 mm to saturate the substrate. The water on all surfaces was removed with a dry sponge and the substrate was then immediately weighed and wrapped with Parafilm "M" laboratory film and sealed with melted paraffin wax except for the treated surface of the substrate which was left unwrapped. The substrates were then placed in an oven at 40°C. The substrates at different times were weighed and the water vapour transmission values were then calculated as below:

$$\text{Water vapor transmission (\% by weight)} = \frac{Wo - Wt}{Wa} \times 100 \qquad (2.2)$$

where W_a was the weight of water which was absorbed by the substrates before wrapping. W_o was the initial weight of the substrates before placing in the oven and W_t was the weight of substrate at time t. The water vapour transmission results may be then plotted against the test time.

2.5.5 Resistance to water absorption under hydrostatic pressure

The water absorption of the substrate under hydrostatic pressure was carried out in order to examine the water resistance ability of the water repellent layer of the substrate under wind pressure by the RILEM tube test. A RILEM test tube was vertically fixed at the centre of the substrate surface by using Blu-Tack re-usable adhesive (see Figure 2.10). The tube was filled with water to a head of 100 mm which is equivalent to the maximum pressure of driven rain forced by blown wind (normally vertical surface pressure by wind blowing at a velocity of 140 km/hr is taken as 95 mm) on a vertical wall according to Noll [29]. To avoid water losses from evaporation from the tube, the water surface was covered with a few drops of paraffin oil.

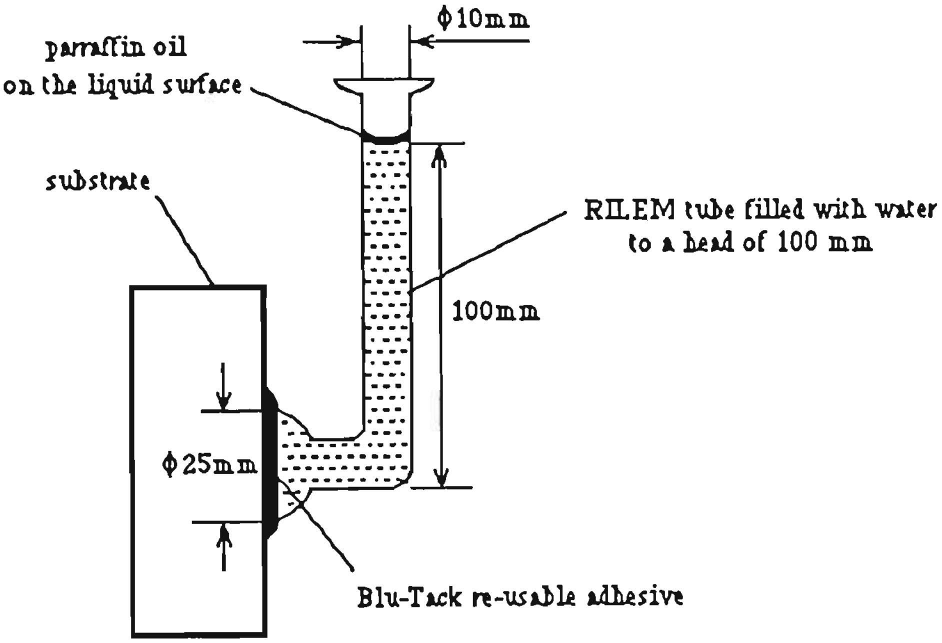


Figure 2.10 Diagram of water absorption test under hydrostatic pressure

The decrease in water from the tube recorded at different intervals was then recorded as the water absorption values (by volume) under hydrostatic pressure. The water lost was added to keep the water level constant at 100 mm. The results may then be plotted against the time of the test.

2.5.6 Resistance to efflorescence

This test assessed the ability of an impregnant to resist the passage of salts through the impregnated part of the substrate and permit the formation of efflorescence. The substrates were placed with the untreated face downward at a depth of 15 mm in a bath of a 10% aqueous sodium sulphate (Na_2SO_4) solution for 7 days. A metal wire (d=1 mm) of U shape is placed between the substrate and the bath to avoid the close contact of the substrate surface with the bottom of the bath to allow sufficient absorption of the salt solution into the substrate (shown in Figure 2.11). The liquid level was maintained constant throughout the test. The treated face of the substrate was examined visually after the test for efflorescence of the substrate.

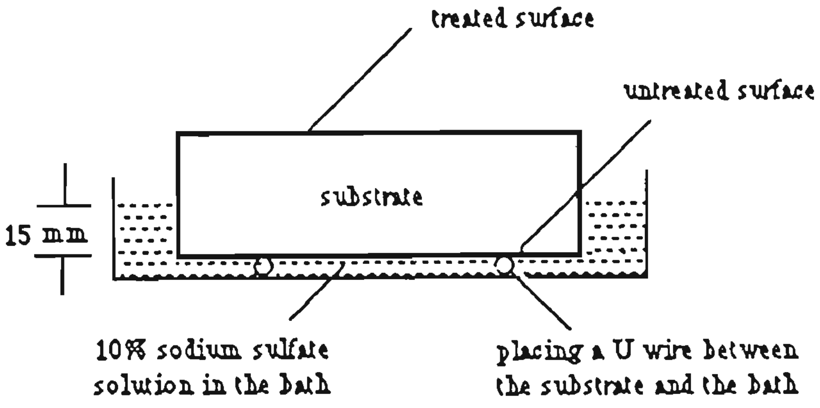


Figure 2.11 Efflorescence test in 10% sodium sulphate solution

2.5.7 Wetting and drying weathering test

The wetting and drying cycling is an accelerated weathering test to examine the durability of the substrate under alternate wet and dry conditions. The test was conducted where the substrate was subjected to the sponge water absorption test for 24 hours followed by drying the substrates at ambient conditions for another 24 hours. The wetting and drying weathering was carried out for 24 weeks (or 84 wet and dry cycles) under these laboratory conditions. The water absorption values, the surface beading effect, and photographs were recorded before and after the wetting and drying weathering test in order to compare the performance of the substrate.

2.5.8 UV and condensation weathering test

The UV and condensation weathering test was conducted in a QUV Accelerated Weathering Tester (Q-Panel Company, U.S.A.) to determine the effect of the resistance of the substrates to UV radiation and condensation weathering as shown in Figure 2.12. Rectangular substrates of size 75x105x30 mm were placed with the treated surfaces facing the UV and condensation chamber of the weathering tester. The operation conditions of the QUV tester included cycles of four hour UV radiation at 60°C followed by four hour condensation on the treated substrate surfaces at 50°C. The accelerated weathering test was performed for 6 months. The water absorption values, the surface beading effect, and photographs were recorded to compare the performance of the substrate before and after the weathering test.

2.5.9 Outdoor exposure weathering test

The purpose of the outdoor exposures was to determine the effect of natural weathering. For this test, rectangular substrates with size of 75x105x30 mm were prepared by impregnating one surface and four relevant edges with the impregnants. The substrates were placed with the untreated side downward onto a wire (d=5 mm) grill which was set in a plastic tray full of holes (d=12 mm) on the bottom. The specimens were exposed in a horizontal position on the roof of D-building, VUT, Footscray, Victoria, for 6 months from April to October of 1994 as shown in Figure 2.13. The water absorption values, the surface beading effect, and photographs were recorded to compare the performance of the substrates before and after the natural weathering test.

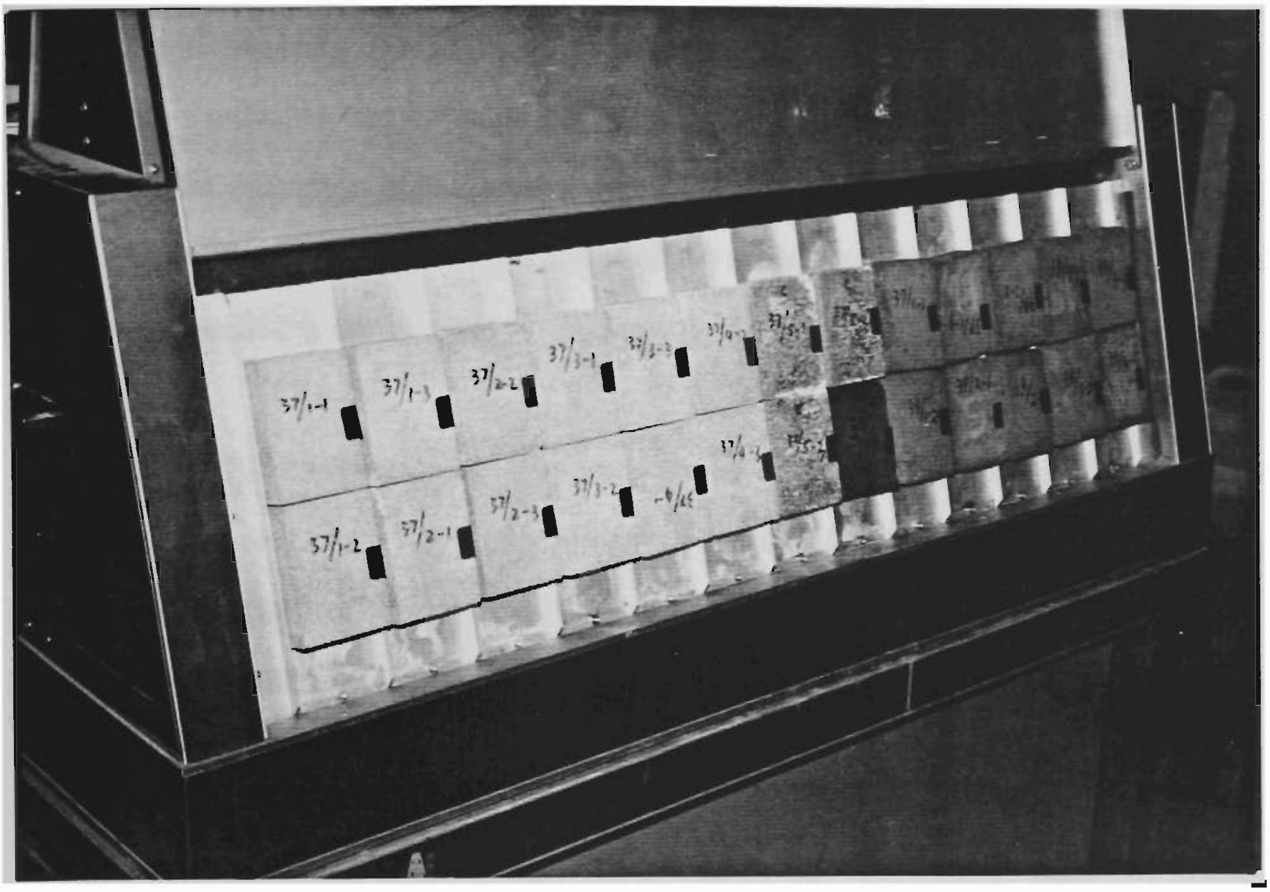


Figure 2.12 UV and condensation weathering test

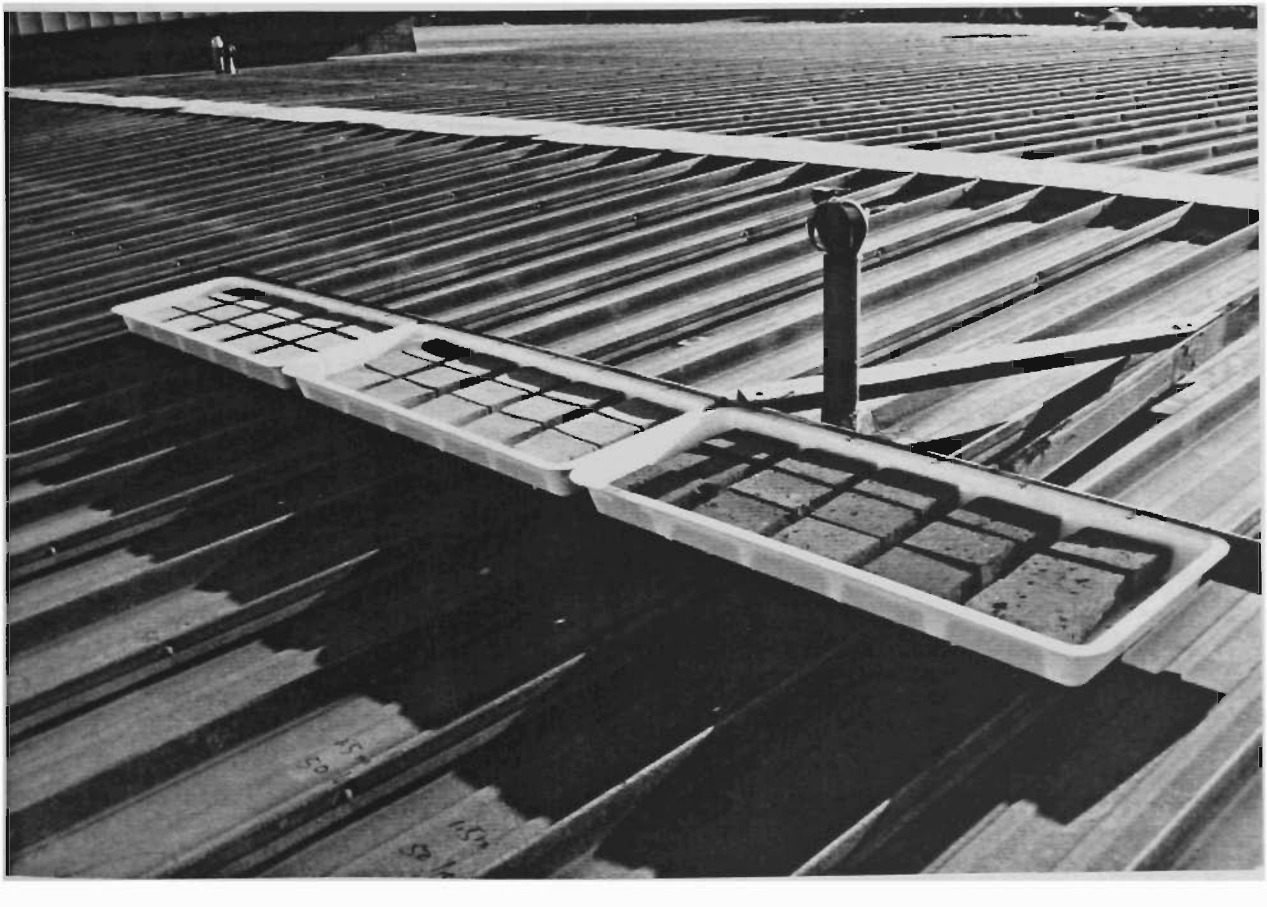


Figure 2.13 Outdoor exposure weathering test from April 1994 to October 1994

2.6 Interactions between the substrates and the impregnants

Mud brick substrates treated with sodium silicate followed by impregnation with a silane/siloxane emulsion were investigated by FTIR spectrometry and Gel Permeation Chromatography (GPC). The FTIR spectra of the substrates were recorded using the same instrument operated under the same conditions as described in §2.3.1.

For qualitative FTIR investigation, the samples were obtained by mixing 1 part of soil/sand mixture with 5 parts by weight of impregnant solution for 1 minute. The mixture was centrifuged and the treated powder was then dried at ambient conditions for 7 days. For quantitative study, a sample was carefully scratched from the surface of the impregnated substrate with a spatula. The substrate powder was ground into fine particles and then mixed with infrared grade potassium bromide (KBr) powder in a vibration mill for 1 minute before being pressed into KBr pellets. The ratio of sample to KBr was carefully controlled so that it was possible to quantitatively compare the intensity of the particular band in the spectrum. The ratio of the sample to KBr was varied depending on measuring silicate gel or the organic polysiloxane in the substrates in order to obtain the strongest peak at a particular region of the spectra but less than 1.5 infrared absorbance. In the case of measuring the intensity of the strong absorbance band of silicate gel SiOSi stretching [143] at 1078 cm^{-1}, 2 mg of sample with 300 mg KBr powder was used while 30 mg of sample with 300 mg of KBr powder was used for determining the weak band of alkyl C-H (organopolysiloxane) stretching [143] at 2859-2957 cm^{-1}. The neat spectrum of the impregnant residue on the substrate was obtained by digitally subtracting the spectrum of the initial substrate from that of the treated substrate, a method described by Ishida and Koenig [49]. The physisorbed silicone may be removed by tetrahydrofuran (THF) washing using a method described by Ishida and Miller [52]. The substrate was washed with THF (1 gram of the substrate powder was mixed with 15 ml of THF for 30 minutes and then centrifuged and dried at ambient condition to evaporate the solvent). The solvent washings were submitted to GPC analysis to determine the molecular weight of the silicone polymer.

The chemisorbed silicone on the substrate was then obtained from the spectrum of the substrate after washing with THF.

The GPC spectra were recorded with a Waters Ultra Styra Gel 100 Å column, equipped with a Bio-Rad HPLC Model 1330 pump and a Varex Evaporative Light Scattering MKIII ELSD detector. The elution solvent was THF at room temperature, nominally 25°C. The samples for GPC were directly obtained from the above solvent washings of the substrate without further dilution. The solvent washings were filtered using a micro-filter before injection into the GPC column. Only qualitative analysis was undertaken by GPC. The molecular weight of the silicone polymer as the molecular weight of the physisorbed silicone was then determined based on the polystyrene standards. This may only determine the relative molecular weight of the silicone polymer. However, these results were adequate enough to be used to study the same system.

3. METAL HIGHER ALKYLSILICONATE IMPREGNANTS

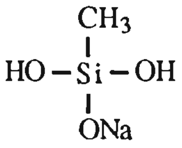
3.1 General

This chapter reviews the novel metal higher alkylsiliconate impregnants. The aim of this work was to develop stable diluted higher alkylsiliconate impregnants to be able to impart a satisfactory water repellent effect to alkaline substrates. The first step was to stabilise commercial potassium propylsiliconate (PPMS) by alkylalcohol ethoxylate nonionic surfactants. Secondly, the development of a novel potassium octyl/methyl siliconate (POMS) by hydrolysing octyltriethoxysilane (OTES) in potassium methylsiliconate (PMS) in the presence of an alkylalcohol ethoxylate nonionic surfactant was investigated. The mechanisms of the surfactant micellar catalysis of the silane hydrolysis and solubilisation of higher alkylsiliconate were studied and discussed.

3.1.1 Chemical and physical properties of metal alkylsiliconates

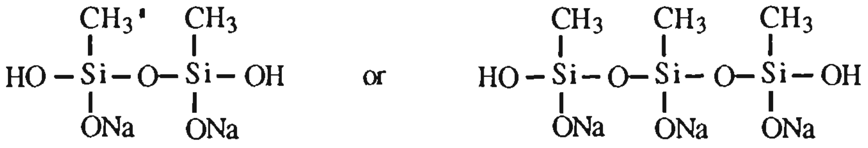
Metal alkylsiliconates have been used as water-based masonry water repellent impregnants since the first commercial sodium methylsiliconate (SMS) product was developed by researchers at the General Electric Company [86, 87] in 1951. Metal alkylsiliconates are obtained by hydrolysing alkyltrichlorosilanes to form polymonomethylsiloxane products and then dissolving the product in an aqueous NaOH solution according to Elliott and Krieble [86]. They may also be prepared by hydrolysing alkylalkoxysilanes in a KOH or NaOH solution according to Traver and Schryer [95] or by hydrolysing siloxanes in alkali metal hydroxides according to Hyde et al.[144].

The exact structure of the metal alkylsiliconate in aqueous solution is not known. However, SMS is generally described as having the basic formula as below(Scheme 3.1). Freezing point data indicates that in dilute solution, SMS exists largely in a monomeric form according to Kather and Torkelson [87]. Due to partial intermolecular condensation, siloxanes such as di- and tri-siliconate oligomers (Scheme 3.2) are also present in the siliconate solution according to Noll [29]. Such di- or tri-oligomers of SMS may be mainly present in solution in the form of cyclic structures (Scheme 3.3) according to Freeman [145]. By employing the Lentz Technique, Plueddmann [76] has proven that sodium vinylsiliconate (10% vinylsilanol in a solution with equal moles of NaOH) contained 45% monomer, 31% dimer, 20% trimer and 4% tetramer.



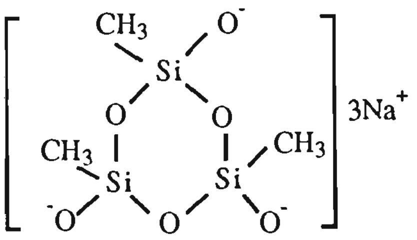
$$\mathrm{HO-\underset{ONa}{\overset{CH_3}{Si}}-OH}$$

(Scheme 3.1)



$$\mathrm{HO-\underset{ONa}{\overset{CH_3}{Si}}-O-\underset{ONa}{\overset{CH_3}{Si}}-OH} \quad \text{or} \quad \mathrm{HO-\underset{ONa}{\overset{CH_3}{Si}}-O-\underset{ONa}{\overset{CH_3}{Si}}-O-\underset{ONa}{\overset{CH_3}{Si}}-OH}$$

(Scheme 3.2)



(Scheme 3.3)

SMS solutions are affected by acids, with the formation of silanols resulting in precipitates of polymethylsiloxanes in various stages of polymerisation [29, 87] (see Scheme 3.4 and 3.5). Carbon dioxide, phenol, and other weak acids accomplish this reaction. Once the SMS is applied to the masonry substrate, it reacts with carbon dioxide to form silanols which then condense and crosslink with the substrate to form hydrophobic polymethylsiloxane on the substrate to impart water repellency (refer to Scheme 1.12).

$$[CH_3Si(OH)_2O]^-Na^+ \;+\; H_3O^+ \longrightarrow CH_3Si(OH)_3 \;+\; Na^+ + H_2O$$

(Scheme 3.4)

or

$$n\,CH_3Si(OH)_3 \longrightarrow [CH_3SiO_{1.5}]_n \;+\; 3n/2\;H_2O$$

(Scheme 3.5)

3.1.2 Alkali stability of substrates treated with metal alkylsiliconates

Methylsiliconates are known to be not alkali stable due to the formation of calcium methylsiliconate precipitate [90] by reaction with the free lime in the substrate or the hydrolysis of the polymethylsiloxane formed after impregnation [29] (refer Scheme 1.13 and 1.14). The siloxane can be hydrolysed by metal hydroxide according to Voronkov et al.[118] (see Scheme 3.6). It is believed that siloxane hydrolysis is via a nucleophilic substitution mechanism (S_N2-Si) under basic conditions with a similar mechanism to that of silane hydrolysis according to Brinker and Scherer [146]. The base-catalysed mechanisms of silane hydrolysis will be discussed in ξ3.3.1.

$$\equiv SiOSi\equiv \;+\; MOH \rightleftharpoons \;\equiv SiOM \;+\; HOSi\equiv$$

(Scheme 3.6)

The nucleophilic substitution mechanisms for silane hydrolysis are affected by both steric and inductive factors [146]. Electron-providing substituents such as alkyl substituents should reduce the hydrolysis rate by an inductive effect. The existence of bulky higher alkyl substituents on the silicon should decrease the hydrolysis rate due to both steric hindrance and an inductive effect. The hydrolysis rate of alkylalkoxysilanes in basic conditions significantly decreases with the increase of size of the substituent [75].

Alkali stability of masonry substrates treated with higher alkylsiliconates such as propylsiliconate is significantly improved over that of substrates treated with methylsiliconates [93] due to the large alkyl group in the silicone imparting better resistance to hydrolysis of the polysiloxane formed in the substrate [21].

3.1.3 Stability of the diluted metal alkylsiliconate aqueous solutions

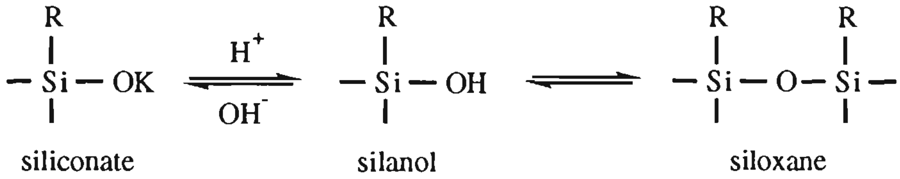
The stability of aqueous metal alkylsiliconate solutions is dependent on the alkyl substituent attached to the silicone. Table 3.1 lists the stability of PMS and PPMS solution at various concentrations after dilution. PMS is stable in any concentration while PPMS is only stable in either very concentrated state or very dilute state. However, the suitable concentration for application may be from 2% to 5% [92, 93]. Following dilution, the PPMS solutions were observed to turn to blue first and then gradually precipitate from the solution.

Table 3.1 *Stability of diluted PMS and PPMS solutions in various concentrations*

Siliconates	Concentration (%)	Stability after dilution (20°C)
PMS	any concentration	stable solution
PPMS*	<0.21	stable solution
	0.21	stable but hazy at 40°C
	0.50	precipitate after 24 hours
	1.0	precipitate within 4 hours
	1.2	precipitate after 10 minutes
	2.1	precipitate within 10 minutes
	5.1	precipitate after 5 minutes
	10.3	precipitate within 5 minutes
	15.4 or more	stable solution

*The initial concentration of PPMS is 20.5%.

Precipitation of the siliconate by dilution is presumably due to the condensation of the siliconate in the solution. It is assumed that dilution of the siliconate solution reduces the concentration of KOH but increases the carbon dioxide concentration, resulting in lowering the pH of the solution. This, in turn, causes the formation of silanols which then condense to siliconate oligomer. Higher alkylsiliconate oligomers are less soluble in water and finally precipitate from the solution. Methylsiliconates are stable on dilution due to their higher solubility due to the small hydrocarbon moiety. The stability of the siliconate solution may be illustrated in the equilibrium reaction shown in Scheme 3.7. Lowering the pH of the solution would shift the equilibrium to the siloxane via the silanol while higher alkalinity keeps the solution in the stable siliconate state.



(Scheme 3.7)

The condensation of silanols in solution is believed to be catalysed by base with a mechanism involving two steps according to Pohl and Osterholtz [147]. Hydroxyl anion reversibly reacts with silanetriol in a rapid first step leading to an equilibrium concentration of siliconate anion ($RSi(OH)_2O^-$) shown in Scheme 3.8. Siliconate anion reacts with neutral silanetriol in a slower rate-determining step resulting in dialkyl tetrahydroxy disiloxane and regeneration of hydroxyl anion (Scheme 3.9). The condensation of the silanol is also proposed to occur by a nucleophilic substitution mechanism according to Grubb [148] and Swain et al.[149]. The condensation rate is observed to be first-order in hydroxide concentration [OH^-] and second-order in silanetriol concentration [$RSi(OH)_3$] according to Pohl and Osterholtz [147]. Therefore, increasing the silanol concentration induced by dilution would greatly enhance the condensation rate.

$$RSi(OH)_3 + OH^- \underset{\substack{k_{-1}\\ \text{fast}}}{\overset{k_1}{\rightleftharpoons}} RSi(OH)_2O^- + H_2O$$

(Scheme 3.8)

$$RSi(OH)_2O^- + RSi(OH)_3 \underset{\substack{k_{-2}\\ \text{slow}}}{\overset{k_2}{\rightleftharpoons}} RSi(OH)_2-O-Si(OH)_2R + OH^-$$

(Scheme 3.9)

As the pH of the siliconate in the concentrated state is more than 13, the silanol in the solution would stay most likely in the stable deprotonated state. However, lowering the pH of the solution induced by dilution favours the formation of silanols resulting in greatly increasing the condensation rate. The equilibrium of Scheme 3.7 would be shifted to the right. Plueddemann [76] found that the stability of the vinylsilanol solution is very low at pH 5.5 to 10.8 but increases if further NaOH is added to increase the pH of the solution.

Further dilution of the siliconate may reduce the condensation rate due to a low concentration of the reactants in the solution. In addition, ultimate dilution of the siliconate would favour the formation of siliconate monomers [87] which should be more soluble than that of the oligomer. This would explain the higher stability of the very low concentration of the PPMS solution.

The stability of silanols in solution is also dependent on the alkyl substituents. Plueddemann [76] has reported that the relative stability of silanol $RSi(OH)_3$ in aqueous solution is: R = methyl > ethyl > propyl > n-butyl.

In order to stabilise higher alkylsiliconate aqueous solutions, up to 50% of water-miscible solvents and other additives as stabilisers replacing water as diluting agents may be used as reported by previous workers [92, 93, 95]. Bosch et al.[92] reported a method to dilute various higher alkylsiliconate solutions by using a diluting agent containing 40% isopropanol, 0.1% trisodium salt of nitrilotriacetic acid and 59.9% water.

3.2 Stabilisation of diluted PPMS solutions by nonionic surfactants

It has been found that diluted PPMS solutions can be stabilised by the addition of surfactants. Table 3.2 lists the stability of PPMS solutions stabilised with different surfactants. The PPMS concentrate was diluted to 2.5% solution containing 0.12% of different surfactants as stabilisers. It was generally observed that diluted PPMS solution with the addition of a surfactant, particularly a polyoxyethylene nonionic surfactant, significantly retards precipitation. The stabilised PPMS solution was observed from a clear solution to colloidal blue until cloudy and the presence finally of a precipitate.

***Table 3.2** Stability of 2.5% PPMS solutions stabilised by various surfactants at 40°C*

Surfactants	Stability at (40°C)
with no surfactant addition	immediately blue and then precipitation
with nonionic surfactants	
Teric G12A12	blue after 1 day & colloidal within 5 days
Teric 16M15	blue after 3 days & colloidal within 7 days
Teric GN30	blue after 2 days & colloidal within 4 days
Tween 80	blue after 1 day & colloidal after 3 days
with anionic surfactants	
LABSA	immediately cloudy & precipitation
Gardilene IPA/94	immediately cloudy & precipitation
Hostapur SAS 60	blue after 4 days & precipitation after 15 days precipitation if more surfactant added
Hostapon KA	cloudy after 2 days.
with cationic surfactants	
Vantoc N40	immediately cloudy & precipitation clear if more surfactant added
Vantoc CC30	immediately cloudy & precipitation clear if more surfactant added

3.2.1 Mechanism of stabilisation of PPMS by surfactants

3.2.1.1 Stabilisation by polyoxyethylene type nonionic surfactants

a) Surfactant solubilisation

When the concentration of surfactant in water is over the "critical micelle concentration" (CMC), surfactant molecules form micelles in aqueous solution with their hydrophobic hydrocarbon inside the micellar core and with the hydrophilic moieties towards the micellar surfaces as shown in Figure 3.1. One of the important properties of surfactant micelles in solution is solubilisation. Solubilisation is the dissolution of a water insoluble substance in an aqueous surfactant solution at or above its CMC to form a clear homogeneous solution.

The increasing solubility of water insoluble organic materials in aqueous solutions of surfactants is due to the organic compound 'dissolving' in the surfactant micelle where the environment will closely approximate that of an organic phase. As nonionic surfactants can form micelles with large aggregation numbers at concentrations appreciably lower than that of the anionics or the cationics, nonionic surfactants are very useful and effective for solubilising organic materials in aqueous solution according to Porter [112] and Shinoda [150].

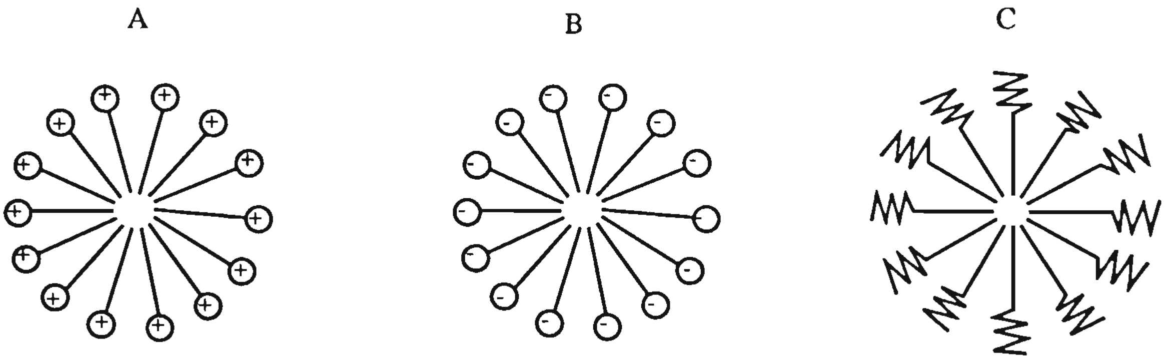


Figure 3.1 Surfactant micelles in aqueous solution; (A) a cationic micelle with positively charged surface, (B) an anionic micelle with negatively charged surface, and (C) a polyoxyethylene nonionic micelle with ethoxylate chains forming a palisade layer on the surface

In the initial diluted PPMS solution, siliconate, silanol and short siliconate oligomers may exist in the solution. The comparison of PPMS structures in the solution with the structure of an alkylalcohol ethoxylate nonionic surfactant shows there are similarities in both the PPMS and the surfactant structures. The propyl group in the siliconate molecule may be considered as the "hydrophobic tail" while the siliconate [$-Si(OH)_mOK$] or the silanol [$-Si(OH)_n$] groups may be regarded as the "hydrophilic head". In this respect, propylsiliconate possesses a structure equivalent to simple surfactant molecules (shown in Figure 3.2).

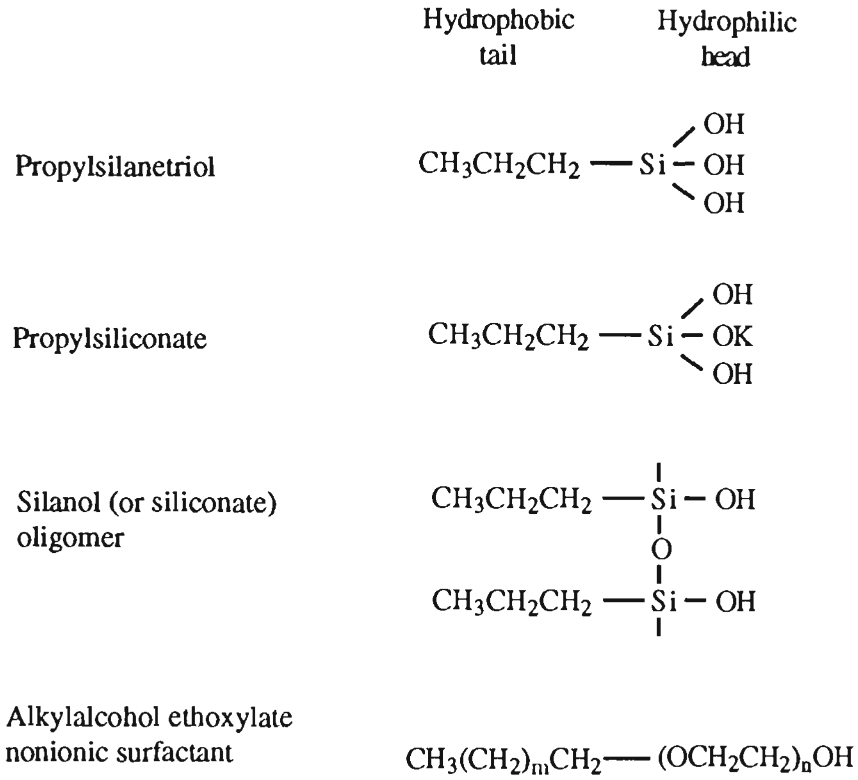


Figure 3.2 *Comparison of PPMS structures in diluted aqueous solution and the structure of alkylalcohol ethoxylate nonionic surfactant*

Having similar structures as that of a surfactant, PPMS may aggregate to form "micelles" in diluted aqueous solution with the propyl tail inside the micellar core while the hydrophilic heads of [-Si(OH)$_m$OK] or [-Si(OH)$_n$] are at the micellar surface towards the water just like a surfactant micellar solution (see Figure 3.3). However, this PPMS "micelle" may be very short-lived since the siliconate may rapidly condense to siloxane oligomers or insoluble polysiloxanes resulting in precipitation from the solution. Experiments have shown that following dilution of PPMS, the PPMS solution is only clear for a short time, and then turns colloidal resulting in an observation initially of blue light scattering but precipitation from the solution in a short time.

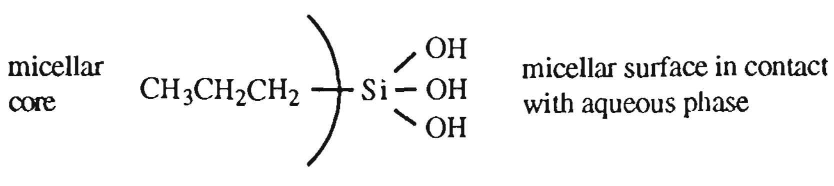


Figure 3.3 *Proposed structure of the PPMS micelle in aqueous solution*

Plueddemann [151] stated that dilute aqueous solutions of hydrophilic organofunctional silanes will retain much silanetriol, or low-molecular weight oligomeric silanol structures, particularly at pH 3-5. These silanol structures form micelles with their hydrophilic silanol groups at the water interface. The silanol groups will be relatively isolated from each other and stabilised by hydrogen bonding to water. However, in higher pH range, these silanol micelles would not be stable but would rapidly precipitate from the solution due to the high condensation rate of silanol under alkaline conditions.

When a polyoxyethylene type nonionic surfactant is added into the diluted PPMS solution, both surfactant and siliconate in the solution may form separate micelles. However, the siliconate micelle may not be chemically stable and it may soon condense to form large aggregates and lose water solubility. According to Fendler and Fendler [152], formation of a micelle or a solubilised micelle may reduce the free energy of the solution resulting in a dynamically stable system. Therefore, in order to achieve a dynamic stable system, these PPMS molecules may then migrate into surfactant micelles to form a "Joint Micelle". This would be like a mixed surfactant system composed of a nonionic surfactant and silanol, siliconate and their oligomers. With the "Joint Micelle" model, most of the experimental phenomena of the stabilisation effect of the siliconate by surfactants particularly polyoxyethylene nonionic surfactants may be explained.

Evidence for the solubilisation of organic molecules with other surfactant systems has been developed by various techniques by many workers [153-158]. This work shows the location of solubilisate in the surfactant micelle may depend on its polarity. Donbrow and Rhodes [154] have reported that benzoic acid can be solubilised by solutions of the nonionic surfactant hexadecanol and cetomacrogol (fatty alkylalcohol) ethoxylates (20-24 EO). This study showed that the most probable orientation of the benzoic acid molecule is with the hydrophobic benzene ring enclosed in the hydrocarbon core and the hydrophilic carboxylic acid group protruding into the polar ethoxylate layer. Hydrogen bonding could occur between the acid proton and the innermost oxygen atom resulting in a reduction of the mobility of the solubilisate. Such hydrogen bonding between the solubilisate and the surfactant ethoxylate chain has also been reported by Mulley and Metcalf [159]. Fendler et al. [158] reported that the solubilisation site of benzophenone and acetophenone in micelles of nonionic nonylphenol ethoxylates (15 EO) is between the ethoxylate chain palisade layer and the hydrocarbon core but closer to the latter. Benzophenone appeared to be closer to the micellar core than acetophenone in these systems as benzophenone is less polar. The PPMS structures in solution have high polarity and therefore are assumed to be located at the junction of the hydrocarbon and the ethoxylate chain palisade area but closer to the latter. The active hydrophilic head groups may be within the palisade layer where they possibly form hydrogen bonds with the ethoxylate chains of the surfactant while the propyl groups may stay toward the hydrocarbon core. This possible structure of the joint micelle is shown in Figure 3.4.

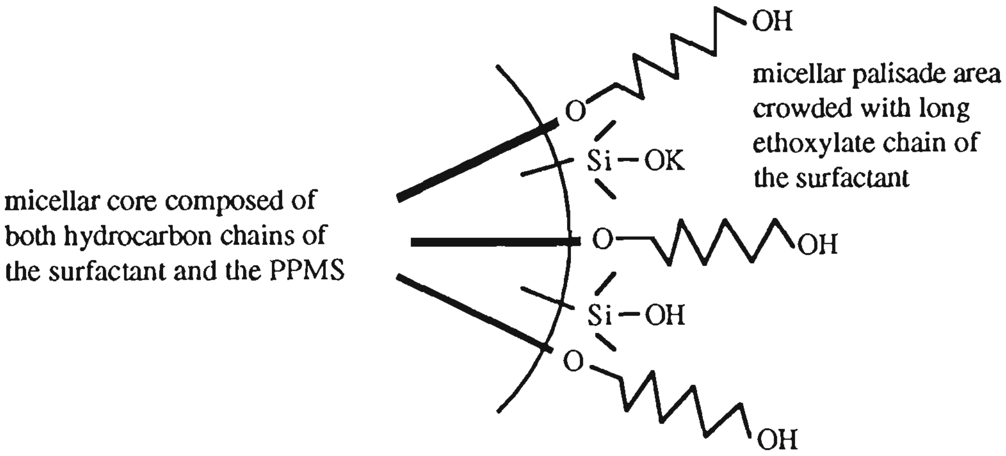


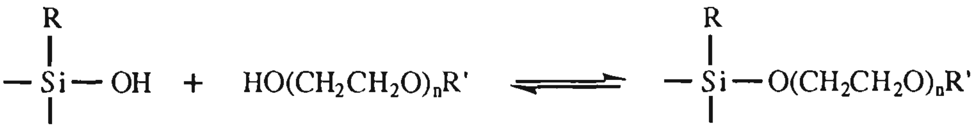
***Figure 3.4** Possible structure of the joint micelle of polyoxyethylene nonionic surfactant and PPMS*

In the joint micelle, it is postulated that siliconate molecules may be kept apart from each other by surfactant molecules. Due to possible interactions such as hydrogen bonding between the siliconate and the surfactant, the mobility of the silicone molecule will be restricted. As the area of the palisades near the micellar surface can be expected to be sterically crowded with polyethoxylate chains, the reactive siliconate head groups which most probably stay in the palisades of the micelle are kept away from direct contact with other siliconate molecular "heads" from either the bulk solution or other micelles. Therefore, condensation between siliconate molecules is proposed to slow down resulting in increased stability of the PPMS solution. However, condensation of the silanol in joint micelle solution cannot be stopped and the oligomeric siloxane may still be gradually formed resulting in changing the joint micelle into siliconate sol in solution (further discussed in ξ3.2.2.3). The observation of blue light scattering of the solubilised PPMS solution is most likely induced by siliconate condensation resulting in sol formation. Further, so-formed siliconate sol may still be spontaneously stabilised by adsorption of the surfactant on the sol surface to prevent further aggregation of the siliconate molecule by a steric effect until the eventual formation of larger molecular weight polysiloxanes which then precipitate from the solution. According to Shinoda [150], the mechanism of dissolving water-insoluble polymers and proteins in aqueous solution by surfactant solubilisation is due to the adsorption of surfactants on the polymer molecule preventing the aggregation of the polymer. Solubilisation of the PPMS in diluted solution may be similar to solubilisation of a polymer when the siliconate sol is formed in the solution.

The solubilisation of the PPMS solutions by surfactants may be the most important factor in stabilisation of diluted PPMS solution.

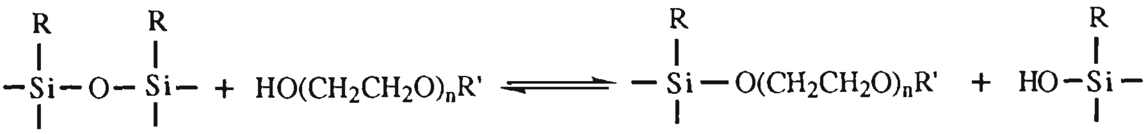
b) Interactions between the siliconate and the surfactant ethoxylate chain

The stabilisation of PPMS solution may also be attributed to the interaction between the surfactant and the siliconates. Apart from the hydrogen bonding between $-Si(OH)_mOK$ or $-Si(OH)_n$ groups of the siliconate and the ethoxylate chains of the surfactant, it is assumed that the re-esterification of silanol by the hydroxyl of the surfactant ethoxylate chain to form a permanent bond between the surfactant and the siliconate may occur (Scheme 3.10). The alcoholysis of the siliconate oligomers (or siloxanes) by the hydroxyl of the surfactant may also occur (Scheme 3.11). Iler [160] reported that it is possible to esterify colloidal silica with various alcohols such as glycol with one end bonding to the sol and the other end at the outer surface of the particle to obtain a modified silica sol which is soluble both in water and alcohols. According to Brinker and Scherer [146] and Voronkov et al.[118], alcoholysis is catalysed under basic conditions and the re-esterification and alcoholysis reactions may be via a S_N2-Si mechanism. As dilution of PPMS concentrate may result in the formation of silanols and siliconate oligomers (or siloxanes), both re-esterification and alcoholysis may occur. The re-esterification may replace the reactive silanol group of the siliconate with inert surfactant ethoxylate resulting in reduction of the further condensation of the siliconate and an increase in the hydrophilicity of the siliconate oligomer in solution. It appears that the re-esterification or the alcoholysis may gradually play a part in stabilisation of diluted PPMS solution particularly in the later state of the stabilisation while evidences (discussed later) show that the major stabilisation effect may be due to the surfactant solubilisation.



$$-\overset{R}{\underset{|}{\overset{|}{Si}}}-OH + HO(CH_2CH_2O)_nR' \rightleftharpoons -\overset{R}{\underset{|}{\overset{|}{Si}}}-O(CH_2CH_2O)_nR'$$

(Scheme 3.10)



$$-\overset{R}{\underset{|}{\overset{|}{Si}}}-O-\overset{R}{\underset{|}{\overset{|}{Si}}}- + HO(CH_2CH_2O)_nR' \rightleftharpoons -\overset{R}{\underset{|}{\overset{|}{Si}}}-O(CH_2CH_2O)_nR' + HO-\overset{R}{\underset{|}{\overset{|}{Si}}}-$$

(Scheme 3.11)

Such re-esterification and alcoholysis reactions between the diluted siliconate and alkylalcohol ethoxylate nonionic surfactants have not been reported in the literature. The examination of these reactions in the complex siliconate system is beyond the scope of this project. However, certain adverse effects induced by the surfactant on the water repellency of the substrates treated with the PPMS and POMS impregnants may give indirect evidence to support the involvement of the surfactant in reaction with the siliconate water repellent. This will be discussed in ξ3.2.3 and ξ3.3.

3.2.1.2 Stabilisation by anionic and cationic surfactants

It was expected that PPMS solution may be stabilised by anionic and cationic surfactants. However, test results in Table 3.2 show that the stabilisation effects of PPMS solution by both anionic and cationic surfactants is less efficient but more complex. Therefore, ionic surfactants may not be the ideal stabilisation agents for the diluted PPMS solution.

Anionic surfactants, for example, show a complex but inferior solubilisation effect depending on the surfactant chosen (see Table 3.2). Firstly, the joint micelle of the anionic surfactant and the PPMS may exist but may not be stable. As both anionic surfactant and the siliconate contain negatively charged hydrophilic groups (e.g. $-SO_3^-$ of the anionic surfactant and $-Si(OH)_nO^-$ of the siliconate), the electrostatic repulsive force between the negatively charged hydrophilic groups may result in unstable micellar packing. Secondly, the joint micelles may provide less protection of the siliconate active groups to reduce the condensation rate. The siliconate reactive groups are assumed to stay on the joint micelle surface where the condensation may still occur due to there being no steric hindrance induced by the surfactant. Thirdly, some anionic surfactants (e.g. LABSA) may provide acidity and further reduce the pH of the solution to accelerate the siliconate condensation.

Generally, solubilisation of PPMS solution by cationic surfactants is less efficient than solubilisation by nonionic surfactants. The test results in Table 3.2 show that cationic surfactants Vantoc N40 and Vantoc CC30 show a poor stabilisation effect for the PPMS solution. Only when using a high concentration of the surfactant, can a clear solution be obtained. The stability of the solution is observed to be much lower than that of a solution with nonionic surfactant. The surfactant and siliconate joint micelle may exist but it may be ephemeral. Firstly, the interaction between the negatively charged siliconate and the positively charged quaternary ammonium reduces the surface activity of the surfactant and makes the surfactant unable to form stable joint micelles (see Scheme 3.12). Secondly, the joint micelle has less effect in preventing siliconate condensation due to the location of the siliconate on the micelle surface as for anionic surfactants.

(Scheme 3.12)

3.2.2 Properties of the PPMS solution stabilised by nonionic surfactants

From the previous discussion, it may be concluded that polyoxyethylene type nonionic surfactants impart the best stabilisation effect to the diluted PPMS solution. Through studying the properties of the stabilised PPMS solution, it is helpful to confirm the mechanism of the stabilisation of the diluted PPMS solutions and to optimise the stabilisation effect.

3.2.2.1 Solubilisation and the surfactant structure

The solubilisation effect of diluted PPMS solution by polyoxyethylene nonionic surfactant varies according to the surfactant structure. Various alkylalcohol ethoxylate and nonylphenol ethoxylate nonionic surfactants with different hydrophilic and lipophilic chain length have been tested for solubilisation effects for the diluted PPMS solution. A standard test was carried out at 20°C by titrating concentrated PPMS into distilled water which contained 0.1% of a surfactant, where the solution just started to change from clear to colloidal, resulting in the observation of blue light scattering (Tyndall Effect [137]), due to the condensation of PPMS in the solution. The quantity of PPMS added before this effect appeared was considered as the solubilisation ability of that surfactant. The solubilisation ability of the surfactant as a function of the surfactant hydrophilic chain length is shown in Figure 3.5.

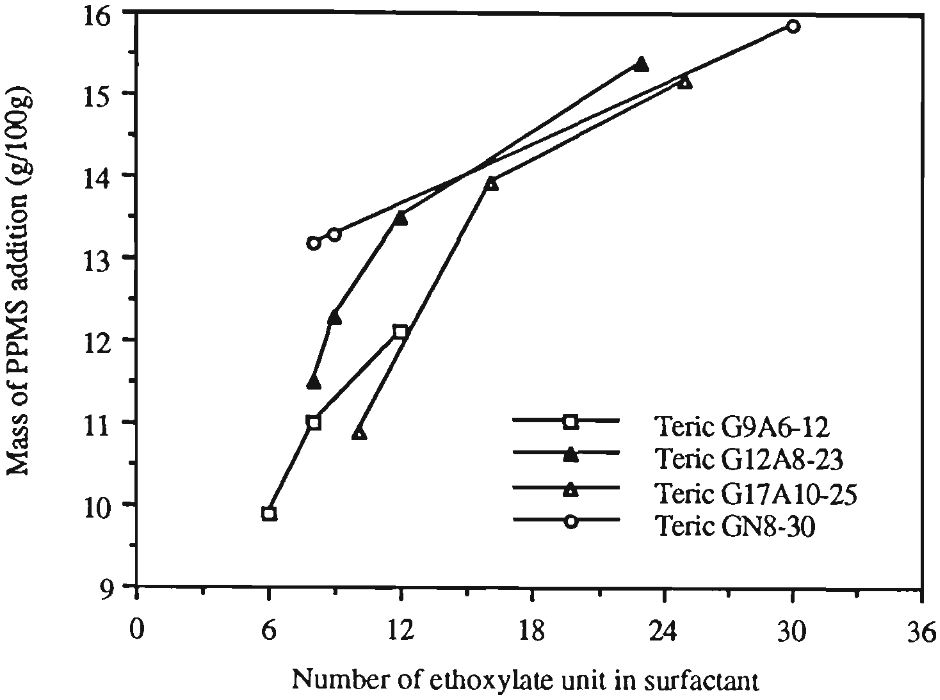


Figure 3.5 Relationship between solubilisation and the surfactant ethoxylate chain length

It is quite clear that the solubilisation ability was improved with the increase in the ethoxylate chain length of surfactants. As the reactive heads of the siliconate may effectively be hidden in the palisade layer of the "Joint Micelle", surfactants with long ethoxylate chains may give better protection in preventing siliconate aggregation by condensation by steric hindrance in the joint micelle palisade layer. In addition, as the ratio of hydrophilic moiety to lipophilic moiety of the surfactant (HLB) is increased with the increase of the surfactant ethoxylate chain length. A high HLB of the surfactant may give the joint micelle better water affinity, this achieving a more stable joint micelle in aqueous solution. This has been further shown by results which illustrate an almost linear relationship between HLB values of the tested surfactants and their solubilisation ability (Figure 3.6).

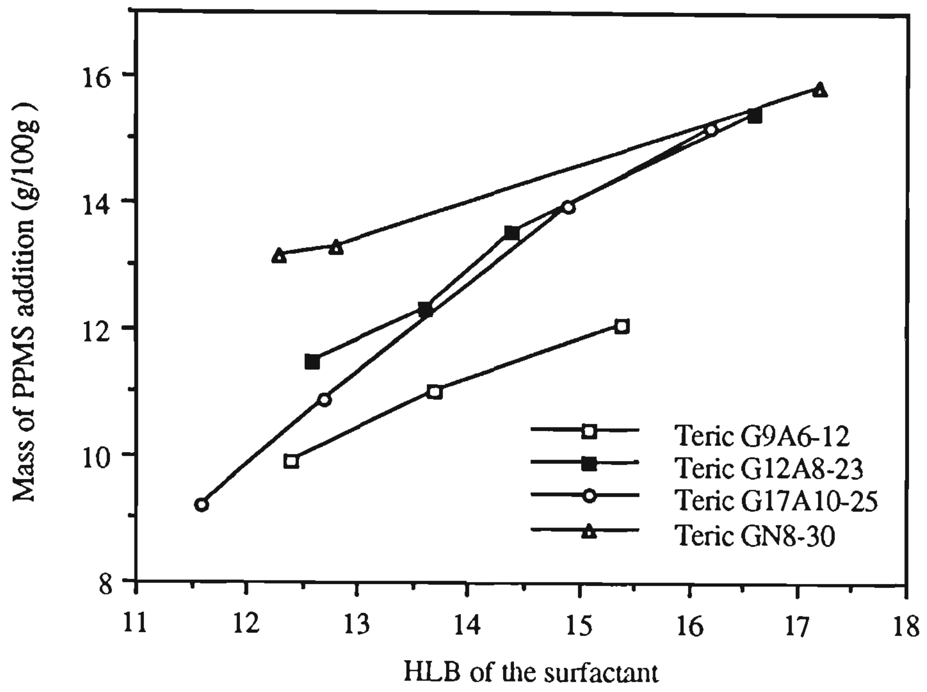


Figure 3.6 Relationship between HLB of the polyoxyethylene nonionic surfactants and solubilisation

Figure 3.7 shows the relationship between the solubilisation ability and the surfactant hydrophobic chain length. The solubilisation effect is increased with an increase in hydrocarbon chain length only within a certain range. However, the relationship between the hydrophobic chain length of surfactants and the solubilisation effect is not significant when the ethoxylate chain length is short. The reason for this is that for any increase in hydrocarbon chain length, the HLB of the surfactant is decreased. Therefore, the solubilisation effect is decreased. This shows that the HLB of nonionic surfactants may be the key factor in controlling the solubilisation of PPMS solution. According to Shinoda [150], the hydrocarbon chain length is less important than that of the ethoxylate chain in determining the solubilisation power of nonionic surfactants. However, test results herein still show that a longer hydrophobic chain achieved a better solubilisation effect if the surfactant has a sufficient HLB value. This is probably because that a surfactant with a longer hydrocarbon chain may form a more rigid joint micelle or stabilised sol with its longer hydrocarbon chain being well compacted in the micelle core or the siliconate sol. In addition, the micellar packing shape may also explain this because the geometric packing of the hydrophobe in the micelle, being wedge shaped, has more solubilisation capacity if the chain length of the hydrophobic moiety is increased [112]. This could further explain the higher solubilisation ability of nonylphenol ethoxylate nonionic surfactants (Teric GN) as shown in Figure 3.5 and Figure 3.6, at least at lower ethoxylate chain length or lower HLB values, is due to the hydrophobic chain containing a large aromatic ring.

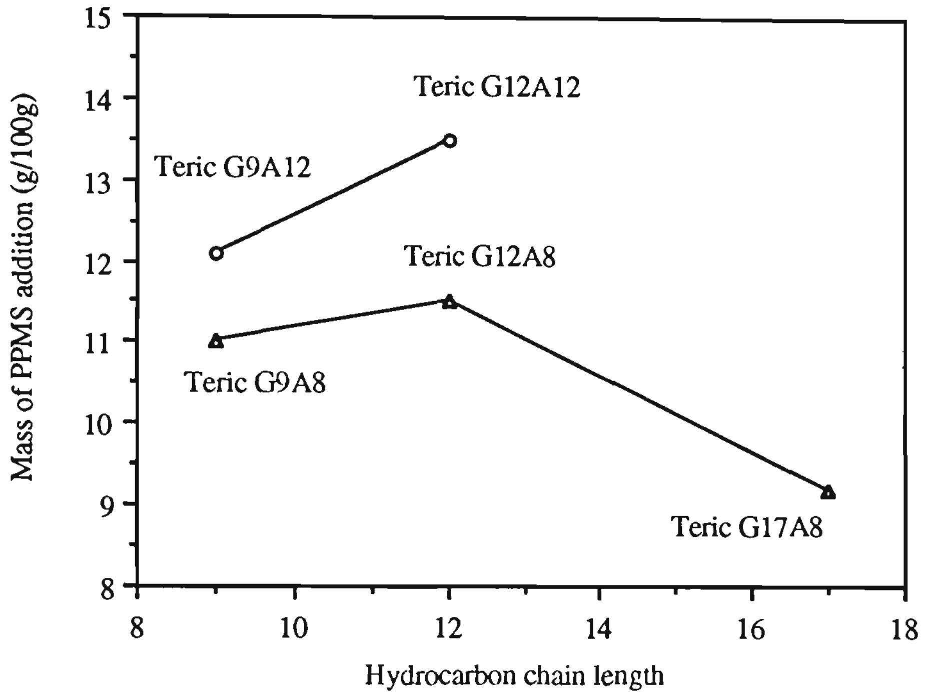


Figure 3.7 Relationship between solubilisation and the surfactant hydrocarbon chain length

It appears that nonionic surfactants with longer hydrocarbon and longer ethoxylate chain or with higher HLB value are more efficient for solubilisation of the PPMS solution. Particularly, a surfactant with a long ethoxylate chain and high HLB value may be the best selection. Table 3.3 lists the stability of PPMS solutions stabilised by various nonionic surfactants. These results confirm that the best surfactants for stabilising PPMS are those with both longer hydrocarbon and ethoxylate chain, or higher HLB. In summary, surfactants with hydrocarbon chain length of 12 and ethoxylate chain length of 12, or with a HLB value of about 14 or more such as Teric G12A12 are satisfactory to stabilise PPMS solutions.

***Table 3.3** Stability of 2.5% PPMS solutions stabilised by various nonionic surfactants*

Surfactant	HLB	Surfactant concentration	Stability *	
			at ambient condition	at 40°C
Teric G9A6	12.4	0.61%	about 4 months	about 2 days
Teric G9A8	13.7	0.61%	about 4 months	about 13 days
Teric G9A12	15.4	0.61%	> 12 months	about 2 months
Teric G12A8	12.6	0.61%	about 4 months	about 1 month
Teric G12A12	14.4	0.61%	>12 months	about 2 months
Teric G12A23	16.6	0.61%	>12 months	>2 months
Teric G17A25	16.2	0.61%	>12 months	>2 months
Teric GN 30	17.2	0.61%	>12 months	about 2 months
Teric 16M15	13.8	0.61%	>12 months	about 2 weeks
Tween 80	15	0.61%	>12 months	about 1 month

* Stability end point is defined as the appearance of cloudiness or precipitate in the solution.

3.2.2.2 Cloud point (T_c) and its depression in solubilised PPMS solutions

It is known that the T_c of the polyoxyethylene nonionic surfactants is a parameter affected by physical or chemical factors and additives [136]. Some alkaline materials such as sodium silicate [114] strongly depress the T_c while certain organic materials such as benzoate salts [136] raise the cloud point. Studying the T_c change of the nonionic surfactant solutions which contain siliconates may help to understand the solubilisation or the interaction between the surfactant and the additives. A test was carried out by adding various amounts of PMS and PPMS into 1% Teric G9A6 solution. The T_c change as a function of the amount of siliconate addition is shown in Figure 3.8. The test results show that the relationship between T_c depression and PMS addition is linear. This may be explained as PMS is a strongly alkaline solution and the effect on the T_c of the nonionic surfactant may be similar to that of sodium silicate which has a strong dehydration effect on the surfactant solution according to Schönfeldt [114]. However, the relationship of T_c depression against PPMS addition is not linear and the curve becomes a plateau when PPMS addition is over a certain concentration (e.g. 1.5 g of PPMS per 100g of surfactant solution). This may be due to the joint micelle effect. The T_c of the surfactant solution with the PPMS should be similar to the solution containing PMS because PPMS is also a strongly alkaline solution. This is shown in Figure 3.8 where the T_C depression curve of the solution containing PPMS goes down sharply with the increase in PPMS addition particularly in the low concentration range. However, when further PPMS is added, PPMS could not stay in solution and more PPMS molecules may migrate into the micelles to form joint micelles. As the hydrophilic "head" of PPMS in the joint micelle surface improves the water affinity of the surfactant micelle this may result in an increase in the T_C of the surfactant solution. El-Khordagui [136] reported that an increase in T_C of octylphenoxy polyethoxy ethanol (Triton X-114) solution with the addition of benzoate salts was related to the solubility-enhancing action of benzoate salts. It appears that PPMS may have both the effect of decreasing the T_C due to the strong alkalinity of PPMS solution and increasing the T_C due to the formation of joint micelles in the solution. Both effects on the T_C depression of the surfactant solution may depend on the concentration of the PPMS resulting in a decrease in the T_C depression effect with the further increase in PPMS addition.

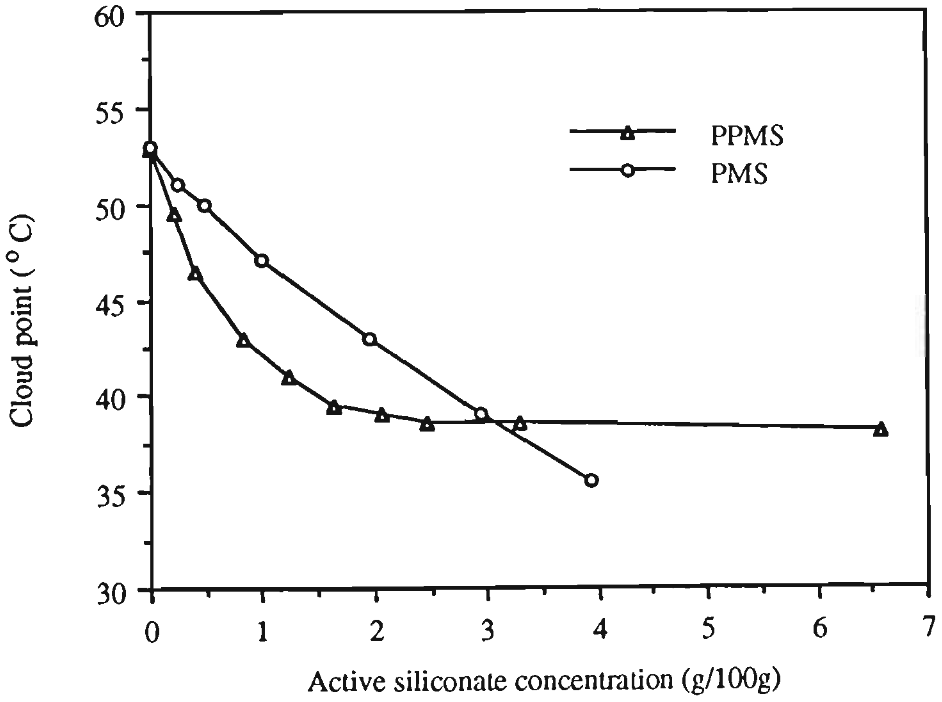


Figure 3.8 Cloud point depression of 1% Teric G9A6 surfactant solution by PPMS and PMS

Results showed that the T_c of PPMS-surfactant solutions are not constant and they increase with time. Temperature rise accelerates this effect. This is shown in Figure 3.9 by measuring the T_c of the solution containing 1% Teric G9A6 and 2.5% PPMS at different periods. Figure 3.9 shows that the T_c of the solution eventually increases to a temperature close to the cloud point of the pure surfactant solution and then becomes constant. At 40°C, the T_c reaches the constant temperature faster. This may be explained by the joint micelle concept. When PPMS is added into the surfactant solution, the concentration of PPMS in the bulk solution may be high initially, but condensation to oligomers commences which are less soluble and then migrate into joint micelles to achieve the best dynamic stability of the solution. The more molecules there are in the micelle, the more hydration effects the micelle has and the T_c of the solution increases. As the condensation takes time, T_c of the solution increases with time. An increase in temperature which accelerates the condensation of the siliconate can obviously accelerate this effect.

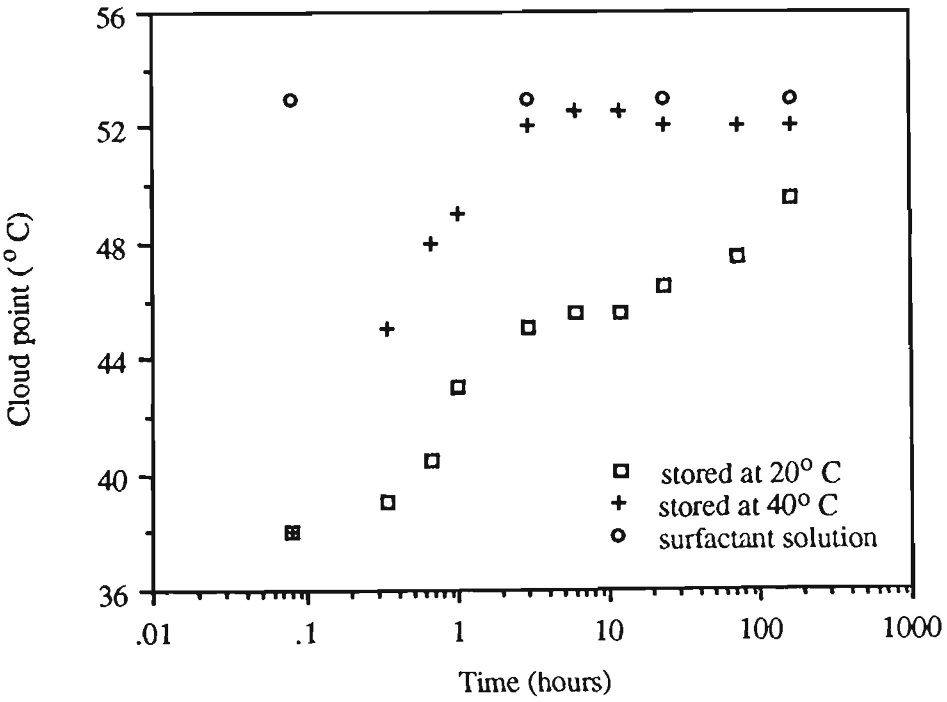


Figure 3.9 Change of cloud point of the PPMS-surfactant solutions with time at different temperature.

Further, it was found that increasing the ethoxylate chain length of the surfactant decreases the T_c change of the solution. Table 3.4 lists the T_c change of three PPMS-surfactant solutions (contained 1% surfactant and 2.5% PPMS) in which surfactants have different ethoxylate chain length at either ambient conditions or 40°C.

Table 3.4 *Change of cloud point of the PPMS-surfactant solutions*

Surfactant	T_c of surfactant (°C)	T_c of PPMS-surfactant solution (°C)			
		initial	after 3 days	after 14 days	after 35 days
at ambient conditions					
Teric G9A6	53	38	47.5	49.5	51
Teric G9A8	78	62.5	64.5	65.5	66
Teric G9A12	97.5	83	83	83	82.5
at 40 °C					
Teric G9A6	53	38	51.5	51	50.5
Teric G9A8	78	62.5	67	67.5	68
Teric G9A12	97.5	83	83	82.5	82.5

As discussed previously, water affinity of the joint micelle is attributed to either siliconate hydrophilic groups or surfactant ethoxylate chains in the palisade layer of the joint micelles. Accordingly, the water affinity of the micelle may be mainly attributed to the siliconate when the surfactant has a short ethoxylate chain, while the main water affinity may be attributed to the long ethoxylate chain of the surfactant if the surfactant has a longer ethoxylate chain. In the case of a surfactant with a long ethoxylate chain, the palisade area of the micelle is sterically crowded with long polyoxyethylene chains of the surfactant with relatively little room left for water to directly contact the siliconate hydrophilic groups to provide water affinity (see Figure 3.10). Therefore, the rate of T_c change was decreased with an increase in the ethoxylate chain of the surfactant. It may be further concluded that a surfactant with a longer ethoxylate chain may achieve better solubilisation for the PPMS solution in terms of preventing PPMS directly contacting the aqueous media and postponing the condensation.

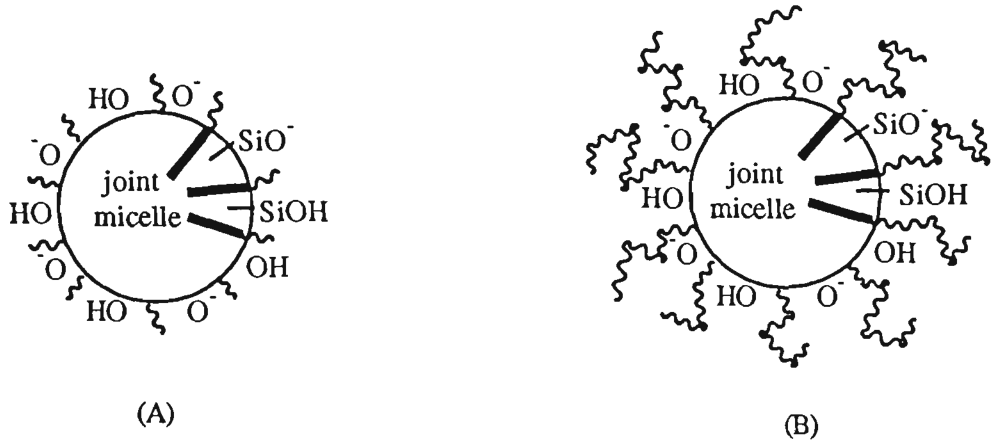


Figure 3.10 Hydration of the micelle mainly attributed to; (A) OH or O^- groups of PPMS, and (B) to ethoxylate chains of the surfactant

3.2.2.3 Stability of the solubilised PPMS solutions

The PPMS solution stabilised by polyoxyethylene nonionic surfactants was observed to change gradually from a clear solution to a light scattering blue and eventually to a cloudy or a precipitate containing solution in the end. Temperature accelerates the change. Table 3.5 lists the change of stabilised PPMS solution containing 0.61% Teric G9A8 and 2.5% PPMS in terms of the increase in the particle size at 20°C and 40°C. These observations are helpful to further understand the stabilisation mechanism discussed previously. The test results are consistent with the following model. According to the Tyndall Effect, the change of a solution from clear to blue then cloudy may be due to an increase in the particle size of the solute [137, 138]. It appears that the particles in the solution become larger when stored. This may imply that the solution turns from a joint micelle solution to a siliconate sol which then grows until a precipitate is formed. The particle sizes were analysed by means of Photon Correlation Spectroscopy. This confirmed that the particle size starts from less than 3 nm which is in the range of micellar size [152] and progresses to 7 nm at 20°C and to 30 nm at 40°C within 40 days.

Table 3.5 The change of the stabilised PPMS solution with time at different conditions

Time (days)	Scattered light of the solution		Particle size (nm)	
	at 20°C	at 40°C	at 20°C	at 40°C
initial	none (clear)	none (clear)	<3	<3
1 day	none (clear)	slight blue	<3	17.3
18 days	none (clear)	weak blue	-	24.8
29 days	none (clear)	blue	-	26.2
40 days	very slight blue	blue (colloidal)	7	30.2

The joint micelle is not chemically stable. Surfactant may slow down the condensation of PPMS by means of steric hindrance with its ethoxylate chain. However, it cannot stop the condensation of the active silanol in the solution. It is well known that a surfactant micelle or solubilised surfactant micelle is not static or rigid, and consequently a solubilised substrate in the micelle or the surfactant itself is relatively mobile. The micellar formation and the solubilisation is a dynamic equilibrium process [152]. Solubilisate residence times in the micelle have been estimated to be 10^{-10} second according to Waggoner et al.[161]. The siliconate in the joint micelles may react with siliconate in other micelles or siliconate in the bulk solution resulting in an increase in the molecular weight of the siliconate or the production of oligomers which have less water affinity than that of the monomers. Further increasing the molecular weight of the oligomer may gradually cause the disappearance of the joint micelle with formation of a siliconate sol, which may be spontaneously stabilised by the surfactant which adsorbs on the sol surface. The particle size of the sol may further grow by condensation until there is precipitation from the solution due to either insufficient water affinity or gravity.

The stability of solubilised PPMS solution depends on the surfactant concentration in the solution. Table 3.6 shows the stability of stabilised PPMS solutions with different surfactant concentrations. It was found that the stability of the solution is improved by increasing the surfactant addition. However, there is a limit to the amount of surfactant addition because the surfactant decreases the water repellency and in particular the alkali stability of the treated substrates (further discussed in ξ3.2.3). Table 3.6 also shows that a minimum of 0.12% Teric G12A12 is necessary to significantly solubilise 2.5% PPMS solutions.

Table 3.6 Stability of solubilised PPMS with different surfactant additions

Surfactant concentration (%)	Stability of the solubilised solution*	
	at ambient temperature	at 40°C
<0.12	unsatisfactory	unsatisfactory
0.12	3 months	within 5 days
0.36	6 months	2 months
0.61	12 months	4 months

* Stability end point is defined as the appearance of cloudiness or precipitate.

3.2.3 Effect of surfactant on the PPMS treated substrates

The major effects of surfactant on the substrate treated with PPMS solution stabilised by surfactant are to decrease the water repellency of the siliconate treated substrate particularly in the case of very alkaline substrates such as fresh cement mortar. Figure 3.11 shows that alkali stability in terms of water absorption of very fresh cement mortar substrates (1 week old DIN 1164 cement mortar discs) treated with the 2.5% PPMS solution containing Teric G12A12 as the stabiliser. The water absorption significantly increases with the increase in surfactant concentration. Only when the surfactant concentration is at 0.12%, is the surfactant effect reduced to a minimum and the water absorption result shows a similar value to that of the PPMS diluted with the water-isopropanol (1:1 by weight) mixture.

Surfactant is known to impart a hydrophilic effect to the substrate due to the adsorption of the surfactant onto the substrate. According to Schönfeldt [114] and Iler [160], polyoxyethylene nonionic surfactants are believed to adsorb on the substrate surface (or substrate capillary wall surface) via the ether oxygen of the ethoxylate chain by hydrogen bonding to the silanol of the masonry substrate. This results in a hydrophilic layer on the substrate surface (shown in Figure 3.12). The adsorbed surfactant on the substrate surface may be the major factor in the reduction of the water repellency of the impregnated substrate due to the surfactant hydrophilic effect.

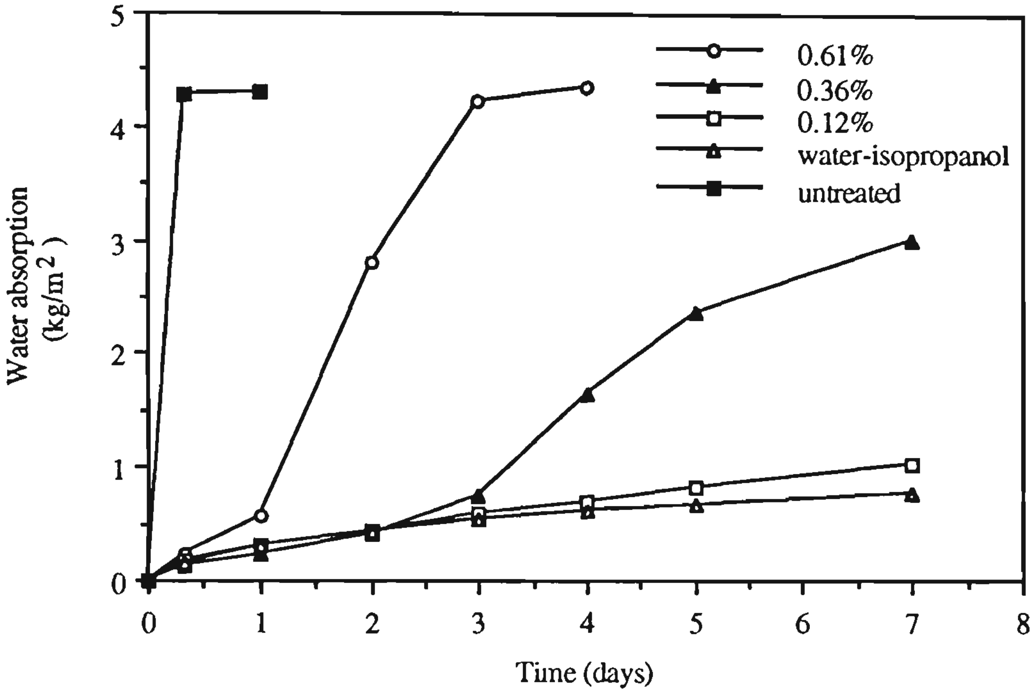


Figure 3.11 Water absorption of alkaline substrates treated with 2.5% PPMS solutions containing various amounts of Teric G12A12

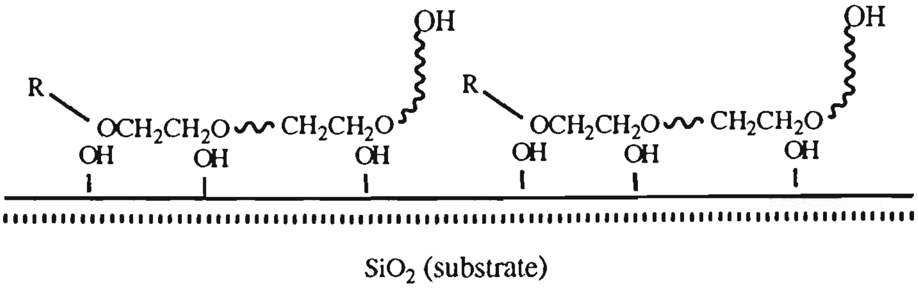


Figure 3.12 Adsorbed polyoxyethylene nonionic surfactant by hydrogen bonding between ether oxygen of the surfactant ethoxylate chain and the silanols of the masonry substrate

In siliconate treated substrates, the surfactant effect is assumed to include both the hydrophilic effect induced by the adsorbed surfactant layer and the effect of an acceleration of the hydrolysis of the polysiloxane formed in the substrate. The effect of the acceleration of the hydrolysis by the surfactant may be the major factor in the reduction of the water repellency when an alkaline substrate is impregnated. As trace water may penetrate into the polysiloxane hydrophobic layer in the substrate, the water is then held by the ethoxylate chain of the surfactant which stays close to the polysiloxane and the siloxane bond between the polymer and the substrate. Significantly, under alkaline conditions, this water can hydrolyse the siloxane resulting in formation of soluble siliconate which may then be gradually dissolved by further penetrating water until all the hydrophobic layer is fully decomposed.

The hydrophilic effect induced by the surfactant in a siliconate treated substrate may be minor compared to that of the hydrolysis effect. The water repellency of the hydrophobic layer in the substrate surface is assumed to be greater at the very surface. As carbon dioxide concentration near the very surface is higher than that inside, the degree of siliconate condensation to form hydrophobic polysiloxane both with the substrate and itself is higher resulting in a higher molecular weight polysiloxane structure which gives an effective barrier near the very surface to stop the water penetration. Although the surfactant still exists in the substrate, it may not achieve a hydrophilic effect as the very surface is dominated by the hydrophobic layer. This has been shown by treating less alkaline substrates with the PPMS solutions. Figure 3.13 shows that there is almost no difference in water absorption of 8 weeks old AS 3700 M3 cement mortar substrates treated with 2.5% PPMS solutions containing various amount of Teric G12A12 surfactant except at a very high concentration of the surfactant.

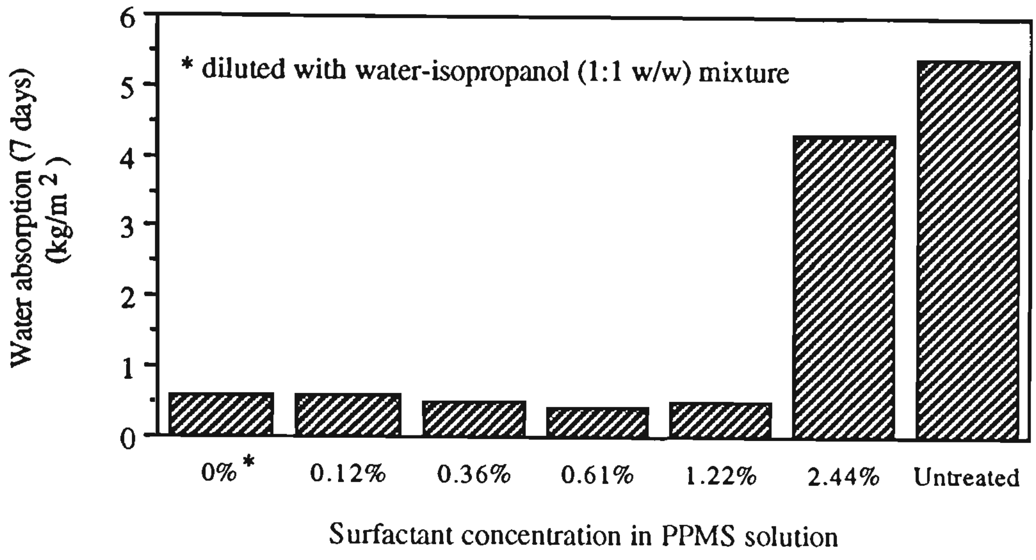


Figure 3.13 Water absorption of substrates treated with 2.5% PPMS solutions containing various amount of Teric G12A12

The depth of impregnation was found to increase with the addition of the surfactant for both DIN 1164 and AS 3700 M3 cement mortar substrates (see Table 3.7). It is known that surfactant aids liquid spreading on solid substrates by lowering the surface tension of the liquid [137]. However, it is observed from Table 3.7 that the surfactant has little effect on the surface tension of PPMS solution. The surface tension of the siliconate solution is known to be low [162], probably due to the similarity of the structure to that of a surfactant. The effect of improvement of depth of impregnation by surfactant may be explained as the surfactant reducing the chemical activity of the siliconate. It is assumed that the siliconate may react spontaneously with substrate silanols and condense to form a polysiloxane hydrophobic water repellent layer which stops further penetration of the aqueous solution. As discussed previously, by adding the surfactant, the reactivity of the PPMS may be reduced by forming the surfactant-siliconate joint micelle resulting in a higher penetration depth. This has been further confirmed by the lower depth of impregnation of PPMS solution containing cationic surfactants. It has been observed that the depth of impregnation of PPMS solution containing Vantoc N40 is only one half of that of the solution containing Teric G12A12. This may be because the cationic surfactant-siliconate joint micelle has less effect in reducing the reactivity of the siliconate. In addition, the surfactant itself may also interact with the substrate due to the different electric charges on the surfactant and the substrate.

***Table 3.7** The surface tension of 2.5% PPMS solutions containing Teric G12A12 surfactant at different concentrations and the impregnation depth of the treated substrates*

Surfactant addition (%)	Surface tension (dyne/cm, 20°C)	Depth of impregnation (mm)	
		DIN 1164 mortar	AS 3700 M3 mortar
0% *	26.7	<1	2.0
0.12%	29.9	<1	2.0
0.36%	-	1	2.5
0.61%	30.7	1.5	3.0
1.22%	-	2	4.0

* Diluted with water-isopropanol (1:1 w/w) mixture.

There is another unique effect on alkali stability induced by the surfactant. The alkali stability of the substrate treated with the PPMS impregnant decreases with the increase of the storage time of the diluted PPMS solution. Table 3.8 lists the water absorption of very alkaline substrates (1 week old DIN 1164) and less alkaline substrates (8 weeks old AS 3700 M3) treated with 2.5% PPMS solutions which were diluted and stored for different periods. The alkali stability is significantly reduced with the increase in the storage time. However, there is no effect on less alkaline substrates. This may be due to the re-esterification or the alcoholysis of the siliconate by polyoxyethylene nonionic surfactant because the re-esterification or the alcoholysis may gradually occur after dilution. In the presence of an alkali, the bonded surfactant may have more effect on accelerating the hydrolysis of siloxane in the substrate than that of un-bonded surfactant. The water is attracted by the bonded surfactant so closely to the siloxane bonds between the substrate and the silicone that hydrolysis of the silicone can easily occur. This effect will be further detailed in ξ3.3.

Table 3.8 *Water absorption of solubilised PPMS solution treated substrates **

Storage time of PPMS solutions after dilution	Water absorption (7 days, kg/m^2)	
	DIN 1164 mortar	AS 3700 M3 mortar
Fresh	1.03	0.47
1 day	1.35	-
8 days	1.43	-
6 months	-	0.43
Untreated substrate	4.3 (1 day)	5.4 (1 day)

* PPMS solutions contained 0.12% Teric G12A12 for DIN 1164 mortar and 0.24 % Teric G12A12 for AS 3700 M3 mortar.

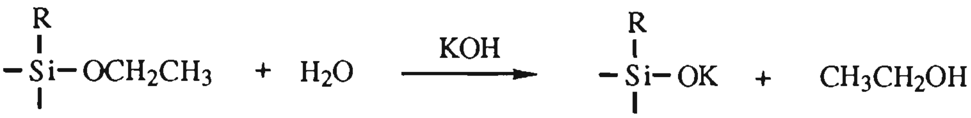
It has been shown that the stabilisation effect is increased by increasing the surfactant addition while the water repellent performance of the PPMS impregnant is decreased with increase in the surfactant level except for the depth of impregnation which is improved. The best condition for stabilising diluted PPMS impregnant may be the use of minimum surfactant to achieve a stability of the diluted PPMS solution to a practical value but with minimum negative effect imparted on the water repellent performance particularly for alkaline substrates. The test results show that a minimum 0.12% of alkylalcohol ethoxylate nonionic surfactant Teric G12A12 may be necessary to stabilise the diluted 2.5% PPMS solution but this achieves only a slightly negative effect on the alkaline stability of the substrates. It is suggested that the diluted solution is used as soon as possible particularly when very alkaline substrates are impregnated in order to reduce the effect induced by possible re-esterification or the alcoholysis by the surfactant.

3.3 Potassium octyl/methyl siliconate (POMS)

A novel POMS impregnant made by hydrolysing octyltriethoxysilane (OTES) in PMS in the presence of a polyoxyethylene nonionic surfactant has been successfully developed in this work [163]. The novel POMS was found to be soluble in aqueous solution and to impart masonry substrates and in particular very alkaline substrates with a satisfactory water repellency. The alkali stability of POMS treated substrate was found to be equivalent to that of the solvent-based OMMS-Sn impregnant.

3.3.1 Hydrolysis of octyltriethoxysilane in PMS solution

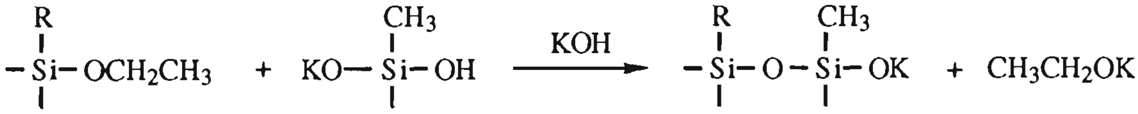
Hydrolysis of OTES in PMS is complex. Basically, PMS is a strongly alkaline solution which contains PMS, KOH and water. Therefore, OTES may be hydrolysed to form potassium octylsiliconate in strongly alkaline conditions (Scheme 3.13).



$$-\underset{|}{\overset{\overset{R}{|}}{Si}}-OCH_2CH_3 + H_2O \xrightarrow{KOH} -\underset{|}{\overset{\overset{R}{|}}{Si}}-OK + CH_3CH_2OH$$

(Scheme 3.13)

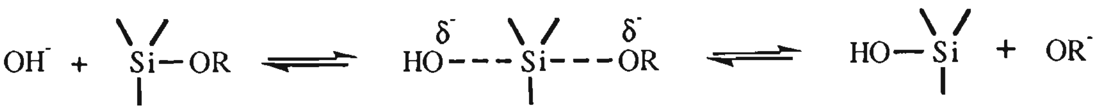
According to Voronkov et al.[118], an alkoxysilane can react with a metal siliconate with the silane ether being replaced by the siliconate anion. Therefore, OTES may react with PMS resulting in an oligomeric siliconate structure or siloxane structure under strongly alkaline conditions (Scheme 3.14)



$$-\underset{|}{\overset{\overset{R}{|}}{Si}}-OCH_2CH_3 + KO-\underset{|}{\overset{\overset{CH_3}{|}}{Si}}-OH \xrightarrow{KOH} -\underset{|}{\overset{\overset{R}{|}}{Si}}-O-\underset{|}{\overset{\overset{CH_3}{|}}{Si}}-OK + CH_3CH_2OK$$

(Scheme 3.14)

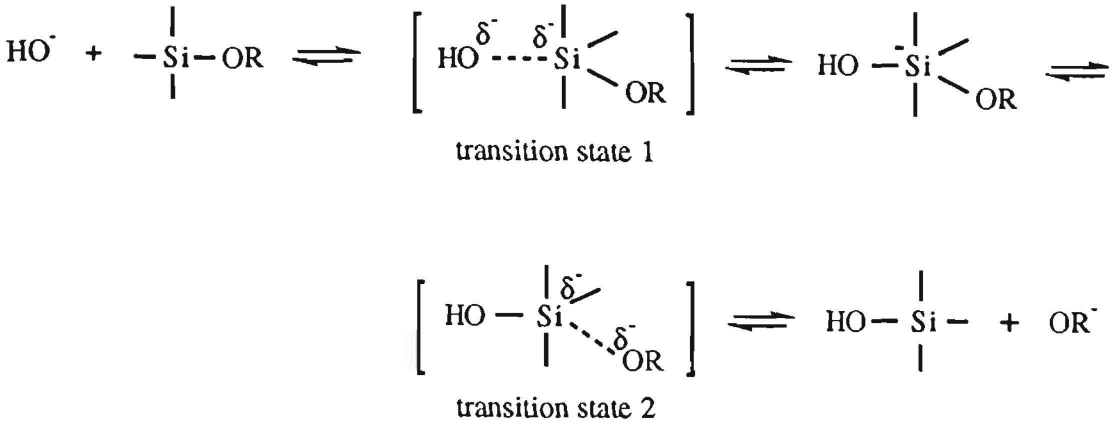
Both of these reactions are believed to operate via a S_N2-Si mechanism where the anion OH^- or the siliconate anion $CH_3(OH)_2SiO^-$ are the nucleophiles which attack the silicon of the silane to replace the ethoxy groups according to Brinker and Scherer [146] (Scheme 3.15).



$$OH^- + \underset{|}{\overset{\diagdown\,\diagup}{Si}}-OR \rightleftharpoons \overset{\delta^-}{HO}---\underset{|}{\overset{\diagdown\,\diagup}{Si}}---\overset{\delta^-}{OR} \rightleftharpoons HO-\underset{|}{\overset{\diagdown\,\diagup}{Si}} + OR^-$$

(Scheme 3.15)

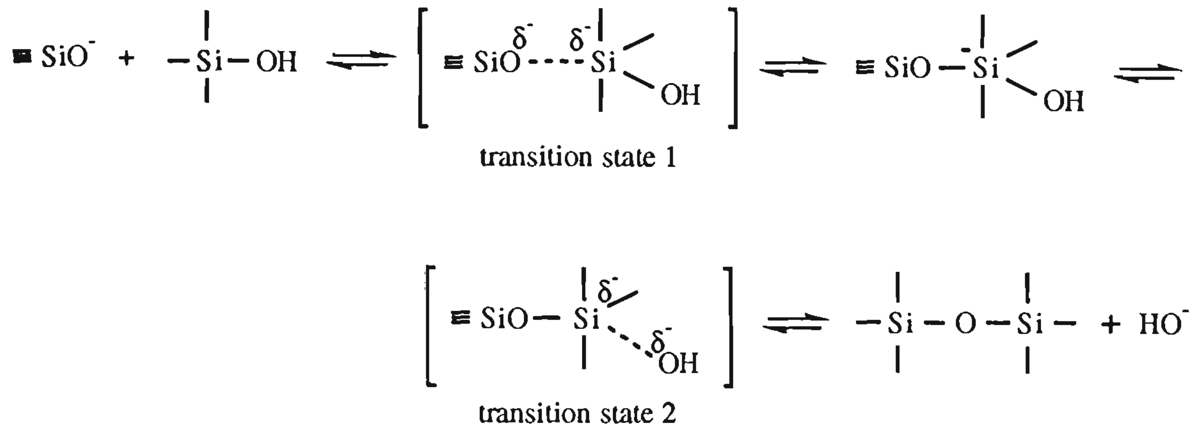
According to Pohl and Osterholtz [147], the mechanism of the nucleophilic substitution reaction could be via a S_N2^{**}-Si or a S_N2^{*}-Si mechanism involving a stable negatively charged 5-coordinated intermediate (Scheme 3.16).



(*Scheme 3.16*)

Both of the above nucleophilic substitution mechanisms for silane hydrolysis are affected by steric and inductive factors. Accordingly, larger alkyl or alkoxy groups on the silicone atom will retard the reaction rate. Once the first alkoxy substituent on the silicone is replaced by hydroxyl anion or siliconate anion, then the reaction rate would be enhanced since both hydroxyl anion or siliconate anion groups are electron withdrawing substituents which would stabilise the negatively charged intermediate [146].

The condensation of the initial silane hydrolysis products may occur but it will proceed slowly. Condensation of silanol under basic conditions may be via the same mechanism as that of hydrolysis in which the siliconate anion acts as a nucleophile to attack the backside of the silicone to displace the hydroxyl anion. The S_N2^{**}-Si or S_N2^{*}-Si mechanism for condensation according to Swain et al.[149] is shown in Scheme 3.17. As the condensation rate is second-order in silanol concentration according to Pohl and Osterholtz [147], the condensation rate would be very slow in the concentrated PMS solution containing silane hydrolysis product as almost all the silanols are deprotonated under highly alkaline conditions by formation of stable siliconate [76]. However, the condensation will occur when the siliconate is diluted.



(Scheme 3.17)

3.3.2 Micellar catalysis of silane hydrolysis in PMS solution

Without the addition of water-miscible solvents to a higher alkylalkoxysilane alkaline hydrolysis system, the reaction is very slow. Generally, solvents are added to prevent liquid-liquid phase separation and to form a homogeneous solution during the initial stages of the hydrolysis reaction to allow the reactants such as hydroxyl anion to sufficiently access the silicon atom to effect the silane hydrolysis. Chemically, water-miscible solvents may accelerate or retard the silane hydrolysis and may take part in the silane hydrolysis or condensation as discussed in the literature [118, 146, 164]. However, the chemical effect of the solvents may be far less than that of the physical effect of achieving a homogeneous hydrolysis system.

Surfactants are well recognised as agents which affect the rate of chemical reactions. Many chemical reactions, especially those in which one reactant is soluble in water and the other in oil, may exhibit a significant enhancement in reaction rate when carried out in the presence of surfactant micelles [165]. This is because the organic reactant may be solubilised in surfactant micelles which dissolve in the aqueous reaction medium and then the enhancement of reaction rate may be attributed to two possible mechanisms: (i) the palisade region of the micelle provides a transition zone of reaction medium between an insoluble hydrophobic organic reactant and an aqueous reactant medium, and (ii) the micelle actually serves as a reservoir of insoluble organic reactant, resulting in an increase in the available concentration of reactants [165].

The reaction rate enhancement by surfactant micelle may also depend on the nature of surfactant, the additives and the reaction system. In acidic or basic hydrolysis of an organic material catalysed by ionic surfactants electrostatic interactions [152, 165] may dominate the micellar catalysis. An anionic surfactant micelle may retard a basic hydrolysis by negative-negative charge repulsion between the micelle and hydroxyl anion while a cationic micelle accelerates the hydrolysis due to the electrostatic attraction between the micelle and the anion [166-169]. In nonionic surfactant catalysis, the reaction rate enhancement may be due to the surfactant micelle providing a transition reaction zone between the hydrophobic substance and the anion in an aqueous reaction medium. This is termed hydrophobic interaction [152, 165].

The hydrolysis reaction of OTES in PMS solution has been found to be significantly accelerated by either cationic or nonionic surfactants but anionic surfactants show much less effect on the reaction rate. The mixture of PMS, surfactant Teric G12A12 and OTES turns from cloudy to a homogeneous hazy suspension first and then becomes a clear solution within about 60 minutes at 25°C, whereas without addition of surfactant the mixture remains cloudy or separates into two phases after the stirring is ceased. The reaction products (POMS) from the silane hydrolysis in surfactant solution can then be diluted with water to form a clear solution which can be used to impregnate masonry substrates. The surfactant within the solution in turn stabilises the diluted POMS by the same effect as that of surfactant within the PPMS solution as discussed in ξ3.2.

3.3.2.1 Mechanism of micellar catalysis of OTES hydrolysis by surfactants

As discussed before, in nucleophilic substitution of the silane by hydroxyl anion and siliconate anion, nucleophiles need to attack the silicon atom to replace the alkoxy of silane. OTES is not soluble in the aqueous phase of PMS solution and therefore sufficient access between the oil and aqueous phase is not possible resulting in a very slow reaction rate. With addition of a surfactant, the organic phase of the silane may be solubilised or emulsified by surfactant to form micelles or emulsion droplets which are homogeneously suspended in the aqueous phase of PMS. As an alkylalkoxysilane has a polar structure, orientation of silane in the surfactant micelle may be shown with the polar groups of $-Si(OR')_3$ in the micellar palisades with possible hydrogen bonding to the ethoxylate chain of nonionic surfactant while the hydrocarbon remains in the micellar core (Figure 3.14). The silane hydrolysis may occur mainly in the palisade area. As the palisade area is the transition between the hydrophobic and the hydrophilic phase, water, hydroxyl anion and siliconate anion of PMS can easily penetrate into the palisade region of the micelle to attack the silicon atom of the silane to effect reaction.

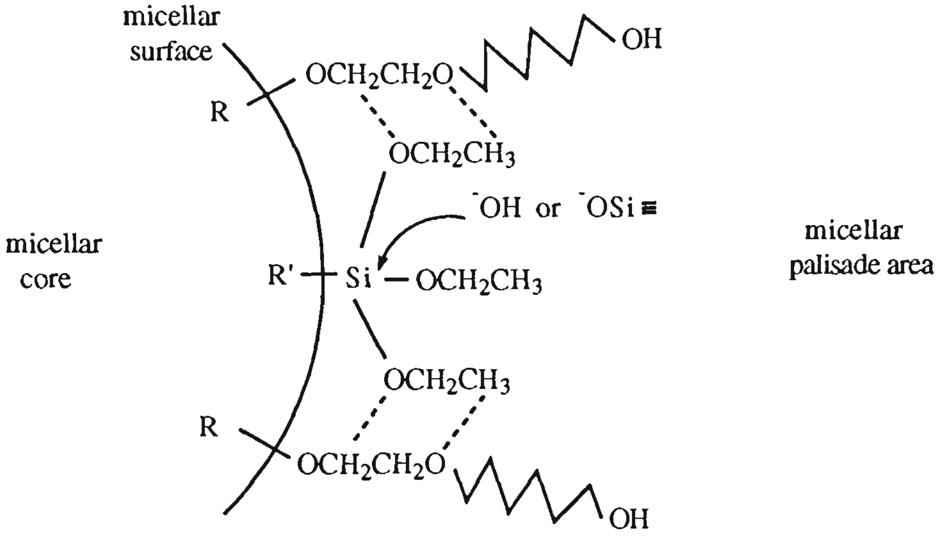


Figure 3.14 Possible silane orientation in a surfactant micelle from a nonionic surfactant and nucleophilic substitution of the silane by hydroxyl anion and siliconate anion

The micellar catalytic effect of the silane reaction in PMS by surfactants may be attributed to both electrostatic and hydrophobic interaction. The silane hydrolysis generates ethanol (see Scheme 3.13 and 3.14) so the hydrolysis rate can be related to the ethanol production from the hydrolysis reaction. Figure 3.15 plots HSGC peak area ratio of ethanol/n-propanol against the reaction time as described in Chapter 2. This summarises the effect of ionic and nonionic surfactants on the silane hydrolysis rate.

The cationic surfactants such as Vantoc N40 show enhancement of the reaction rate similar to that exhibited by the polyoxyethylene nonionic surfactant Teric G12A12. However, anionic surfactants such as Hostapon KA show much less effect in enhancing the reaction rate. The hydrolysis rate enhancement by cationic surfactant Vantoc N40 may be attributed to electrostatic interaction. The electrostatic attraction between positively charged micelle and anion (hydroxyl and siliconate) increases the concentration of anion around the micellar surface where the hydrolysis occurs and therefore there is an acceleration. The anionic Hostapon KA does not enhance the rate of silane hydrolysis probably due to the negative-negative repulsion between the micelle and the anion resulting in a decrease in the concentration of nucleophiles around the micellar surface. However, a slightly higher reaction rate than that of the hydrolysis without surfactant is probably due to the hydrophobic interaction.

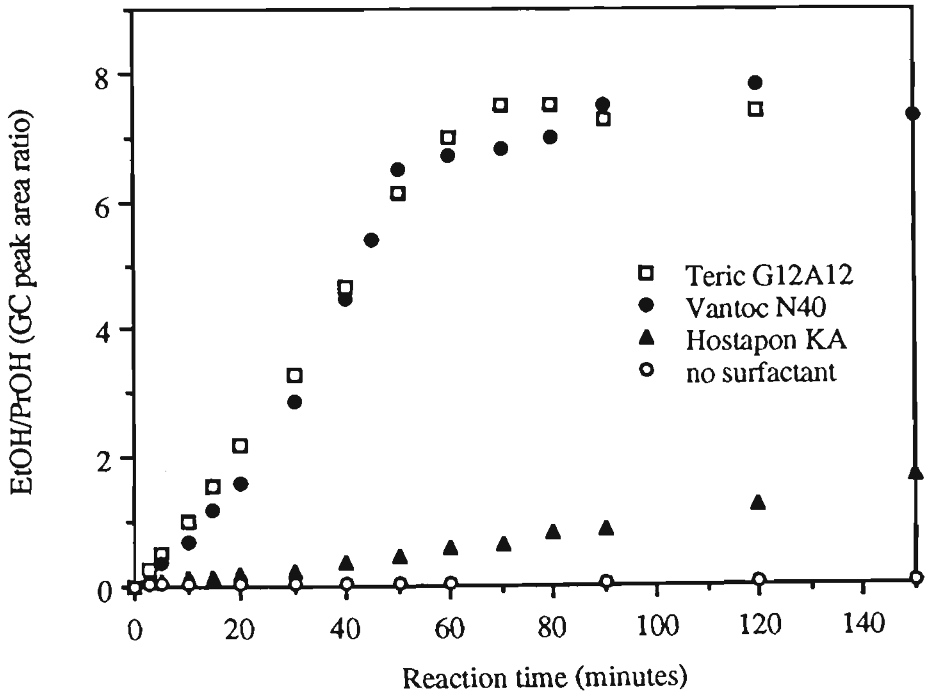


Figure 3.15 The effect of ionic and nonionic surfactants on the OTES hydrolysis in PMS solution (The reaction medium was 10.00 g PMS, 0.73 g surfactant and 1.75 g OTES at 25°C)

Bunton et al.[169] studied the catalytic effect of nitrophenyl phosphate hydrolysis in base by cationic surfactant. They found that only cationic surfactant accelerated the hydrolysis reaction whereas anionic and nonionic surfactants showed a retarding effect on the hydrolysis rate. The hydrolysis in base of carboxylic esters as well as many other materials show these same effects as exhibited in the hydrolysis of the phosphates [152].

From the results shown in Figure 3.15, polyoxyethylene nonionic surfactants show the same hydrolysis rate enhancement effect as exhibited by cationic surfactants. It may be concluded that hydrophobic interaction may also play an important part in silane hydrolysis in PMS solution.

The effect of micelles on the rate of organic hydrolysis is explicable in terms of the location of the substrate solubilised in the micelle. In a comparison with the phosphate hydrolysis in a cationic micelle, the silane has less polarity and may locate within the micelle with the polar groups $-Si(OCH_2CH_3)_3$ very close to the inner surface of the micelle while the polar group of the phosphate may stay in the surface of the micelle. It is obvious that the hydrolysis of phosphate may occur easily at the micellar surface where the anion concentration is the highest, whereas for the silane hydrolysis the nucleophiles still need to penetrate the very surface of the micelle to react with the silicone. In the case of nonionic micellar catalysis, the polar groups stay in the palisade area of the nonionic micelle where the anions have access to the silicone to complete the reaction. Therefore, the electrostatic interaction for the micellar catalysis of silane hydrolysis may be not as significant as that for phosphate hydrolysis. The hydrophobic interaction for nonionic surfactants plays the same important role as that of the electrostatic for cationic surfactants.

In addition, polyoxyethylene nonionic surfactants can further stabilise the diluted silane hydrolysis products as discussed previously. Therefore, it may be concluded that nonionic surfactants would be the best choice for both catalysis of the silane hydrolysis and subsequent stabilisation of the hydrolysis products.

Investigation of various effects of nonionic surfactants on silane hydrolysis has been carried out to further confirm the micellar catalysis mechanism and to optimise the catalysis effect.

a) Effect of the surfactant structure on the silane hydrolysis rate

The effect of ethoxylate chain length of alkylalcohol ethoxylates on silane hydrolysis is shown in Figure 3.16. It was found that a decrease in the ethoxylate chain length increases the silane hydrolysis rate. This may be explained by the hydrophobic interaction of the micelle. As discussed, it is assumed that the polar groups of the silane stay in the micellar palisade area where the nucleophiles approach the silicone. However, a long ethoxylate chain in the surfactant may impart steric hindrance for the nucleophiles as they approach the silicon atoms, resulting in less of a rate acceleration. Obviously, the steric hindrance increases with the increase in ethoxylate chain length. However, such a steric hindrance effect may not be significant unless the ethoxylate chain is very long. It was observed that Teric G12A23 shows a significantly lower hydrolysis rate enhancement in a comparison with other surfactants but still enabled hydrolysis to occur.

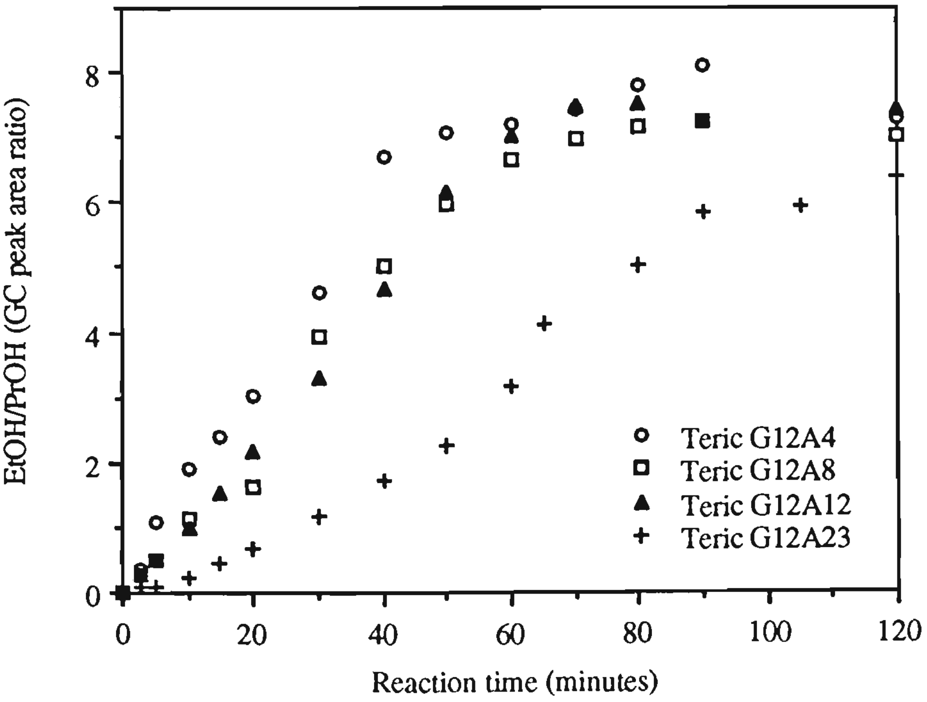


Figure 3.16 The effect of surfactant ethoxylate chain length on OTES hydrolysis rate in PMS (The reaction medium was 10.00 g PMS, 0.73 g surfactant and 1.75 g OTES at 25°C)

The hydrocarbon chain length of the surfactant is found to be less important in affecting the rate of silane hydrolysis. Figure 3.17 shows that the rate of silane hydrolysis is similar for surfactants with $(CH_2)_n$ where n is from 9 to 17 in the surfactants. The slightly lower hydrolysis rate induced by Teric G17A8 may be due to the HLB of the surfactant being too low to properly solubilise the silane in aqueous PMS solution to form a homogeneous reaction mixture. These results once again show the hydrophobic interaction mechanism of micellar catalysis of silane hydrolysis.

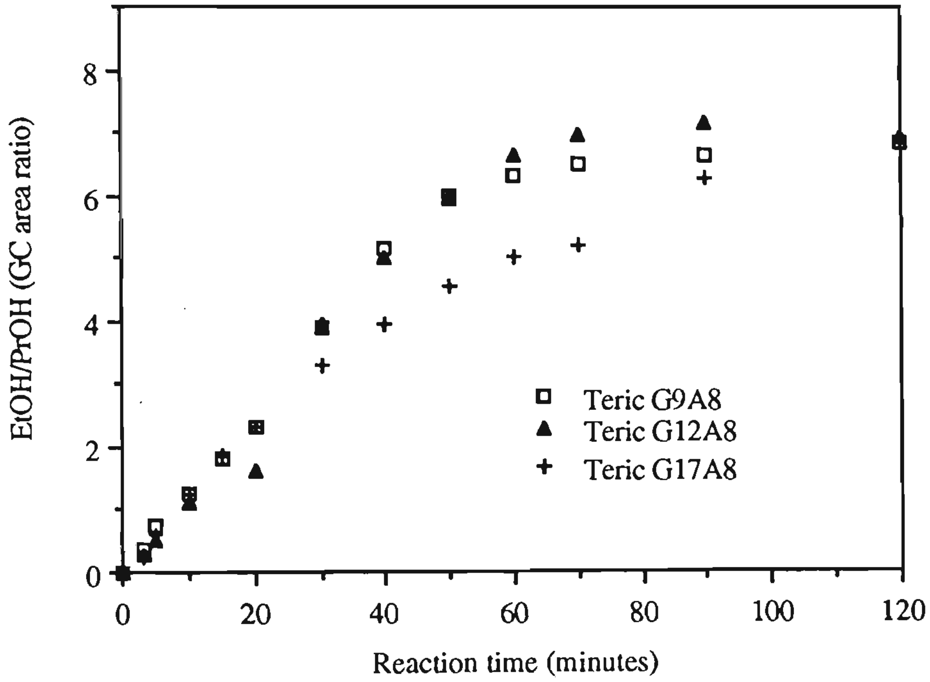


Figure 3.17 The effect of surfactant hydrocarbon chain length on the OTES hydrolysis rate in PMS (The reaction medium was 10.00 g PMS, 0.73 g surfactant and 1.75 g OTES at 25^{o}C)

b) Effect of the surfactant concentration on the silane hydrolysis rate

It is understandable that the silane is solubilised by the nonionic surfactant micelle and the hydrolysis mainly occurs within the micelle. Increasing the surfactant concentration should improve the solubilisation effect and therefore increase the rate of silane hydrolysis. Figure 3.18 shows the rate of silane hydrolysis at different concentrations of surfactant (Teric G12A12 addition at 0%, 30%, 70% and 150% based on active OTES calculated as

$CH_3(CH_2)_7SiO_{1.5}$ or 0.00 g, 0.31 g, 0.73 g, 1.57 g Teric G12A12 respectively based on the hydrolysis system of 10.00 g PMS and 1.75 g OTES). The results confirm this effect which once again shows the hydrophobic interaction mechanism of micellar catalysis by the nonionic surfactant.

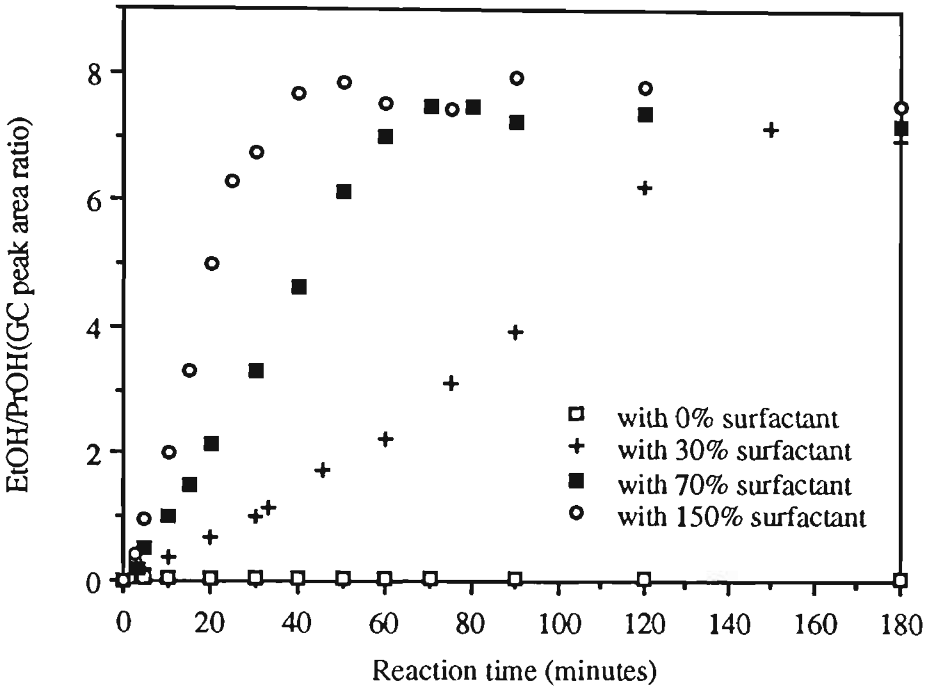


Figure 3.18 The effect of surfactant concentration on the OTES hydrolysis rate in PMS (The reaction medium was 10.00 g PMS, various Teric G12A12 and 1.75 g OTES at 25°C)

c) Effect of temperature on the rate enhancement by the surfactant

Increasing the temperature from 25°C to 60°C is found to further accelerate the silane hydrolysis in PMS in the presence of nonionic surfactant as shown in Figure 3.19. Increasing the temperature is known to accelerate chemical reaction rates. However, the silane hydrolysis without surfactant addition shows almost no rate acceleration effect with increase in the reaction temperature. This again implies that the hydrophobic interaction effect in silane hydrolysis is significant. Therefore, as well as the effect on reaction rate by temperature, the rate enhancement of the silane hydrolysis by temperature may also be attributed to the solubilisation power of the nonionic surfactant. According to Shinoda [150] and Shinoda and Haruhiko [170], the solubilisation power of nonionic surfactants is increased with an increase in temperature and reaches a maximum at near the cloud point. At a higher temperature (at or less than the surfactant T_c), more silane would be solubilised by the surfactant micelle and therefore a higher hydrolysis rate would result.

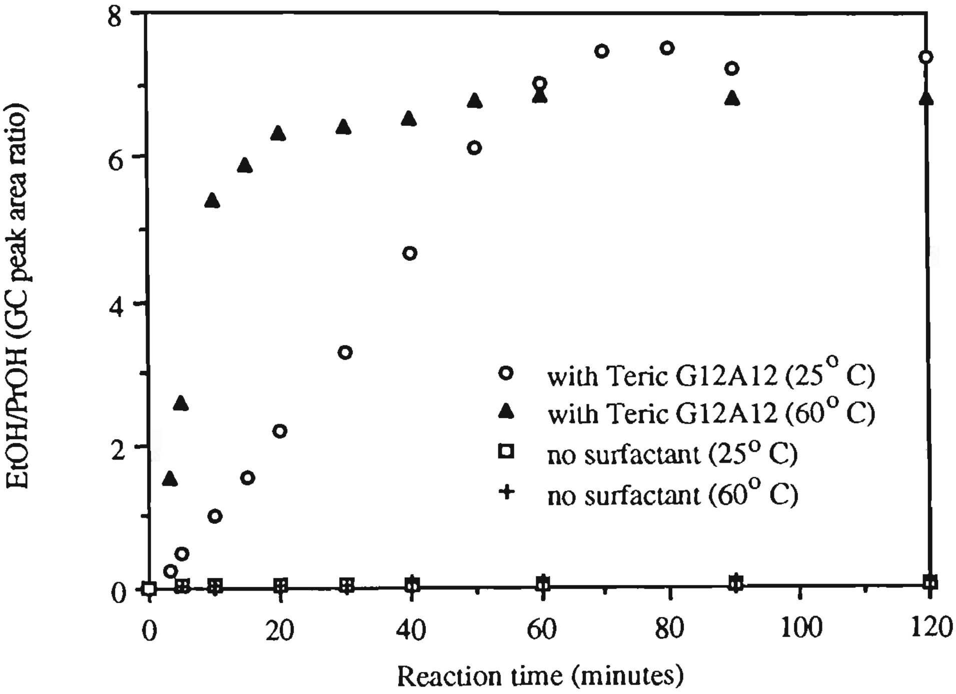


Figure 3.19 The effect of hydrolysis temperature on the OTES hydrolysis rate in PMS (The reaction medium was 10.00 g PMS, 0.73 g Teric G12A12 and 1.75 g OTES at 25°C)

From the above discussion, it may be concluded that the alkylalcohol ethoxylate surfactant Teric G12A12 may be the most suitable surfactant for acceleration of the OTES hydrolysis in PMS. The surfactant concentration at above 30% (calculation based on the active octylsiliconate $RSiO_{1.5}$) and the temperature at either 25°C or 60°C may be adequate to undertake the OTES hydrolysis in PMS to prepare POMS impregnant.

3.3.2.2 Proposed structures of the products from OTES hydrolysis in PMS

Alkylalkoxysilane hydrolysis products have been proved to be a mixture of either monomers or oligomers by many workers previously. Plueddemann [76] investigated the hydrolysis products of vinyltrimethxoysilane by using the Lentz Technique and found that these mixtures contained various silanol or siliconate monomers, dimers, trimers and tetramers depending on the nature of the solution. Nishiyama et al.[131, 171] found by using ^{29}Si NMR combined with ^{13}C NMR that the products of γ-methacryloxy-propyltrimethoxysilane (γ-MPTS) initially contained mainly monomeric silanols and then dimers, trimers and oligomers were formed gradually. Cyclic oligomeric products have been shown to exist in the hydrolysis products. Brown and Vogt [172, 173] identified cyclic tetramer structures by studying the hydrolysis products of cyclohexyltrichlorosilane and phenyltrichlorosilane. Savard et al.[126] proposed a cyclic trimer and tetramer structure for the hydrolysis products of γ-MPTS. Peace et al.[124] postulated a cyclic tetramer structure of the tetraethoxysilane hydrolysis product in the solution by using GC and ^{1}H NMR techniques.

The exact structure of the silane hydrolysis product in PMS is difficult to determine. However, the products of OTES hydrolysis in the PMS solution are believed to exist as a mixture. As discussed previously, the silane reaction occurring in the system includes silane hydrolysis by hydroxyl anion and siliconate anion. At the same time the condensation of the hydrolysis products proceeds involving methylsiliconate. Thus, various siliconate mixtures other than silanol or siliconate monomers may be the main products in the system. The mixture may include monomers, dimers and oligomers and octyl/methyl siliconate co-oligomers including dimers, trimers, tetramers and so forth. The trimers, tetramers or the oligomers may exist as cyclic structures. To obtain some evidence as to the composition of the hydrolysis products, FTIR and ^{29}Si NMR spectrometric studies have been carried out on the mixtures and the results obtained are in concordance with the results in the literature for other systems.

By monitoring the silane hydrolysis by FTIR technique, the change in the silane structure during the hydrolysis was observed. Figure 3.20 shows the FTIR spectrum of OTES and the spectrum (subtracted spectrum obtained as described in ξ2.3.1) of the OTES hydrolysis product 24 hours after commencement of hydrolysis. The strong doublet bands at 1106 cm^{-1} and 1082 cm^{-1} and the bands at 1168 cm^{-1} and 956 cm^{-1} in the OTES spectrum may be assigned to the asymmetric Si-O-C stretch for the silane ethoxy groups [174, 175]. Those bands have disappeared in the spectrum of the hydrolysis products. Instead new bands in the range 1000-1100 cm^{-1} are obtained, which are believed to be the asymmetric Si-O-Si stretching vibration [143, 174, 175]. The broad doublet bands at 1080-1100 cm^{-1} could be due to the stretching of linear or cyclic oligomeric siloxane structures [143]. Bands appearing at 1020-1000 cm^{-1} are assumed to be due to short cyclic structures such as trimers [143]. Bands at 1000-950 cm^{-1} may be due to the stretch of Si-O-K in the different oligomeric siliconates of either linear or cyclic structures or in the monomer [175]. Table 3.9 summarises the band assignment for the alkylalkoxysilane and its hydrolysis products. The concentrated state of the hydrolysis product of the silane in PMS appears to contain various siliconates including oligomeric structures of either linear or cyclic composition.

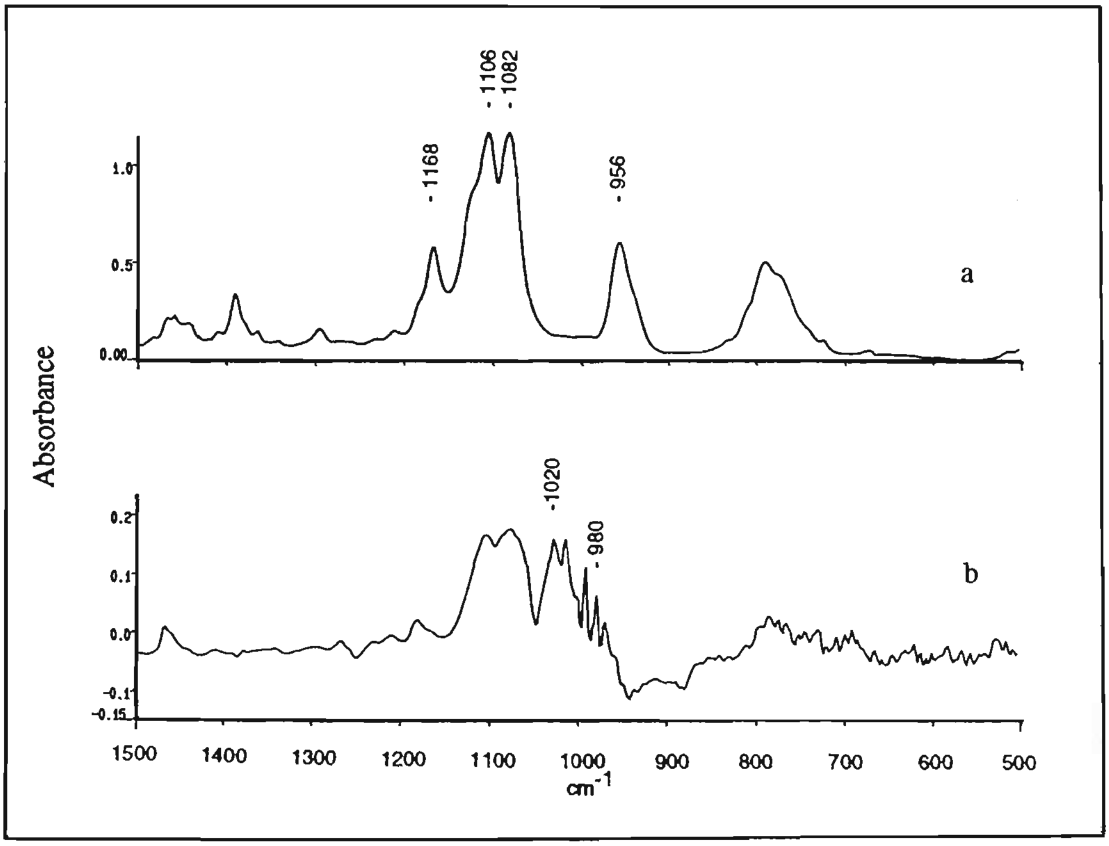


Figure 3.20 The FTIR spectra; (a) initial OTES, and (b) hydrolysis products (the hydrolysis medium was 10.00 g PMS, 0.73 g Teric G12A12 and 1.75 g OTES at 25°C for 24 hours)

Table 3.9 Assignments of infrared bands for the silane and its hydrolysis products

Band assignment	Band frequency (cm^{-1})	Comments	
Si-O-Et [a]	1106 and 1082	asymmetric stretch (strong doublet)	
	1168, 956	asymmetric stretch	
Si-O-Si [a,b,c]	cyclic: 1080-1010	trimers:	1020-1010
		tetramers:	1090-1080
		larger rings:	1080-1050
	linear: 1600-1000	short chain:	1093-1076
			1055-1020
		longer chain:	1160-1000 (broad)
Si-O-K [c]	1000-900		
C-OH [d]	1090, 1050, 880		

a) according to Anderson [174], b) to Bellamy [143], c) to Launer [175] and d) to Colthup et al.[132]

Figure 3.21 clearly shows the change of structures of the products during the hydrolysis by monitoring the FTIR spectra of the silane hydrolysis. The intensity of ethoxy bands at 1168, 1106, 1082 and 956 cm $^{-1}$ decrease gradually resulting in formation of new bands at 1020-1010 cm^{-1} due to cyclic structures such as trimers. The negative band at 1050 cm^{-1} at the beginning is due to the subtraction of the ethanol band (see ξ2.3.1) but disappears after hydrolysis is completed. This band implies the ethanol is produced from the silane during the hydrolysis reaction. The other negative bands at 1000-950 cm^{-1} gradually form during the hydrolysis but then disappear with the formation of new bands at about the same position during hydrolysis. This is assumed to be the change from the methylsiliconate Si-O-K bands to the octylsiliconate or octyl/methylsiliconate Si-O-K bands. The methylsiliconate disappears due to the reaction between the PMS and the OTES but the POMS forms to impart new but complex Si-O-K bands in the same frequency range after hydrolysis.

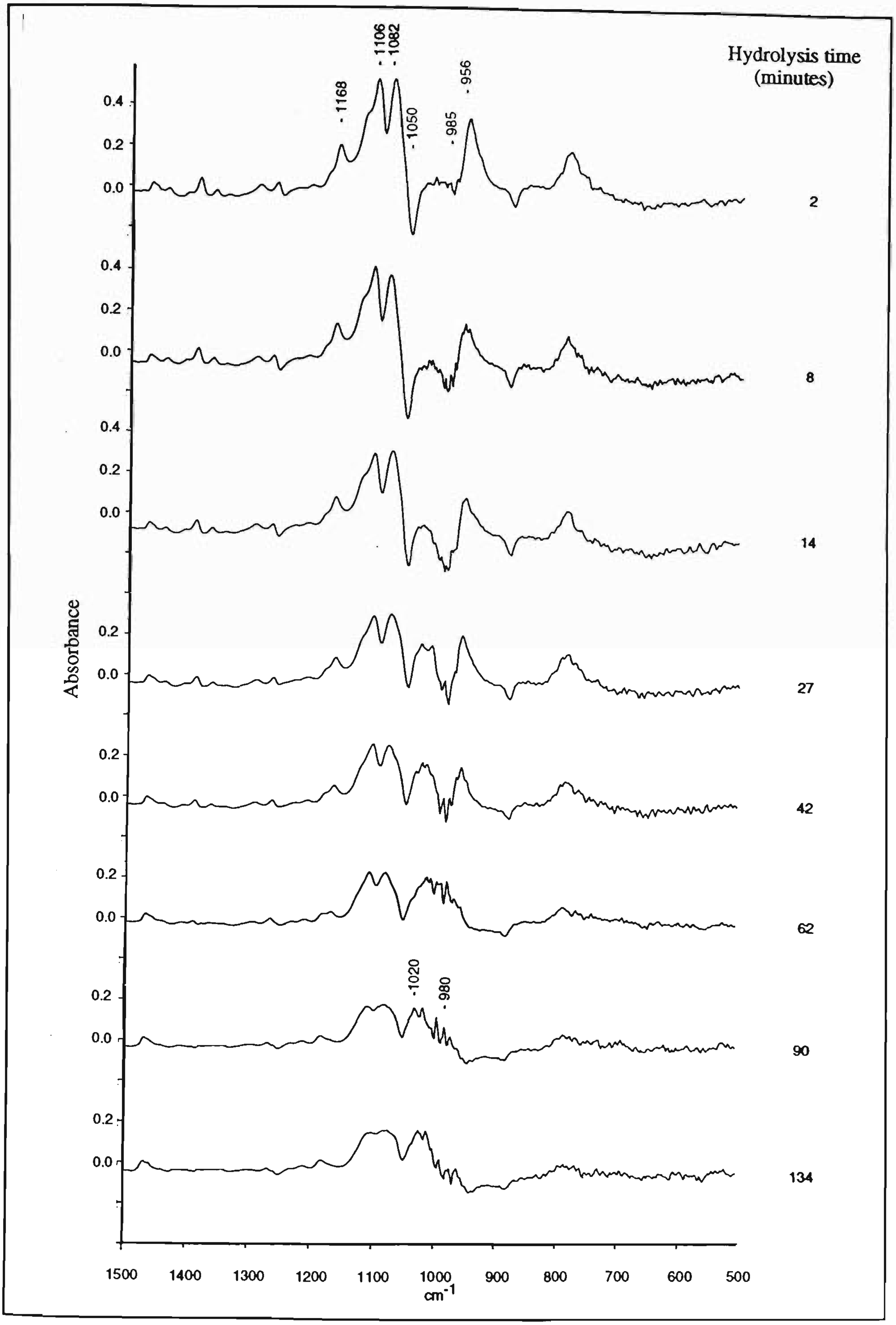


Figure 3.21 *The FTIR spectra of various states of the OTES hydrolysis during the hydrolysis (The reaction medium was 10.00 g PMS, 0.73 g Teric G12A12 and 1.75 g OTES at 25^{o}C)*

Figure 3.22 shows the intensity change of the silane ethoxy band at 1106 cm^{-1} and cyclic trimer band at 1020 cm^{-1} during the hydrolysis reaction time, which clearly shows the change during the hydrolysis. The intensity of the silane ethoxy band (at 1106 cm^{-1}) decreases to a constant value and the intensity of the cyclic trimer band (at 1020 cm^{-1}) increases to a constant value at about 60-90 minutes, which is consistent with that of the GC results of ethanol cleavage during the hydrolysis of the same reaction system containing Teric G12A12 (refer to Figure 3.15) .

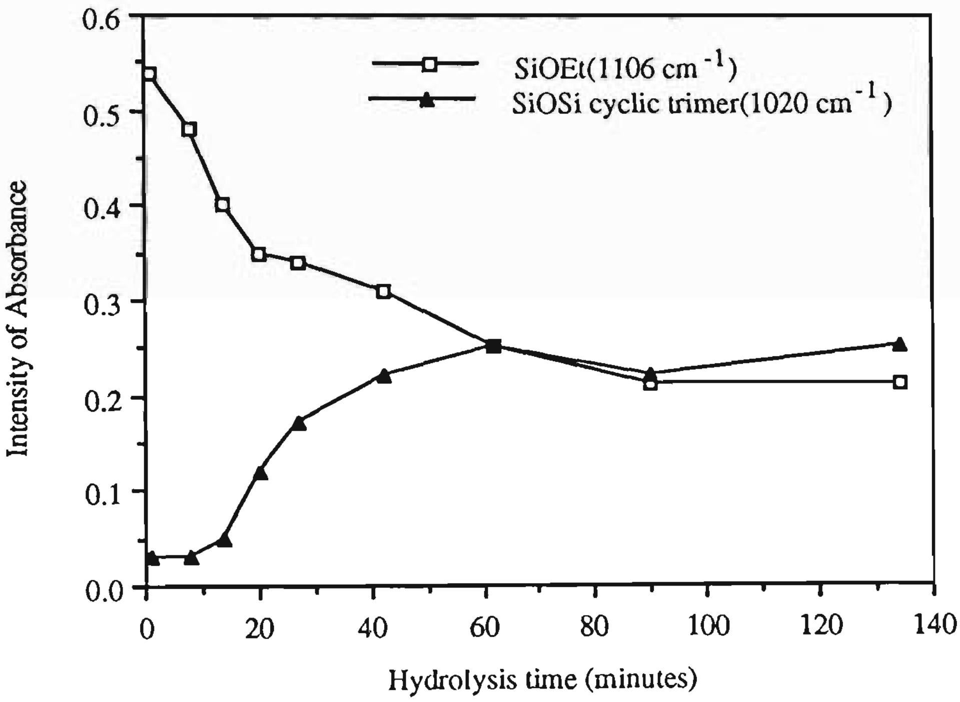
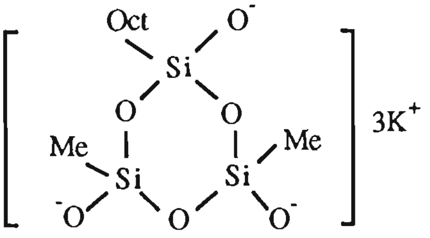


Figure 3.22 A plot of band intensity change of SiOEt (at 1106 cm^{-1}) and SiOSi (at 1020 cm^{-1}) versus hydrolysis time (the hydrolysis medium was 10.00 g PMS, 1.73 g Teric G12A12 and 1.75 g OTES at 25°C)

The cyclic oligomeric structure may be more stable than those of linear structures. By forming the cyclic structure, two functional groups in each silicon tetrahedron bond to the other silicons by covalent bonds with only one un-bonded silanol on each silicon which may form siliconate with a potassium ion. Scheme 3.18 shows the proposed octyl/methyl oligomeric cyclic siliconate trimer structure as one of the possible silane hydrolysis structures in PMS. This cyclic structure may explain the high stability of the concentrated alkylsiliconate because there is no silanetriol or even silanol groups in the siliconate molecules in the solution. Formation of silanol in the siliconate solutions is the precursor to silicone condensation. Only when the siliconate concentrate is diluted with water with formation of silanols which cause condensation, the cyclic structure may break resulting in the stability of the siliconate solution being lost. (However, diluted POMS may be spontaneously stabilised by the surfactant resulting in stable siliconate solution but the structure of POMS in the diluted solution may change.) This conclusion is in agreement with results reported in the literature [146]. According to Brinker and Scherer [146], at above pH 12, deprotonated silanols (siliconates or silicates) may be the major components in solution as cyclic trimers and tetramers . These cyclic structures are stable at this pH due to formation of the planar, cyclic configuration (D_{3h} symmetry) which permits the greatest separation of charge between the deprotonated sites [146]. Dent Glasser and Lachowski [176, 177] reported that the cyclic trimer of a silanol appears to exist in very alkaline solution. At such high pH the protonation of all silanol groups will be quite low, and this might result in the stabilisation of configurations that could not exist at a lower pH such as pH <10.



(Scheme 3.18)

The structures of the silane hydrolysis products in PMS were further studied by ^{29}Si NMR spectrometry. However, only diluted hydrolysis product (sample was diluted with D_2O before the analysis as described in ξ2.3.2) was able to be analysed by ^{29}Si NMR. The structure of the OTES hydrolysis product in diluted state is assumed to be different from that of the concentrated state. However, the evidence from ^{29}Si NMR may still provide valuable information to indirectly identify the structure of the OTES hydrolysis product.

Figure 3.23(a-c) shows that ^{29}Si NMR spectra of OTES, PMS and the OTES hydrolysis products. Guidance to assignment of the major peaks in the spectra was obtained from the work of Nishiyama et al.[131, 171]. The spectra include three groups of peaks which are assigned to the silicone monomers, dimers and oligomers (such as trimers). Table 3.10 shows the peak assignment of the ^{29}Si NMR spectrum. It was found from the spectral indications that the major components of the hydrolysis products of the silane are similar to those of the starting material PMS in diluted state. The only difference is that there are new peaks in the region of the dimers and oligomers of the spectrum of the hydrolysis products. There is greater complexity in the spectrum than that of the PMS. This may imply that the OTES is hydrolysed to form oligomeric siliconates (most probably the octyl/methyl co-oligomeric structures such as dimers, trimers or other oligomers) without formation of octylsiliconate monomers resulting in a complex peak pattern and new peaks in those regions. This assumption is further confirmed by studying the splitting pattern of the hydrogen-coupled ^{29}Si NMR spectrum of the silane hydrolysis product.

Table 3.10 Assignment of ^{29}Si NMR spectra according to Nishiyama et al.[131, 171]

Assignment	Chemical shift δ (ppm)
monomer groups	-44 to -45
dimer groups	-51 to -54
oligomers (trimers et al.)	-58 to -61

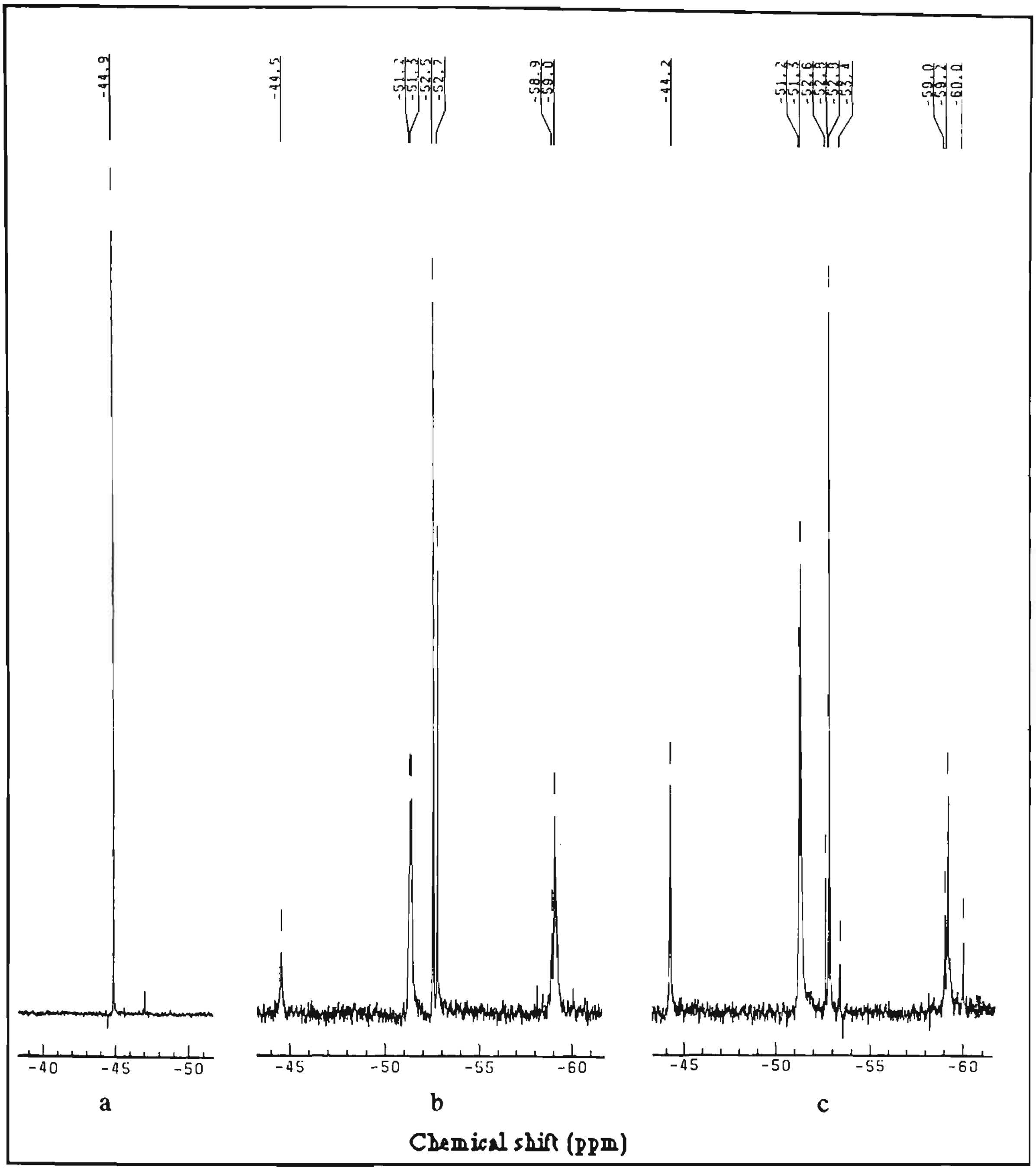


Figure 3.23 *The ^{29}Si NMR spectra; a) OTES in $CDCl_3$, b) PMS in D_2O, and c) OTES hydrolysis product in D_2O (The hydrolysis medium was 10.00 g PMS, 0.73 g Teric G12A12 and 1.75 g OTES at 25°C)*

Figure 3.24 shows the hydrogen-coupled ^{29}Si NMR spectrum of the silane hydrolysis product. The expanded peak at about -44 ppm clearly shows a quartet which may be assigned to the methylsiliconate environment, which implies that the monomer is the methylsiliconate. No evidence was obtained to show the existence of octylsiliconate monomers (which should be triplets in the hydrogen-coupled ^{29}Si NMR spectrum) in the final silane hydrolysis products.

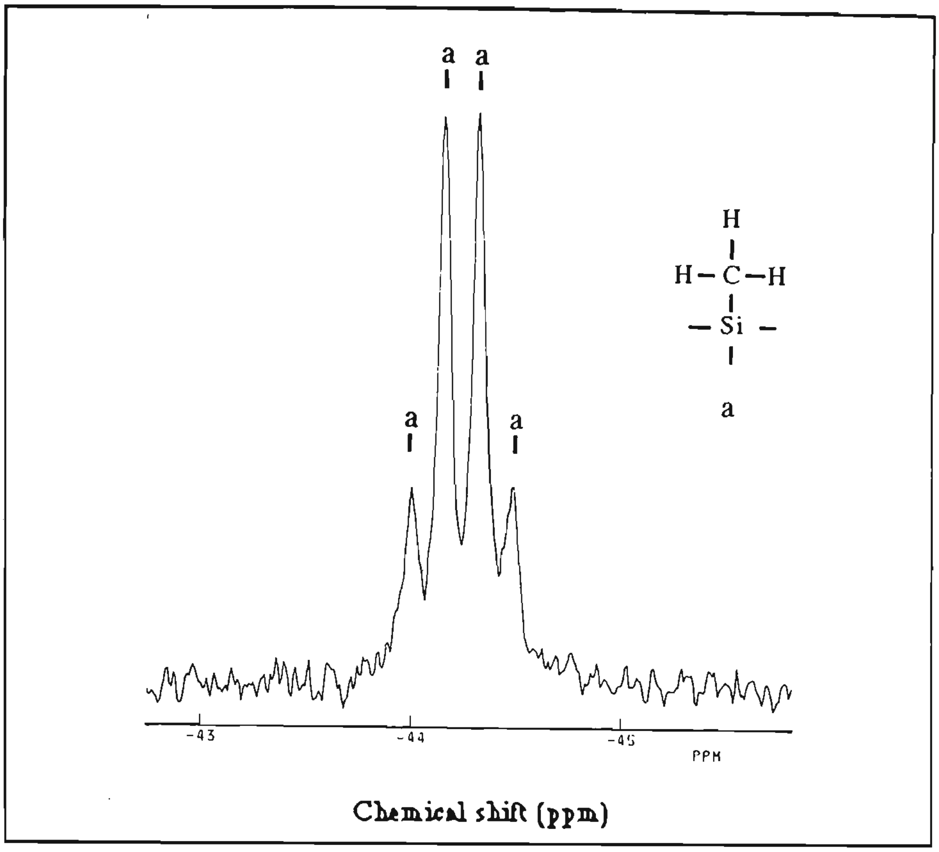


Figure 3.24 The hydrogen-coupled ^{29}Si NMR expanded spectrum of the silane hydrolysis product at chemical shift about -44 ppm

Figure 3.25 (a) shows the peaks in the region of -51 ppm to -54 ppm of the hydrogen-coupled ^{29}Si NMR expanded spectrum of the silane hydrolysis products. The peaks at ca. -51 ppm may be considered to be two overlapping quartets which are assigned to be methylsiliconate dimers. The peaks at ca. -53 ppm may be considered as the overlapping quartets and triplets which may be assigned as the dimers of octyl/methyl co-oligomeric siliconates. In comparison, Figure 3.25 (b) shows the peaks in the same region of the hydrogen-coupled ^{29}Si NMR expanded spectrum of PMS. The peaks at -51 ppm and -53 ppm may be considered as two overlapping quartets which may only be assigned as methylsiliconate dimers.

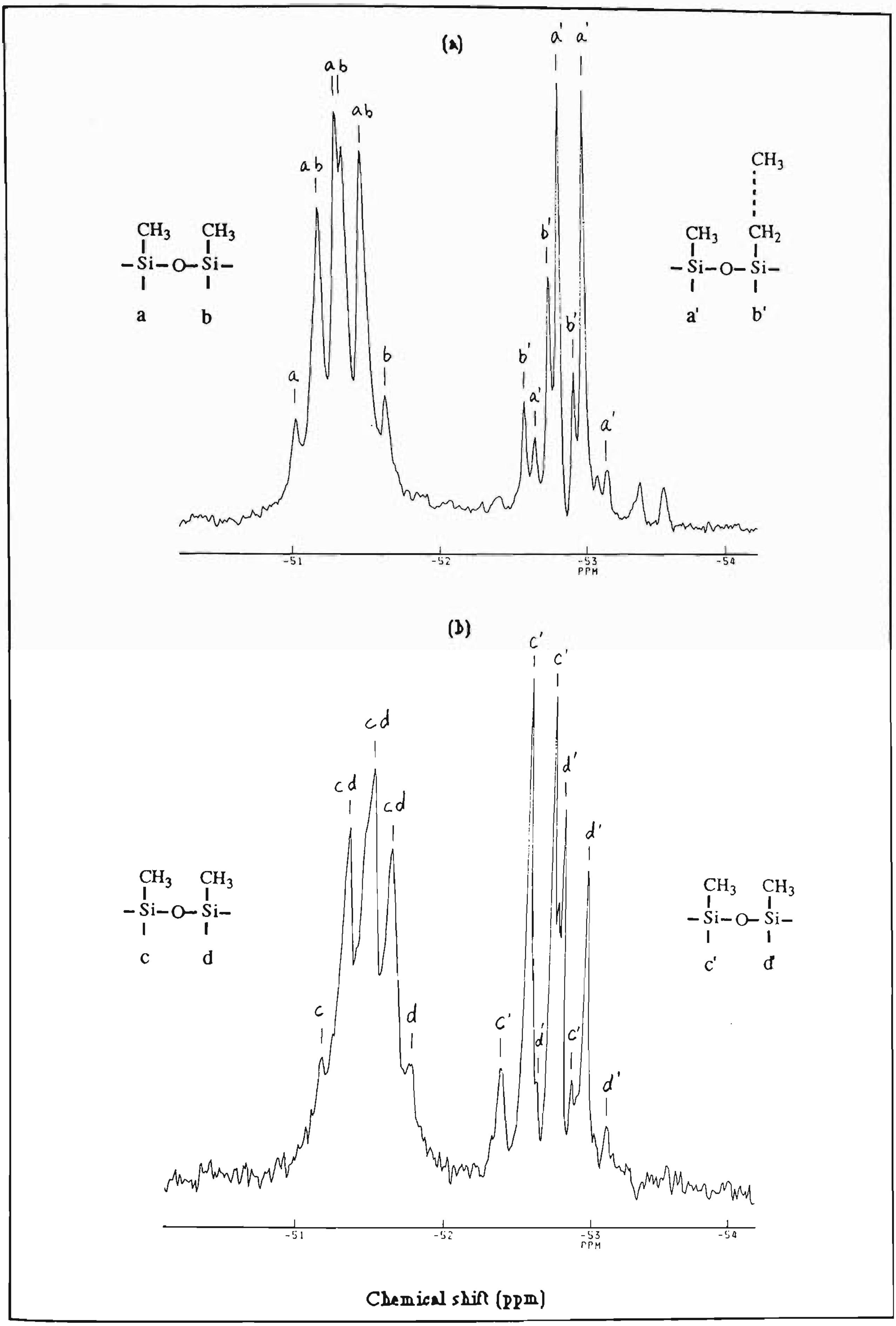


Figure 3.25 *The expanded peaks of hydrogen-coupled* ^{29}Si *NMR spectra at the region of about -51 ppm and -53 ppm; a) the silane hydrolysis products, and b) the potassium methylsiliconate*

Figure 3.26 shows the expanded peaks at the region of oligomers of the hydrogen-coupled ^{29}Si NMR spectrum of the silane hydrolysis products. The splitting pattern of oligomers (such as trimers) is complex because the oligomers may contain linear, branched, and cyclic structures. The peaks in that region may be regarded as many overlapping quartets and triplets. However, no evidence shows that the splitting pattern is composed of only quartets or triplets. This may imply that the oligomers are co-oligomeric octyl/methyl siliconates.

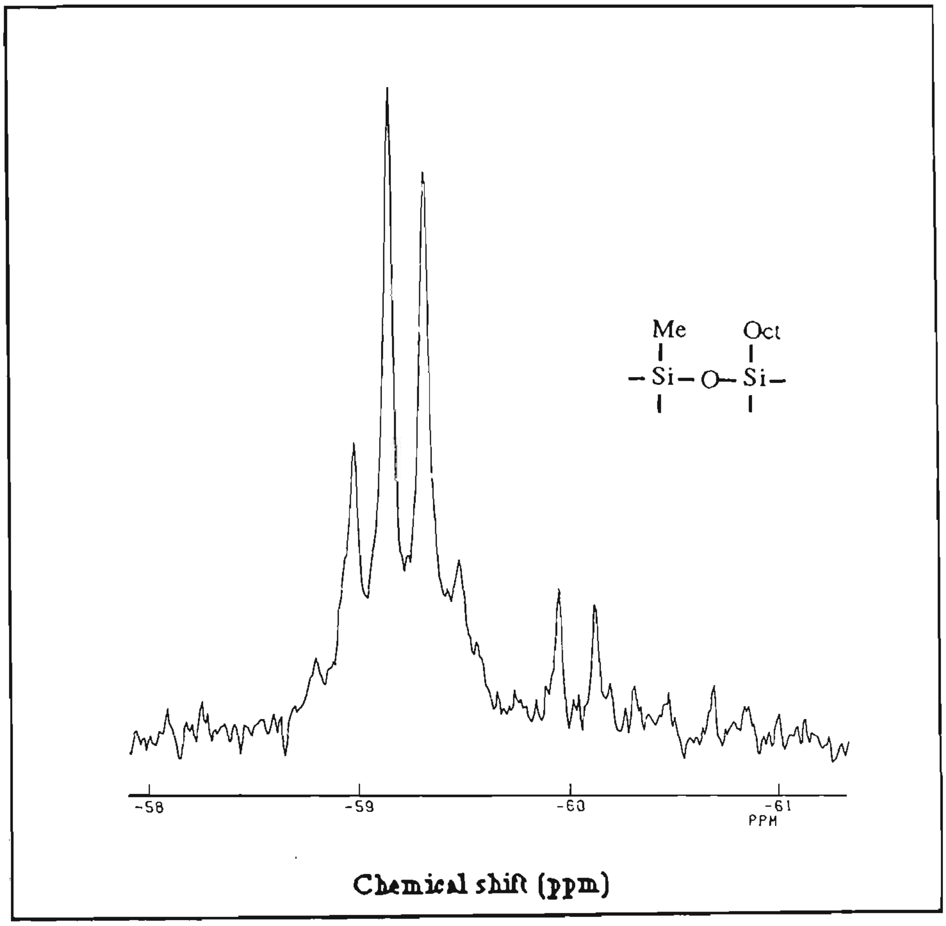


Figure 3.26 *The expanded peaks of hydrogen-coupled ^{29}Si NMR spectra of the silane hydrolysis product in the region of -58 to -61 ppm*

3.3.3 Stability of the OTES hydrolysis products

Concentrated POMS solutions have been observed to be stable for more than one year at room temperature possibly due to the presence of oligomeric siliconate cyclic structures under strongly alkaline conditions as discussed in ξ3.3.2.2.

Diluted solution was also physically stable for more than one year at room temperature. The stabilisation effect is attributed to the surfactant in the POMS due to similar effects as described for PPMS solution in ξ3.2. The surfactant in POMS has a dual effect. It accelerates the hydrolysis of the silane by micellar catalysis and then stabilises the final diluted solution by surfactant solubilisation and/or by possible re-esterification or alcoholysis with the siliconate. The stability of the diluted POMS solution very much depends on the selected surfactant. The surfactants with short ethoxylate chains and low HLB such as Teric G9A2-4, Teric G12A3-4 and Teric G17A2 cannot stabilise the solutions due to the reasons discussed in ξ3.2. However, these surfactants can significantly accelerate the silane hydrolysis (see ξ3.3.2.1). Figure 3.27 summarises the solubilisation effect by nonionic surfactants in terms of measuring the particle size of the POMS solution after dilution. The formation of large particles implies less solubilisation effect of the surfactant.

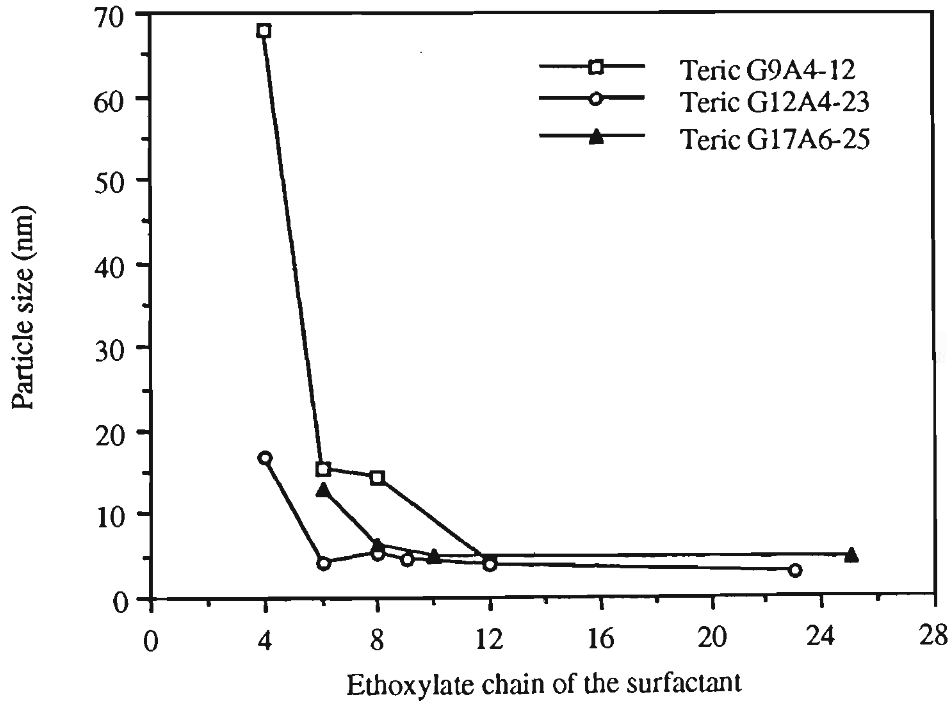


Figure 3.27 Particle size of 2% POMS solutions containing various nonionic surfactants within 2 hours of dilution (The reaction medium was 10.00 g PMS, 0.73 g surfactant and 1.75 g OTES at 25°C for 24 hours)

The results show that surfactants with longer ethoxylate chain achieve better stabilisation in terms of achieving smaller particle size of the diluted POMS solution. However, the surfactant with a short ethoxylate chain has a better catalysis effect. A further increase in the surfactant ethoxylate chain greater than 12 appears to offer little improvement in solubilisation effect to the POMS solution. The hydrocarbon chain of the surfactant has less effect on the particle size of the solution but surfactants with longer hydrocarbon chains appear to impart slightly better performance as observed from Figure 3.27. Teric G12A12 alkylalcohol ethoxylate nonionic surfactant was found to be a suitable surfactant to stabilise POMS solution and to accelerate the OTES hydrolysis in PMS as discussed in ξ3.2 and ξ3.3.2. From Figure 3.27, Teric G12A12 also appears to be the most suitable surfactant for stabilisation of the POMS solution.

Table 3.11 shows the particle size change of the diluted POMS solution at room temperature over one year. The POMS was prepared by mixing 10.00 g PMS, 0.73 g Teric G12A12 and 1.75 g OTES at 60°C for 30 minutes and the concentrate was diluted to 2% before test. Physically, this solution is quite stable as there is only a slight change in the particle size over one year at ambient conditions.

Table 3.11 Change of particle size in 2% POMS solution over one year

Time (month)	Particle size (nm)
Initial	3.7
After 2 months	3.9
After 6 months	4.7
After 12 months	6.7

The main solubilisation effect of the POMS by the surfactant is assumed to be the stabilised POMS sol which is mainly composed of oligomeric octyl/methyl siliconate. The joint micelle may exist but may have a short life. Unlike PPMS solution, POMS contains the longer alkyl group which has less solubility and has a high tendency to condense to the siliconate sol in diluted solution. However, this sol may then be spontaneously adsorbed by the nonionic surfactant to form a stabilised sol. The surfactant reduces the further condensation of the sol by the ethoxylate steric hindrance resulting in slowing down the further growth of the sol particle size in the solution.

Figure 3.28 shows the FTIR spectra of the diluted POMS solution (2%) at different times over a period at room temperature. In the initial diluted solution, both bands centred at 1120 cm^{-1} and 1030 cm^{-1} may be attributed to the oligomeric siloxane bond. However, the band at 1120 cm^{-1} gradually shifts to 1140 cm^{-1} during storage. One of the possible explanations of the shift in the band position from 1120 cm^{-1} to 1140 may be that the molecular weight of the oligomer (sol) gradually increases during storage. However, there is no evidence to show that a high molecular weight product from POMS is formed in the solution by comparing the spectrum of the POMS solution with that of a POMS polymer. The POMS polymer whose FTIR spectrum is presented in Figure 3.28 was made from POMS by adding acid. Siloxane polymer shows a broad band covering the entire region from 1160 cm^{-1} to 1000 cm^{-1} according to Anderson [174] and Launer [175].

The stabilisation effect in the diluted POMS solution may also be attributed to the interaction between the siliconate and the surfactant by means of physical and chemical bonds. These interactions improve the hydrophicility of the siliconate sol to make the sol particle more stable in the aqueous media. Physically, the hydrogen bonds and Van der Waals forces between the POMS molecule and the surfactant certainly exist . The re-esterification or the alcoholysis of the siliconate by the surfactant as discussed in ξ3.2 is also possible in the diluted POMS solution. One other explanation of the shift in the band position from 1120 cm^{-1} to 1140 cm^{-1} in Figure 3.28 may be that the surfactant became bonded to siliconate. An investigation of this possible reaction in such dilute, reactive and complex mixtures is beyond the scope of this project.

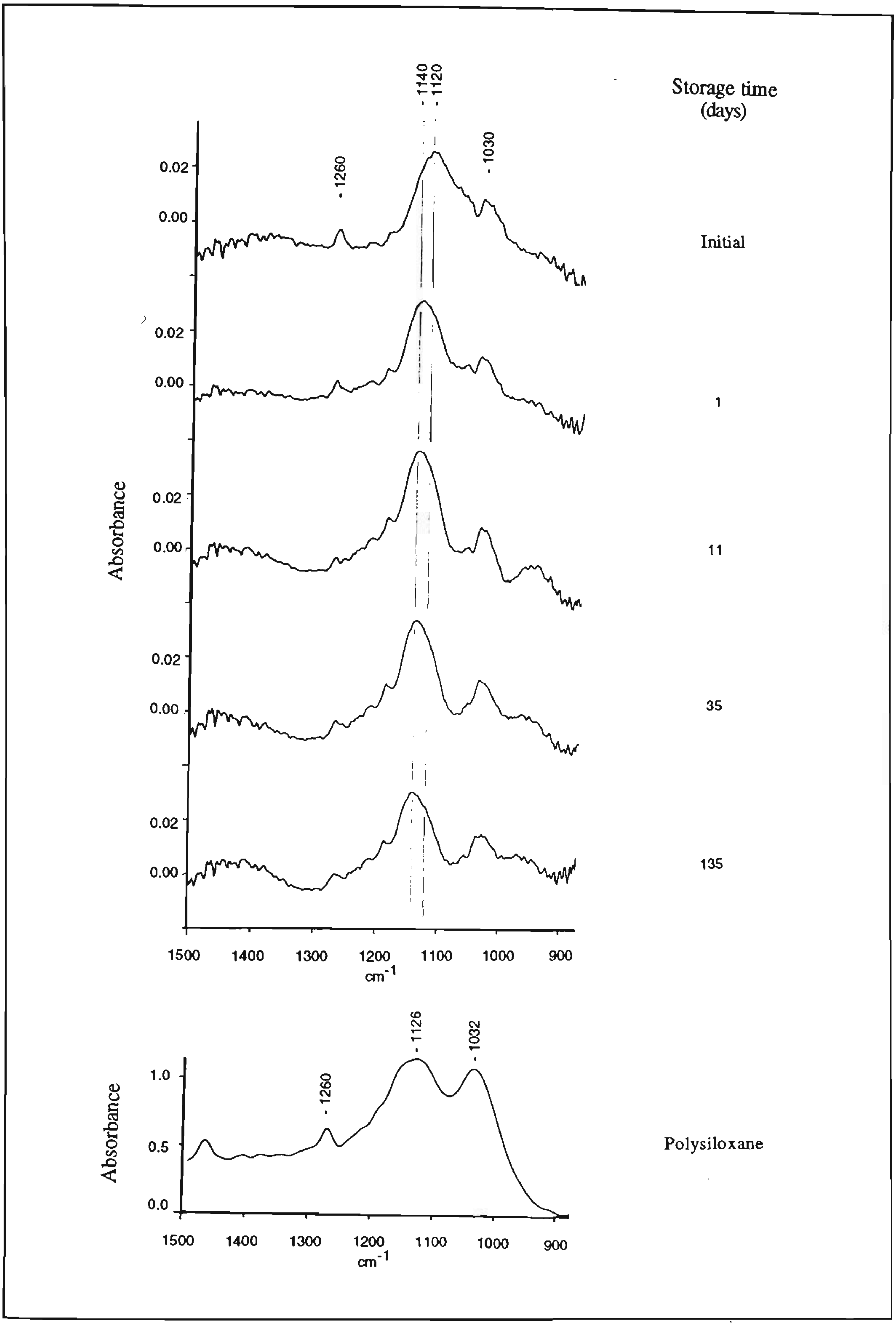


Figure 3.28 The FTIR spectra of 2% POMS solution with storage at room temperature (The POMS concentrate was prepared by mixing 10.00 g PMS, 0.73 g Teric G12A12 and 1.75 g OTES at 25°C for 24 hours and then was diluted to 2%)

3.3.4 Alkali stability of substrates treated with the POMS impregnants

Alkali stability in terms of water absorption of very alkaline substrates (1 week old DIN 1164 cement mortar) treated with the POMS is shown in Figure 3.29. The commercial PMS, PPMS and the organic solvent-based OMMS-Sn impregnants were also tested as comparisons (the PPMS contained 0.12% Teric G12A12 surfactant as a stabiliser and was diluted with distilled water). From Figure 3.29, alkali stability of the substrates treated with the POMS is found to be significantly increased in a comparison with substrates treated with the commercial siliconates particularly PMS. The results are equivalent to that of substrate treated with the OMMS-Sn impregnant. The high alkali stability achieved by the POMS is attributed to the long hydrocarbon chain which is attached to the siliconate.

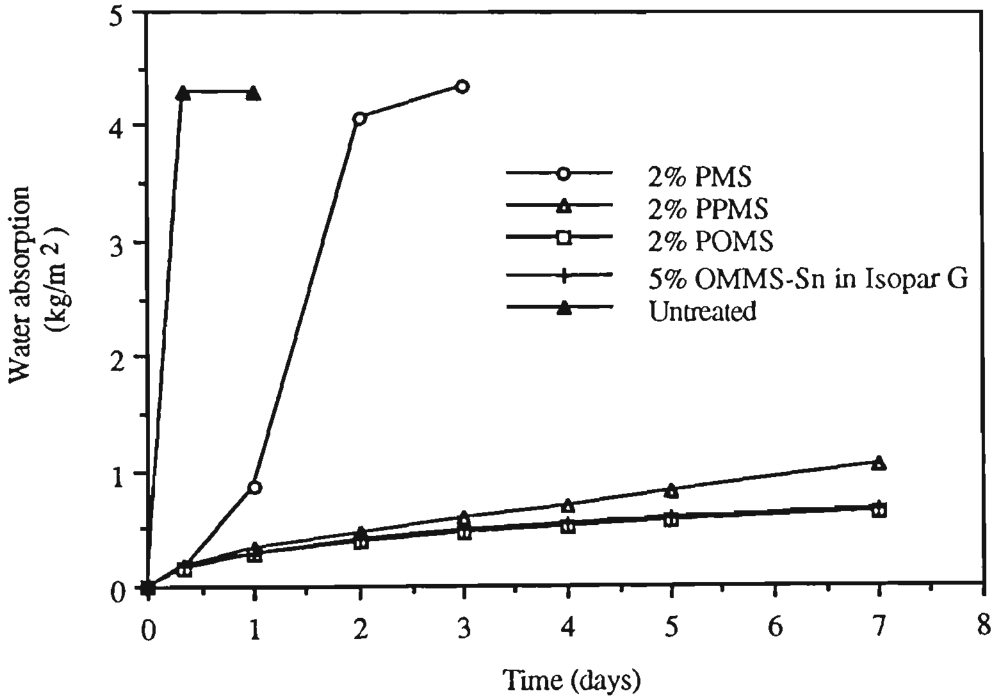


Figure 3.29 A plot of alkali stability test results (POMS concentrate contained 10.00 g PMS, 0.73 g Teric G12A12 and 1.75 g OTES and was diluted to 2% before application)

The depth of impregnation of the above impregnants is shown in Table 3.12. The depth of impregnation of POMS is higher than those of the commercial siliconates particularly PPMS and is similar to that of the OMMS-Sn impregnant. The high depth of impregnation of the POMS may be attributed to the surfactant (see ξ3.2.3) and the existence of the PMS (see ξ3.3.2.2) in the POMS impregnant. The PMS, although it contains no surfactant, shows a higher depth of impregnation than that of the PPMS possibly due to the smaller molecular weight of the PMS (shown in Table 3.12).

***Table 3.12** Impregnation depth of 1 week old DIN 1164 cement mortar substrates*

Impregnant	Concentration (%)	Depth of impregnation (mm)
2% PMS	2	2
2% PPMS	2	<1
2% POMS	2	3
5% OMMS-Sn	5	3

Further, it was found that only a small amount of OTES is needed in the preparation of the POMS to impart sufficient alkali stability in the substrate. Figure 3.30 shows the alkali stability of the POMS impregnants containing various amounts of active OTES in terms of water absorption on 1 week old DIN 1164 cement mortar substrates. The active OTES is calculated on the basis of $CH_3(CH_2)_7SiO_{1.5}$.

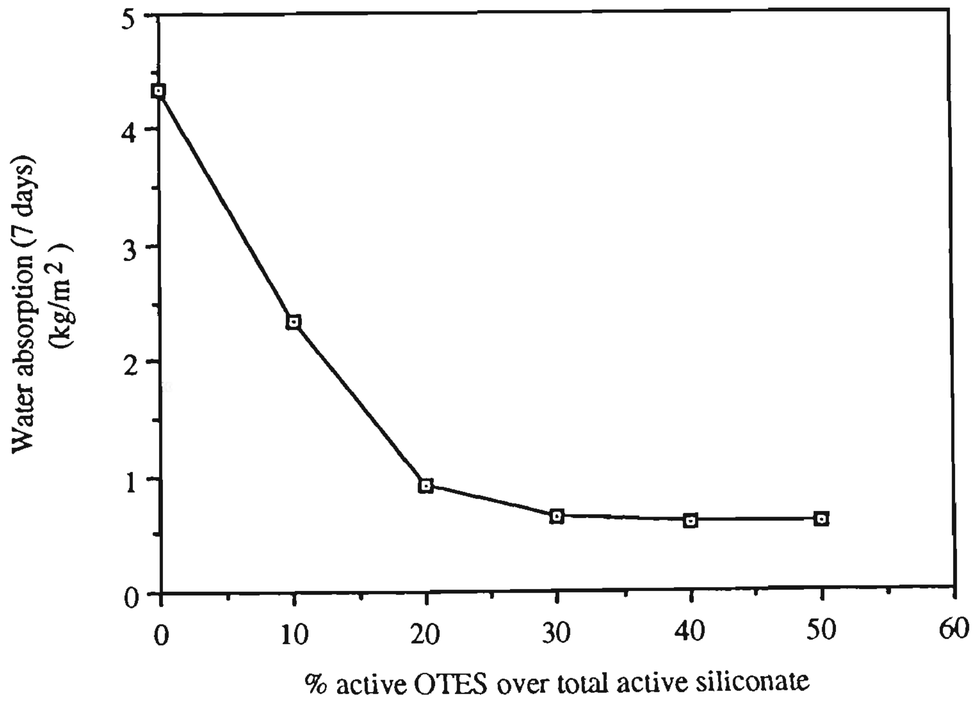


***Figure 3.30** Water absorption of substrates treated with 2% POMS solutions containing from 0 to 50% of active OTES over total active siliconate*

The results show that the alkali stability increases with the increase in the active OTES concentration up to 30%. Above 30%, the water absorption becomes constant with further increase in the OTES concentration. By adding 30% active OTES, the alkali stability is equivalent to that of the OMMS-Sn treated substrate (see Figure 3.29). This ratio of 30% octyl to 70% methyl in the final siliconate product is quite consistent with that of the commercial OMMS-Sn siloxane impregnant which was found to contain about 30% octyl and 70% methyl in its co-oligomeric siloxane structure by ^{1}H NMR in this research. This commercial siloxane product is claimed by the manufacturer to be suitable for alkaline substrates. Good alkali stability of the POMS solution composed of minor octyl but major methyl siliconate may be attributed to the formation of co-oligomeric octyl/methyl siliconate which improves the alkali stability of the substrates by forming a crosslinked co-polysiloxane structure.

Figure 3.31 shows the effects of concentration of the POMS on impregnation performance in terms of the depth of the impregnation and water absorption on 1 week old DIN 1164 cement mortar substrates. The results show that 2% POMS solution is sufficient to impart satisfactory depth of impregnation and satisfactory alkali stability to the substrate. Decreasing the concentration to less than 2% significantly reduces the depth of impregnation while increasing the concentration to greater than 3% increases the water absorption value. This may be due to the surfactant which affects both the depth of impregnation and the alkali stability as described for PPMS in ξ3.2.3. A decrease in POMS concentration also decreases the active concentration of surfactant in the final impregnant resulting in reduction in the depth of impregnation. Also, an increase in POMS concentration increases the active surfactant concentration in the final impregnant resulting in a reduction in the alkali stability and an increase in water absorption. Therefore, it may be concluded that 2% POMS solution is the most suitable concentration of the POMS impregnant in treating alkaline substrates. The surfactant effect on POMS treated substrates will be further discussed in the next section.

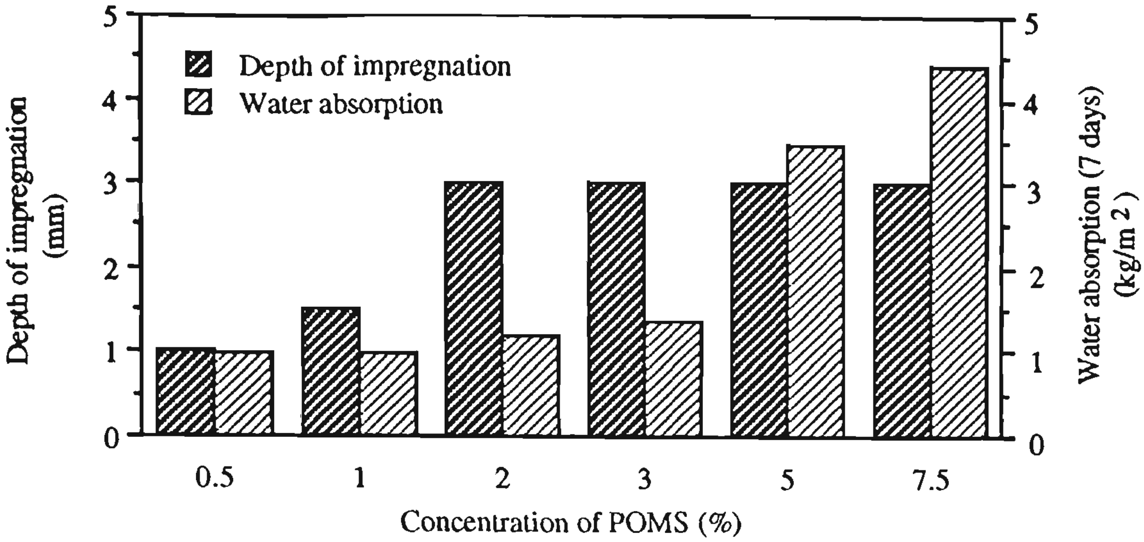


Figure 3.31 *Effects of concentration of POMS on the impregnation performance (POMS contained 30% active OTES over total active silicone and 70% Teric G12A12 based on active OTES)*

3.3.5 Surfactant effects on the substrates treated with the POMS solution

Generally, the surfactant has the same effect on the quality of the substrates treated with the POMS solutions in the case of the PPMS solutions as described in ξ3.2.3. Table 3.13 lists the depths of impregnation and the water absorption values of the 1 week old DIN 1164 cement mortar substrates treated with the 2% POMS solutions containing various amounts of Teric G12A12 surfactant and 30% active OTES over total active siliconate. The depth of impregnation is increased with an increase in surfactant addition but tends to be constant when the surfactant addition is greater than 70%. Apart from the 20% surfactant addition, water absorption is low in the range of surfactant addition from more than 20% to 70% but increases with further increase in the surfactant addition. Using 20% or less surfactant the POMS cannot impart either satisfactory water repellency or satisfactory depth of impregnation probably due to the insufficient penetration ability of the impregnant containing less surfactant.

Table 3.13 *Depth of impregnation and water absorption results of substrates treated with 2% POMS containing various amounts of Teric G12A12*

G12A12 addition over active OTES	G12A12 concentration in final POMS	Impregnation depth (mm)	Water absorption (7 days, kg/m^2)
20%	0.12%	<0.5	1.32
30%	0.18%	2	0.64
50%	0.30%	2-3	0.70
70%	0.42%	3	0.70
100%	0.60%	3	0.94
150%	0.90%	3	2.93
untreated	-	-	4.70*

*1 day water absorption value which is the maximum water absorption of the substrate.

Another effect observed with the PPMS treated substrates is also observed with substrates treated with POMS impregnants. The water repellency decreases sharply with the increased storage time of the diluted POMS solution particularly for very alkaline substrates. Table 3.14 lists the depth of impregnation and water absorption values of the 1 week old DIN 1164 cement mortar substrates treated with the 2% POMS solutions which have been stored for various periods at room temperature. The concentrated POMS contained 30% active OTES over total active siliconate and 70% Teric G12A12 based on the active OTES. As discussed in ξ3.2, this effect is attributed to the surfactant which may react with the POMS by re-esterification or alcoholysis after dilution. The surfactant in the substrate appears to accelerate the hydrolysis of the siloxane within the substrate.

However, the results show no significant effect on the water repellent performance if the concentrated POMS is stored. Table 3.15 shows the quality of the 1 week old cement mortar substrates treated with the POMS solutions which have been stored as a concentrate for various periods and then diluted to 2% before application. The POMS contained 30% active OTES over total active siliconate and 70% Teric G12A12 based on the active OTES. The test results show that there is no significant difference in the depth of impregnation and the water absorption values of the substrates treated with either 7 month old, 3 month old or freshly prepared POMS solutions. The contrast between storage ability of concentrated and diluted POMS solution may again be explained by the re-esterification or the alcoholysis by the surfactant. As the pH of the POMS is very high in the concentrated state, either the POMS or surfactant hydroxyl may be substantially deprotonated resulting in a very low re-esterification or alcoholysis rate by the surfactant.

Table 3.14 *Depth of impregnation and water absorption values of substrates treated with 2% POMS solutions stored for various periods after dilution*

Storage time of 2% POMS solution	Depth of impregnation (mm)	Water absorption (7 days, kg/m^2)
Fresh	3	0.70
4 hours	3	0.82
8 hours	3	0.90
24 hours	3	2.51
7 days	3	3.16
Untreated	-	4.70*

* 1 day water absorption value

Table 3.15 *Performance of the substrates treated with the 2% POMS solutions which have been stored as the concentrates for various periods before application*

Storage period of concentrate POMS	Depth of impregnation (mm)	Water absorption (7 days, kg/m^2)
Fresh	3	0.70
3 months	3	0.63
7 months	3	0.67

Accordingly, it is reasonable to predict that either reducing the surfactant addition in the POMS or increasing the concentration of KOH in the diluted POMS solution may reduce the re-esterification or the alcoholysis. This was examined for a diluted POMS solution stored for 24 hours containing less surfactant and one containing extra KOH. The results from Table 3.16 show that using less surfactant or the addition of KOH into the diluted

POMS solution significantly reduces the surfactant effect induced by storing the diluted POMS solution before application. The results once again support the re-esterification or the alcoholysis reaction. However, addition of KOH into the diluted solution may involve inconvenience in application. Adding less surfactant may be a useful method to reduce the reesterification and alcoholysis effect. However, the disadvantage of using less surfactant in the POMS is that it reduces the depth of impregnation and the initial hydrolysis rate of the octyltriethoxysilane. From Table 3.13 and Table 3.16, it may be concluded that the surfactant concentration in POMS may be reduced to the minimum 30% based on active OTES in order to minimise the adverse effect of reduced alkali stability in application performance of the POMS solution.

Table 3.16 *Performance of the 1 week old DIN 1164 cement mortar substrates treated with the 2% POMS solutions stored for 24 hours after dilution*

Additives based on active OTES in POMS solution*	Depth of impregnation (mm)	Water absorption (7 days, kg/m^2)
70% Teric G12A12	3	2.51
70% Teric G12A12 & 3.5 mole KOH	3	1.65
30% Teric G12A12	2	1.39

* Concentrated POMS contained 30% active OTES over total active siliconate.

3.3.6 Preferred conditions to prepare POMS impregnants

Alkylalcohol ethoxylate nonionic surfactant significantly accelerates the OTES hydrolysis in PMS to form POMS and then in turn stabilises the diluted POMS solution before application. The stabilisation effect of the surfactant for diluted PPMS solution as described in ξ3.2 is also significant. The alkali stability of substrates treated with POMS solution has been found to be exemplary. However, surfactant reduces the alkali stability in the treated substrates, particularly when the diluted siliconate solution is stored. Reducing the surfactant addition decreases the surfactant effect. However, reducing the surfactant concentration decreases the depth of impregnation in the treated substrate. The preferable condition to prepare the POMS is summarised as follows:

a) 30% Active OTES over total active siliconate in POMS is needed to achieve the required alkali stability in the substrate compared to that of substrate treated with commercial organic solvent-based siloxane (OMMS-Sn) impregnant.

b) From 30% to 70% (based on active OTES) alkylalcohol ethoxylates Teric G12A12 is the most suitable surfactant to accelerate the silane hydrolysis, to stabilise the diluted POMS solution, and to improve the depth of impregnation.

c) The preferred conditions to hydrolyse OTES in PMS is by using 30% to 70% Teric G12A12 (based on active OTES) and by using 30% active OTES (based on total active siliconate) at either room temperature (about 25°C) or 60°C. The hydrolysis time is from 0.5 to 1 hours or more depending on the conditions.

d) Both the concentrated and the diluted (2%) POMS solution are quite stable (more than 1 year) in terms of clarity of the solutions. However, it is necessary to use the diluted solution as soon as possible and preferably within 8 hours after dilution in order to avoid the significant adverse effects on the water repellency induced by the surfactant.

One of the preferred examples of POMS preparation is as follows: 0.73 g of melted Teric G12A12 is mixed into 10.00 g PMS solution under continuous stirring to form a homogeneous reaction mixture. Then 1.75 g OTES is added dropwise into the mixture with continuous stirring to give a homogenous suspension. With continuous stirring the reaction is heated from room temperature to 60°C within 10 minutes. The reaction mixture is maintained at 60°C until it becomes clear and the mixture is then stirred for a further 30 minutes. The clear POMS concentrate is cooled to room temperature. After dilution it is ready to be applied to the substrate.

3.4 Application data for POMS impregnant

In order to examine the quality of the novel POMS impregnant on various masonry substrates, a POMS preparation (refers to ξ3.3.6) was diluted to 2% and the fresh diluted solution was then applied to the substrates by the methods described in ξ2.4. A 2% PMS solution and a 5% organic solvent-based siloxane (OMMS-Sn in Isopar G solvent) were used as comparisons for each test conducted for the POMS solution. Untreated substrate was used as a control. Substrates included 4 weeks old DIN 1164 cement mortar discs, Indian fired bricks and mud bricks. Mud bricks were impregnated with 79 g/litre sodium silicate 24 hours before silicone impregnation (this will be discussed in Chapter 5). Application conditions are listed in Table 3.17. The test results are outlined below.

Table 3.17 Impregnant consumption on various substrates at ambient conditions

Substrates	Impregnant consumption (kg/m^2)		
	2% POMS	2% PMS	5% OMMS-Sn in Isopar G
Cement mortar	0.454	0.465	0.430
Indian fired bricks	2.004	2.118	1.423
Mud bricks*	0.935	0.898	0.917

* Consumption of 79g/litre sodium silicate solution was 0.998 kg/m^2.

3.4.1 Beading effect

The beading effect of various substrates treated with POMS impregnant is shown in Table 3.18. The beading effect of the substrates treated with 2% POMS solution is the same as those treated with 5% solvent-based siloxane impregnant. In addition, the beading effect of the substrates shows no difference between the substrates treated with POMS and the ones with PMS in non-alkaline substrates but POMS shows better beading effect than PMS in cement mortar substrates.

***Table 3.18** Beading effect of various substrates treated with different impregnants*

Impregnants	Cement mortar	Indian fired brick	Mud brick
2% POMS	2	2-3	2
2% PMS	3	2-3	2
5% OMMS-Sn in Isopar G	2	2	2
Untreated	7	7	7

3.4.2 Water absorption and alkali stability

Water absorption tests were conducted for 24 weeks (168 days) in order to examine the long term water repellent performance of POMS impregnant. Water absorption of cement mortar substrates is plotted in Figure 3.32(A). The test results indicate that the water absorption value of the substrate treated with 2% POMS is equivalent to that of 5% solvent-based siloxane treated substrate. However, substrate treated with 2% PMS failed the water absorption test within a few days of the test. The test results show that POMS impregnant is satisfactory to render alkaline substrates water repellent while PMS is not suitable for alkaline substrates.

Figure 3.32(B) and 3.32(C) shows the water absorption test results of Indian fired bricks and mud bricks respectively, treated with various impregnants. The results show that 2% POMS can significantly reduce water absorption values of both substrates. It was found that the water repellent effect of POMS impregnant in terms of water absorption is similar to that of PMS impregnant. Therefore, it may not be necessary to use POMS impregnant to treat non-alkaline substrates such as fired bricks and mud bricks. It was also observed that both POMS and PMS impart less water repellency to those substrates than that of solvent-based siloxane impregnant particularly to the mud bricks. Therefore, siliconate impregnants are less effective in rendering substrates such as mud bricks water repellent.

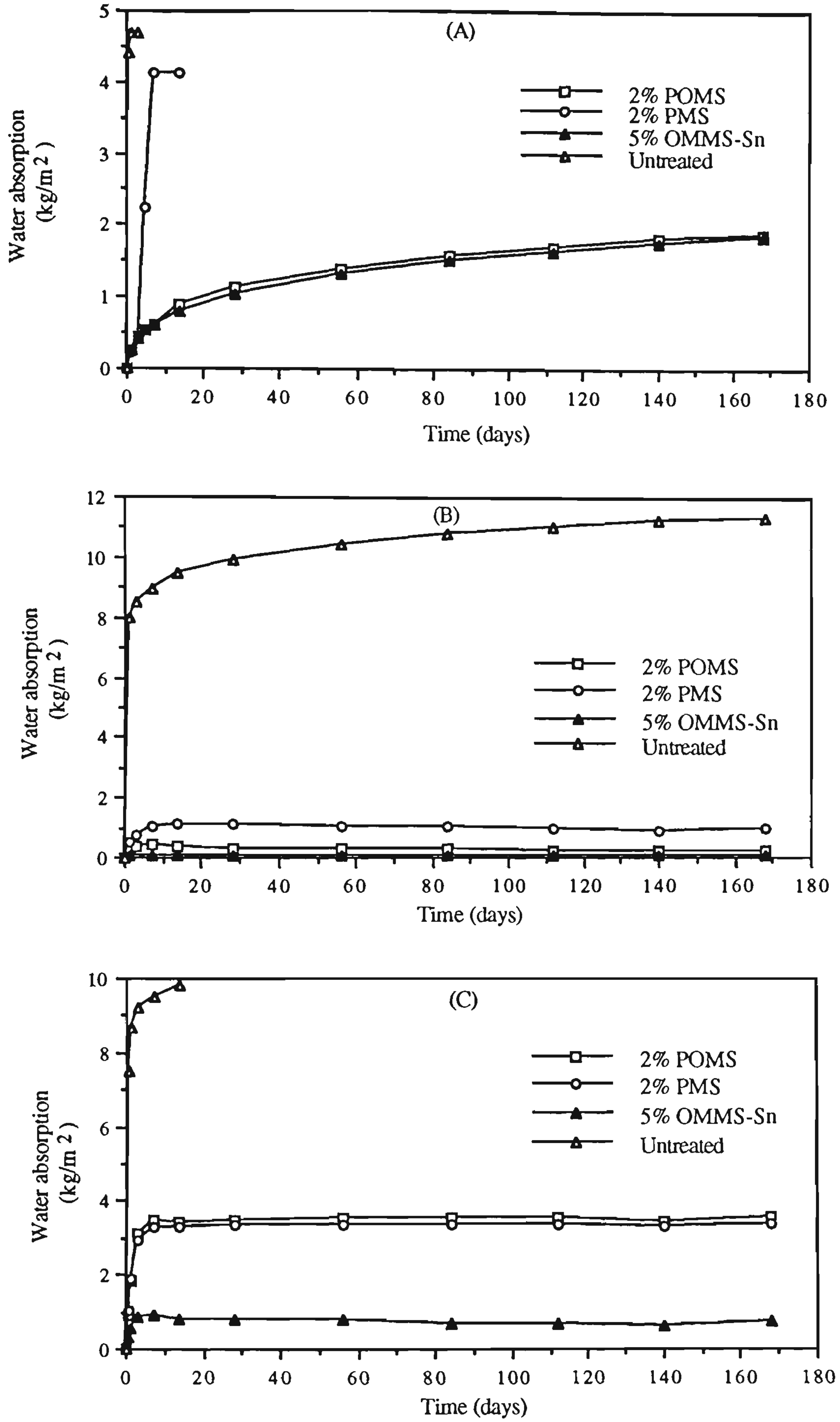


Figure 3.32 *Water absorption of; (A) cement mortar, (B) Indian fired bricks, and (C) mud bricks treated with POMS, PMS and solvent-based siloxane (OMMS-Sn in Isopar G) impregnants*

The alkali stability results for POMS impregnant in a 10% KOH solution absorption test on 4 week old DIN 1164 cement mortar substrate are shown in Figure 3.33. As in the water absorption test results for very alkaline substrates, 2% POMS shows a comparative test result to that of solvent-based siloxane impregnant. Again PMS impregnant shows a very poor alkali stability.

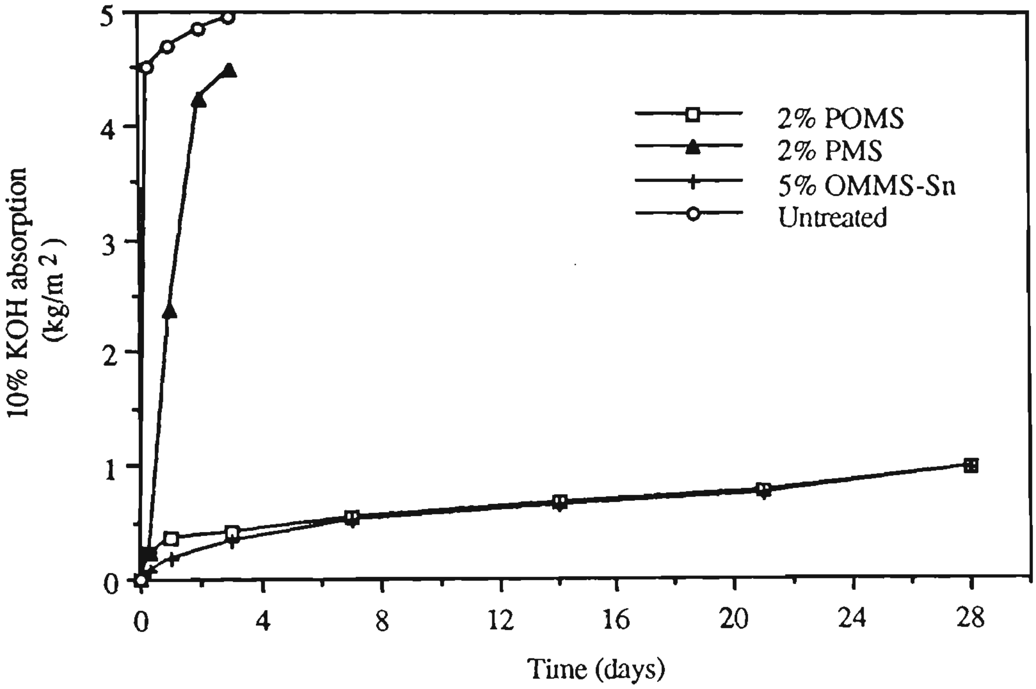


Figure 3.33 10% KOH absorption of cement mortar substrates treated with various impregnants

3.4.3 Depth of impregnation

Table 3.19 shows the depth of impregnation of various substrates treated with 2% POMS impregnant. The results show that POMS impregnant achieves significant depth of impregnation to various substrates similar to those achieved by the solvent-based siloxane impregnant and PMS impregnant. As discussed previously, the high impregnation depth of POMS impregnant is attributed to surfactant and PMS in the POMS solution. Both surfactant and PMS is assumed to increase the penetration ability of the POMS.

Table 3.19 Depth of impregnation of various substrates treated with different impregnants

Impregnants	Cement mortar (mm)	Indian fired brick* (mm)	Mud brick (mm)
2% POMS	3	20	2
2% PMS	2	20	2
5% OMMS-Sn in Isopar G	3	20	2

* Very high depth of impregnation may be due to the high permeability of the substrates.

3.4.4 Water vapour permeability

The water vapour permeability of substrates treated with different impregnants is shown in Figure 3.34 in terms of a water vapour transmission test on 4 week old DIN 1164 cement mortar substrates. The test results show that the water vapour transmission rate of the substrates treated with 2% POMS is similar to those of the substrates treated with 2% PMS and 5% solvent-based siloxane. The water vapour transmission rates of all the treated samples are less than that of the untreated sample at the beginning but tend to become the same rate after a few days of the test. The initial higher rate in untreated substrate may be because the substrate was wetted right to the surface which was open to air while the surfaces of silicone treated substrates were dry. After the surface of untreated substrate was dry, the vapour transmission rates of all substrates would become similar. It may be concluded that permeability of the substrate remains unaffected by impregnation with 2% POMS impregnant. This is also true for the other impregnants used in the test.

3.4.5 Resistance to water absorption under hydrostatic pressure

The test for resistance to water absorption under hydrostatic pressure was carried out on 4 weeks old DIN 1164 cement mortar substrates and the results are plotted in Figure 3.35. The test results clearly show that 2% POMS imparts to the substrate significant resistance to water penetration under 100 mm hydrostatic pressure. The test results show that the ability to resist water absorption under hydrostatic pressure of the substrate treated with 2% POMS is the same as that of the substrate treated with 5% solvent-based siloxane. The substrate treated with 2% PMS failed the test after 1 day due to its poor alkali stability.

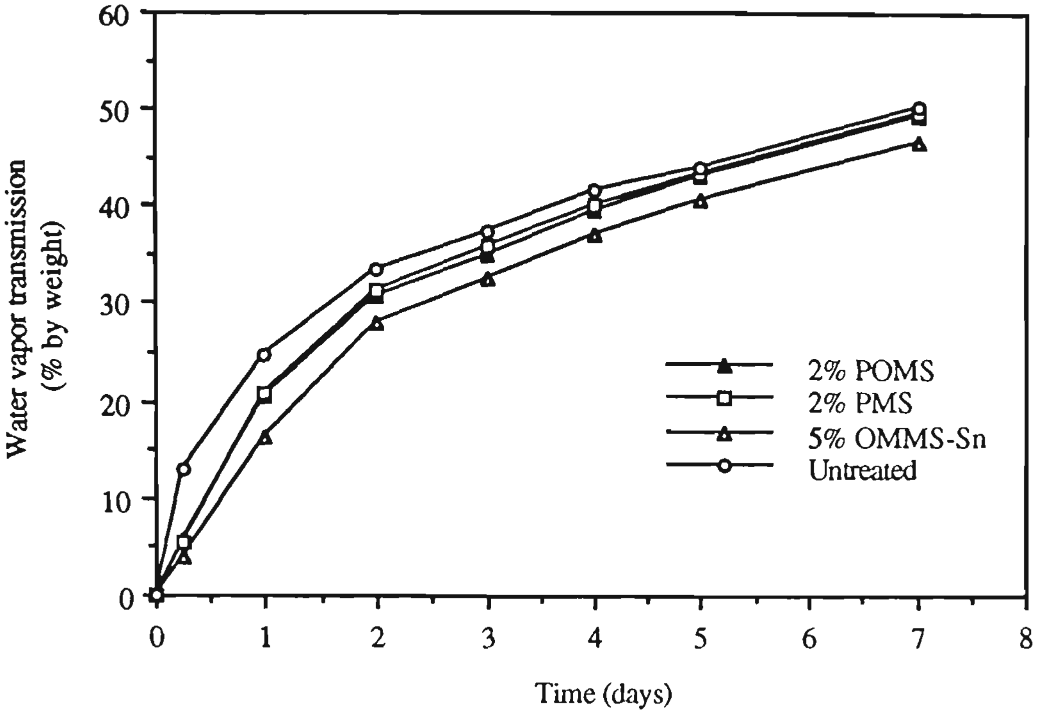


Figure 3.34 Water vapour transmission of cement mortar substrates treated with different impregnants

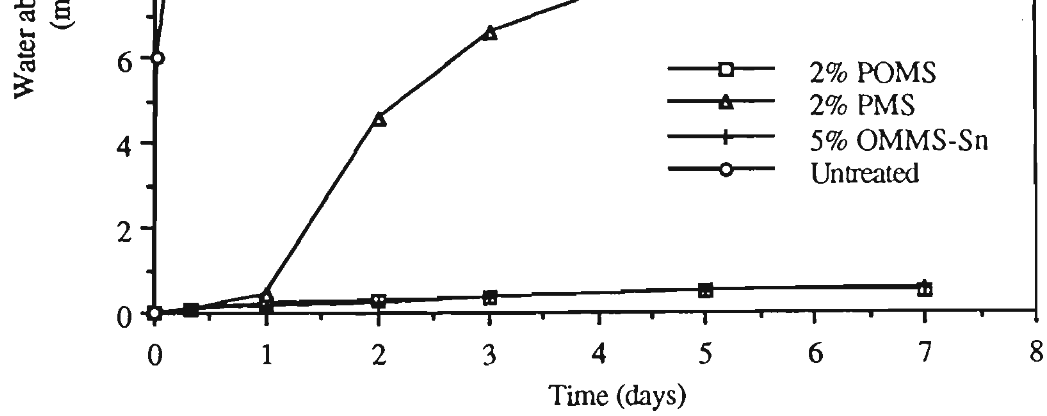


Figure 3.35 Water absorption under hydrostatic pressure of 100 mm water head

3.4.6 Resistance to efflorescence

The tests for resistance to efflorescence were carried out on both 4 week old DIN 1164 cement mortar substrates and Indian fired brick substrates. After 7 days of the test, the surfaces treated with either 2% POMS or 2% PMS or 5% OMMS-Sn impregnants showed no efflorescence. Heavy efflorescence was only observed on untreated mortar substrates and brick substrates.

3.4.7 Resistance to wetting and drying weathering

The wetting and drying weathering test was carried out for 24 weeks (84 wetting and drying cycles) on various substrates . The beading effect before and after wetting and drying weathering is listed in Table 3.20. The beading effect of the substrates treated with 2% POMS impregnant shows very similar results to those of the substrates treated with 5% solvent-based siloxane impregnant on various substrates. The beading effect is decreased after the weathering test but is still significant in comparison to untreated samples. Decrease in beading effect is probably due to the hydrolysis of hydrophobic polysiloxane on the very surface of the substrate by water and alkali (if substrate is basic). However, the beading effect of the mortar substrate treated with 2% PMS solution shows a very poor result after the weathering test due to the poor alkali stability of the PMS impregnant. For the Indian fired brick and mud brick substrates, PMS shows a similar beading effect to that of the POMS impregnant after 24 weeks of the wetting and drying weathering test.

Table 3.20 Beading effect of the treated substrates before and after wetting and drying weathering test

	Cement mortar		Indian fired brick		Mud brick	
Impregnants	before	after	before	after	before	after
2% POMS	2	4	2-3	3	2	3-4
2% PMS	3	6-7	2-3	3	2	3-4
5% OMMS-Sn in Isopar G	2	4	2	3	2	3
Untreated	7	7	7	7	7	*

* Untreated mud brick substrates collapse after a few cycles of wetting and drying weathering.

Water absorption values of substrates before and after wetting and drying weathering test are shown in Table 3.21. For cement mortar substrates, water absorption of the substrate treated with 2% POMS impregnant increases slightly after the weathering but is still significantly lower than that of the untreated sample. The water absorption result is very similar to that of the sample treated with 5% solvent-based siloxane impregnant. However, PMS impregnant failed the water absorption test after the weathering. The water absorption of Indian fired brick treated with 2% POMS impregnant decreases slightly after the weathering but the value for the mud brick substrate treated with the same impregnant increases. To both Indian brick and mud brick substrates, POMS and PMS show similar test results either before and after the weathering. POMS does not show a superior effect to PMS impregnant in terms of a reduction of water absorption of the substrates after the weathering test. However, the solvent-based siloxane imparts to these substrates a better water repellent effect than both POMS and PMS impregnants either before or after weathering.

***Table 3.21** Water absorption values (24 hours, kg/m^2) before and after the weathering test*

	Cement mortar		Indian fired brick		Mud brick	
Impregnants	before	after	before	after	before	after
2% POMS	0.24	0.53	0.30	0.10	1.77	2.89
2% PMS	0.21	3.18	0.45	0.21	1.64	2.85
5% OMMS-Sn in Isopar G	0.25	0.43	0.05	0.05	0.52	0.30
Untreated *	4.53	4.06	8.08	7.90	8.71	**

* A drop in water absorption of untreated substrates after the test may be due to the contamination of the surfaces by the impregnants decomposed from the treated substrate surfaces by water or alkali or UV et al under the test conditions during the weathering test.

** Untreated mud brick substrates collapse after a few cycles of wetting and drying weathering.

3.4.8 Resistance to UV and condensation weathering

The UV and condensation weathering test was conducted for 6 months. The appearance of the substrate surfaces before and after the weathering was almost the same. However, the beading effect of almost all the substrates treated with 2% POMS was significantly decreased after the UV and condensation weathering as shown in Table 3.22. A decrease in the beading effect is because the UV may decompose the hydrophobic polysiloxane on the very surface of the substrate. The water from the condensation test may then cause hydrolysis of the silicones on the very surface of the substrate under the test conditions. The beading effect of the substrates treated with solvent-based siloxane is also significantly reduced after the test. 2% PMS shows the same test results as those of the 2% POMS.

Table 3.22 Beading effect of the treated substrates before and after UV and condensation weathering test

	Cement mortar		Indian fired brick		Mud brick	
Impregnants	before	after	before	after	before	after
2% POMS	2	5-6	2-3	3	2	6-7
2% PMS	3	5-6	2-3	3	2	6-7
5% OMMS-Sn in Isopar G	2	5	2	2-3	2	5-6
Untreated	7	7	7	7	7	7

The water absorption results before and after the UV and condensation weathering are shown in Table 3.23. The water absorption test results are similar to those after wetting and drying weathering shown in Table 3.21. This proves that the UV may only destroy the polysiloxane on the very surface of the substrate resulting in significantly reducing the beading effect but the hydrophobic layer inside the substrate remains unaffected.

Table 3.23 Water absorption values (24 hours, kg/m^2) before and after the weathering test

	Cement mortar		Indian fired brick		Mud brick	
Impregnants	before	after	before	after	before	after
2% POMS	0.28	0.57	0.33	0.15	1.34	2.56
2% PMS	0.20	3.87	0.37	0.21	1.35	3.07
5% OMMS-Sn in Isopar G	0.23	0.53	0.07	0.03	0.49	0.32
Untreated *	4.44	4.27	6.99	6.94	10.22	7.88

* A drop in water absorption of untreated substrates after the test refers to the comment under Table 3.21.

3.4.9 Resistance to outdoor exposure weathering

The outdoor exposure weathering test was carried out for 6 months. The appearance of the substrate surfaces before and after the weathering remained the same except for the untreated mud bricks which collapsed during the weathering test. As shown in Table 3.24 the beading effect of the substrates treated with 2% POMS impregnant slightly decreased after the weathering and the results are similar to those of the substrates treated with solvent-based siloxane impregnant. A decrease in beading effect is again attributed to the decomposition of the hydrophobic layer on the very surface of the substrates by the natural weathering. The test results show that POMS is able to withstand this weathering test. However, the beading effect of the mortar substrate treated with 2% PMS impregnant is significantly reduced due to poor alkali stability of the PMS impregnant. For Indian brick and mud brick substrates, the beading effect after the weathering shows no difference between substrates treated with POMS and PMS impregnants.

Table 3.24 Beading effect of the treated substrates before and after outdoor exposure weathering test

	Cement mortar		Indian fired brick		Mud brick	
Impregnants	before	after	before	after	before	after
2% POMS	2	3-4	2-3	2-3	2	3
2% PMS	3	5-6	2-3	2-3	2	3
5% OMMS-Sn in Isopar G	2	3-4	2	2-3	2	3
Untreated	7	7	7	7	7	*

* Untreated mud brick substrates collapsed during outdoor exposure weathering.

Water absorption test results before and after the outdoor exposure weathering are shown in Table 3.25. The results are similar to those in the wetting and drying weathering test in Table 3.21 except that the mortar substrate treated with 2% PMS is less affected by this weathering test than the other weathering tests. This may be because the weathering conditions were not as severe as those of the wetting and drying weathering and the UV and condensation weathering. However, it is assumed the hydrophobic polysiloxane inside the substrate formed from PMS would eventually be decomposed if the weathering test continued.

***Table 3.25** Water absorption values (24 hours, kg/m^2) before and after the weathering test*

	Cement mortar		Indian fired brick		Mud brick	
Impregnants	before	after	before	after	before	after
2% POMS	0.24	0.44	0.36	0.17	1.48	2.51
2% PMS	0.20	0.40	0.47	0.24	1.05	2.40
5% OMMS-Sn in Isopar G	0.24	0.32	0.08	0.06	0.56	0.30
Untreated	4.38	4.36	6.67	6.72	10.22	*

* Untreated mud brick substrates collapsed during outdoor exposure weathering.

It may be concluded that POMS impregnant can impart a significant water repellent effect to masonry substrates and in particular alkaline substrates. In a comparison with PMS impregnant, the alkali stability of the POMS is significantly improved. Various test results showed that 2% POMS can achieve the same water repellent effect and alkali stability to alkaline substrates as that of 5% solvent-based siloxane impregnant. It is possible to replace 5% solvent-based siloxane impregnant with 2% POMS impregnant to render alkaline substrates such as fresh mortar substrates water repellent. However, it was found that POMS shows no or almost no superior effect to PMS impregnant in rendering non-alkaline substrates such as Indian fired bricks and mud bricks water repellent. Therefore, it may not be necessary to use POMS to render non-alkaline masonry substrates water repellent. In addition, the water repellency of these substrates and in particular mud brick substrates treated with both POMS and PMS impregnant were found to be less than those of substrates treated with the solvent-based siloxane impregnant.

4. SILANE/SILOXANE EMULSION IMPREGNANTS

4.1 General

The important advantage of the siliconates in practice is certainly their low cost and their solubility in water. The POMS obtained from the hydrolysis of OTES in PMS in the presence of a nonionic surfactant developed in this research is a novel siliconate water repellent. It is completely soluble in water and imparts sufficient water repellent effect to very alkaline substrates, whereas other commercially available siliconates suffer problems due to water insolubility or unsatisfactory alkali stability. However, the disadvantage of the siliconates is their high alkalinity, which is inconvenient in application particularly for general water repellent treatment of mass buildings. In addition, the surfactant in novel POMS solutions or the PPMS solutions imparts some adverse effects to the water repellency (see Chapter 3) particularly when the diluted solution is stored. This limits the application of the siliconates in practice. The alternative water-based, environmentally friendly silicone water repellents may be silicone emulsions. This work describes the development of a novel silane/siloxane emulsion as a masonry water repellent and the emulsion stabilisation mechanism.

4.1.1 Emulsions and emulsion stability

An emulsion is defined according to Becher [178] as a heterogeneous system, consisting of at least one immiscible liquid intimately dispersed in another in the form of droplets, whose diameter, in general, exceeds 0.1 μm. Such systems possess a minimal stability, which may be increased by such additives as surface-active agents, finely divided solids, and other materials.

Making an emulsion, for example, an oil in water (O/W) emulsion, involves greatly increasing the new interfacial area between the oil and water by 10^6 times according to

Myers [165] resulting in an increase in the free energy of the system. An emulsion is a thermodynamically unstable system and there is a tendency for the interfacial energy between the oil and water phases to reduce the interface, causing the droplets to flow together resulting in droplet coalescence and eventually a breaking of the emulsion. Consequently, in order to obtain a stable O/W emulsion, external energy (such as shear mixing or other homogenisation mixing) must be provided to the oil/water system to break the oil phase into small oil droplets. In addition, surface active materials such as surfactants have to be added to the emulsifying system to either reduce the interfacial energy between oil and water phases to achieve the smallest droplets, or to form a rigid barrier in the oil/water interface. This slows down the coalescence of the emulsion droplets, or imparts an electric charge to the interface, resulting in the formation of an electric double layer that lessens the frequency and effectiveness of close droplet approach and contact leading to droplet growth. An O/W emulsion may be pictured as shown in Figure 4.1.

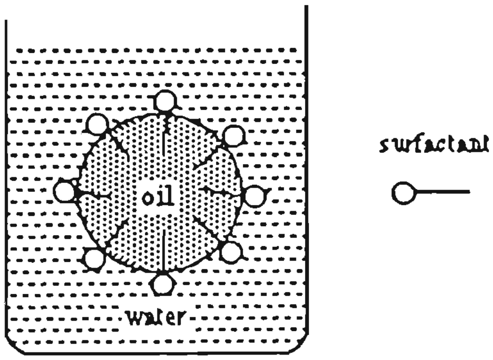


Figure 4.1 Schematic drawing of an O/W emulsion droplet

It is an unfortunate fact that there exists no single coherent theory of emulsion formation and stability. Certain theories of emulsion stability have been developed but prediction of emulsion behaviour still largely depends on practice. Modern developments in the theory of emulsion stability have focused on the nature of the interfacial film [165, 178] which is assumed to play an important role in determining the stability of the emulsion. A stable emulsion is assumed to have a rigid, viscous and/or charged interfacial film which stays permanently in the interface and protects against the coalescence of the emulsion droplets.

The nature of the oil and water phases of the emulsifying system are an important factor in forming a stable interfacial film but surfactant may be the most important component. Firstly, a surfactant having a proper balanced HLB would be best able to stay in the interface of the oil and water to form a stable surfactant layer without diffusing to either the oil or the water phase. Secondly, a surfactant having a longer or branched hydrophilic chain may form a viscous, less mobile and rigid interfacial film to impart repulsive force to inhibit droplet coalescence [165], or stabilise the emulsion by steric hindrance according to Schubert and Armbruster [179]. Thirdly, in the most popular view of emulsion stability theory, ionic surfactant may impart an electric charge to the interfacial film resulting in formation of a double layer [178] to the oil droplet to impart sufficient repulsive force between the charged emulsion particles to inhibit the particle coalescence (shown in Figure 4.2). Further, surface active polymer in the emulsion may also help to stabilise the emulsion by forming a viscous interfacial film at the interface [165, 178], or by polymeric steric stabilisation according to Napper [180].

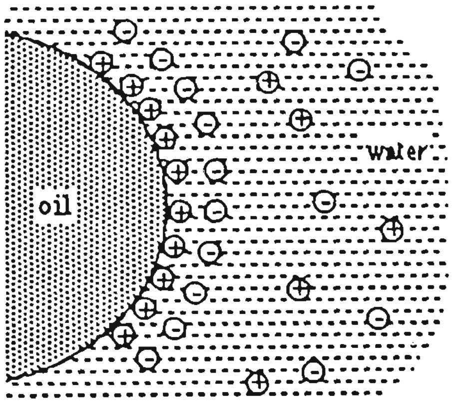


Figure 4.2 Schematic diagram of double layer of a cationic oil droplet dispersed in aqueous phase

4.1.2 Silicone emulsions as masonry water repellents

Various methods to make silicone emulsions as masonry water repellents have been reported in the literature [96-104]. Apart from consideration of the physical emulsion stability and impregnation performance, particular attention must also be paid to two important factors: hydrolysis of silicone components in the emulsion and wetting effect induced by the surfactant. The wetting effect due to the emulsion is very difficult to avoid as the surfactant is the major part in making a physically stable emulsion. This wetting effect has not been seriously considered by previous workers who developed silicone emulsions. Therefore, wetting effects are able to be observed in the substrates treated with many masonry water repellents which are commercial silicone emulsions.

The novel silane/siloxane emulsion developed by this research [181] was found to be highly effective in rendering various masonry substrates water repellent including alkaline, acidic and neutral materials. This effectiveness on different pH substrates is extraordinary in an emulsion without catalyst addition. The performance of the emulsion is comparable to the commercial organic solvent-based siloxane water repellents. The significant water repellent performance and the long-term stability of the novel silane/siloxane emulsion is due to the design with particular silane and siloxane composition in the presence of an acidified alkylamine ethoxylate surfactant at a particular pH. Various different emulsions can be produced with the technology and the performance on many different substrates means that this may be regarded as a new class of masonry water repellents.

The siloxane used in the silane/siloxane emulsion was found to greatly improve the water repellent performance of the emulsion. The high reactivity, the early water repellency, and the good film-forming properties of the siloxane enables the silane/siloxane emulsion to impart significant water repellency to various masonry substrates. In addition, the siloxane significantly increases the stability of the emulsion by taking part in the formation of the interfacial film at the oil/water interface acting as a co-surfactant due to the partial hydrolysis of the siloxane. The hydrolysis and condensation of siloxanes in the emulsion may not significantly affect performance and stability of the emulsion but may impart long-term stabilisation properties to the silane/siloxane emulsion.

The major role of the silane is to achieve higher depth of impregnation. In addition, the silane may act as a solvent in the silane/siloxane emulsion to significantly reduce the viscosity of the oil phase and to increase the stability of the emulsion by means of reducing the emulsion particle size.

The design of the surfactant is probably the most important part of the silane/siloxane emulsion. The selection and assessment of the potential commercial surfactants with adequate emulsifying properties together with benign properties as far as silane ether hydrolysis is concerned and satisfactory effects on masonry surfaces is an intellectually demanding and time-consuming task. The acidified alkylamine ethoxylate surfactants possess the properties of both cationic and nonionic surfactants and are prepared by neutralising the alkylamine ethoxylates by addition of acetic acid. These modified alkylamine ethoxylates have been found to be satisfactory in stabilising the silane/siloxane emulsion. Moreover, they impart no wetting effect to the treated substrates and induce low hydrolysis rates of silane ethers in the emulsion due to their cationic nature and weak alkalinity.

4.2 Development of silane/siloxane emulsions

A silicone emulsion may include three major components; organic silicone oil (such as silane, siloxane or polysiloxane), water and surfactant. The key factors to develop a stable silicone emulsion may include selecting the components, their proportion and imparting external energy to the system to shear the oil phase to form a stable suspension in water. Through studying emulsion stability, particle size, interfacial tension, viscosity, and zeta potential integrated with studying the water repellent performance on substrates by various techniques, the best emulsion composition was obtained. The mechanism of the emulsion stabilisation and the various emulsion properties may then be understood.

4.2.1 Selecting silicones as the emulsion oil phase

4.2.1.1 Effects of silicones on water repellent performance

The major task in developing a silicone emulsion is to design the emulsion to be useful as a masonry water repellent impregnant. Therefore, the first factor in selecting the silicones as the oil phase of the emulsion is to consider the final water repellent performance of the emulsion for various substrates and particularly for low-cost substrates.

Many organic silicones such as alkylalkoxysilanes, alkylalkoxysiloxanes and polysiloxanes can be used as water repellents for masonry substrates. There are advantages and disadvantages in the choice of each component. In general, a silicone with a large molecular weight such as a polysiloxane achieves early water repellency and a good film-forming effect according to Roth [54]. However, polysiloxanes possess poor penetration ability due to the high molecular size and high viscosity. In the case of a polysiloxane emulsion, poor depth of impregnation is achieved as there are no organic solvents as the penetration carrier in the system. Water in an emulsion as a penetration carrier is far inferior to organic solvents. In addition, silicone emulsions may break after application to the substrate leaving the polysiloxane on the surface. Therefore, polysiloxanes may not be suitable as water repellent components in emulsions and were rejected as the candidate oil component for the emulsion.

The advantage of using silanes either neat or dissolved in hydrocarbon solvents are their high penetration ability into masonry substrates due to their low molecular weight [21]. However, the volatility of silanes in application conditions results in unsatisfactory water repellency. A high concentration of silane is suggested for use in order to achieve satisfactory water repellent performance [21]. This increases the cost of the treatment and is obviously not suitable for treating low-cost buildings. In addition, the relatively poor film-forming effect means that silanes are less efficient in treating neutral or slightly acidic materials such as bricks, stone and mud bricks. In such substrates a satisfactory water repellent effect may only be developed when crosslinked hydrophobic polysiloxane is formed on the substrate capillary wall. Silane hydrolysis may be accelerated in the presence of moisture and either acid or base [54]. However, crosslinked hydrophobic polysiloxane is favoured under alkaline conditions as base significantly accelerates hydrolysis and condensation of the silane [75]. Therefore, silanes are effective in treating alkaline substrates but not satisfactory for neutral or acidic substrates. Consideration of these factors shows that emulsions using silanes as the oil phase are not suitable for all types of masonry substrates.

Alkylalkoxysiloxanes in hydrocarbon solvent have to be regarded as the preferred silicone water repellent impregnant [21, 54]. An oligomeric molecular structure imparts substrates with early and effective water repellency as with polysiloxanes but they still achieve a reasonable depth of impregnation due to their moderate molecular weight. Co-oligomeric octyl/methyl methoxysiloxanes known as Wacker 290 (with catalyst) and VP1268 (without catalyst) are water repellent impregnants provided by Wacker-Chemie GmbH of Germany [182]. In low concentration they are very effective in rendering various masonry materials water repellent including acidic, neutral and alkaline substrates according to test data from the manufacturer [182]. Therefore, an oligomeric octyl/methyl methoxysiloxane without organic tin (OMMS) was chosen as one part of oil phase for the potential silicone emulsion impregnant. The presence of tin catalyst in the emulsion design was deemed to be unnecessary and undesirable due to problems induced by the tin catalyst in the catalysis of hydrolysis and crosslinking during storage.

The combination of the silanes and the siloxanes to make a silicone emulsion may include the advantages of both the silane and the siloxane. A high depth of impregnation may be achieved due to the low molecular weight of the silane, and satisfactory water repellent performance in various masonry substrates may also be achieved due to the octyl/methyl methoxysiloxane. Therefore, part of the design of the silicone emulsion was the use of a mixture of silane and siloxane. The selection of silane and siloxane and their proportion as the oil phase in terms of achievement of water repellent performance of the emulsion is outlined below.

a) Volatility of the alkylalkoxysilanes

Figure 4.3 shows the evaporation rate of various silanes at room temperature (25°C) as determined by evaporation studies herein. It is not surprising that silanes with short alkyl and alkoxy chains have a very high evaporation rate. It has been suggested that silanes must be used in high ready-for-use concentrations of about 40% or even more [21] to overcome evaporation losses and obtain a satisfactory water repellent performance. It is not suitable to use high ready-for-use concentrations of silanes to treat low-cost buildings or for that matter most buildings due to the high cost of the treatment. Therefore a silane with a low evaporation rate such as octyltriethoxysilane was selected as the potential silane for the silane/siloxane emulsion.

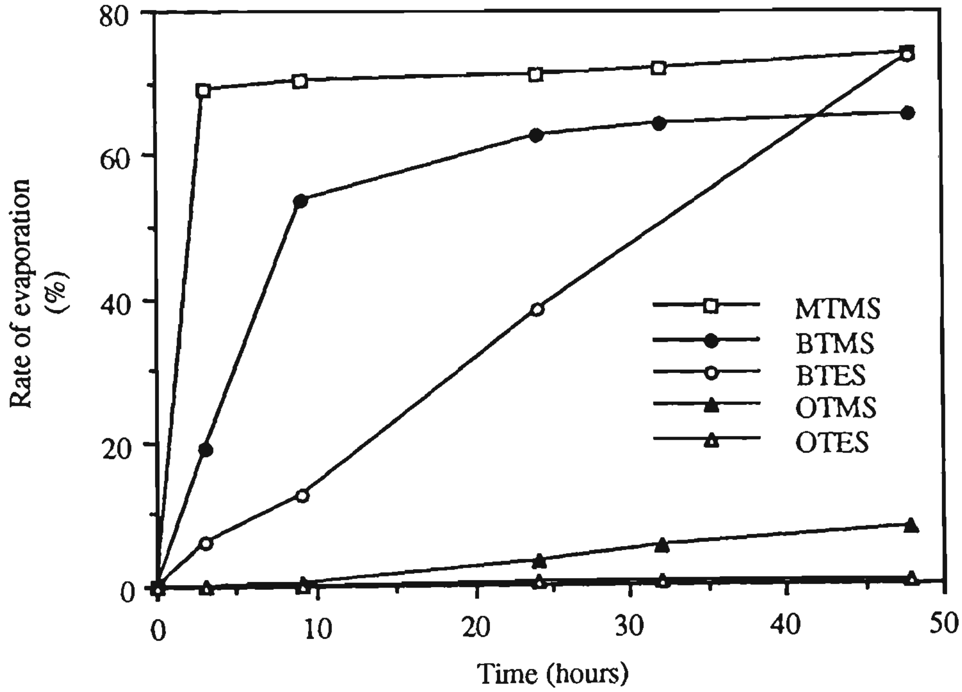


Figure 4.3 Evaporation rate of methyltrimethoxysilane (MTMS), isobutyltrimethoxysilane (BTMS), isobutyltriethoxysilane (BTES), octyltrimethoxysilane (OTMS), and octyltriethoxysilane (OTES) at 25°C

b) Penetration ability of silanes and the siloxane

Figure 4.4 shows the relationship between the depth of impregnation and the silane concentration in the oil phase of the silane/siloxane emulsion on substrates (1 week old

DIN 1164 cement mortar) treated with 5% emulsion. It is clear that the penetration ability of the octylsilane (OTES) and butylsilane (BTES) to the substrates is much higher than that of the siloxane in this system. The BTES has better penetration ability than that of the OTES due probably to the effect of a smaller molecular weight. The depth of impregnation was found to increase with the increase in the silane concentration in the oil phase of the silane/siloxane emulsion. In the case of the OTES emulsion system, the depth of impregnation was not significantly improved by an increase in the silane concentration in the oil phase over 50%.

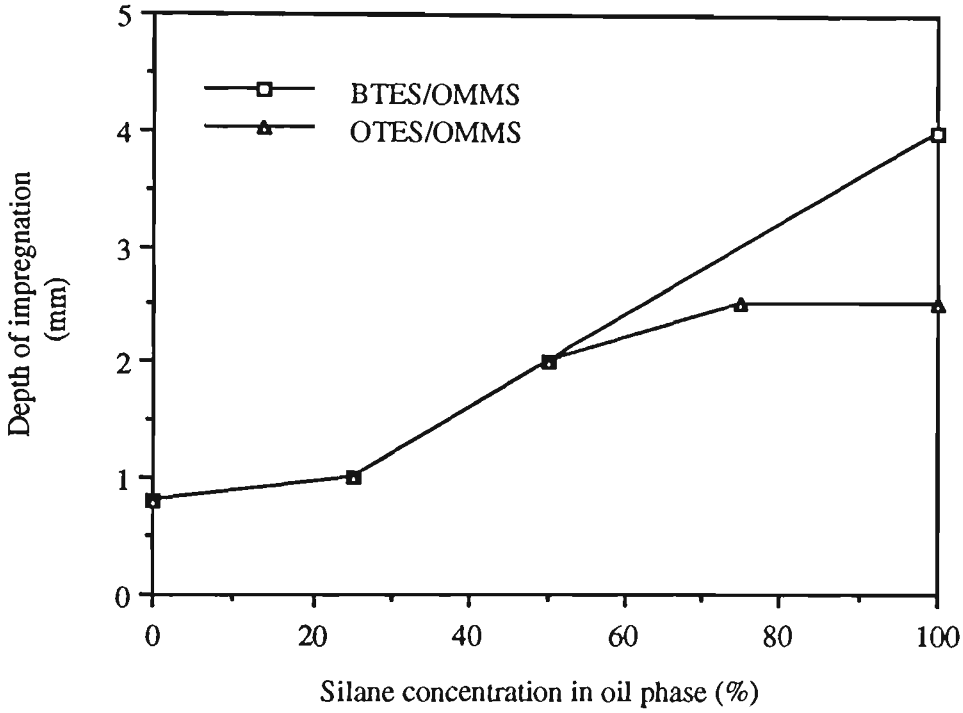


Figure 4.4 *Relationship between depth of impregnation and silane concentration in the oil phase of a silane/siloxane emulsion (Emulsion contained 50% oil phase and 2.3% Teric 16M2-7 and was diluted to 5% before application)*

The higher depth of impregnation of silanes is known to be attributed to the smaller molecular weight of the silanes [21, 54]. However, this may also be attributed to other factors. Figure 4.5 shows another phenomenon observed in this research. An OMMS emulsion with no silane addition but some organic solvent addition such as Isopar G and Exxsol D60 can also impart a higher depth of impregnation in the same substrates used in Figure 4.4.

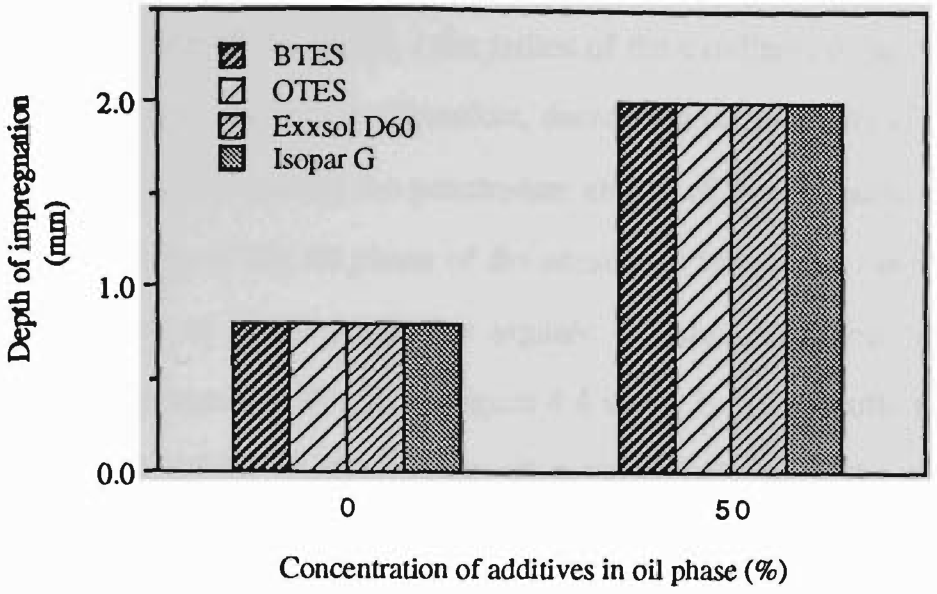


Figure 4.5 Effects of various additives in the oil phase of OMMS emulsions on the depth of impregnation (Emulsion contained 50% oil phase and 2.3% Teric 16M2-7 and was diluted to 5% before impregnation)

This may be explained as the result of reduced viscosity of the oil phase in the emulsion. A silicone emulsion is believed to break after application to the masonry substrate surface [106] leaving the silicone oil on the substrate surface to further penetrate into the capillaries. Particularly, if the emulsion is stabilised with acidified alkylamine ethoxylate surfactant, the emulsion is assumed to rapidly break after application because the surfactant will be abstracted from the oil/water interface by adsorption onto the negatively charged masonry surface according to Wates and James [183]. Eventually the remaining emulsifier is insufficient to stabilise the emulsion resulting in the emulsion breaking. The siloxane is a very viscous liquid. The rate of spreading of a liquid on solid substrate capillaries is known to be adversely affected by the viscosity of the liquid according to Washburn's equation [115]:

$$\frac{ds}{dt} = \frac{\gamma \, r \cos \theta}{4 \, \eta \, s} \qquad (4.1)$$

where ds/dt is the rate of liquid penetration into capillaries, s the distance travelled in time t, γ the surface tension of the liquid, r the radius of the capillary, θ the liquid contact angle and η the viscosity of the liquid. Therefore, decreasing the viscosity of the oil phase of the emulsion results in increasing the penetration ability of the emulsion. Figure 4.6 shows that an examination of the oil phase of the emulsions found that the viscosity decreased with the addition of either particular organic solvents or silanes while the depth of impregnation increased as shown in Figure 4.4 and 4.5. The results are quite consistent with the principle of the Washburn's equation particularly when the silane or the solvent addition was at 50% or less.

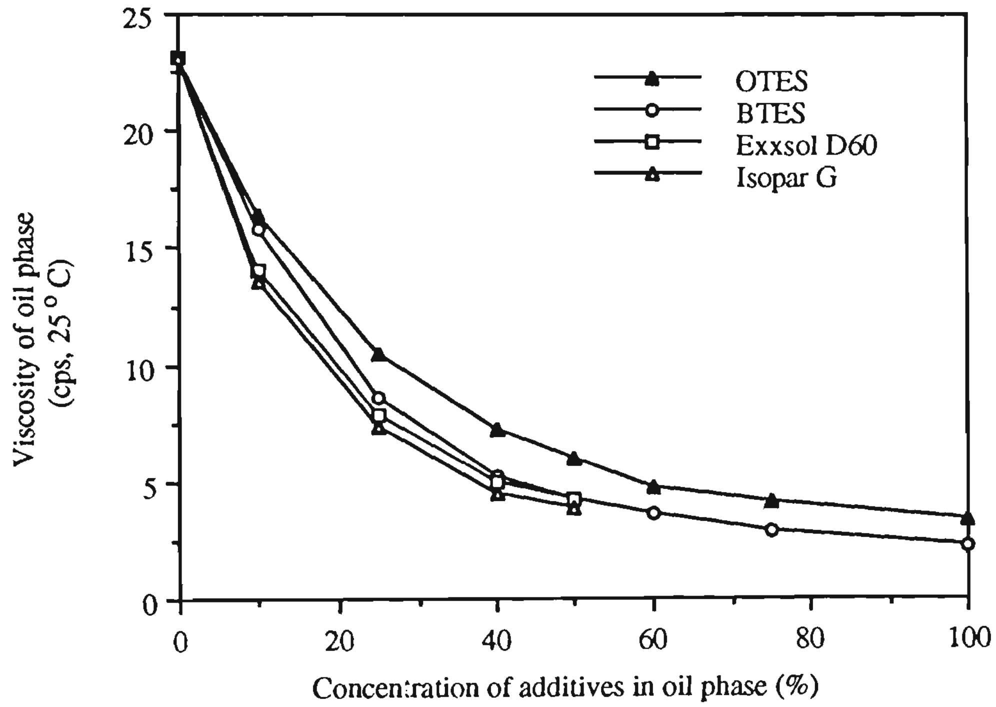


Figure 4.6 Relationship between the viscosity of the oil phase and additives.

Another factor which may affect the depth of impregnation of the silicone emulsion is the so-called aquaplane effect. This effect was termed by Roth [65]. Roth found that isooctyltrimethoxysilane dissolved in hydrocarbon solvent can impart a higher depth of impregnation to the substrate if the substrate is pre-wetted with water. This effect is assumed to be due to a sliding or aquaplaning of the organic phase along a wet capillary wall of the substrate. In the case of impregnating substrates with emulsions, the same aquaplane effect may apply. The emulsion may break into the organic and water phase after application to the substrate [106, 183]. The water may then wet the substrate capillaries first with subsequent penetration of the organic phase. Form the test results shown in Figure 4.5 the effect of increased depth of impregnation with the addition of particular organic solvents may also be attributed to the aquaplane effect. Addition of the silanes into the siloxane may be regarded as adding a solvent and therefore a higher depth of impregnation is then observed because silanes also have low viscosity like organic solvents.

c) Effect on the water repellency of the treated substrates

Figure 4.7 shows the relationship between the water absorption of the treated substrates and OTES concentration in the oil phase of the OTES/OMMS emulsion. There is no difference in water absorption of the treated substrates when the concentration of the silane in the oil phase of the emulsion is varied if cement mortar substrates are impregnated. This is because the alkali in the substrate is an effective catalyst for the silane hydrolysis and condensation. The silane can form crosslinked hydrophobic polysiloxane through hydrolysis and condensation to achieve the same water repellency as that of the siloxane. However, for non-alkaline substrates such as Indian fired bricks, the water repellent effect is decreased with the increase of the silane in the oil phase particularly when the concentration of the silane is over 50% in the oil phase of the emulsion. This effect is more significant when using BTES to replace the OTES in the emulsions to treat mud brick substrates. Figure 4.8 shows the relationship between water absorption of treated mud brick substrates and the silane concentration in the oil phase. The mud bricks were impregnated with 79 g/litre sodium silicate 24 hours before the emulsion impregnation. The same effect is observed for both the silanes. However, the BTES shows much poorer results than those of the OTES. This difference is explained as the loss of the BTES due to its higher evaporation rate compared to OTES (refer to Figure 4.3).

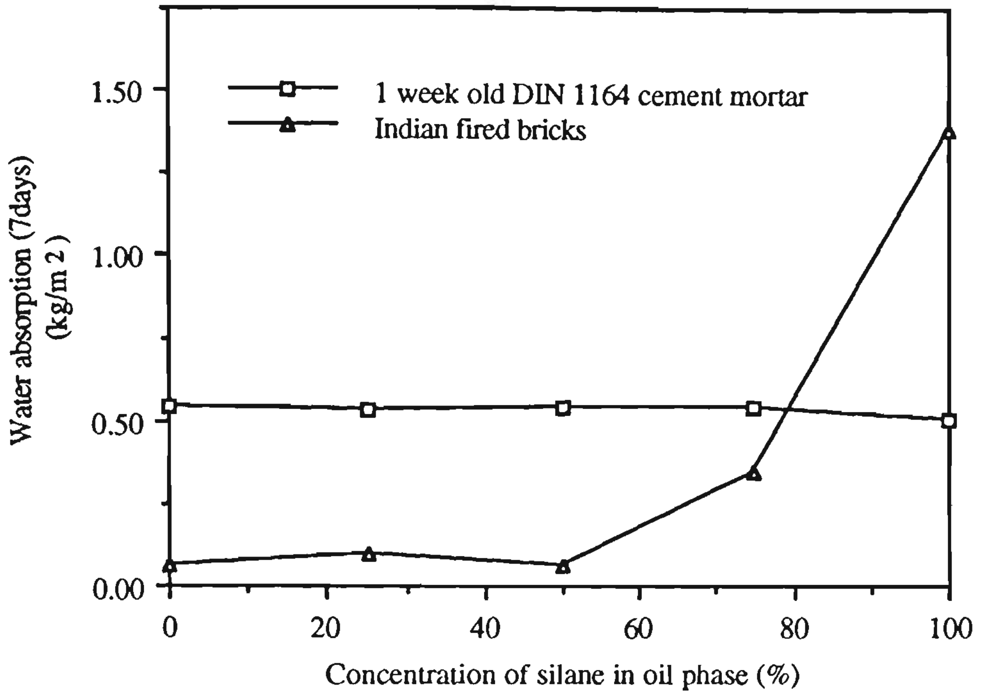


Figure 4.7 *Relationship between water absorption of treated substrates and OTES concentration in the oil phase of the OTES/OMMS emulsion (Emulsion contained 50% oil phase and 2.3% Teric 16M2-7 and was diluted to 5% before impregnation)*

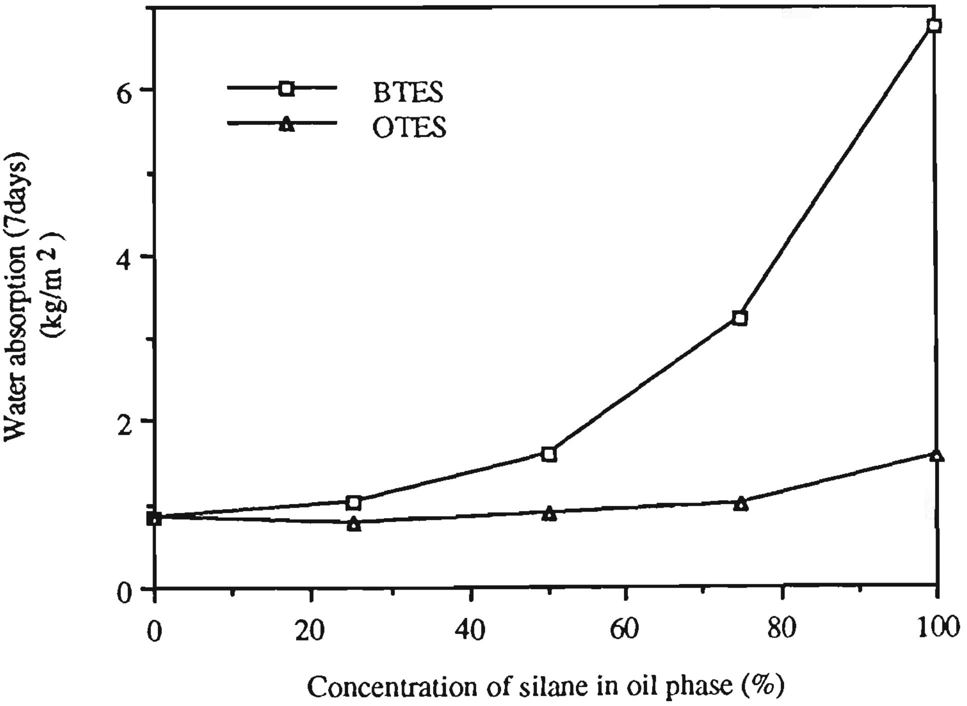


Figure 4.8 *Relationship between water absorption of treated mud brick and silane concentration in oil phase of the silane/siloxane emulsion (Emulsion contained 50% oil phase and 2.3% Teric 16M2-7 and was diluted to 5% before impregnation)*

In conclusion, pure siloxane emulsions and pure silane emulsions cannot impart satisfactory impregnation performance in terms of either penetration ability or water repellency to masonry substrates which include cement mortar, fired bricks and mud bricks. An emulsion with a mixture of silane and siloxane as the oil phase imparts satisfactory performance. Although the BTES in a silane/siloxane emulsion can impart a significant depth of impregnation, it achieves poor water repellency for non-alkaline substrates, particularly for mud brick substrates. However, OTES achieves relatively better water repellent performance in non-alkaline substrates. The concentration of the OTES in the oil phase of the emulsion was found to be best at about 50%. With this concentration, the OTES/OMMS emulsion can impart a satisfactory (≥ 2 mm) depth of impregnation and good water repellency for various substrates. Increasing the silane proportion may decrease the water repellent effect but does not significantly improve the depth of impregnation. With a decrease in the silane concentration, the penetration ability of the emulsion is sharply reduced.

4.2.1.2 Effects of silicones on the emulsion stabilisation

An emulsion is a dynamic, unstable system. Any components of the emulsion may affect emulsion stability. In the case of silane/siloxane emulsions, the stability may also include the chemical stability of the silane and siloxane because silicones may hydrolyse and condense to change the properties of the oil phase to affect the emulsion stability and to decrease the final impregnation performance of the emulsion. The effects induced by the silane/siloxane in the oil phase on the stability of the emulsion are outlined below.

a) Hydrolysis and condensation of the silane/siloxane in the emulsion

Silanes, particularly with short alkyl and short alkoxy chains, are easily hydrolysed into silanols and then condensed to polysiloxanes in water according to Osterholtz and Pohl [75]. The hydrolysis of the silane with formation of silanols and siloxanes changes the chemical properties of the oil phase which may result in a breaking of the emulsion. Examination of silane/siloxane emulsions containing short alkyl substituted trimethoxysilanes such as methyltrimethoxysilane (MTMS) or isobutyltrimethxoxysilane (BTMS) shows they are not stable and the emulsions are observed to separate into two phases with very viscous polysiloxane forming at the bottom of the emulsion within a few days. However, the long alkyl substituted triethoxysilanes have retarded hydrolysis rates in the emulsions resulting in more stable emulsions. Figure 4.9 shows emulsion stability in terms of oil separation rate within two day storage at room temperature from silane/siloxane emulsions containing various silanes. The emulsions contained 50% silane/siloxane at a ratio of 1:1 as the oil phase and were emulsified by 2.3% Teric 16M2-7 surfactant.

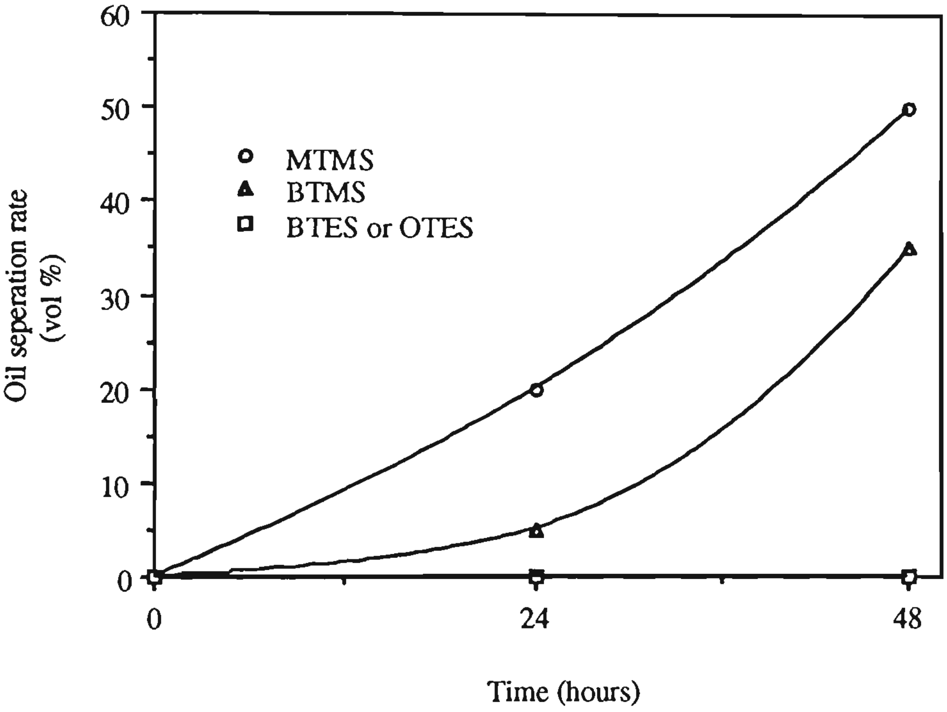


Figure 4.9 Separation rate of the silane/siloxane emulsions upon storage at room temperature

The stability of the emulsions containing the silanes with higher alkyl and ethoxy substituents (e.g OTES and BTES) are less affected due to a low hydrolysis rate. Unfortunately, some silane hydrolysis must be accepted when making silane/siloxane emulsions. Even long alkyl triethoxysilanes such as OTES can also hydrolyse in the emulsion after preparation. The hydrolysis of OTES was investigated in this emulsion system. Figure 4.10 shows the OTES hydrolysis in terms of monitoring the ethanol cleavage from the silane in the emulsion (Scheme 4.1) by HSGC. The emulsion contained

50% OTES/OMMS at a ratio of 1:1 as the oil phase. The emulsion was stored at 40°C in order to assess hydrolysis at an accelerated rate. From Figure 4.10 the hydrolysis rate of the OTES greatly depends on the emulsifier system used in the emulsion. The surfactant effect on the hydrolysis of silane will be discussed in §4.2.2.2. The hydrolysis rate may be retarded to a minimum by properly selecting the surfactant.

$$R-\overset{|}{\underset{|}{Si}}-OCH_2CH_3 + H_2O \longrightarrow R-\overset{|}{\underset{|}{Si}}-OH + CH_3CH_2OH$$

(Scheme 4.1)

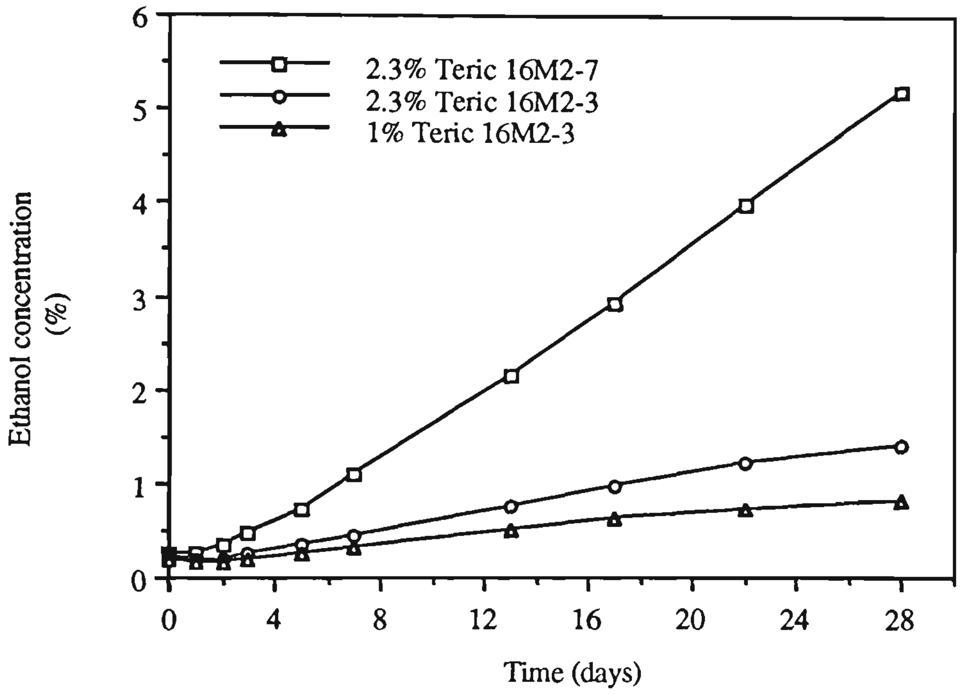


Figure 4.10 Ethanol concentration in the OTES/OMMS emulsions during storage at 40°C

Oligomeric octyl/methyl methoxysiloxane (OMMS) is easy to hydrolyse due to the presence of methoxy groups. The pure OMMS emulsion is observed to become very viscous with some gel separation from the emulsion. The same trend was also observed with the OTES/OMMS emulsions. Figure 4.11 shows the accelerated viscosity change of both pure OMMS and the OTES/OMMS emulsions by storing the emulsions at 40°C. The increase in the viscosity of the emulsion is assumed to be due to the hydrolysis and condensation of the siloxane. The initial decrease in viscosity may be explained as an increase in the degree of hydration of the oil droplet as has been discussed for other systems by Sunderland and Enever [184]. The hydrolysis of the siloxane would result in the formation of siloxanol which would impart a hydrophilic effect to the emulsion particle to increase the hydration of the oil droplet in the emulsion. Formation of the interfacial film in the oil/water interface by siloxane will be discussed in §4.3. The subsequent gradual increase in viscosity may be due to the condensation of the siloxane resulting in further growth of the molecular weight of the siloxane. The siloxane emulsion may then be changed from a oil/water emulsion to a polysiloxane colloidal dispersion finally when all the siloxane is polymerised. The viscosity change of the silane/siloxane emulsions may be attributed to the hydrolysis of both silane and siloxane. However, it was shown that the major effect was induced by the siloxane hydrolysis and condensation because addition of silane within the oil phase of the siloxane emulsion significantly retards the increase in viscosity (Figure 4.11).

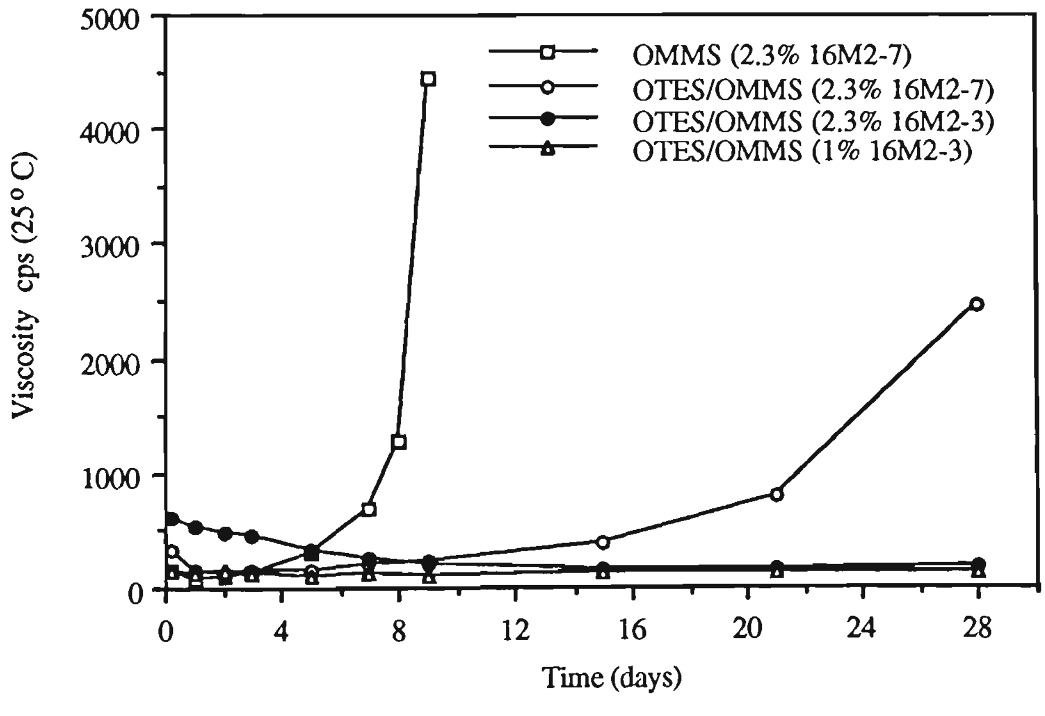


Figure 4.11 Viscosity of the OMMS and the OTES/OMMS emulsions during storage at 40°C

The siloxane hydrolysis is further confirmed by monitoring the methanol cleavage from the emulsion (Scheme 4.2). Figure 4.12 shows the methanol concentrations in both OMMS and OTES/OMMS emulsions during storage at 40°C. From Figure 4.12, the methanol concentration of the siloxane emulsion increases sharply during the first 7 days and then tends to reach a constant value. This may be best explained as that the major reaction at the beginning is the hydrolysis of the methoxy ethers to produce methanol and then condensation to increase the molecular weight of the siloxane.

$$-\underset{OCH_3}{\overset{R}{Si}}-O-\underset{OCH_3}{\overset{R}{Si}}- \; + \; H_2O \longrightarrow -\underset{OCH_3}{\overset{R}{Si}}-O-\underset{OH}{\overset{R}{Si}}- \; + \; CH_3OH$$

(Scheme 4.2)

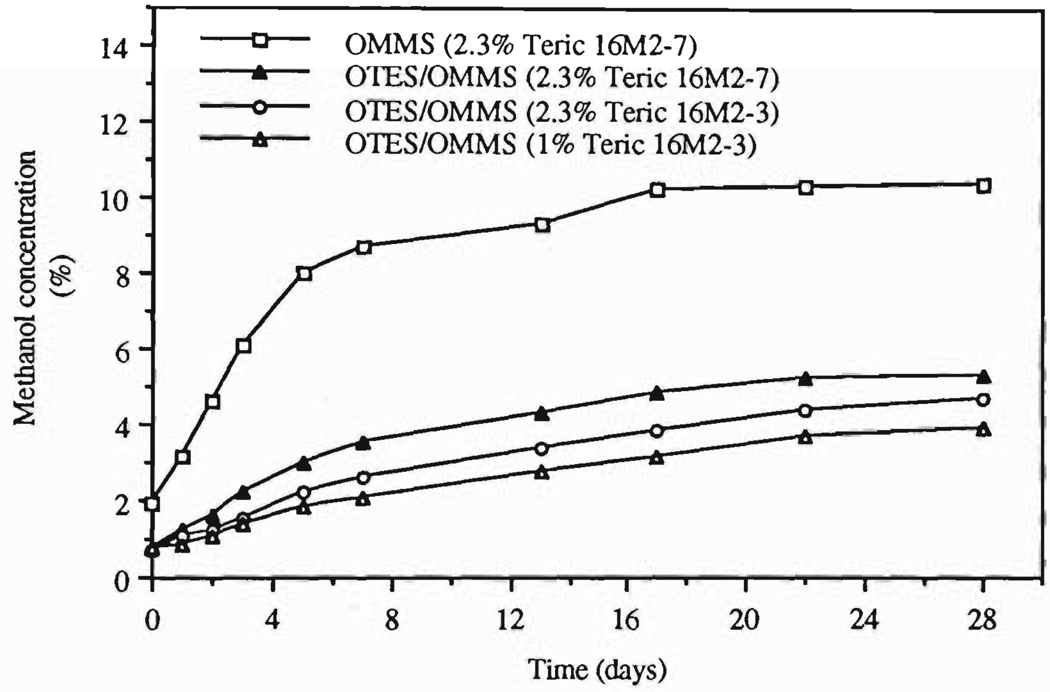


Figure 4.12 *Methanol concentration of the OMMS emulsion and the OTES/OMMS emulsions during storage at 40°C*

Further confirmation that the change in the viscosity of the emulsion is due to the hydrolysis of the siloxane was obtained by replacing the methoxy ether of the siloxane using alcoholysis (see Chapter 2). The hydrolysis of the siloxane in the emulsion prepared with the ethoxysiloxane (OMES) was significantly retarded due to the lower hydrolysis rate of the ethoxy ether of the siloxane. The hydrolysis rate of ethoxysilane ethers is well known to be significantly lower than that of methoxysilane ethers [75]. Figure 4.13 shows the viscosity change of the emulsion made with the OTES/OMES. The increase in viscosity of the OTES/OMES emulsion is significantly lower compared to that of the emulsion made with the methoxysiloxane (OTES/OMMS) during long term storage at 40°C.

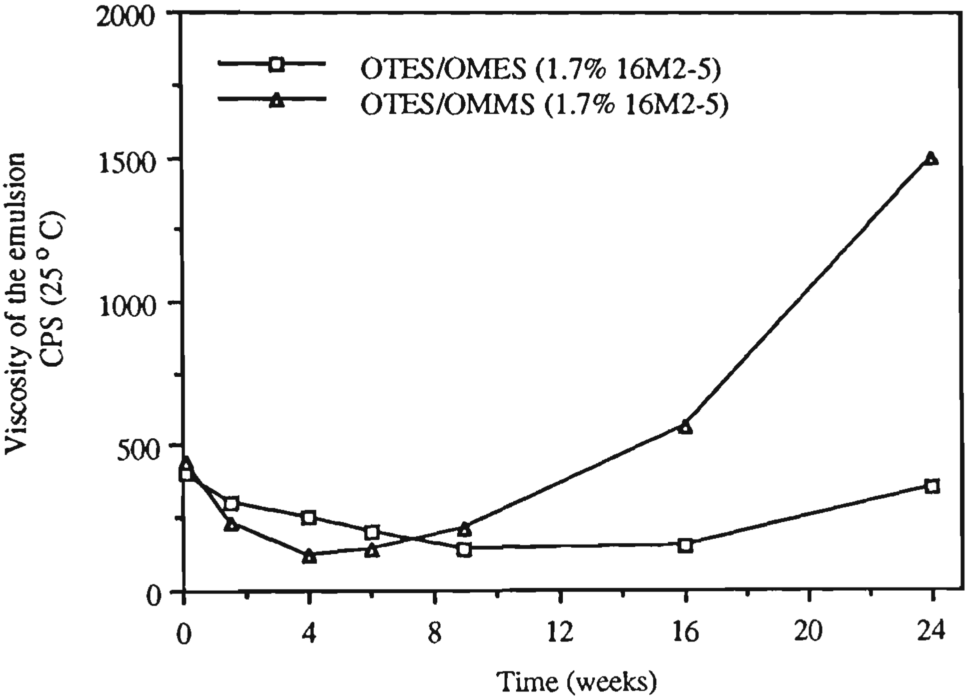


Figure 4.13 Viscosity change of the silane/siloxane emulsions during long term storage at 40°C

Unfortunately, the ethoxysiloxane is not yet commercially available. Therefore, methoxysiloxane is the only choice of siloxane for silane/siloxane emulsion preparation. However, Figure 4.11 and Figure 4.12 show that the hydrolysis of the siloxane in the silane/siloxane emulsion is also affected by the emulsifying systems. The degree of siloxane hydrolysis may be controlled to an acceptable level by carefully selecting the emulsifying system and the surfactant addition. The surfactant effect on the hydrolysis of the siloxane will be discussed in ξ4.2.2.2.

Partial hydrolysis of silane/siloxane in the emulsion does not appear to significantly affect the emulsion stability and the impregnation performance. Table 4.1 shows the emulsion stability and the impregnation performance of a silane/siloxane emulsion after up to 10 months storage at room temperature. The emulsion contained 50% OTES/OMMS at a ratio of 1:1 as the oil phase and was stabilised by 1% Teric 16M2-3 surfactant. The test results indicate that there is no significant change in emulsion stability in terms of the emulsion particle size and viscosity from initial state to 6 and 10 month storage state at room temperature. The impregnation performance in terms of water absorption tests conducted on 1 week old DIN 1164 cement mortar substrates remains unaffected except the depth of impregnation is slightly reduced probably due to an increase in the molecular weight of the siloxane.

Table 4.1 *Stability and impregnation performance of the OTES/OMMS emulsion before and after storage at room temperature*

Storage time	Initial	After 6 months	After 10 months
Stability (optical)	stable	stable	stable
Particle size (μm)	0.51	0.53	0.44
Viscosity (cps, 25°C)	155	150	150
Water absorption (kg/m^2, 7 days)	0.48	0.53	0.57
Depth of impregnation (mm)	2	1.5-2	1.5

In fact, hydrolysis of the siloxane may take part in the stabilisation of the silane/siloxane emulsion with the silanols enjoining with the surfactant in the formation of the interfacial film. In addition, an increase in the molecular weight of the siloxane induced by condensation may help to stabilise the silane/siloxane emulsion by polymeric stabilisation according to Napper [180]. This will be discussed in the next section and in ξ4.3.

b) Effects of silane/siloxane on the physical stability of the emulsion

It has been discussed that the pure OMMS emulsion is not stable due to the high rate of hydrolysis of the siloxane in the emulsion. It was also found that the pure silane emulsion was not stable in terms of poor physical stability. However, the emulsion made with the silane/siloxane mixture as the oil phase had the best stability in terms of the chemical and physical stability of the emulsion. By investigating the interfacial tension at the oil/water interface in the presence of acidified alkylamine ethoxylate surfactant Teric 16M2-3, it was found that the static oil/water interfacial tension of silane/siloxane mixtures are always lower than those of either pure silane or pure siloxane. Figure 4.14 shows the change of static oil/water interfacial tension of both OTES/OMMS and BTES/OMMS mixtures with change of concentration of silanes in the oil phase. The emulsion particle size analysis results also show that the emulsions with the small particle size are those made with mixtures of silane/siloxane as the oil phase (Figure 4.15). This implies that the best physical stability of the emulsion occurs with a silane/siloxane mixture rather than with pure silanes or with siloxane as the oil phase. It appears that the best silane concentration in the emulsion oil phase is 50% because the emulsion has the lowest static oil/water interfacial tension and the smallest emulsion particle size. However, both the static interfacial tension and the particle size show no great difference in the silane concentration range from 25% to 75% in the oil phase of the emulsion. By referring to the previous discussion in ξ4.2.1.1, the best silane/siloxane emulsion in terms of satisfactory impregnation performance was the emulsion made with OTES at the silane concentration of 50% in the oil phase. Therefore, it may be concluded that the mixture of OTES/OMMS as the oil phase of the emulsion not only favours impregnation performance of the impregnant but also improves the stability of the emulsion. The best ratio of silane to siloxane in the oil phase of the emulsion appears to be 1:1 by weight.

It is not surprising that the results of the change in static interfacial tension with the change in silane concentration in the oil phase in Figure 4.14 are not quite consistent with the change of the particle size shown in Figure 4.15. Therefore, static interfacial tension cannot fully explain the stability of the silane/siloxane emulsions in terms of the change in emulsion particle size. These phenomena are also observed with those in another system reported by Nakajima et al.[185]. Other factors apart from static interfacial tension must exist to affect the stability of the silane/siloxane emulsion. The role of the silane/siloxane oil phase in the stabilisation of the emulsion will be discussed in ξ4.3.

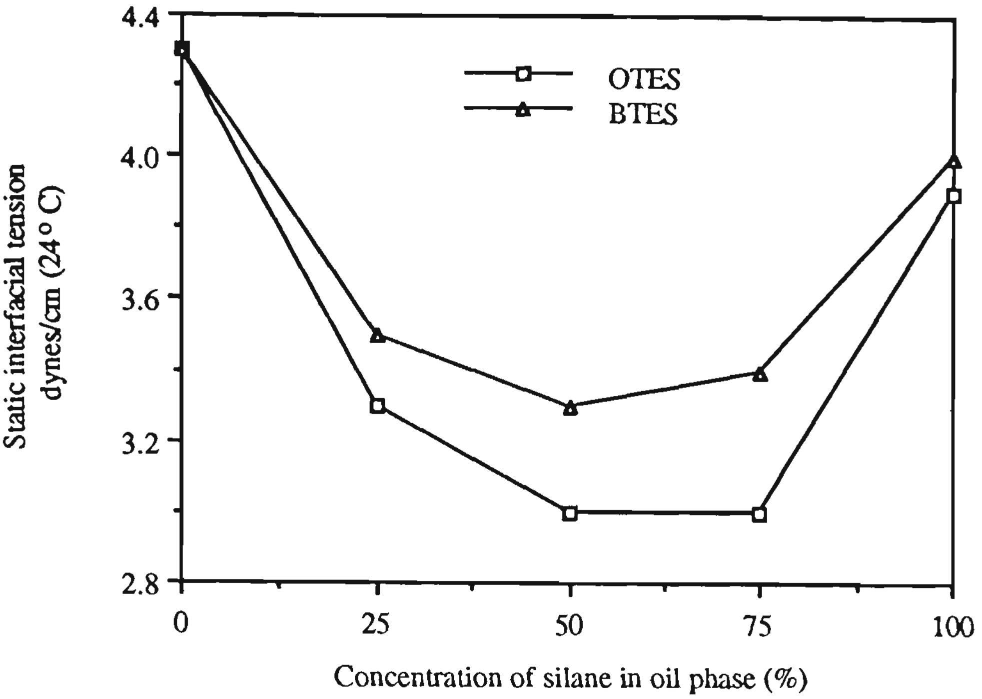


Figure 4.14 Relationship between the static interfacial tension and the silane concentration in the silane/siloxane oil phase (The aqueous phase contained 4.6% Teric 16M2-7 which was equivalent to 2.3% in the relevant emulsion)

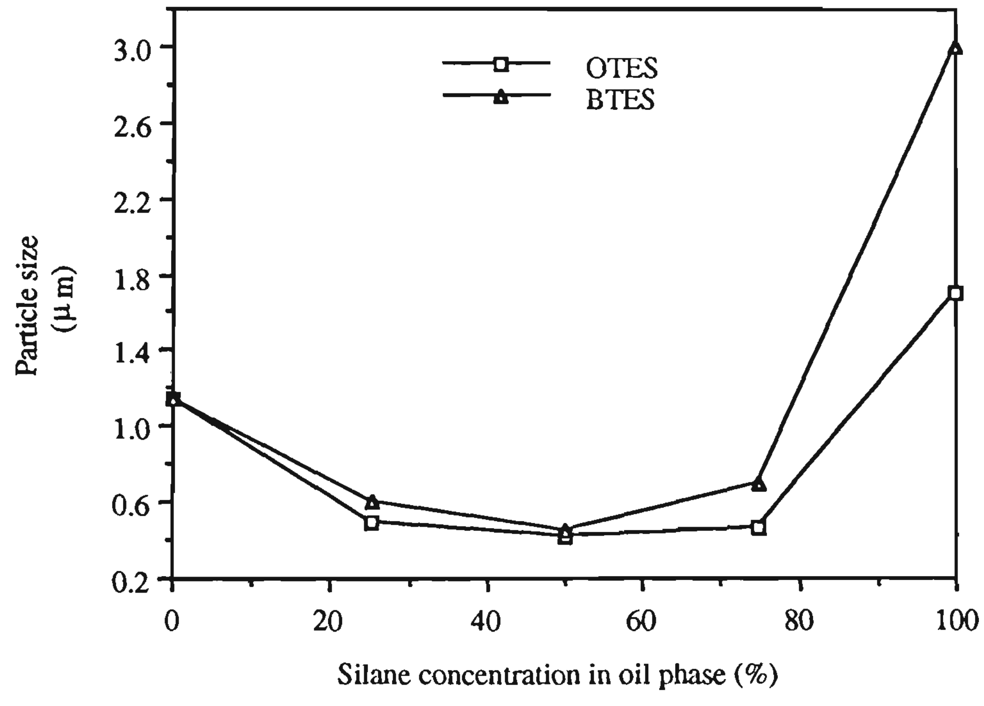


Figure 4.15 Relationship between the particle size and the silane concentration in the silane/siloxane emulsion oil phase (The emulsion contained 50% oil phase and 2.3% Teric 16M2-7)

4.2.2 Selecting the emulsifier system for the OTES/OMMS emulsion

4.2.2.1 Surfactant effects on the impregnation performance

a) Wetting effect induced by the surfactants in the emulsion

The inclusion of surfactants into impregnants normally imparts a wetting effect to the substrates. There is the situation that the surfactant can produce a stable emulsion but impart a wetting effect to the treated substrate surface. This wetting effect is found to exist in a few commercial silicone emulsions which are used as masonry water repellents. The surfactant wetting effect in terms of the beading effect and the water absorption of Indian fired bricks treated with two commercial silicone emulsions and a solvent-based siloxane (OMMS-Sn in Isopar G) water repellent were examined. Table 4.2 shows that the water repellency is significantly decreased in comparison with the substrate treated with the solvent-based siloxane impregnant.

Table 4.2 *The beading effect and the water absorption of Indian fired bricks treated with various commercial water repellent impregnants at 10% concentration*

Name of impregnant	Beading Effect	Water Absorption (7 days, kg/m^2)
Goldschmidt ZFR 899 [a]	6-7	3.51
Hydrozo Enviroseal 40 [b]	6-7	1.42
OMMS-Sn in Isopar G solvent	2	0.07
Untreated	7	8.92

a. Goldschmidt ZFR 899 is a 50% silane/siloxane emulsion provided by Th. Goldschmidt AG, Germany.

b. Hydrozo Enviroseal 40 is a 40% silane emulsion provided by Hydrozo Inc., USA.

The surfactant effect imparted to the substrate from the silicone emulsion is more significant than that from the siliconates containing surfactants such as PPMS or POMS solution. As discussed in Chapter 3, the major surfactant effect in siliconates is to reduce the alkali stability of the siliconate solution. There is no significant surfactant wetting effect observed in substrates treated with siliconate solutions unless the surfactant is at very high concentration. In addition, by comparing the water repellent performance of non-alkaline substrates treated with the OTES/OMMS emulsion and the POMS siliconate solution, it is surprising to find that even though the concentration of the surfactant in the final siliconate impregnant solutions is much higher than that of the emulsion, the water repellent performance of the siliconate remains unaffected. Table 4.3 shows the test results for Indian fired bricks treated with 2% POMS siliconate impregnant containing Teric G12A12 nonionic surfactant and 10% OTES/OMMS emulsion containing the same surfactant. The emulsion contained 50% OTES/OMMS at the ratio of 1:1 as the oil phase.

Table 4.3 *The beading effect and the water absorption of Indian fired bricks treated with 2% POMS siliconate solution and 10% OTES/OMMS emulsion*

Water repellent Impregnants	Concentration of the surfactant in final impregnant solution	Beading Effect	Water Absorption (7 days, kg/m^2)
2% POMS	0.42%	2-3	0.41
10% OTES/OMMS emulsion	0.20%	6-7	1.67
Untreated	–	7	8.92

The difference in water repellent performance between the siliconate treated substrate and the emulsion treated substrate in Table 4.3 may be attributed to the difference in the reactivity of siliconate solution and silane/siloxane of the emulsion on the substrate. It is known that siliconates are very reactive and their ability to form a hydrophobic layer on the substrate only depends on the presence of atmospheric carbon dioxide [29, 54]. Generally, water repellency on the very surface of the substrate is formed very soon after impregnation as the availability of atmospheric carbon dioxide on the very surface of the substrate is high. Therefore, it is to be expected that the water repellency will be excellent on the very surface of the substrate and this dominates the surface to the exclusion of the surfactant wetting effect. However, the reactivity of the silane/siloxane in the emulsion is less than the siliconate and the reactivity depends on the presence of moisture and the pH of the substrate [21, 54]. It takes longer for the silane/siloxane to hydrolyse and then condense to form a hydrophobic layer in the substrate capillaries. During this period, the silane on very surface of the substrate may evaporate [21] resulting in less concentration of silicone on the very surface. In the case of alkaline substrates, the pH of the substrate at depth is higher than that of the surface due to carbonation and this results in a lesser degree of crosslinking of polysiloxane on the very surface. Therefore, the water repellency on the very surface of the substrate treated with silane/siloxane emulsion is generally less than the water repellency inside. The surfactant at the very surface of the substrate may then dominate the surface to impart a wetting effect on contact with water.

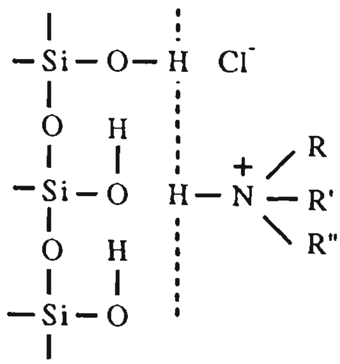
Most nonionic and anionic surfactants in the emulsion systems are found to impart unsatisfactory impregnation performance due to the surfactant wetting effect. However, cationic surfactants show a unique surface effect different to those of other surfactants. Table 4.4 lists the beading effect and the water absorption values of substrates treated with OTES/OMMS emulsions stabilised with various surfactants. The emulsion contained 50% OTES/OMMS at the ratio of 1:1 as the oil phase and is stabilised by 1% of various surfactants or surfactant mixtures, and then the emulsions are diluted to 10% before impregnation.

Table 4.4 *Beading effect and water absorption of Indian fired bricks treated with 10% concentration of various emulsions*

Emulsions or Impregnants	Surfactant in emulsions	Beading effect	Water absorption (7 days, kg/m^2)
Emulsion with anionic	Hostapur SAS60 (soluble)	6-7	1.84
	Gardilene IPA/9 (insoluble)	6-7	0.69
Emulsion with nonionic	Teric G9A6 (HLB 12.4)	6	0.44
	Teric G16A16 (HLB 14.9)	6-7	1.88
Emulsion with cationic	Vantoc N40 (soluble)	3	0.17
Emulsion with mixed cationic & nonionic	Vantoc N40 & Teric G9A2	4	0.31
Emulsion with acidified alkylamine ethoxylates	Teric 16M2-3	2-3	0.12
Solvent-based siloxane	OMMS-Sn in Isopar G solvent	2	0.07
Untreated		7	8.92

In a comparison with the substrate treated with solvent-based siloxane impregnant, the test results show that the emulsions made with anionic surfactants of either high or low water solubility impart more or less wetting effects resulting in poor beading effects and high water absorption values. The emulsions with nonionic surfactants of either high or low HLB also show similar effects to those of the anionic surfactants. However, the emulsion made with the cationic surfactant Vantoc N40 achieves satisfactory water repellent performance. The emulsion with the mixed cationic and nonionic surfactants shows some surfactant wetting effect. The emulsion made with acidified alkylamine ethoxylate surfactant shows a satisfactory water repellent performance and the test results are competitive with those of the solvent-based siloxane impregnant.

The phenomenon of an insignificant wetting effect of the emulsion made with cationic surfactants is due to the strong adsorption of the positively charged nitrogen of the surfactant to a negatively charged solid substrate surface (e.g. textiles and pigments) with hydrophobic groups oriented away from the surface according to Porter [112]. This results in formation of a hydrophobic surfactant hydrocarbon layer on the surface to produce a water repellent effect. Iler [160] assumed that the interaction between a silica surface and a hydrochloride salt of an alkylamine may be represented by the following scheme (Scheme 4.3), in which the electronegative chlorine, oxygen and nitrogen atoms are associated through hydrogen bonds. This orientation of amine on the silica surface also results in a hydrophobic surface. The orientation of cationic surfactant on the masonry substrate surface is assumed to be similar to that discussed by Porter and Iler resulting in a hydrophobic surfactant layer on the surface (as shown in Figure 4.16). That a purely cationic surfactant is unsatisfactory to stabilise the silane/siloxane emulsion and addition of a nonionic co-surfactant such as an alkylalcohol ethoxylate is necessary will be discussed later. However, introduction of a nonionic surfactant into the emulsifying system causes the surfactant wetting effect to the substrates (see Table 4.4).



(Scheme 4.3)

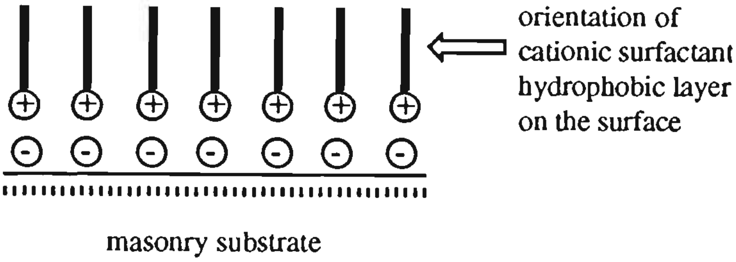
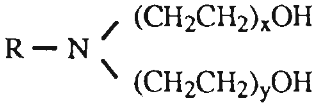


Figure 4.16 Adsorption of cationic surfactants to masonry substrate surface

The good performance of the emulsion with an acidified alkylamine ethoxylate surfactant is due to the surfactant which is assumed to be cationic in nature. It is also observed that the acidified alkylamine ethoxylate surfactant significantly stabilises the silane/siloxane emulsion without addition of any nonionic co-surfactants.

b) Properties of alkylamine ethoxylate nonionic surfactants

Alkylamine ethoxylate surfactants have a general formula of alkylamine with two ethylene oxide (EO) chains attached to the nitrogen of the amine (shown in Scheme 4.4) [112].



$$R-N\begin{cases}(CH_2CH_2)_xOH\\(CH_2CH_2)_yOH\end{cases}\qquad x+y=n$$

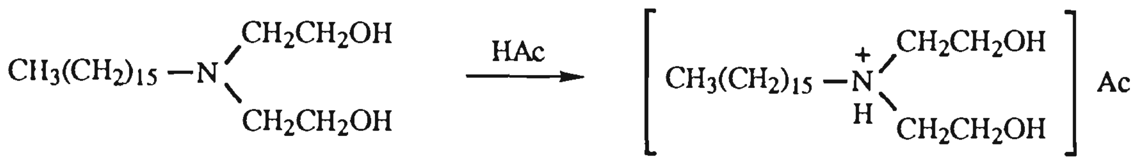
(Scheme 4.4)

Whether alkylamine ethoxylates are classified as nonionic or cationic surfactants depends on the number of ethylene oxide units they contain and the pH at which they are used. At low ethylene oxide levels they are cationic in nature but at high ethylene oxide levels they behave similarly to nonionic surfactants [112]. The results in Table 4.5 show that amine ethoxylate surfactants with longer ethoxylate chains such as Teric 16M15 and Teric 16M5 impart surfactant wetting effects to substrates treated with the emulsions made with those surfactants. This implies that the surfactants still behave similarly to the nonionics because longer hydrophilic ethoxylate chains in the surfactant still impart a similar effect to those of the polyoxyethylene nonionic surfactants. However, the surfactant with a low number of EO units (i.e. Teric 16M2) achieves good water repellent performance both in the unmodified and acidified state. This shows that the amine ethoxylate with low number of EO units behaves similarly to the cationics in the silane/siloxane emulsion. The results from the examination of the zeta potential of the emulsion also confirmed this conclusion (see ξ4.3.2).

Table 4.5 *Beading effect and water absorption of Indian fired bricks treated with 10% emulsions stabilised with various alkyamine ethoxylate surfactants*

Surfactant used in the emulsion	Beading effect	Water absorption (7 days, kg/m^2)
Teric 16M15 (with 15 EO)	6-7	1.83
Teric 16M5 (with 5 EO)	6-7	1.38
Teric 16M2 (with 2 EO)	2-3	0.10
Teric 16M2-3 (acidified 16M2)	2-3	0.12

The pH of the alkylamine ethoxylates is an important factor in controlling the properties of the surfactant. Addition of acid to alkylamine ethoxylates introduces more positive charge to the nitrogen to produce the amine salt according to Biermann et al.[186] (Scheme 4.5) Such acidified alkylamine ethoxylate surfactants have strong affinity for mineral surfaces and have been used to make bitumen emulsions [183, 187]. An examination of Table 2.1 shows that the addition of acid into Teric 16M2 increases the solubility of the surfactant resulting in an increase in the HLB of the surfactant. However, the addition of acid may bring some free acid into the emulsifying system and lower the pH of the emulsifier, which may then accelerate the hydrolysis of both silane and siloxane in the emulsion. The various effects on the silane/siloxane emulsion induced by acidified alkylamine ethoxylate surfactant will be discussed in ξ4.2.2.2.



(Scheme 4.5)

In summary, the silane/siloxane emulsion stabilised by either nonionic or anionic surfactant achieves unsatisfactory water repellent performance due to the surfactant wetting effect. Cationic surfactants impart less wetting effect to the substrate but a nonionic co-surfactant is necessary to stabilise the silane/siloxane emulsion. The mixed cationic-nonionic surfactant system also imparts a surfactant wetting effect to the substrate. Alkylamine ethoxylate surfactant with short ethoxylate chains (Teric 16M2) is found to not only stabilise the silane/siloxane emulsion but also achieve a satisfactory water repellent performance in terms of imparting no wetting effect to the substrate. Under these parameters, alkylamine ethoxylate surfactants were chosen as the emulsifier for the silane/siloxane emulsion.

4.2.2.2 Surfactant effects on the stability of the emulsion

a) Effect of surfactants on the hydrolysis of the silane/siloxane

It is known that surfactants may accelerate organic hydrolysis by means of micellar catalysis according to Fendler and Fendler [152]. The surfactant acts as a reaction medium between the organic and the aqueous phases. Within chapter 3, the acceleration of the hydrolysis rate of OTES in PMS in the presence of a surfactant in terms of hydrophobic or electrostatic interaction has been discussed. In a similar manner, the surfactant in the silane/siloxane emulsion may also accelerate the hydrolysis of the silane and the siloxane. Although an emulsion oil droplet is much larger than a surfactant micelle, the surfactants in emulsions still provide an enormous area at the oil/water interface where hydrolysis may occur. The alkoxy ether groups are more polar than the alkyl chain in silanes or siloxanes, and therefore they should have more chance to be located in or near the interface of the emulsion droplet where they are easily approached by the water. In the case of pH adjustment induced by the surfactant to either acidic or alkaline, the hydrolysis rate will be further accelerated according to Osterholtz and Pohl [75]. However, the rate of acid hydrolysis is significantly greater than base hydrolysis according to Arkles et al.[188].

Figure 4.17 shows the methanol and ethanol concentration produced by hydrolysis in the silane/siloxane emulsions which were stabilised with various surfactants and stored at room temperature for 6 months. The silane/siloxane emulsions contained 50% OTES/OMMS at a ratio of 1:1 as the oil phase and stabilised with 1% of various anionic, nonionic and cationic surfactants. The properties of the surfactants used are shown in Table 4.6.

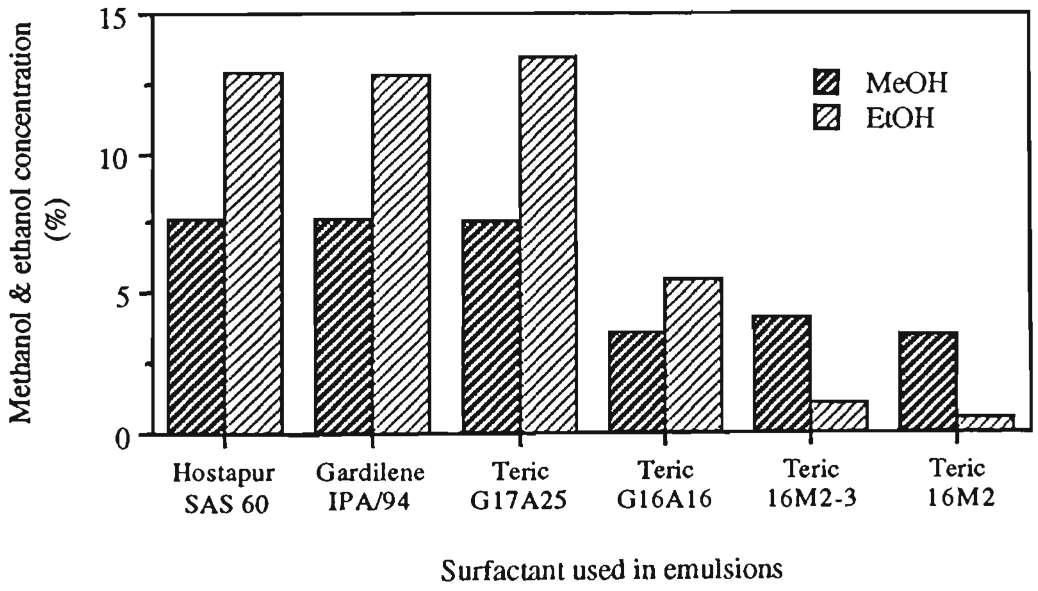


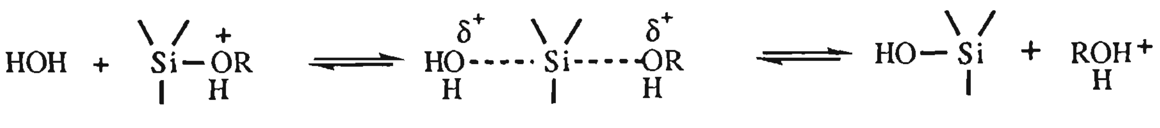
Figure 4.17 *Methanol and ethanol concentration in OTES/OMMS emulsions after 6 months storage at room temperature*

Table 4.6 Some properties of the surfactants

Surfactant name	Property	pH of the surfactant
Hostapur SAS 60	anionic	6.2
Gardilene IPA/94	anionic	5.7
Teric G17A25	nonionic	3.4
Teric G16A16	nonionic	5.2
Teric 16M2-3	acidified alkylamine ethoxylates	7.5
Teric 16M2	alkylamine ethoxylates	9.0

Anionic surfactants such as sodium alkane sulphonate (Hostapur SAS60) and isopropylamine alkylbenzene sulphonate (Gardilene IPA/94) exhibit significant acceleration of hydrolysis for both silane and siloxane in the emulsions. Nonionic surfactants also accelerate the silane/siloxane hydrolysis but the effect on the hydrolysis rate appears to depend on the pH of the surfactant. Alkylamine ethoxylate (Teric 16M2) or acidified alkylamine ethoxylate surfactants (Teric 16M2-3) show the lowest acceleration of hydrolysis effect particularly for the hydrolysis of the OTES in the emulsions. However, all the emulsions in Figure 4.17 show more or less silane/siloxane hydrolysis due to either surfactant micellar catalysis or the change of pH induced by the surfactants.

Alkoxy ether hydrolysis as in the silane/siloxane emulsion appears to undergo acid-catalysed hydrolysis with S_N2-Si mechanism. According to Osterpholtz and Pohl [75], an alkoxy ether is protonated in a rapid first step, followed by the slow step of the formation of a positively charged transition state. The transition state decays by displacement of alcohol accompanied by inversion of the silicon tetrahedron (shown in Scheme 4.6).



(Scheme 4.6)

By reference to this acid-catalysed hydrolysis mechanism, the acceleration of the hydrolysis rate of silane/siloxane in the emulsion stabilised by anionic surfactants may be explained.

Firstly, the negatively charged emulsion droplet has strong electrostatic attraction to the positively charged hydronium ions which find it easy to access the silicones in the oil/water interface to protonate the alkoxy ethers. Fendler and Fendler [152] have discussed the catalysis by anionic surfactant micelles of reactions involving cations where catalysis is due to the electrostatic interaction between the cations and the anionic micelles. In addition, lowering the pH below neutrality as induced by the anionic surfactant increases the hydronium ion in the emulsion resulting in an increase in the hydrolysis rate.

As distinct from anionic surfactants, the alkylamine ethoxylates or the acidified alkylamine ethoxylates impart positive charges to the emulsion particles. Under the acid-catalysed hydrolysis conditions, electrostatic repulsion may exist between the emulsion particle and hydronium ions resulting in retarding the hydrolysis rate. Alkali may also accelerate the silane/siloxane hydrolysis under a base-catalysed hydrolysis mechanism [75]. However, the weakly alkaline conditions induced by the alkylamine ethoxylates or the acidified amine ethoxylates is not sufficient to induce significant hydrolysis rate. The results in Figure 4.17 show that the acid-catalysed hydrolysis mechanism may dominate the hydrolysis under these conditions. Other results (discussed later) also confirm this assumption.

Apart from the hydrophobic interaction, nonionic surfactants may not impart electrostatic interaction effect in the silicone hydrolysis and therefore the hydrolysis would then be highly dependent on the pH of the surfactant. The results in Figure 4.17 are in agreement with this assumption.

In order to ascertain the hydrolysis effect induced by the acidified alkylamine ethoxylate surfactant, the methanol and ethanol concentration in the silane/siloxane emulsions made with different pH of acidified alkylamine ethoxylate surfactant Teric 16M2 were examined. Figure 4.18 shows the hydrolysis effect on the silane/siloxane induced by the surfactant with addition of various amounts of acetic acid. The emulsion contained 50% OTES/OMMS at a ratio of 1:1 as the oil phase and was stabilised by 1% acidified alkylamine ethoxylates at the acid addition ratio of HAc/16M2 from 0:1 to 0.24:1 with pH from 9 to 6.5. The surfactant detail appears in Table 2.1.

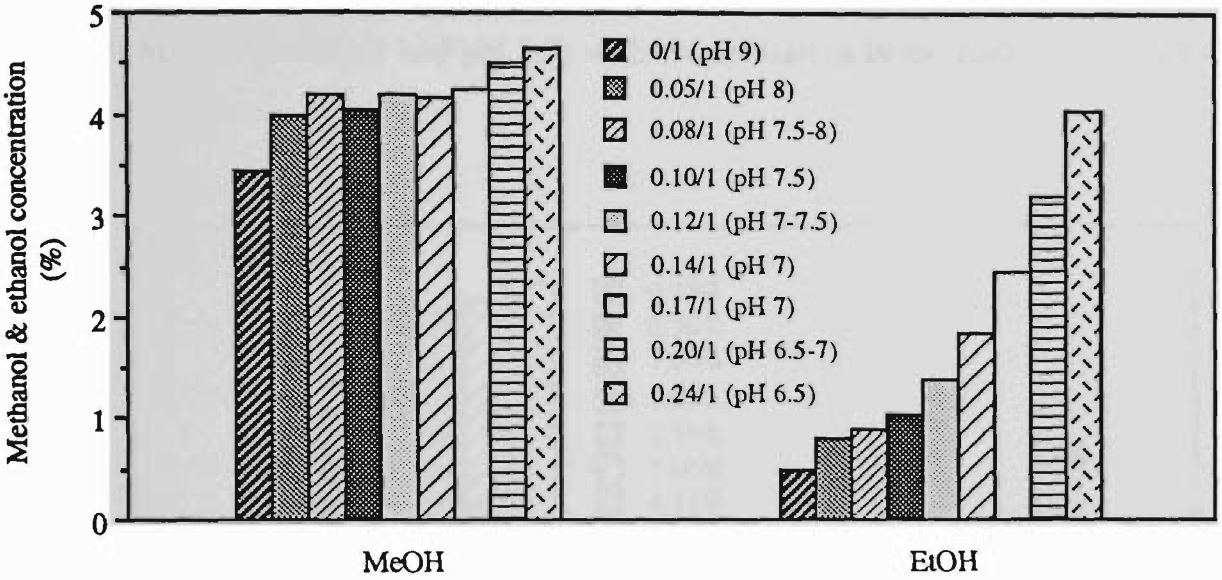


Figure 4.18 *Methanol and ethanol concentration in OTES/OMMS emulsions after 6 months storage at room temperature*

The test results show that both silane and siloxane hydrolysis in terms of methanol and ethanol concentration increases with increase in the acid addition to the surfactant. However, the siloxane hydrolysis shows a lesser dependency on the acid addition whereas the hydrolysis of the silane greatly depends on the acid addition to the surfactant. The high hydrolysis rate of the siloxane may be attributed to the methoxy ether which is much more easily hydrolysed than ethoxy or longer alkoxy groups. The surfactant without acid addition shows the lowest hydrolysis rate of the silane/siloxane. The surfactants with acid addition at the ratio of HAc/16M2 at 0.1/1 or less show a similar effect to that of the surfactant without acid addition and a much lower silane hydrolysis rate than those of the higher acid addition. These results imply that the silane/siloxane hydrolysis rate, particularly the octyltriethoxysilane hydrolysis rate, in the silane/siloxane emulsion is low in weakly alkaline conditions. These results again confirm the acid-catalysed hydrolysis as the most important mechanism for silane/siloxane hydrolysis.

The hydrolysis of the silicones in the emulsion also depends on the concentration of the surfactant. Figure 4.19 shows the concentration effect on silane/siloxane hydrolysis in terms of both the methanol and the ethanol concentration in the emulsion. The emulsion contained 50% silane/siloxane at a ratio of 1:1 as the oil phase and was stabilised by Teric 16M2-3 (HAc/16M2 = 0.1/1 and pH 7.5) with concentration in the range from 0.25% to 4.17%.

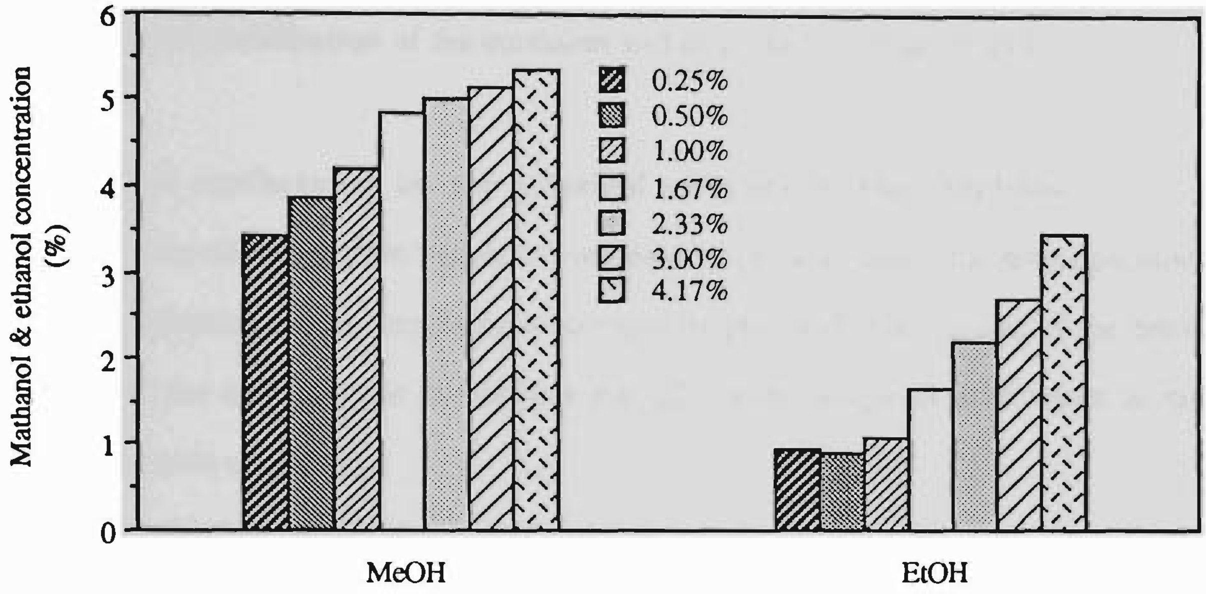


Figure 4.19 Methanol and ethanol concentration in OTES/OMMS emulsions after 6 months storage at room temperature

The test results in Figure 4.19 show that both silane and siloxane hydrolysis in terms of methanol and ethanol concentration increases with increase in the surfactant concentration in the emulsions. This may be explained by the hydrophobic interaction of the emulsion particles. However, the siloxane hydrolysis shows lesser relationship to the surfactant concentration whereas the silane hydrolysis greatly depends on the surfactant concentration. A surfactant concentration of 1% or less shows a much lower hydrolysis rate particularly for the silane hydrolysis.

As discussed before, the silane/siloxane hydrolysis in the emulsion appears to favour the acid-catalysed hydrolysis mechanism. Surfactant has a significant effect on the acceleration of the silane/siloxane hydrolysis in the emulsion. If the pH of the emulsion is reduced to 7 or less, the hydrolysis is further accelerated. The alkylamine ethoxylate and the acidified alkylamine ethoxylate surfactants show a lesser accelerating effect than that of either anionic or nonionic surfactants. The acidified alkylamine ethoxylates with acid addition ratio of HAc/16M2 at 0.1/1 or less and at concentration of 1% or less shows a low rate of silicone hydrolysis in the emulsions. The silane hydrolysis appears to be very dependent on the surfactant, whereas the siloxane shows relatively a higher hydrolysis rate with less relationship to the surfactant. However, the hydrolysis of the siloxane in the emulsion may impart physical stabilisation of the emulsion and this will be discussed in ξ4.3.

b) Effect of surfactants on the physical stability of the emulsion

Apart from the silicone hydrolysis effect induced by the surfactant, the major parameter in surfactant selection for the emulsion is to consider physical stabilisation of the emulsion. The role of the surfactant is to stabilise the oil droplet suspension in water to make a physically stable emulsion.

Many nonionic surfactants were used in the earlier stages of this research to develop silane/siloxane emulsions. However, the nonionic surfactants investigated could not stabilise the silane/siloxane emulsions. The surfactants used included; alkylalcohol ethoxylates (Teric series), alkylphenol ethoxylates (Teric series), alkylamine ethoxylates (Teric series with long EO chains), sorbitan ester (Span series) or ethoxylated sorbitan fatty acid esters (Tween series) and fatty alkyl polyglucosides (Alkadet). In addition, nonionic surfactants show a wetting effect (see Table 4.4) and an acceleration of hydrolysis (see Figure 4.17). Therefore, nonionic surfactants are found to be unsatisfactory surfactants for the development of silane/siloxane emulsions as water repellents for masonry materials. This poor performance of emulsions with nonionic surfactants has not deterred many workers from filing substantial patent protection for such technology [96, 97, 99].

Anionic surfactants such as sodium alkane sulphonate (Hostapur SAS60), isopropylamine alkylbenzene sulphonate (Gardilene IPA/94) and linear alkylbenzene sulphonic acid were found to be effective in stabilisation of silane/siloxane emulsions. However, the wetting effect induced by anionic surfactants is found to be significant (see Table 4.4). In addition, the acceleration of hydrolysis effect induced by the anionic surfactant is significant (see Figure 4.17). The hydrolysis of silicones, particularly that of the silane, is found to decrease the long term stability of the emulsion. Silane/siloxane emulsions stabilised by anionic surfactants were observed to have some bottom precipitation of gel within 6 months of storage at room temperature. Therefore, anionic surfactants were found to be ineffective in making silane/siloxane emulsions.

As discussed previously, cationic surfactants apart from acidified alkylamine ethoxylates are unsatisfactory in stabilising silane/siloxane emulsions unless a co-surfactant such as an alkylalcohol ethoxylate nonionic surfactant is used. It was found that cationic surfactants such as myristyltrimethyl ammonium bromide (Vantoc N40) or cetyltrimethyl ammonium chloride (Vantoc CC30) in combination with alkylalcohol ethoxylate nonionic surfactants such as Teric G9A2 as a co-surfactant can make a more stable silane/siloxane emulsion than those stabilised only with cationics. However, addition of nonionic surfactant may cause a wetting effect on the substrate surface. Further, long term stability of silane/siloxane emulsions stabilised by mixed cationic and nonionic surfactants was not sufficient and the emulsion was observed to separate within 6 months storage at room temperature. Therefore, either cationic surfactants or mixed cationic and nonionic surfactants may not be the ideal emulsifier for silane/siloxane emulsions.

Being cationic in nature but possessing some nonionic properties, alkylamine ethoxylate surfactant Teric 16M2 was found to be the best emulsifier for silane/siloxane emulsions in terms of imparting long term emulsion stability and achieving no surfactant wetting effect to the treated substrate surface. The effect of alkylamine ethoxylate surfactants on the physical stability of the emulsion is outlined below.

Apart from affecting the hydrolysis of silicones in the emulsion, addition of acid to the alkylamine ethoxylates also affects the surface activity of the surfactant. Figure 4.20 shows the change of interfacial tension at the oil/water interface with the addition of acid into the alkylamine ethoxylate surfactant. Interfacial tension is reduced by addition of acid into the surfactant until a minimum interfacial tension value is observed at a HAc/16M2 ratio of 0.1/1. Then the interfacial tension increases again with an increase in acid addition but tends to a constant value on further acid addition. The change of interfacial tension at the oil/water interface should affect the emulsion properties, for example, the emulsion particle size. Figure 4.21 shows the emulsion particle size change with different acid addition. The emulsion contained 50% OTES/OMMS at a ratio of 1:1 as the oil phase and was stabilised by 1% acidified alkylamine ethoxylate surfactant containing various amounts of acetic acid.

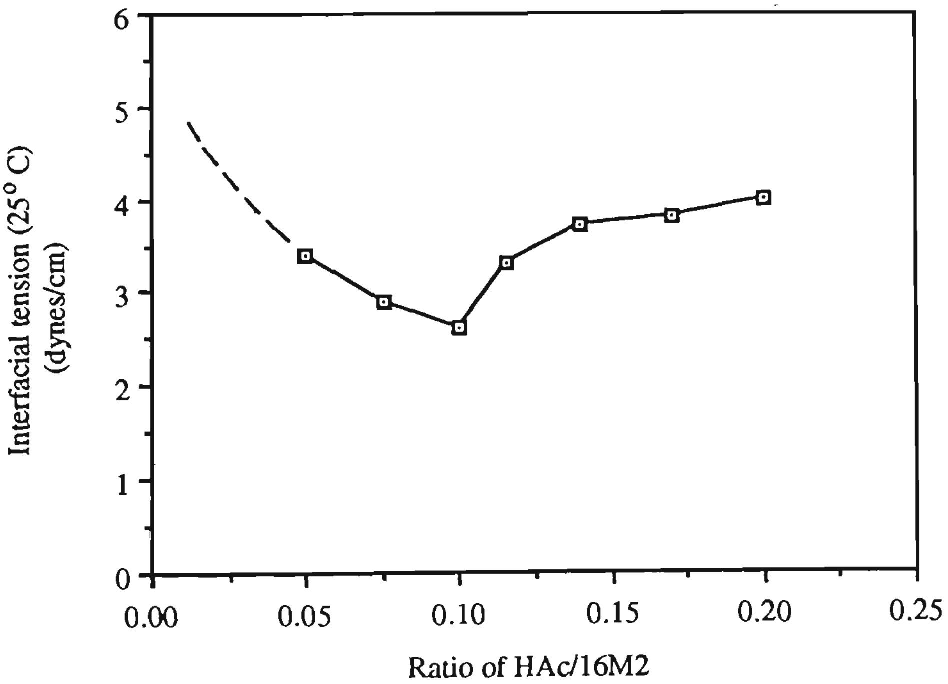


Figure 4.20 Relationship between interfacial tension at the oil/water interface and acid addition to the alkylamine ethoxylate surfactant (The dotted line is extrapolated as the surfactant is insoluble in aqueous phase in that range)

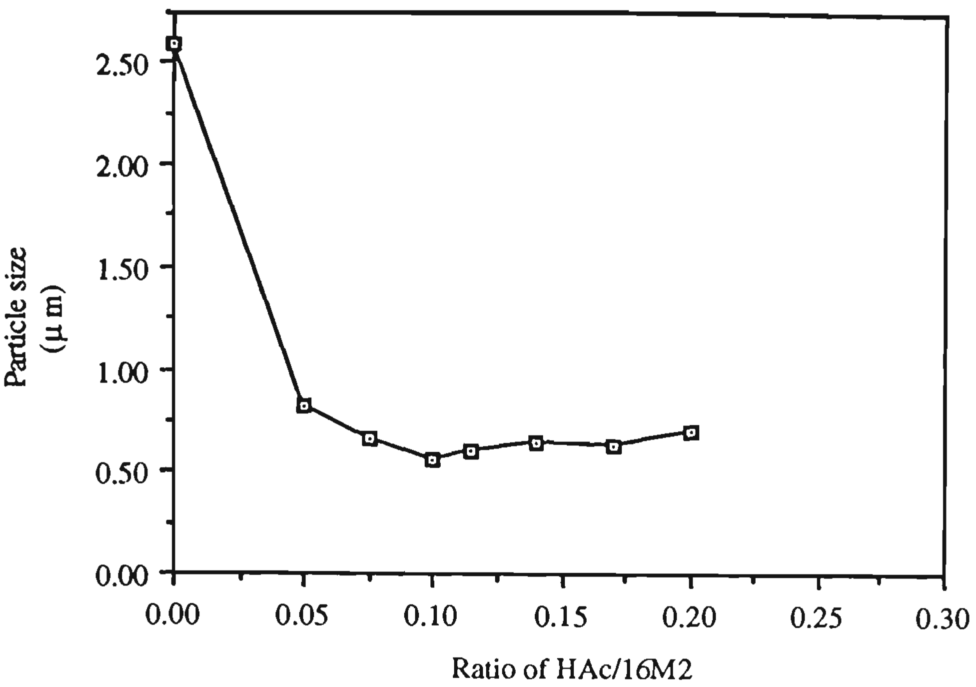


Figure 4.21 Relationship between particle size of emulsions and acid addition to the surfactant

The particle size decreases sharply with acid addition and then slowly decreases to a minimum at a HAc/16M2 ratio of 0.1/1. The particle size then increases slightly with the further increase in acid addition. In a comparison with interfacial tension change shown in Figure 4.20, the result of the particle size change is consistent with that of interfacial tension change. In addition, the particle size distribution is also affected by the acid addition to the surfactant. Results in Figure 4.22 show that the particle size distribution of the silane/siloxane emulsion stabilised by the surfactant with various acid additions. The best particle size distribution was exhibited by the emulsion stabilised by the surfactant with acid addition at a ratio of HAc/16M2 at 0.1/1. The results are also consistent with those shown in Figure 4.20.

The test results imply that addition of acid to the surfactant increases the surface activity of the surfactant resulting in improvement in the physical stability of the emulsion in terms of a reduction in particle size and a better particle size distribution. However, a further increase in acid addition at a HAc/16M2 ratio of over 0.1/1 contributes no further to an increase in the surface activity of the emulsifier. The results in the previous section have already shown that further increasing acid addition at a HAc/16M2 ratio of over 0.1/1 significantly increases the silicone hydrolysis. Therefore, a HAc/16M2 ratio of 0.1/1 may be the best ratio by a consideration of surfactant surface activity and surfactant effect on silicone hydrolysis.

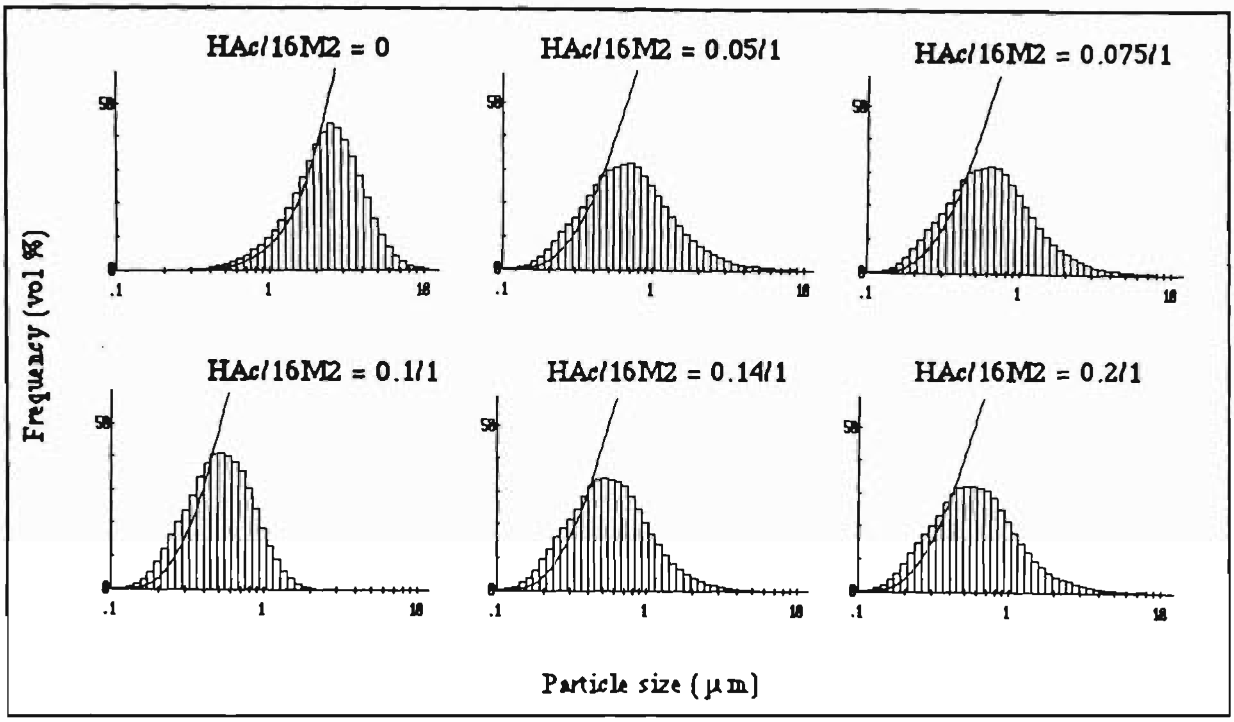


Figure 4.22 Relationship between emulsion particle size distribution and acid addition to the surfactants

The effect of the surfactant concentration on the physical properties of the emulsions is significant. Figure 4.23 shows the relationship between the interfacial tension at the oil/water interface and the concentration of the surfactant (Teric 16M2-3 with HAc/16M2 ration at 0.1/1). It is clear that increasing the surfactant concentration significantly decreases the interfacial energy at the oil/water interface. Consequently, the stability of the emulsion in terms of particle size and particle size distribution should be improved. Figure 4.24 shows that the particle size is significantly reduced with the increase in the surfactant concentration. Further, Figure 4.25 shows that the emulsion particle size distribution is improved with an increase in the surfactant concentration.

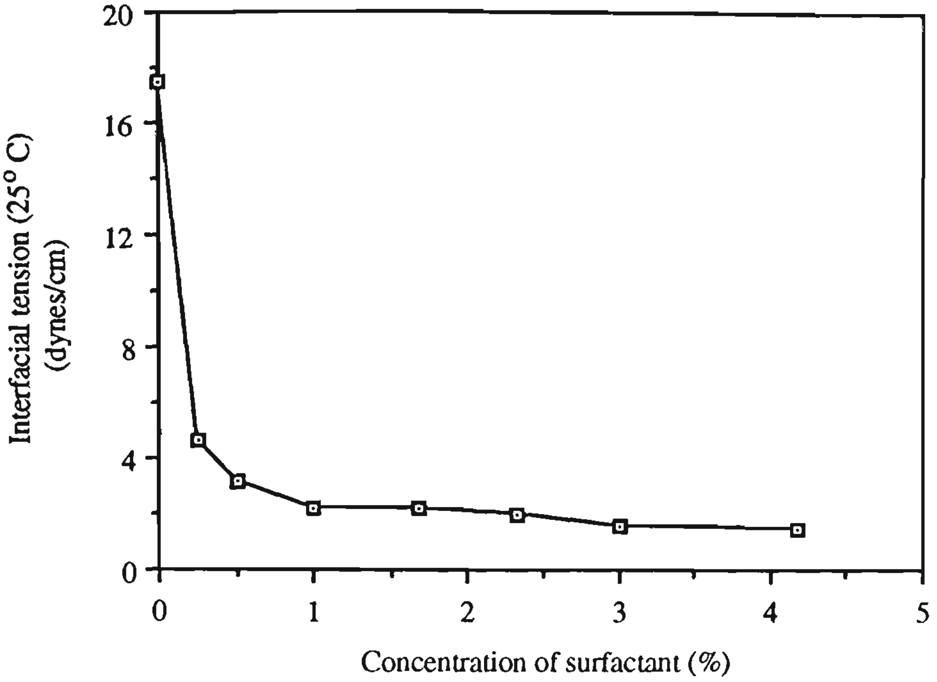


Figure 4.23 Relationship between the interfacial tension at the oil/water interface and the surfactant concentration (16M2-3) in relevant OTES/OMMS emulsion

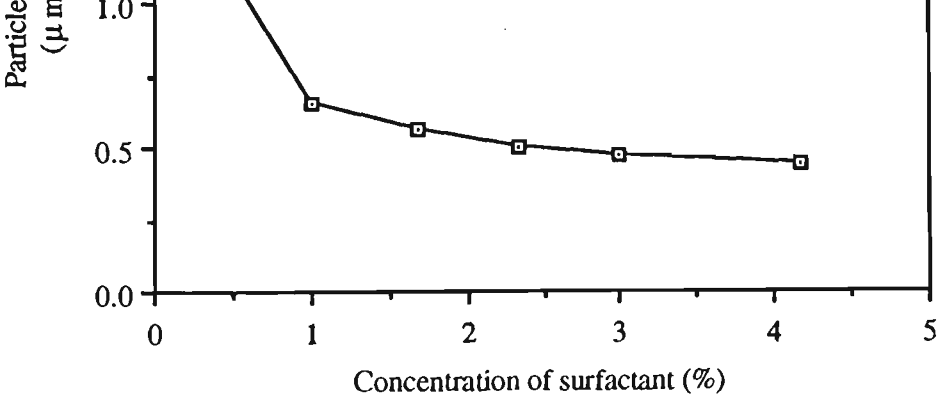


Figure 4.24 Relationship between particle size of OTES/OMMS emulsions and the surfactant (Teric 16M2-3) concentration

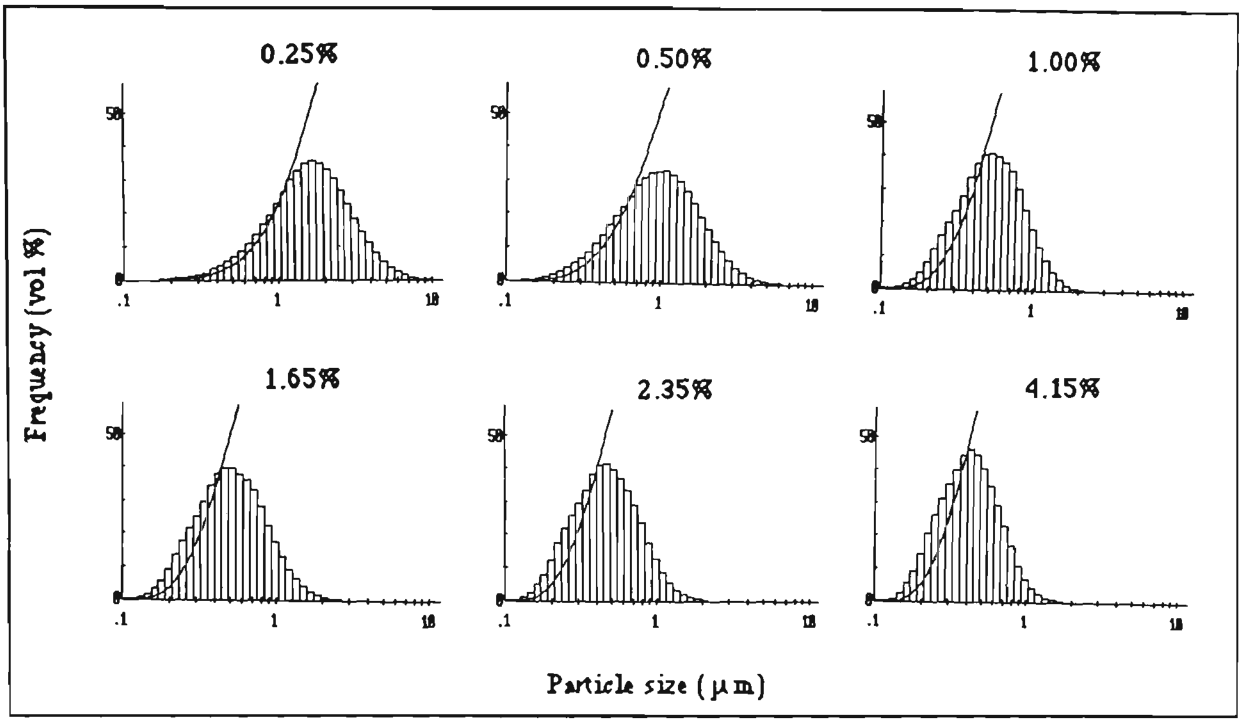


Figure 4.25 Relationship between particle size distribution of the OTES/OMMS emulsion and the surfactant concentration (16M2-3)

However, further increasing surfactant concentration over 1% makes no significant contribution to increasing the surfactant surface activity in terms of reducing the particle size and improving the particle size distribution. On the other hand, further increasing surfactant concentration greatly increases the hydrolysis rate, particularly that of the silane hydrolysis (see Figure 4.19). Therefore, the best surfactant (Teric 16M2-3) concentration is 1% . At this concentration, the surfactant shows almost the maximum surface activity but imparts almost a minimum hydrolysis effect.

4.2.3 Shear strength

To break the oil phase into an emulsion droplet to be dispersed in the aqueous phase, external energy must be provided. A shear mixer was used to provide external energy to the emulsifier system of the silane/siloxane emulsion. Shear strength used was found to greatly affect the emulsion stability. Figure 4.26 shows the relationship between the shear strength (shear speed) and the particle size of the emulsion. The emulsion contained 50%

OTES/OMMS at a ratio of 1:1 as the oil phase stabilised by 2.3% Teric 16M2-7 as a surfactant mixed at various speeds by a shear mixer for 10 minutes.

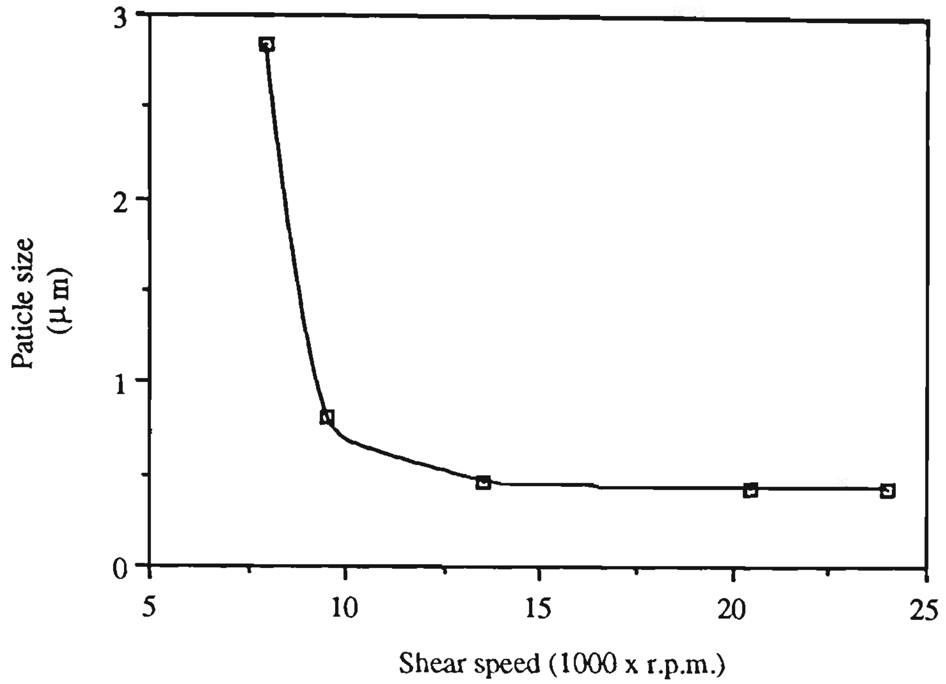


Figure 4.26 Relationship between the OTES/OMMS emulsion particle size and shear speed

The results show that increasing the shear speed provides more external energy to the emulsification system to greatly reduce the particle size of the emulsion. It is known that emulsions with smaller particle sizes are more physically stable [179]. In this case, it was observed that the silane/siloxane emulsions were not stable if a shear speed of less than 10,000 r.p.m. was used which gave relatively large particle size. In addition, the shear strength also affected the emulsion particle size distribution which is another important factor related to the emulsion stability. Figure 4.27 (A) shows the change in the particle size distribution with an increase in the shear speed. It is clear that the emulsion achieves a narrow distribution with an increase in the shear speed.

The time of shearing also affected the particle size and the particle size distribution. However, the particle size is less affected by the shearing time while the particle size distribution is improved with an increase in the shearing time. Figure 4.27 (B) shows the change in emulsion particle size distribution with the increase in shearing time.

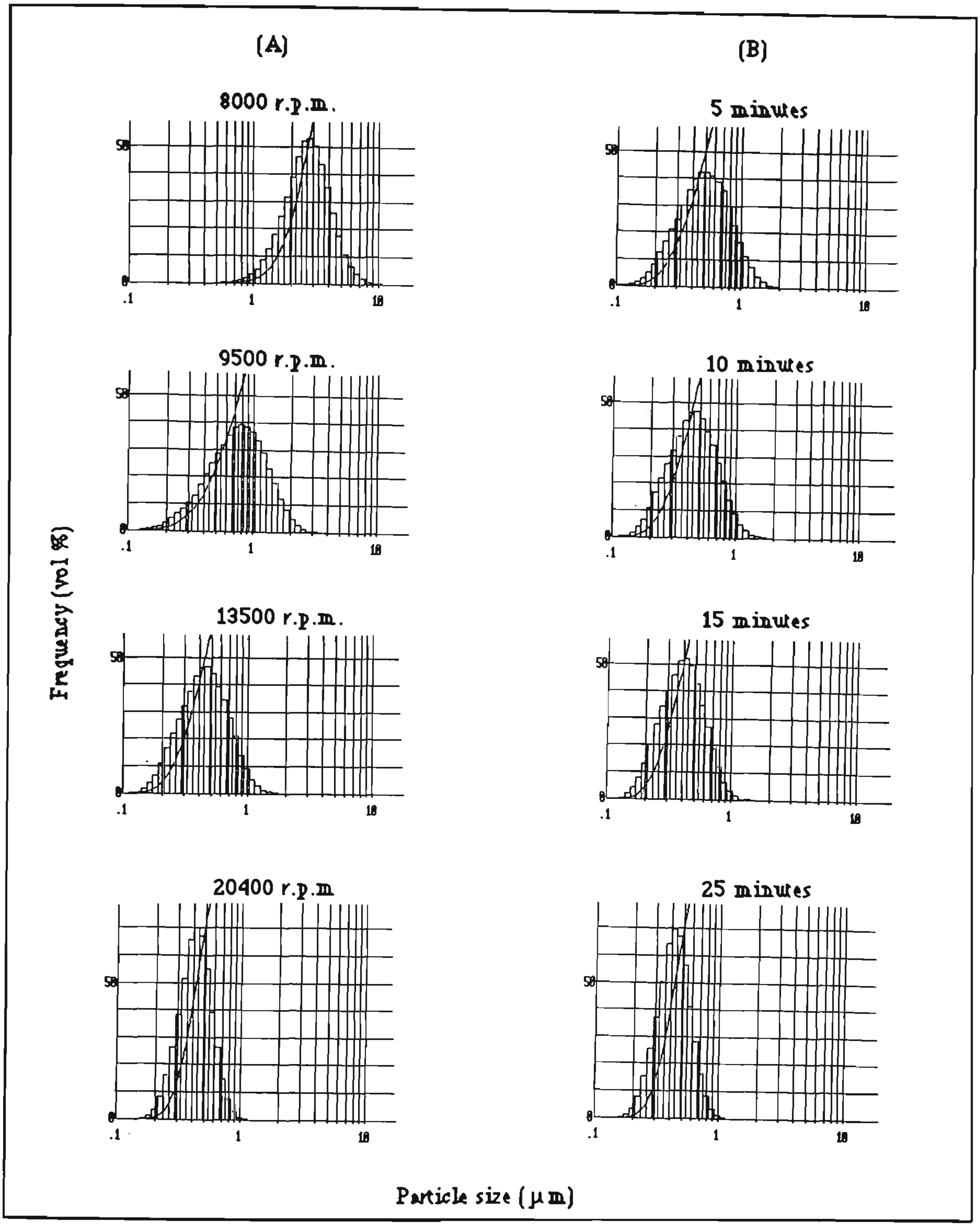


Figure 4.27 (A) and (B) *The change in the particle size distribution of the emulsions with; (A) a change of shearing speed at fixed shearing time of 10 minutes, (B) a change of shearing time at the fixed shearing speed of 13,500 r.p.m [Emulsions contained 50% OTES/OMMS at a ratio of 1:1 as the oil phase stabilised by 2.3% Teric 16M2-7]*

It may be concluded that emulsion stability in terms of emulsion particle size and distribution is greatly affected by shearing strength. Increasing the shearing speed significantly reduces the particle size while an increase in shearing time helps narrow the particle size distribution. However, it was found that, by shearing at 13,500 r.p.m. for 10 minutes, the particle size distribution was sufficient to make a stable emulsion. In fact, it was found that stable silane/siloxane emulsions are always obtained by shearing the emulsion at a speed of 13,500 r.p.m. for 10 minutes with the other factors which achieve the emulsion stability being in place. Further increasing the shearing strength cannot further significantly improve the stability of the silane/siloxane emulsion but may cause practical difficulties particularly in large scale production.

4.3 Proposed mechanisms of silane/siloxane emulsion stabilisation

The physical stabilisation of the emulsion may be attributed to the siloxane and the emulsifier. Basically, the siloxane and the surfactant may affect the formation of the interfacial film in the oil/water interface of the emulsion. Further, polysiloxane formed gradually by the hydrolysis and condensation of the siloxane in the emulsion may in turn impart a long-term stabilisation of the emulsion through polymeric stabilisation. In addition, the positive charge induced by the acidified alkylamine ethoxylate surfactant imparts an electric double layer to the emulsion droplet, which greatly improves the stability. The mechanism of the emulsion stabilisation is outlined below.

4.3.1 Interfacial film at the oil/water interface

4.3.1.1 Role of the surfactant in interfacial film formation

It has been found that the stability of the silane/siloxane emulsion stabilised with a cationic surfactant apart from acidified alkylamine ethoxylates is less than that of the emulsion with a mixture of a cationic and a nonionic surfactant. Rubingh and Jones [189] found that mixed cationic and nonionic surfactants have better surface activity in another system. The stability of the emulsion made with mixed surfactants is due to the formation of a coherent interfacial film. It is known that a coherent interfacial film at the oil/water interface imparts a rigid barrier which possesses greater strength and resistance to emulsion coalescence [190]. Cationic surfactants orient at the interface to form positively charged interfacial films which impart electrical repulsion between the particles to resist particle coalescence. On the other hand, the repulsive force between the positively charged nitrogen of the surfactant molecules in the interface in the single surfactant emulsion may cause instability of the orientation of the surfactants. The surfactant may then leave the interface resulting in a failure in stabilising the emulsion. Introducing another surface active substance consisting of neutral molecules such as a nonionic surfactant effectively between the cationic surfactant molecules reduces the effect of electrostatic repulsive forces between the oriented cationic surfactants. A coherent mixed film with a neutral surfactant molecule between the positively charged cationic surfactant in the interface is then formed resulting in a stable interfacial film to give a stable emulsion. Figure 4.28 shows diagrammatically a coherent mixed film according to Rao [190]. In the case of the silane/siloxane emulsion made with a cationic and a nonionic surfactant, the coherent film may consist of a quaternary ammonium cationic surfactant and an alkylalcohol ethoxylate nonionic surfactant on adjacent sites.

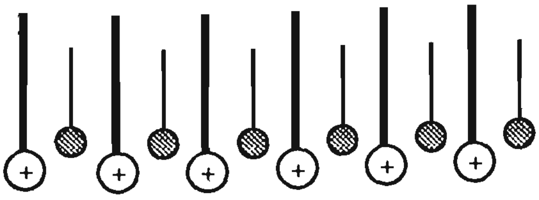


Figure 4.28 Mixed coherent film consisting of a cationic and a nonionic surfactant

Similarly, the interfacial film formed by an alkylamine ethoxylate surfactant, particularly the acidified alkylamine ethoxylate surfactant in the silane/siloxane emulsion, is assumed to have the same properties as that of the mixed cationic and nonionic surfactant. When forming an interfacial film at the oil/water interface, the ethoxylate chains in the surfactant may greatly reduce the electrostatic repulsion between the positively charged ammonium head groups by both charge shielding and steric hindrance. Therefore, the interfacial film formed by the acidified alkylamine ethoxylate is assumed to be more stable than a single cationic surfactant. Although this interfacial film is composed of only one surfactant, the interfacial film may be similar to that formed by a quaternary ammonium cationic surfactant with an alkylalcohol ethoxylate nonionic surfactant. Therefore, a coherent interfacial film formed by the acidified alkylamine ethoxylate surfactant is an important factor in stabilisation of the silane/siloxane emulsion.

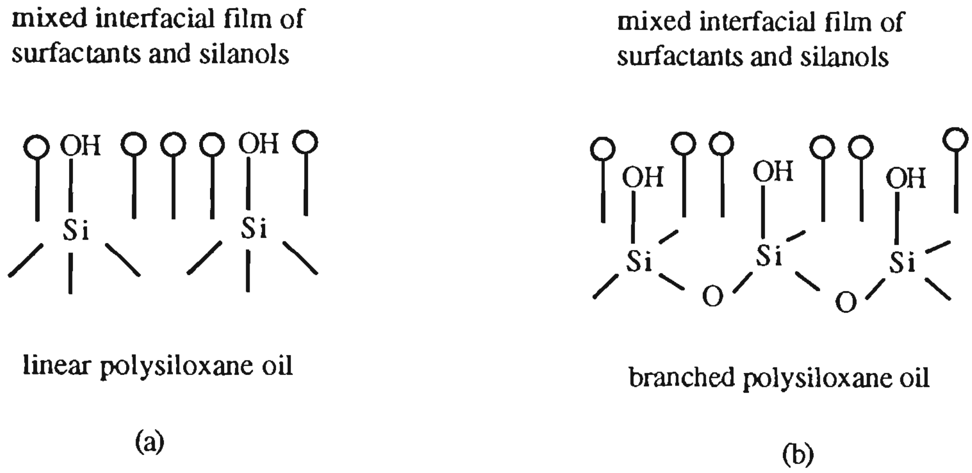
In addition, the acidified alkylamine ethoxylate surfactant used in the silane/siloxane emulsion is not fully neutralised at the HAc/16M2 ratio of 0.1/1 and at pH 7.5 (e.g. Teric 16M2-3). Stoichiometric calculation shows that 1 part of Teric 16M2 needs at least 0.17 part of acetic acid to neutralise the amine in the surfactant. In addition, the amine is a weak base and full protonation may not be obtained unless a large quantity of acetic acid is added. Therefore, only part of the alkylamine ethoxylate present may be acidified and some free amine would still exist in the emulsifier system [191]. As discussed previously, addition of acid into the alkylamine ethoxylate surfactant greatly increases the solubility of the surfactant (see Table 2.1). This implies an increase in the HLB of the emulsifier which is acidified while the HLB of the unacidified surfactant remains low. The acidified alkylamine ethoxylate is assumed to have a HLB of greater than 13 as it can dissolve in water to form a clear aqueous solution according to Becher [178]. The initial Teric 16M2 is insoluble and has a HLB of 9.5. However, in the partially acidified surfactant system, the unacidifed amine may be solubilised by the acidified amine surfactant resulting in formation of a clear aqueous surfactant solution. In fact, the emulsifier system of the silane/siloxane emulsion becomes a mixture of surfactants containing one with a high HLB and one with a low HLB (both of them are assumed to be cationic in nature with ethylene oxide nonionic moieties, see ξ4.2.2.1 and ξ4.3.2). Therefore, the mixed interfacial film must be formed in the oil/water interface with mixed surfactants. It is known that emulsions made with two primary surfactants, one soluble in water and the other in oil, can greatly enhance the stability of an emulsion according to Myers [165] and Becher [178]. It is believed that the effect is related to the production of very low interfacial tensions and the formation of cooperative surfactant complexes in the interface of the emulsion to impart greater strength and coalescence resistance to the oil/water interface [165].

Figure 4.20 shows the appearance of a minimum interfacial tension and the relationship between interfacial tension and acid addition to the surfactant is due to the formation of surfactant complexes of one with low HLB and the other with high HLB. The minimum interfacial tension value exists where the two surfactants are in the right proportion or a correct HLB value is obtained. At the best ratio of two surfactants or the best HLB (e.g. when HAc/16M2 is 0.1/1), the surfactant complex imparts the best surface activity to the emulsifier system resulting in the best stability of the emulsion in terms of imparting the smallest particle size and the best particle size distribution (see Figure 4.21 and 4.22). The system with a ratio of HAc/16M2 at either less than 0.1/1 or more than 0.1/1 acts more as a homogeneous surfactant system of either a low HLB or a high HLB surfactant.

4.3.1.2 Role of the siloxane (OMMS) in interfacial film formation

The particle size detailed in Figure 4.15 shows that the emulsion with the smallest particle size is the one made with the mixed silane and siloxane as the oil phase. In practice, it was observed that the emulsions made with pure silanes of either BTES or OTES were not physically stable and stable emulsions can only be made if mixed silane/siloxane or the pure siloxane is used as the oil phase. Therefore, the siloxane as well as the surfactant is believed to play an important role in stabilisation of the silane/siloxane emulsion. Vergelati et al.[192] have disclosed that polydimethylsiloxanes (PDMS) take part with the surfactant in the formation of the interfacial film at the oil/water interface by participation of their hydroxyl groups. The theoretical models of the mixed interface of surfactants and the silanols of the polysiloxanes as discussed by Vergelati et al. are shown in Figure 4.29.

Therefore, the siloxane in the silane/siloxane emulsion may be assumed to join in the formation of the interfacial film with the surfactant to contribute to the stabilisation of the emulsion. It has previously been shown by HSGC analysis that the hydrolysis of the methoxy ether of the siloxane upon formation of the emulsion is significant. According to Osterholtz and Pohl [75], the initial product of the hydrolysis of the methoxy ethers in siloxanes are the siloxanols and then the siloxanols gradually disappear with the formation of polysiloxane by molecular condensation. Figure 4.12 shows that the initial methanol concentration upon formation of the silane/siloxane emulsion was about 3% based on the siloxane in the emulsion and this implies that partial hydrolysis of the siloxane must occur upon formation of the emulsion. It has been shown by Vergelati et al. [192] that the interfacial energy between an oil/water interface is sensitive to very small variations in the number of hydroxyl groups in the siloxane. Therefore, hydrolysis of the siloxane with formation of siloxanols may greatly decrease the direct interfacial energy at the oil/water interface.



(a)

(b)

Figure 4.29 Interfacial film of surfactants and silanols at the oil/water interface of polysiloxane emulsions; (a) linear polysiloxane oil, and (b) branched polysiloxane oil

From Figure 4.14 and Figure 4.15, it is now clear that the role of the static interfacial tension in the stabilisation of the silane/siloxane emulsion particularly in controlling the emulsion particle size is doubtful. Firstly, the static interfacial tension is an ideal state in which the surfactant is assumed to be fully adsorbed between the oil/water interface. However, in the dynamic environment of an emulsion system, the droplet is disrupted by homogenisation in a very short time. The interface at the time of droplet disruption can not be covered with a saturated monolayer of surfactant since the diffusion of surfactant molecules to the interface of the oil droplet to lower the interfacial tension will require a finite amount of time. This phenomenon has been discussed by Nakajima et al.[185]. Secondly, static interfacial tension cannot include the contribution of the hydrolysis of siloxane with formation of silanols to reduce the interfacial energy between the oil and water during formation of the emulsion. Therefore, static interfacial tension cannot fully explain the change in the particle size with the change of the proportion of the silane/siloxane in the emulsion as shown in Figure 4.14 and 4.15. However, the decrease in the interfacial energy attributed to the hydrolysis of the siloxane can then be regarded as the cause of the decrease in the dynamic interfacial tension which becomes the most important factor in controlling the particle size of the emulsion during the emulsification.

In addition to improved surface energetics, a possible beneficial effect of the siloxane is the formation of an interfacial complex with the surfactant in the emulsion oil/water interface. Current emulsion science contends that interfacial tension effects are less important to overall long-term emulsion stability than are the effects of the nature of the interfacial film [165]. The interfacial film in the oil/water interface of the silane/siloxane emulsion contains surfactant and those siloxane molecules which possess hydroxyl groups due to hydrolysis. Furthermore, the interfacial film may also include some higher molecular weight siloxane (linear or branched) because condensation between the siloxanols ultimately increases the molecular weight of the siloxane. Such an interfacial film is assumed to provide a rigid and highly viscous or elastic barrier at the interface capable of preventing or retarding the coalescence of droplets which would result from random Brownian motion, thermal convection, or mechanical agitation. Myers [165]and Becher [178] have described the composition of such interfacial films. In addition, such a mixed interfacial film has a close molecular packing density and significant lateral interaction between hydrophobic chains resulting in a decrease in the mobility of molecules at the interface. A possible representation of the interfacial film in the silane/siloxane emulsion would be similar to those reported by Vergelati et al. in a different system [192] (as shown in Figure 4.29).

Apart from formation of the interfacial film, the polysiloxane may contribute a stabilisation effect in terms of polymeric (or steric) stabilisation. Polymeric stabilisation has been discussed in detail by Napper[180]. Upon formation of the emulsion and during further storage polysiloxane molecules may be formed due to molecular condensation. It has been previously shown that the hydrolysis of the siloxane gradually increases with an increase in the emulsion viscosity during long-term storage and this implies the formation of polysiloxane. The polysiloxane can adsorb at the interface to keep the emulsion oil droplets apart and reduce the Van der Waals attractive forces and give rise to a repulsion between the particles. Such an occurrence is in accord with the principles of emulsion stability[180, 193, 194]. Following the increase in polysiloxane concentration in the emulsion, the polymeric stabilisation may become effective in stabilisation. Figure 4.30 shows that the particle size of the silane/siloxane emulsion after 10 months storage at room temperature remained almost unaffected. Therefore, polymeric stabilisation may play an important part.

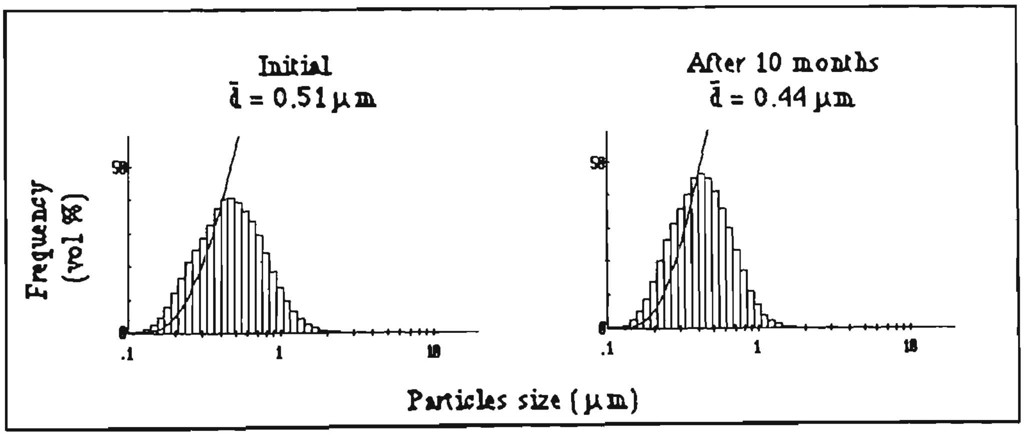


Figure 4.30 Particle size and the particle distribution of the OTES/OMMS emulsion after 10 months storage at room temperature (Emulsion contained 50% oil phase and 1% Teric 16M2-3 mixed at 13,500 r.p.m. for 10 minutes)

The instability of silane emulsions (BTES or OTES) with large particle sizes shown in Figure 4.15 may then be clarified. Firstly, the dynamic interfacial tension may be high during emulsification resulting in a large particle size in the emulsion because there is no siloxane in the oil phase. In addition, poor interfacial film due to the lack of siloxane causes poor stability of the emulsions. Addition of the siloxane into the silane sharply decreased the particle size and significantly improved the stability of the emulsions in practice. Although further increase of the siloxane ratio to where the siloxane proportion was greater than 50% in the oil phase gradually increased the particle size of the emulsion, it was observed that these emulsions including the pure siloxane emulsion were stable. Stability of the emulsion is obviously attributable to the siloxane in the emulsions. The slight increase in the particle size with further addition of the siloxane above 50% in the oil phase may be due to the increase in the viscosity of the oil phase induced by the addition of the viscous siloxane. According to Wu [195], the particle size of emulsions is proportional to the viscosity of the internal phase (or dispersed phase) of an oil in water emulsion when the ratio of the viscosity of the dispersed phase to the continuous phase is greater than 1. This is expressed in Equation 4.2:

$$p_d / \sigma = 4 (\eta_d / \eta)^{0.84} / G \eta \qquad (4.2)$$

where p_d is the particle size of the dispersed phase, σ is the interfacial tension at the oil/water interface, η_d is the viscosity of the dispersed (internal) phase, η is the viscosity of the continuous phase and G is the shear rate.

The viscosity change of the oil phase of a siloxane emulsion with different additives is shown in Figure 4.6. Figure 4.31 shows the change in particle size of siloxane emulsions with the concentration of organic additives comprising silanes or solvents in the siloxane phase of the emulsions. The particle size decreases continuously with an increase in the additive concentration in the oil phase until the level of 50% of additives is reached. These results confirm that the increase in the particle size with increase in the siloxane concentration in the oil phase is induced by the increase in the viscosity of the oil phase.

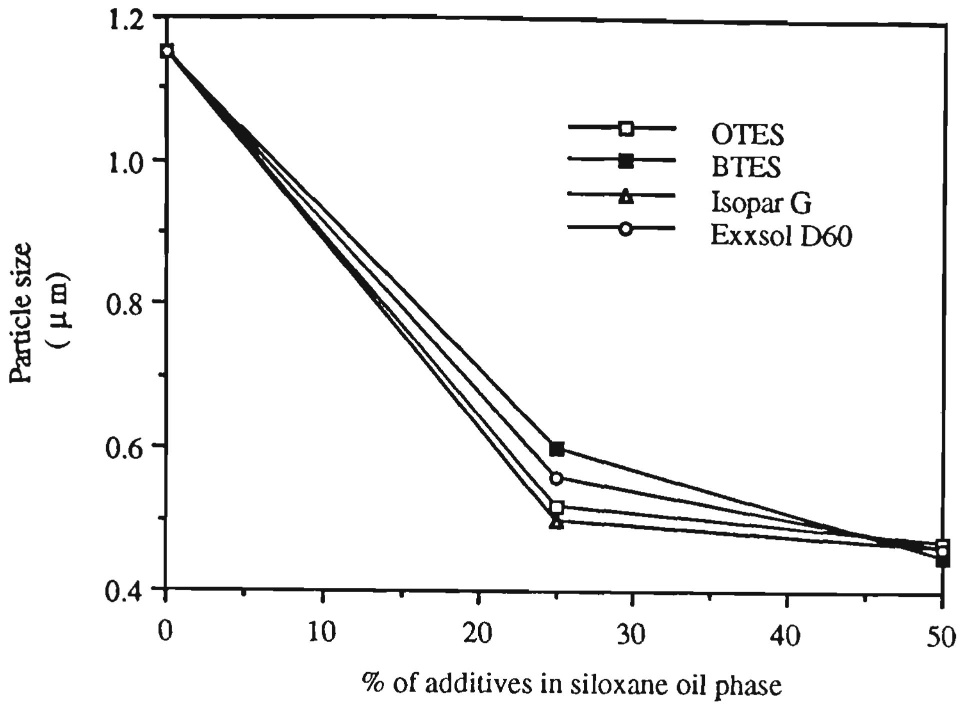


Figure 4.31 Relationship between the particle size and the concentration of organic additives in oil phase of siloxane emulsion (Emulsion contained 50% oil phase and 2.3% Teric 16M2-7 surfactant mixed at 13,500 r.p.m. for 10 minutes)

4.3.2 Electric double layer

Another most important property of the interfacial film in emulsion stabilisation is the charge on the interface termed the electric double layer [165, 178, 179]. Due to the same charge on the particle surfaces, the electric double layers can impart significant potential repulsion between the charged particles to resist the coalescence of the emulsion droplets. As discussed in ξ4.2.2.2, almost all general nonionic surfactants cannot stabilise silane/siloxane emulsions. Ionic surfactants may be used as the emulsifiers. It is generally known that ionic surfactants can introduce electric charge to the emulsion particles [165, 178, 179]. This implies that the formation of electric double layers may be another key factor in controlling the stabilisation of silane/siloxane emulsions. Table 4.7 lists the zeta potential values of emulsions stabilised by various surfactants. Emulsions contained 50% OTES/OMMS at a ratio of 1:1 as the oil phase and 1% surfactant mixed at 13,500 r.p.m. for 10 minutes.

***Table 4.7** Zeta potential and some properties of the emulsions stabilised by various surfactants*

Surfactant used in emulsion	pH of surfactant	Zeta potential of emulsion (mV)	Optical stability of emulsion
Hostapur SAS 60	6.2	-96.6	stable emulsion
Teric G16A16	5.2	-1.9	broke within 24 hrs
Teric 16M15*	8.9	-9.3	creamed within 24 hrs
Teric 16M5*	9.0	+16.8	creamed slightly within 24 hrs
Teric 16M2*	9.3	+51.8	stable emulsion

* pH was read by a pH meter (see ξ2.3.9).

The results confirm that the stability of silane/siloxane emulsions is highly dependent on the zeta potential of emulsions. The emulsion stabilised by anionic surfactant Hostapur SAS60 had a high zeta potential value (negative charge) and therefore it was stable. However, the emulsion stabilised by nonionic surfactant Teric G16A16 had a very short life due to almost zero charge of the particles. In the case of emulsions stabilised by alkylamine ethoxylate surfactants, the stability of emulsions depends on the surfactant ethoxylate chains or the zeta potential value of the emulsions. Surfactant with a long ethoxylate chain (Teric 16M15) behaved similarly to a nonionic surfactant because the emulsion had a low but negative zeta potential value resulting in an unstable emulsion. Surfactant with a short ethoxylate chain (Teric 16M5) behaved similarly to a cationic surfactant. However, the zeta potential value may not be large enough to stabilise the emulsion and therefore the emulsion was not stable. The surfactant with very short ethoxylate chains behaved more like a cationic because the zeta potential value was relatively high resulting in a stable emulsion. As discussed in ξ4.2.2.1, indirect evidence has shown that the alkylamine ethoxylate surfactant with short ethoxylate chains such as Teric 16M2 is cationic in nature. The test results in Table 4.7 confirms this.

It has been discussed in ξ4.2.2.2 that addition of acid into an alkylamine ethoxylate surfactant (e.g. Teric 16M2) changes the properties of the surfactant. Addition of acid into the surfactant is assumed to increase the positive charge in the surfactant resulting in increasing the zeta potential of the emulsion. Table 4.8 shows the zeta potential values of silane/siloxane emulsions and the properties of the emulsions stabilised with either acidified or unacidified alkylamine ethoxylate surfactant. Emulsions contained 50% OTES/OMMS at a ratio of 1:1 as the oil phase and 1% surfactant mixed at 13,500 r.p.m. for 10 minutes. The zeta potential increased with increase in the acid addition. However, all the emulsions were stable. Although the emulsion with unacidified 16M2 had large particle size, the stability of the emulsion remained unaffected. The stability of the emulsion may be explained by the surfactant imparting significant positive charge to the interfacial film to induce electric double layers which impart significant electric repulsion between the particles to resist coalescence. It is known that an emulsion which has an absolute zeta potential value of up to 20 mV is stable as general rule [196]. The emulsion stabilised by unacidified Teric 16M2 had a zeta potential of 51.8 mV and therefore the emulsion was stable. The particle size may depend on the shearing strength and interfacial tension (static and dynamic) which is controlled by the surfactant surface activity or the properties of the oil phase. However, the stability of an emulsion may be highly dependent on the properties of the interfacial film and the charge of the particles.

Table 4.8 Zeta potential and some properties of the emulsions

Surfactant used in emulsion*	pH of surfactant	Zeta potential of emulsion (mV)	Particle size of emulsion (μm)	Optical stability of emulsion
Teric 16M2*	9.3	+51.8	2.59	stable
Teric 16M2-3	7.5	+74.9	0.56	stable
Teric 16M2-8	6.5	+89.4	0.71	stable

* pH was read by a pH meter (see ξ2.3.9).

In order to further illustrate the emulsion stabilisation by the electric double layer induced by the cationic surfactant, a test was carried out to examine the effect of anions on the stability of the emulsion made with 1% Teric 16M2-3. Addition of chloride anions (NaCl), and sulphate anions (Na_2SO_4), was undertaken. Different concentrations of anions were added to the emulsion and then it was centrifuged at 4,000 r.p.m. at room temperature for times up to 400 minutes. The emulsion was observed to break and the organic oil phase then separated during the centrifuge process. The volume percentage of oil separated from the emulsion was recorded at different periods and is shown in Figure 4.32. The results show that the oil separation rate sharply increased with an increase in the anion concentration. In addition, an increase in the charge of the anion significantly increased the oil separation rate.

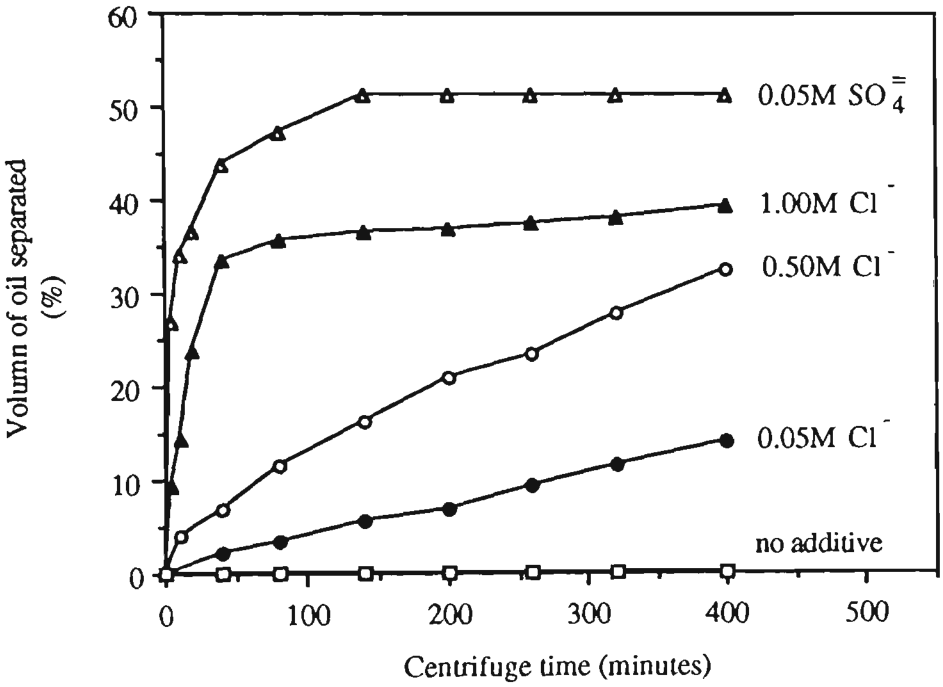


Figure 4.32 Oil separation rate of the emulsion by addition of Cl^- and $SO_4^=$ and centrifuging (Emulsion contained 50% OTES/OMMS as the oil phase and 1% Teric 16M2-3 surfactant mixed at 13,500 r.p.m. for 10 minutes)

It may be concluded that the breaking of the emulsion was due to the collapse of the electric double layers of the emulsion particles. The anions can destroy the positively charged particles by adsorption of the oppositely charged anions resulting in a reduction in the thickness of the double layers. The repulsive potential between the charged emulsion particles is then significantly reduced resulting in flocculation, coalescence and the eventual breaking of the emulsion. Either increasing concentration of the anion or the charge of the anion exacerbates the effect of the breaking of the emulsion.

4.4 Preferred silane/siloxane emulsion composition

Throughout this research, it was found that both the surfactant and the silicones in the organic phase, particularly the siloxane, affect the chemical and physical stability of the emulsion. In addition, the impregnation performance is significantly affected by the silanes and siloxanes used in the emulsion. Further, almost all types of surfactants impart more or less wetting effect to treated substrates except for the cationic surfactants. The modified alkylamine ethoxylate surfactant (Teric 16M2) used in this research is a cationic surfactant in nature and significantly improves the stability of the emulsion.

The preferred silicone emulsion as a water repellent for masonry substrates as determined herein was the silane/siloxane emulsion made with acidified alkylamine ethoxylate surfactant (Teric 16M2-3). The preferred silane was the octyltriethoxysilane (OTES) and the siloxane was the octyl/methyl methoxysiloxane (OMMS) in a proportion of 1:1 as the oil phase. The emulsion contained 50% silicone as the oil phase. The preferred surfactant was the alkylamine ethoxylate Teric 16M2 with addition of acetic acid at the ratio of 0.1/1. The surfactant concentration in the emulsion was controlled at 1% and dissolved in the aqueous phase before making the emulsion. The emulsion was homogenised with a shear mixer at the shearing rate of 13,000 r.p.m. or more for about 10 minutes or more. The emulsion made under the above conditions was stable and can impart significant water repellency to masonry substrates without achieving a surfactant wetting effect. The preferred emulsion composition is shown as follows and the related emulsion properties and the impregnation performance have been listed in Table 4.1:

Organic phase:	Octyltriethoxysilane (OTES)	12.0 gram
	Octyl/methyl methoxysiloxane (OMMS)	12.0 gram
Aqueous phase:	Teric 16M2-3 (10% aqueous solution)	2.4 gram
	Distilled water	9.6 gram
Total emulsion:	(50% OTES/OMMS)	24.0 gram

The emulsification was carried out by adding the organic mixture dropwise into the aqueous phase during 1 minute with constant shearing. After completing the organic addition a further shearing was applied for 10 minutes (also refer ξ2.2.3).

4.5 Application data for the silane/siloxane emulsion

In order to examine the water repellent performance of the silane/siloxane emulsion on various masonry substrates, various tests were conducted (refer to Chapter 2). The silane/siloxane emulsion was made according to ξ4.4. The substrates included 4 week old DIN 1164 cement mortar discs, Indian fired bricks and mud bricks. Mud bricks were impregnated with 79 g/litre sodium silicate 24 hours before silicone water repellent impregnation. Firstly, the effect of concentration of the silane/siloxane emulsion on the impregnation performance of masonry substrates was studied by impregnating the substrates with the silane/siloxane emulsion at various concentrations (shown in Table 4.9). It was generally found that 2% emulsion did not impart satisfactory impregnation performance in terms of impregnation depth and resistance to water penetration (e.g. mud brick substrate). However, 5% emulsion can render the various substrates water repellent. Further increasing the emulsion concentration up to 10% did not significantly improve the impregnation performance but would increase the cost of the treatment. Therefore, dilution of the emulsion to 5% may be the best suitable concentration for various substrates. Further test results also confirmed this.

A comparison of the emulsion with organic solvent-based siloxane impregnant was carried out. The silane/siloxane emulsion was diluted to 5% and then applied to the substrates by the methods described in Chapter 2. A 5% solvent-based siloxane solution (OMMS-Sn in Isopar G) was used as the comparison sample for each test. Untreated substrates were examined as the control. Mud bricks were impregnated with 79 g/litre sodium silicate 24 hours before silicone water repellent impregnation. Application conditions are listed in Table 4.10. The test results are outlined in the following discussion.

Table 4.9 Effect of emulsion concentration on the impregnation performance of substrates

Substrates	Concentration of the emulsion %	Beading effect	Depth of impregnation (mm)	Water absorption (7 days) (kg/m^2)
Cement mortar	2	1-2	1	0.56
	5	1-2	2-3	0.50
	10	2	3	0.48
Indian fired brick	2	2	4-11	0.03
	5	2	20	0.06
	10	2	20	0.08
Mud brick	2	2	1	2.78
	5	2	2	0.76
	10	2	3	0.59

Table 4.10 Impregnant consumption on various substrates at ambient conditions

Substrates	Impregnant consumption (kg/m^2)	
	5% OTES/OMMS emulsion	5% OMMS-Sn in Isopar G
Cement mortar	0.453	0.430
Indian fired bricks	0.487	1.423
Mud bricks*	0.689	0.917

* Consumption of 79g/litre sodium silicate solution was 0.998 kg/m^2.

4.5.1 Beading effect

The beading effect of various treated substrates is shown in Table 4.11. The beading effect of the substrates treated with 5% silane/siloxane emulsion impregnant was significant for three kinds of substrates. No surfactant wetting effect was observed for treated substrates. The results for beading effect were very similar to those of the substrates treated with the solvent-based siloxane impregnant. Good beading effect implies that the silane/siloxane emulsion has a good reactivity and significant film-forming effect to the various substrates including either alkaline or neutral substrates. This shows that the silane/siloxane emulsion developed herein is effective in effecting the water repellency of various substrates.

Table 4.11 *Beading effect of various substrates treated with water repellents*

Impregnants	Cement mortar	Indian fired brick	Mud brick
5% silane/siloxane emulsion	1-2	2	2
5% OMMS-Sn in Isopar G	2	2	2
Untreated	7	7	7

4.5.2 Water absorption and alkali stability

Long term (24 weeks) water absorption tests were conducted on cement mortar, Indian fired brick and mud brick substrates to examine the water repellent performance of the silane/siloxane emulsion impregnant. The water absorption test results are plotted in Figure 4.33(A-C). The test results indicate that water absorption of all the substrates treated with 5% silane/siloxane emulsion are significantly reduced and the emulsion achieves equivalent results to those of the 5% solvent-based siloxane impregnant. The novel silane/siloxane emulsion was found to be as effective as solvent-based siloxane impregnant for not only alkaline substrates but also for the non-alkaline substrates such as Indian fired bricks and mud bricks. In contrast, siliconate impregnants based on either PMS or POMS showed slightly higher water absorption than OMMS-Sn for the non-alkaline substrates (see ξ3.4.2). It may be concluded that the silane/siloxane emulsion is suitable to render various substrates water repellent and the effectiveness is equivalent to the solvent-based siloxane impregnant.

The alkali stability in terms of the 10% KOH absorption test was carried out on 4 week old DIN 1164 cement mortar substrates. The test results are plotted in Figure 4.34. The test results show that the silane/siloxane emulsion imparted the substrate with significant alkali stability and achieved a slightly better test result than that of the substrate treated with 5% solvent-based siloxane impregnant. The excellent alkali stability of the silane/siloxane emulsion may be attributed to the presence of octyltriethoxysilane (OTES) and octyl/methyl methoxysiloxane (OMMS). Both of the silicones are highly alkali stable due to the long hydrocarbon substituents.

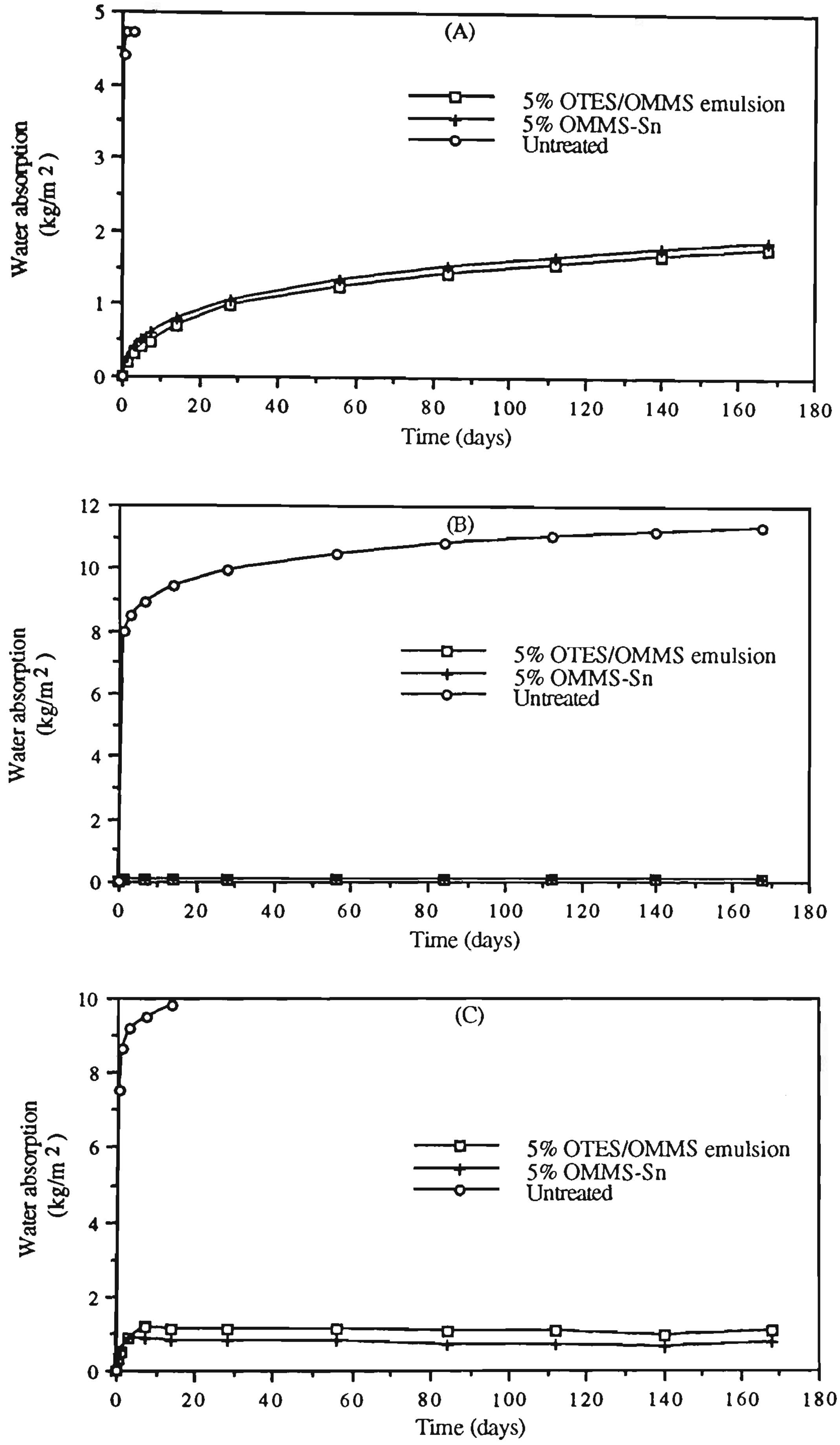


Figure 4.33 *Water absorption of; (A) cement mortar, (B) Indian fired bricks, and (C) mud bricks treated with 5% silane/siloxane emulsion and 5% siloxane impregnants*

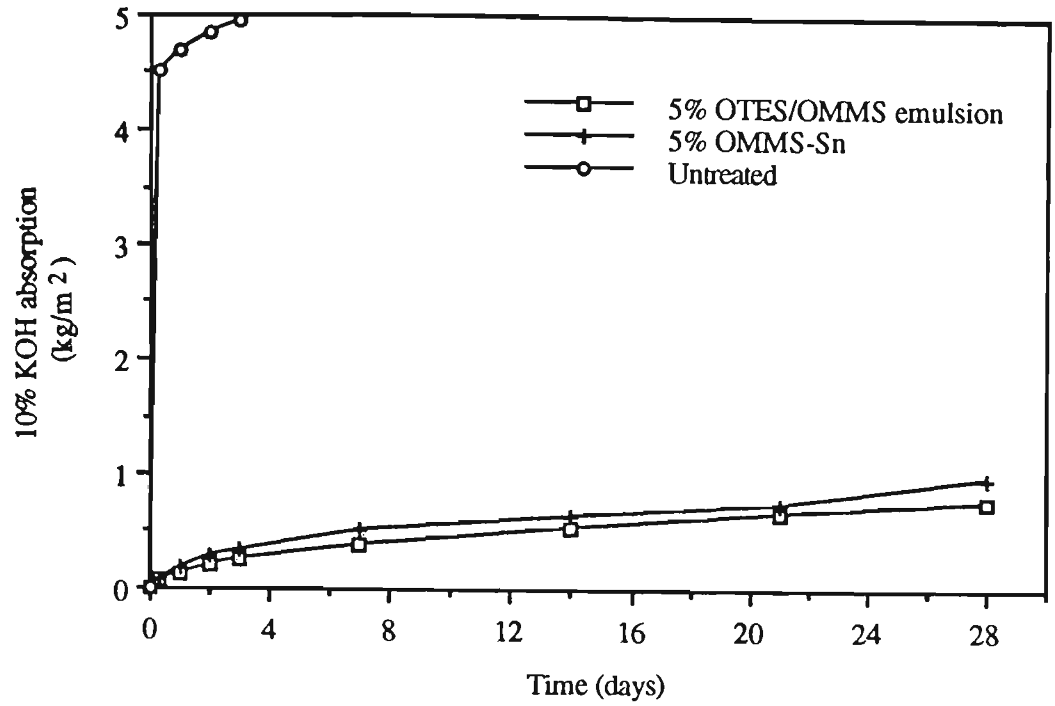


Figure 4.34 Alkali stability of substrates treated with 5% silane/siloxane emulsion and 5% siloxane impregnants

4.5.3 Depth of impregnation

Table 4.11 shows the depth of impregnation for various substrates treated with 5% silane/siloxane emulsion impregnants. The results show that the silane/siloxane emulsion impregnant achieved similar depth of impregnation in various substrates to those of the substrates treated with the solvent-based siloxane impregnant. As discussed in ξ4.2.1.1, good penetration ability of the silane/siloxane emulsion impregnant may be attributed to the silane as one part of oil phase in the emulsion.

Table 4.11 Depth of impregnation of various substrates treated with 5% silane/siloxane emulsion and 5% siloxane impregnants

Impregnants	Cement mortar (mm)	Indian fired brick (mm)	Mud brick (mm)
5% OTES/OMMS emulsion	2-3	20	2
5% OMMS-Sn in Isopar G	3	20	2

4.5.4 Water vapour permeability

Water vapour permeability of the substrate in terms of the water vapour transmission test was conducted on 4 week old DIN 1164 cement mortar substrate. The results are shown in Figure 4.35. The test results show that the water vapour transmission rate of the substrates treated with 5% silane/siloxane emulsion almost remained unaffected. The result is similar to those of the substrates treated with the solvent-based siloxane impregnant. This implies that the impregnant only coats the capillary wall surface without blocking the capillaries. The water vapour transmission rates of both the substrates treated with the emulsion and the siloxane were less than that of the untreated sample at the beginning but tended to become the same as that of the untreated substrate after a few days of the test. The reason for the initially higher water vapour transmission rate in untreated substrate has been discussed in ξ 3.4.4.

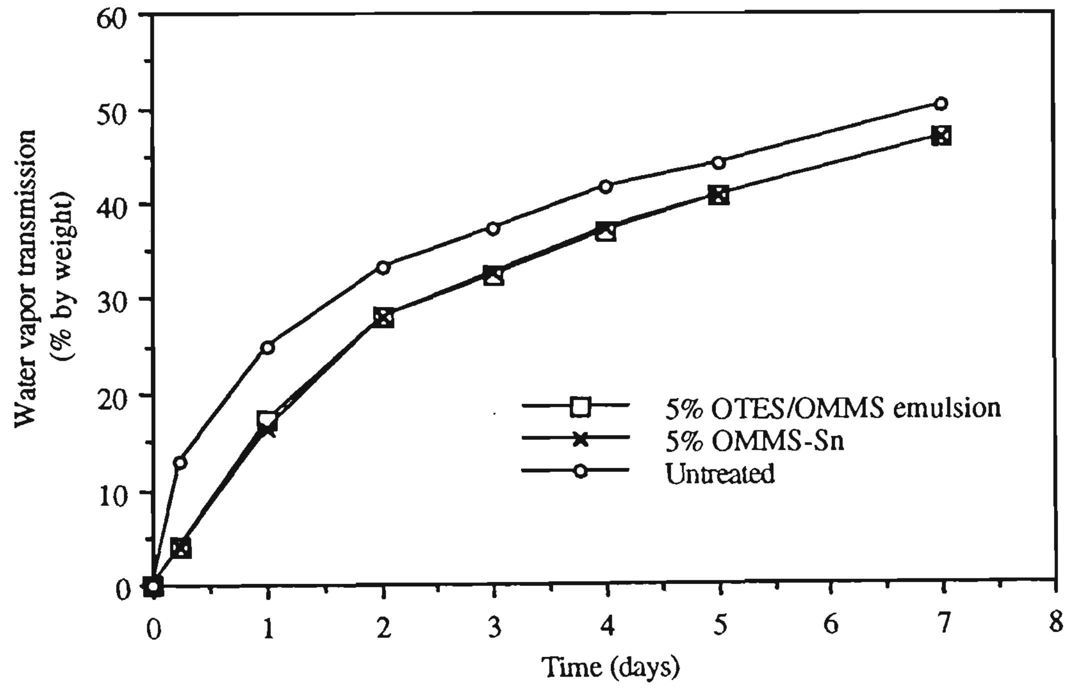


Figure 4.35 Water vapour transmission of substrates treated with the 5% silane/siloxane emulsion and 5% siloxane impregnants

4.5.5 Resistance to water absorption under hydrostatic pressure

The test for resistance to water absorption under hydrostatic pressure was conducted on 4 week old DIN 1164 cement mortar substrates and the results are shown in Figure 4.36. The test results clearly show that 5% silane/siloxane emulsion impregnant imparted to the substrate significant resistance to water penetration under 100 mm hydrostatic pressure at ambient conditions. The result was the same as that of the substrate impregnated with 5% solvent-based siloxane impregnant.

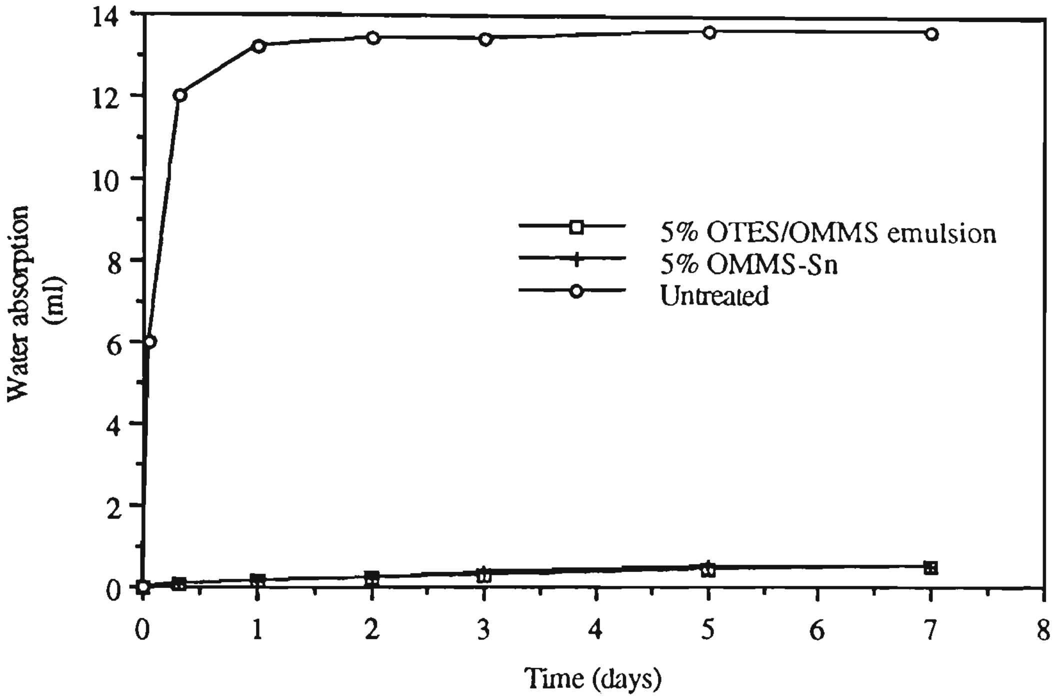


Figure 4.36 Water absorption under hydrostatic pressure of 100 mm head of water

4.5.6 Resistance to efflorescence

The tests for resistance to efflorescence were conducted on both 4 week old DIN 1164 cement mortar and Indian fired brick substrates. After 7 days of the test, the surfaces treated with either 5% silane/siloxane emulsion or 5% solvent-based siloxane impregnants showed no efflorescence. Heavy efflorescence was only observed from both untreated mortar and brick substrates. The silane/siloxane emulsion achieved a significant resistance to efflorescence for the treated substrates.

4.5.7 Resistance to wetting and drying weathering

The wetting and drying weathering test was carried out for 24 weeks (84 cycles of wetting and drying) on various substrates. The beading effect before and after wetting and drying weathering is listed in Table 4.12. The beading effect of the substrates treated with 5% silane/siloxane emulsion decreases but the results are very similar to those of the substrates treated with 5% solvent-based siloxane impregnant. A decrease in the beading effect is probably due to the hydrolysis of the hydrophobic polysiloxane on the very surface of the substrate by water, and alkali if the substrate is basic. The decrease in the beading effect was more pronounced for the alkaline substrates.

Table 4.12 Beading effect before and after wetting and drying weathering test

	Cement mortar		Indian fired brick		Mud brick	
Impregnants	before	after	before	after	before	after
5% OTES/OMMS emulsion	1-2	4	2	3	2	3-4
5% OMMS-Sn in Isopar G solvent	2	4	2	3	2	3
Untreated	7	7	7	7	7	*

* Untreated mud brick substrates collapsed after a few cycles of wetting and drying weathering.

Water absorption of the substrates before and after the wetting and drying weathering test is shown in Table 4.13. For cement mortar substrates, water absorption of the substrate treated with 5% silane/siloxane emulsion impregnant increased slightly after the weathering but was still significantly lower than that of the untreated sample. However, the water absorption of Indian fired brick and mud brick substrates treated with the emulsion remained almost unaffected. A slight decrease in the water absorption of the cement mortar substrate treated with the emulsion could be attributed to the hydrolysis of the silicone by the alkali. Reduction in the water absorption of all substrates by 5% silane/siloxane emulsion impregnation was significant after the weathering test and the water absorption results were very similar to those of the samples treated with 5% solvent-based siloxane impregnant. Again, the test results show that the silane/siloxane emulsion is suitable for treating various masonry substrates including cement mortar, fired brick and mud brick substrates to make them water repellent.

Table 4.13 Water absorption (24 hours) before and after wetting and drying weathering test

	Cement mortar		Indian fired brick		Mud brick	
Impregnants	before	after	before	after	before	after
5% OTES/OMMS emulsion	0.18	0.40	0.02	0.05	0.50	0.37
5% OMMS-Sn in Isopar G solvent	0.25	0.43	0.05	0.05	0.52	0.30
Untreated *	4.53	4.06	8.08	7.90	8.71	**

* A drop in water absorption of untreated substrates after the test refers to the comment under Table 3.21.

** Untreated mud brick substrates collapsed after a few cycles of wetting and drying weathering.

4.5.8 Resistance to UV and condensation weathering

The UV and condensation weathering test was conducted for 6 months on various substrates. The appearance of the substrate surfaces before and after the weathering remained unaffected. However, the beading effect of almost all the substrates treated with 5% silane/siloxane emulsion was significantly decreased after the UV and condensation weathering. The beading effect before and after the UV and condensation weathering is listed in Table 4.14. The decrease in beading effect was obviously because the UV had decomposed the hydrophobic polysiloxane on the very surface of the substrate. The water from the condensation may then cause hydrolysis of the silicones on the very surface of the substrates during the weathering. However, the test results also show that the change in beading effect after weathering of the substrates treated with the emulsion was similar to that of the substrates treated with solvent-based siloxane. Avoiding the decomposition by UV of the silicone impregnant on the very surface of the substrate may be impossible. However, this decomposition does not seriously affect the other impregnation performance such as resistance to capillary water penetration.

Table 4.14 Beading effect before and after UV and condensation weathering test

	Cement mortar		Indian fired brick		Mud brick	
Impregnants	before	after	before	after	before	after
5% OTES/OMMS emulsion	1-2	5	2	2-3	2	5-6
5% OMMS-Sn in Isopar G solvent	2	5	2	2-3	2	5-6
Untreated	7	7	7	7	7	7

The water absorption results before and after the UV and condensation weathering are shown in Table 4.15. The test results show that the water absorption values of the substrates remained almost unaffected after the UV and condensation weathering. This implies that the UV only destroys the polysiloxane on the very surface of the substrate but the hydrophobic layer inside the substrate is unaffected resulting in resistance to capillary water penetration. The silane/siloxane emulsion impregnant performed similarly to the solvent-based siloxane impregnant on various substrates during the UV and condensation weathering.

Table 4.15 Water absorption values (24 hours) before and after UV and condensation weathering test

	Cement mortar		Indian fired brick		Mud brick	
Impregnants	before	after	before	after	before	after
5% OTES/OMMS emulsion	0.16	0.36	0.04	0.05	0.43	0.35
5% OMMS-Sn in Isopar G solvent	0.23	0.53	0.07	0.03	0.49	0.32
Untreated *	4.44	4.27	6.99	6.94	10.22	7.88

* A drop in water absorption of untreated substrates after the test refers to the comment under Table 3.21.

4.5.9 Resistance to outdoor exposure weathering

The outdoor exposure weathering test was carried out for 6 months. The appearance of the substrate surfaces before and after the natural weathering remained the same except for the untreated mud bricks which collapsed during the weathering test. The beading effect of the three kinds of substrates treated with 5% silane/siloxane emulsion impregnant was slightly decreased after the weathering. However, these results were quite similar to those of the substrates treated with solvent-based siloxane impregnant (shown in Table 4.16). The decrease in beading effect was again attributed to the decomposition and the hydrolysis of the hydrophobic polysiloxane layer on the very surface of the substrates by the sun radiation and rain water penetration. However, such weathering conditions may not be as severe as those in the accelerated UV and condensation weathering as shown by the results where less decrease in beading effect of the substrates was recorded for the natural weathering.

***Table 4.16** Beading effect before and after outdoor exposure weathering test*

	Cement mortar		Indian fired brick		Mud brick	
Impregnants	before	after	before	after	before	after
5% OTES/OMMS emulsion	1-2	3-4	2	2-3	2	3
5% OMMS-Sn in Isopar G solvent	2	3-4	2	2-3	2	3
Untreated	7	7	7	7	7	*

* Untreated mud brick substrates collapse after outdoor exposure weathering.

The results of the water absorption test before and after the outdoor exposure weathering are shown in Table 4.17. No significant change in water absorption after natural weathering has been observed for the various tested substrates treated with either 5% silane/siloxane emulsion or 5% solvent-based siloxane impregnants. The silane/siloxane emulsion performed well in resisting the natural weathering.

Table 4.17 Water absorption values (24 hours) before and after outdoor exposure weathering test

	Cement mortar		Indian fired brick		Mud brick	
Impregnants	before	after	before	after	before	after
5% OTES/OMMS emulsion	0.15	0.31	0.08	0.10	0.53	0.38
5% OMMS-Sn in Isopar G solvent	0.24	0.32	0.08	0.06	0.56	0.30
Untreated	4.38	4.36	6.67	6.72	10.22	*

* Untreated mud brick substrates collapse after outdoor exposure weathering.

It may be concluded that the 5% silane/siloxane emulsion can impart significant water repellency to the various substrates including cement mortar, fired bricks and mud bricks. The impregnation performance of the 5% silane/siloxane emulsion is very similar to that of 5% solvent-based siloxane impregnant. Therefore, it is possible to use this novel silane/siloxane emulsion as a water-based alternative to replace the organic solvent-based siloxane as a normal impregnant to render the surface of masonry substrates water repellent.

5. INTERACTIONS BETWEEN IMPREGNANTS AND SUBSTRATES

5.1 General

The application of water repellent impregnants to substrates is usually carried out by impregnation [197]. There are various ways to test the water repellency imparted by this process to masonry substrates [198]. The methods employed in this research to apply the impregnants to masonry substrates and to examine the performance of the impregnated substrates have been described in Chapter 2. The impregnation performance of the various substrates treated with the two novel water repellents developed in this research has been presented and discussed in Chapter 3 and Chapter 4. It was found that both novel water repellents were successful in effecting water repellency in masonry substrates and the impregnation performance was equivalent to those of substrates treated with the organic solvent-based siloxane impregnant.

It was found that the water repellency of mud bricks impregnated with silicone water repellents, either water-based or organic solvent-based was not satisfactory. The mud brick substrates were not effectively made hydrophobic with silicone impregnants unless they were treated with soluble sodium silicate before impregnation. A successful way to treat mud brick to impart water repellency and consolidation effects was developed by treating the substrate with diluted sodium silicate followed by impregnation with the water-based silicone impregnant [12]. The durability of the mud bricks was found to be significantly upgraded through the treatments. In order to understand the specific phenomena of the impregnation of mud bricks and the general impregnation mechanism, the substrates were examined by FTIR spectroscopy and GPC as well as by the general methods used to examine impregnated substrates. It is believed that the consolidation of the earth is attributed to the silicate gel (inorganic polymer) which greatly enhances the adhesion between earth particles. The water repellent effect is due to the formation of hydrophobic polysiloxane in the substrate capillaries. However, pre-treatment with sodium silicate was found to be the key factor to control the water repellency of the mud brick substrates. The pre-treatment improved the crosslinking structure of the polysiloxane by increasing the pH of the substrate, reducing the surface area of the capillary wall and increasing the chemical functionality on the surface of the substrates [199].

Soluble silicates such as sodium silicate have been used to impart water resistant effect and consolidation effects to masonry substrates [25, 37, 38, 68, 69]. However, the water-resistant effect induced in silicate-treated substrates is generally unsatisfactory unless the capillaries of the substrates are fully filled. A new method has been developed herein to improve the water resistant effect of soluble sodium silicate treated masonry substrates by impregnation with diluted sodium silicate followed by impregnation with an alkyl quaternary ammonium salt (cationic surfactant) solution [200]. The effect in reducing the water absorption of the treated substrate was significant. It was found that the water resistant effect was not due to the reduced permeability of the pores by filling of the capillaries with silicate polymer but by the introduction of organic hydrophobic groups into the capillaries attributed to a reaction between the silicate polymer and the cationic surfactant. Such reactions have been observed in systems not involving masonry surfaces [201, 202]. This research provides a new way to improve the water resistant effect of silicate-treated masonry substrate by significantly reducing the water absorption but having almost no effect on the capillary permeability of the substrates. However, the water repellency of the treated substrates was not competitive with those of substrates treated with organic silicone water repellent.

5.2 Water repellency of mud brick substrates

By studying the interaction between the mud brick substrate and the soluble sodium silicate and the silane/siloxane emulsion, the mechanism of the water repellent properties induced in mud bricks may be understood. In addition, general impregnation mechanisms may also be understood. The silane/siloxane (OTES/OMMS) emulsion used herein was made according to ξ4.4.

5.2.1 Water repellency of mud bricks induced by the repellent

Figure 5.1 plots water absorption values of mud brick substrates against time. The water absorption of the substrates A treated with 79g/litre sodium silicate followed by 5% silane/siloxane emulsion impregnation was reduced by about 90% compared to that of untreated substrates D for a long term water absorption test. The substrate B treated only with 5% silane/siloxane emulsion shows a lower water absorption value than that of untreated sample but is unsatisfactory compared to that of the substrate treated with the silicate followed by the emulsion. It was also observed that treatment of the mud bricks with various siliconate or organic solvent-based siloxane impregnants without silicate pre-treatment showed similar poor test results. However, treatment with silicate followed by the siliconate or organic solvent-based siloxane impregnants gave satisfactory results. Sodium silicate alone did not achieve a satisfactory water repellent effect but a higher water absorption value for the treated substrate C compared to that of untreated substrate. This will be discussed in ξ 5.2.3.

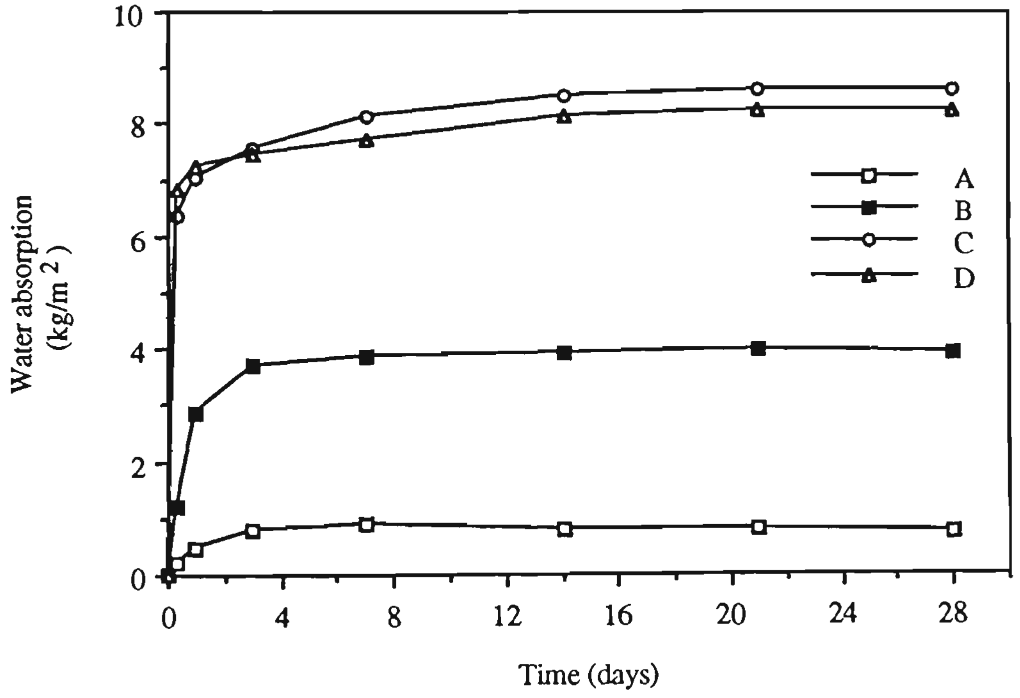


Figure 5.1 Water absorption of mud brick substrates treated in various ways; A) treated with sodium silicate followed by OTES/OMMS emulsion, B) only with the emulsion, C) only with the silicate, and D) untreated

Figure 5.2 shows the infrared spectra of the earth substrates. It clearly shows that the water repellent effect is related to the organic silicone which has been adsorbed on the substrates. This is shown in the spectra at 2859-2957 cm.$^{-1}$ due to CH stretching and at 1270 cm^{-1} due to $SiCH_3$ deformation [132] of the alkylsilane or alkylsiloxane (spectra A and B). For the substrate treated with the silicate and the untreated substrate, there is no organic group shown in the spectra (spectra C and D). No water repellent effect was exhibited in these substrates. Through impregnation, the silicone can adsorb on the substrate capillaries to form a hydrophobic polysiloxane thin film . As discussed in Chapter 1, the hydrophobic polysiloxane can significantly increase the contact angle of water with the substrate capillary wall and reduce the water absorption of the substrate through capillary depression [11, 29]. According to Equation 1.1, increasing the contact angle θ decreases the capillary rise H.

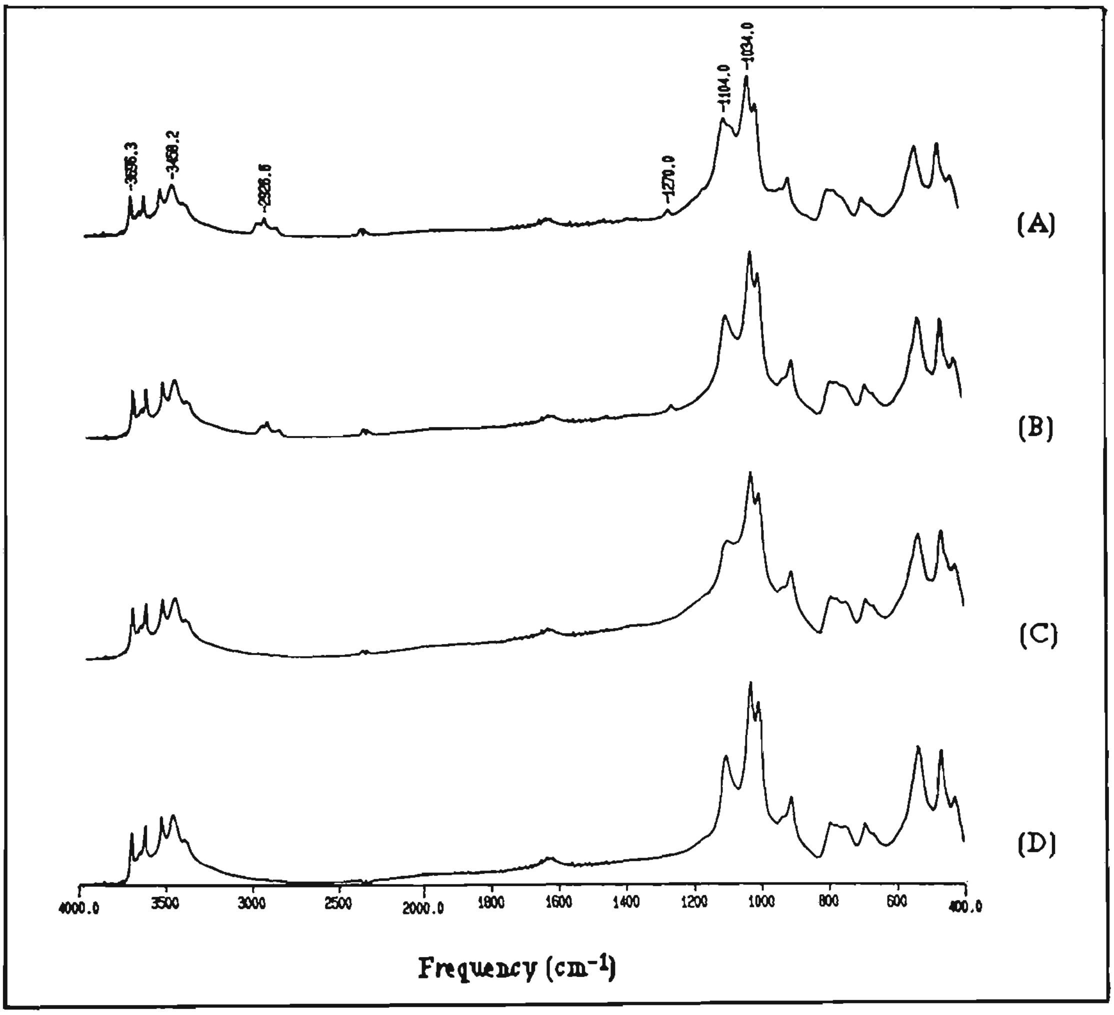


Figure 5.2 FTIR spectra of earth substrates; A) treated with sodium silicate followed by OTES/OMMS emulsion; B) only with the emulsion, C) with the silicate, and D) untreated

The surface of a clay mineral is normally made up of either negatively charged oxygen atoms or hydroxyl groups [2]. The free silanol in the clay silica structure is very reactive with either silane/siloxane or the hydrolysed silanols through a siloxane bonding mechanism. According to Colthup et al.[132] and Grim [2], the silica (SiOSi) absorbs at 1000-1200 cm^{-1} and the silanol (SiOH) absorbs at 3400-3700 cm^{-1}. The Spectrum D of the earth substrate in Figure 5.2 exhibits these absorption bands.

Interaction between silane/siloxanes and silica mineral surfaces through siloxane bonds is described elsewhere [44, 48, 49, 50, 51, 203]. The strong siloxane bonds is thought to form between the silanols of the masonry substrate and the silane/siloxane (refer to Scheme 1.5, 1.6 and 1.7). Condensation between silicone impregnant and the surface or within the hydrolysed silane/siloxane to polysiloxane is also assumed to occur in the substrate capillaries. The possible reactions have been shown in Scheme 1.8 and 1.9.

Figure 5.3 shows the neat spectrum of adsorbed silane/siloxane residue (spectrum A), the chemisorbed (spectrum B) and the physisorbed (spectrum C) spectra obtained as described in ξ2.6. It clearly demonstrates that the majority of silane and siloxane has been adsorbed on the substrate through chemical bonding and the remainder may be deposited on the substrate by physical adsorption (e.g. via hydrogen bonds) which can be removed by the solvent washing process.

Figure 5.4 shows the water absorption values and the infrared band intensity at 2957 cm^{-1} due to CH_3 stretching of the adsorbed silane/siloxane on the substrates as a function of the emulsion concentration. The result demonstrates that further increasing the emulsion concentration to greater than 5% made little contribution in reduction of the water absorption of the substrate. On the other hand, the infrared absorbance intensity at 2957 cm^{-1} increases with the increase in the concentration of the emulsion.

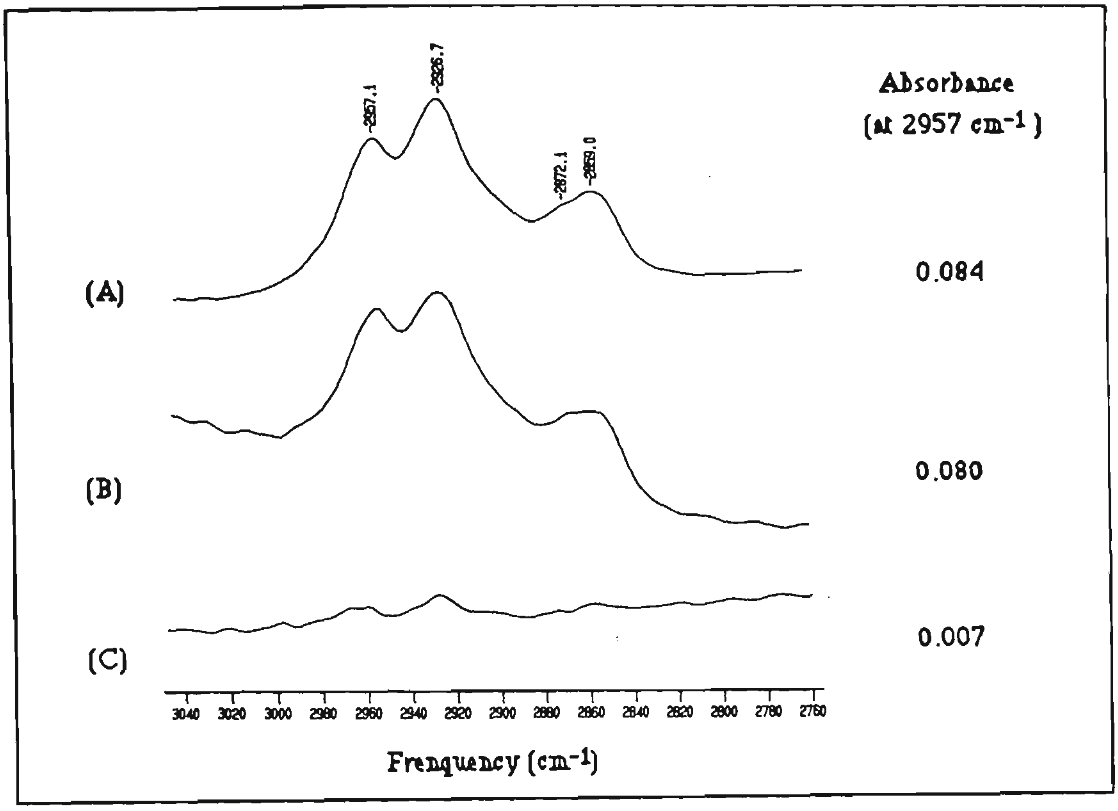


Figure 5.3 Spectra of the substrates treated with 79g/litre sodium silicate followed by 5% OTES/OMMS emulsion; A) neat adsorbed organic silicone on the substrate, B) chemisorbed silicone (with THF washing), and C) physisorbed silicone (A-B)

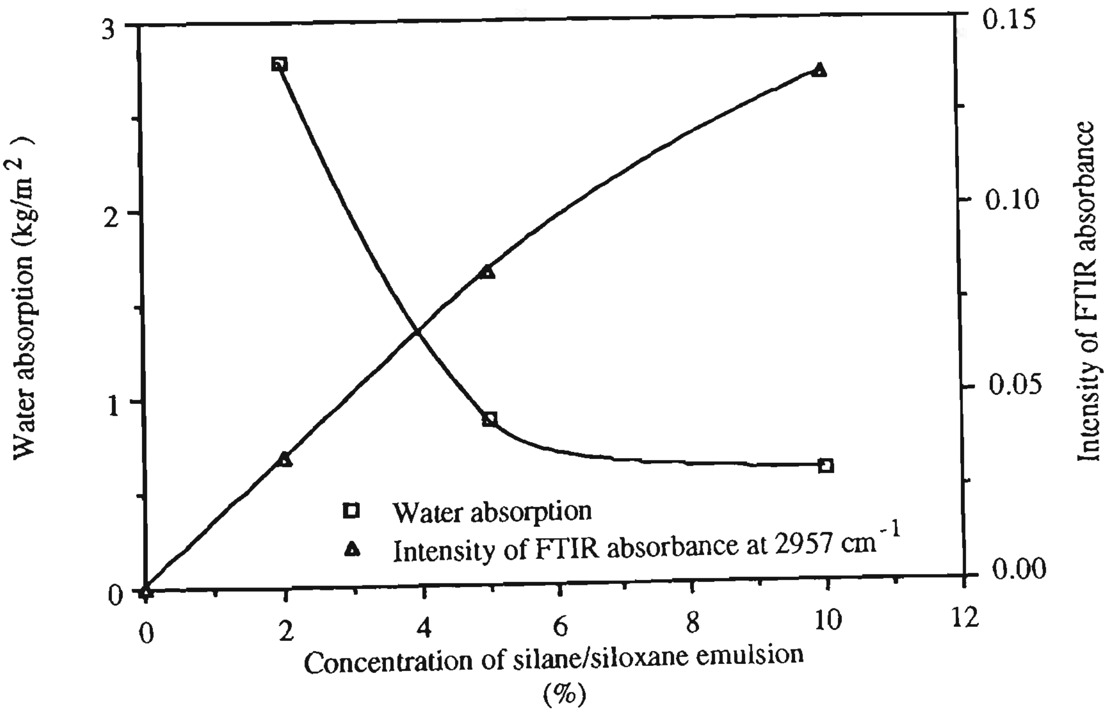


Figure 5.4 Seven day water absorption values and the band intensity at 2957 cm^{-1} as a function of the emulsion concentration for the substrates treated with 79g/litre sodium silicate followed by impregnation with OTES/OMMS emulsion

The water repellent effect in the substrates may depend only on the thin film of hydrophobic polysiloxane structure formed on the capillary wall surface. Figure 5.4 demonstrates that the amount of the silicone (or the thickness of polysiloxane thin film) adsorbed on the substrate surface increases with the increase in the concentration of the organic silicone but this cannot further decrease the water absorption value of the substrates. This could be explained as the contact angle of water could not be further increased once a hydrophobic polysiloxane thin film has been formed at a certain concentration of the silicones as applied to the surface.

5.2.2 Consolidation of mud bricks by sodium silicate impregnation

The test results conducted by totally immersing the mud brick substrates in water in a water bath showed that the untreated portion of the substrate deteriorated within 2 hours immersion whilst the treated portion could stand in the water for more than 4 weeks. The consolidation effect of the substrate treated with the silicate is attributed to the adsorbed silicate gel (inorganic polymer) which is formed in the capillaries by crosslinking with the substrate. Figure 5.5 shows the infrared spectrum (A) of the neat adsorbed silicate obtained by subtracting the spectrum of the untreated substrate from the spectrum of the substrate treated with silicate. The spectrum (B) of the pure precipitated silicate gel is also shown in Figure 5.5. The pure silicate gel was obtained by precipitating the diluted sodium silicate solution with hydrogen chloride (HCl) solution. A comparison of the spectra indicates that the spectrum of adsorbed silicate shows a similarity to that of the pure silicate gel. This implies that the silicate becomes silicate polymer after being applied to the substrate. The strong band at 1078 cm^{-1} in spectrum (A) shows the typical stretching of siloxane bonds (SiOSi) of silicate as reported by Bellamy [143]. The slight shift of position of this siloxane band from 1086 cm^{-1} in pure silicate gel spectrum (B) to lower frequency in the treated substrate spectrum (A) may be due to the bonding of the silicate polymer via the siloxane bond with the surface free silanol. Ishida and Koenig [49] observed a similar phenomenon in studying the interaction between polyvinylsiloxane and a porous silica surface and they believed this was due to the formation of siloxane bonds between the silicone and the substrate. It is apparent that the silicate gel bonded with the substrate in the capillaries imparts sufficient adhesion between the earth particles to consolidate the substrate.

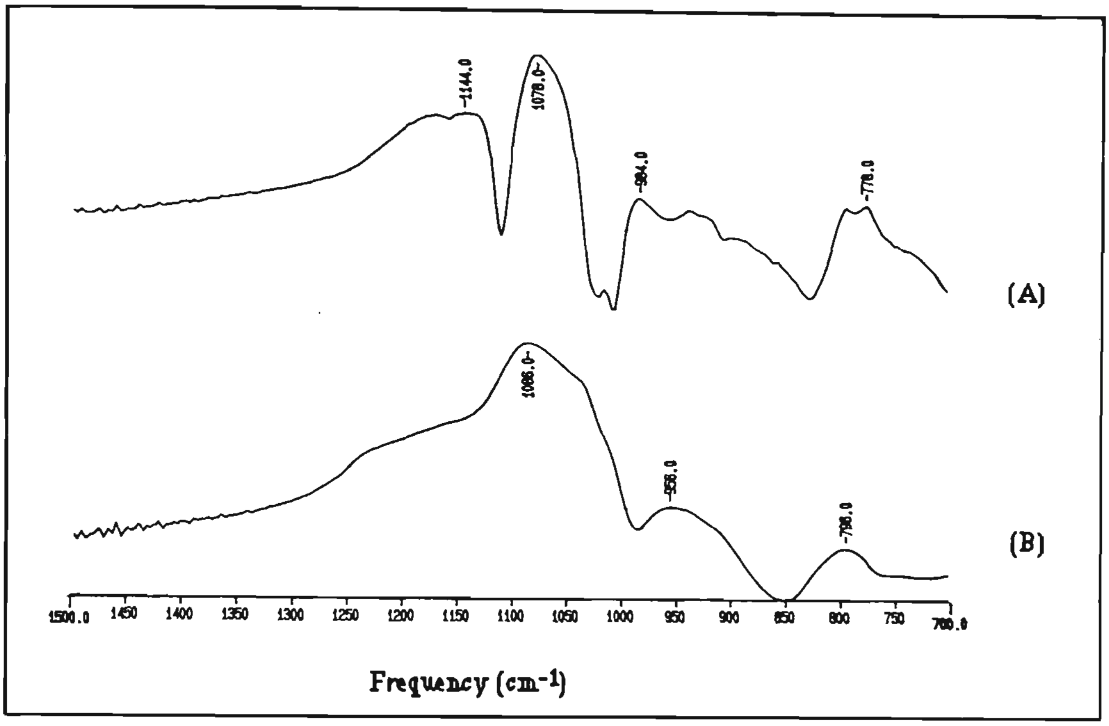


Figure 5.5 Spectra of inorganic silicate gel; A) neat silicate gel on the substrate obtained by subtraction of the spectrum of the substrate from the spectrum of the substrate treated with 79g/litre sodium silicate, and B) precipitated pure sodium silicate gel

5.2.3 The effect of the silicate on the water repellency of the substrates

A unique effect of the sodium silicate in this system is that it enhances the water repellency of the substrate treated with silane/siloxane emulsion. As shown in Figure 5.1, the water absorption value can be significantly further reduced by pre-impregnating the substrate A with the silicate compared to that of the substrate B without silicate pre-treatment. As discussed previously, the water repellent effect is developed by organic silicone which forms a hydrophobic thin film in the substrate capillaries. However, the water repellent effect may vary according to the final structure of the adsorbed silicone in the capillaries. One must assume that a polysiloxane thin film with higher molecular weight and fully crosslinked structure can impart a better water repellency to the substrate than that of a mono-molecular adsorption of the silicone. Ishida and Miller [52] have demonstrated that the final silicone structure on the substrates may be controlled by the pH environment of the substrate, and the physical properties and the chemical functionality of the substrate surface. Table 5.1 shows the change of pH and capillary porosity of the mud brick substrates before and after silicate treatment.

Table 5.1 *The change of pH and capillary porosity of the substrate before and after impregnation with 79 g/litre sodium silicate*

	pH of the substrate	Capillary porosity (%)
Before impregnation	5.2	19.1
After impregnation	10.3	18.3

The pH is known to influence the rate of hydrolysis and condensation of silanes [75, 118, 146]. Similarly, the acid/base nature of the particulate modifies the environment of the deposited silicones and should have a significant effect on their ultimate structures according to Ishida and Miller [52]. In general, both acidic and basic conditions accelerate the hydrolysis of a silane while basic conditions favour the condensation of silanols according to Osterholtz and Pohl [75] and Plueddemann [76]. As shown in Table 5.1, the pH of the untreated substrate is acidic (pH 5.2) and the organofunctional silane or siloxane can be easily hydrolysed into reactive silanols which then spontaneously bond to the substrate surface through siloxane bonds. The crosslinking between silanols of the silane or siloxane through condensation may be slow under such conditions. Therefore, the adsorbed material on the substrate may be mainly the mono-silicone molecules. However, after the substrate is impregnated with sodium silicate, the pH of the substrate is changed from being acidic to alkaline (pH 10.3). The condensation between molecules of hydrolysed silane or siloxane is catalysed and this ultimately enhances the molecular weight and the crosslinking of the organic polysiloxane which in turn greatly improves the water repellent effect of the treated substrate (refer to Scheme 1.7). Figure 5.6 shows the neat spectrum of adsorbed silane/siloxane (A'), and both chemisorbed (B') and physisorbed

(C') spectra of the substrate treated only with silane/siloxane emulsion. A comparison of the spectra of Figure 5.6 with those in Figure 5.3 shows that the band intensity of chemisorbed silicone on the substrate treated only with silane/siloxane emulsion is significant but the water absorption data in Figure 5.1 shows a relatively high value. This implies that the water repellency of the treated substrate is not always proportional to the amount of the organic silicone adsorbed but must depend on the ultimate silicone structure formed in the capillaries. Further, under alkaline conditions (Figure 5.3) there is little physisorbed silicone which can be removed by the solvent from the substrate treated with silicate followed by silane/siloxane emulsion impregnation and this in turn implies that either all the silicones are bonded to the surface or the silicone is crosslinked between molecules to form polysiloxane which cannot be removed by the solvent. However, under acidic conditions, so-called physisorbed silicone cannot crosslink and may then be removed by the solvent washing.

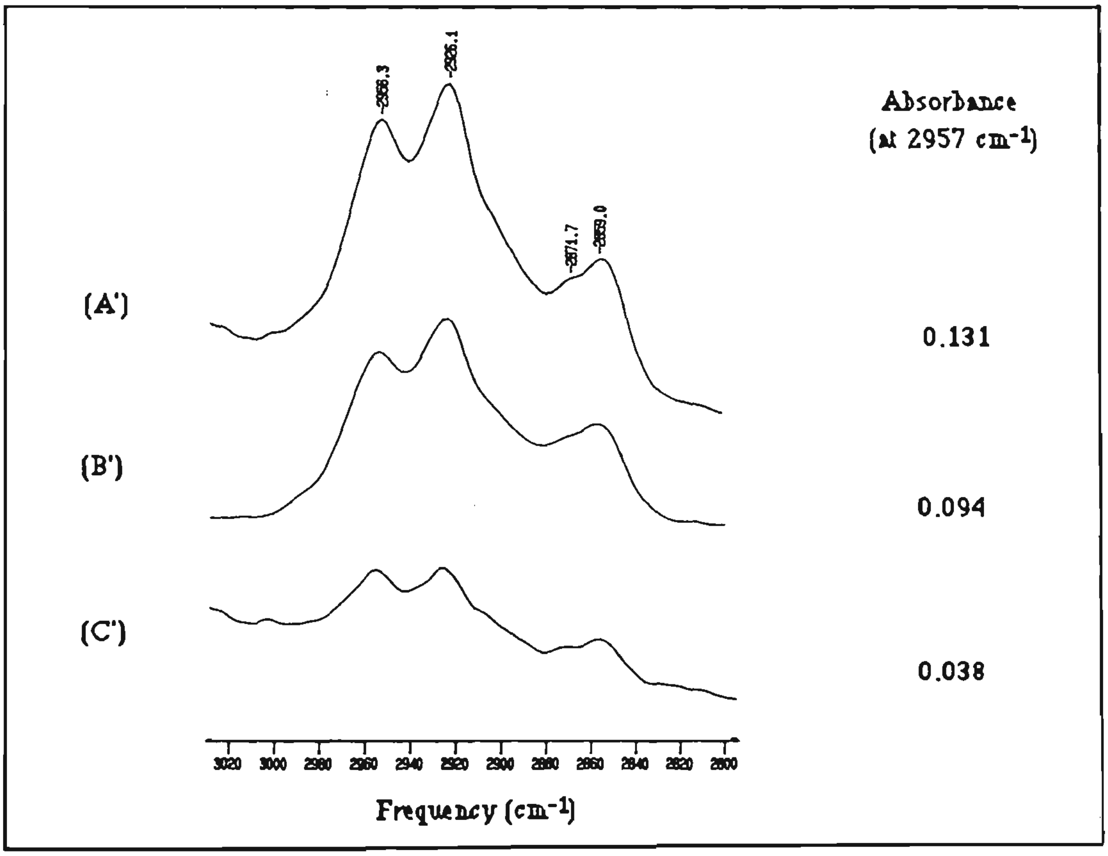


Figure 5.6 *Spectra of substrates treated only with 5% OTES/OMMS emulsion; A') neat adsorbed organic silicone on the substrate, B') chemisorbed silicone (with THF washing), and C') physisorbed silicone (A'-B')*

Table 5.1 also shows that the capillary porosity of the substrate was slightly decreased through the silicate impregnation. By impregnating the substrate with diluted sodium silicate for 1 minute, so-formed silicate polymer may only coat the capillary wall surface but does not block the capillaries. The minor change in capillary porosity may imply that the silicate polymer blocks the very fine capillaries resulting in greatly reducing the surface area of the capillary wall. This may be explained as the total adsorbed silane/siloxane on the substrate after pre-impregnation with silicate is less than that of the substrate without pre-treatment with silicate due to less coverage of the capillary wall surface (see Figure 5.3 and Figure 5.6). The physical role of the substrate surface is known to be extremely important in influencing the structure of the adsorbed polysiloxane [52]. When the silicones are applied to the substrate it is always in small quantities and therefore, the substrate surface determines the effective concentration and mobility of the silicone molecules. According to Ishida and Miller [52], a high surface area in the substrate tends to give low molecular weight siloxane on the substrate surface whilst a low surface area results in a high molecular weight polysiloxane. This is attributed to a high surface area in the substrate reduces the silanol mobility as the silicone molecules may be spontaneously adsorbed on the capillary surface while the few free molecules can further condense on the surface to form a crosslinked polysiloxane structure. Therefore, these results imply that a pre-treatment with silicate reduces the capillary surface area and therefore a higher molecular weight and crosslinked polysiloxane would be expected.

GPC determination of the molecular weight of the physisorbed polysiloxane from the substrate treated with the silicate followed by the impregnation with the emulsion was carried out and two peaks were exhibited with one strong peak at a molecular weight in a range of 110,000 to 4,000 and the other broad peak at about 700. The physisorbed polysiloxane from emulsion treatment only showed one broad peak centred at molecular weight of about 700 which is believed to be in the range of an oligomeric siloxane. The molecular weight and the structure of the chemisorbed silicone may be assumed to be similar to that of the physisorbed siloxane as the reaction environment in the substrate capillaries is the same. Therefore it was indirectly confirmed by GPC analysis that the substrate treated with silicate first followed by impregnation with emulsion contained hydrophobic polysiloxane while the one treated only with the emulsion contained only oligomeric siloxane in its capillaries.

Apart from reducing the surface area of the capillaries, the silicate may change the substrate surface chemical functionality by coating the capillary surface with hydrophilic silicate polymer. This polymer in the pores can not achieve any water repellent effect but may increase the hydrophilicity of the impregnated pores (e.g. the number of the hydroxyls). This would explain why the substrate treated with silicate has a slight higher water absorption value than that of untreated substrate (see Figure 5.1). When silane/siloxanes are applied to the capillaries, they can condense with the hydroxyls of the silicate polymer through siloxane linkage to form crosslinked organopolysiloxane via inorganic silicate gel. Figure 5.7 shows SiOSi band intensity 1078 cm^{-1} of silicate polymer on the substrate and the water absorption value of the substrates with increase of silicate concentration of pre-treatment. An increase in the silicate concentration increases the amount of silicate gel on the substrate. The water absorption of the substrate shows a sharp decrease at first and then tends to be constant but shows a trend of slight increase when silicate concentration is further increased. This can be best explained the reaction medium provided by the silicate polymer for further silane and siloxane condensation is improved with increase in the silicate polymer concentration. However, a further increase in the silicate concentration greater than 79g/litre provides extra hydrophilic silicate structure which cannot be fully crosslinked by the organic silicone and therefore causes an increase in the water absorption of the substrates.

5.2.4 Conclusion

The consolidation and water repellent effect of the earth substrates treated with soluble sodium silicate followed by impregnation with water-based silane/siloxane emulsion was found to be significant. The consolidation of the earth by soluble sodium silicate impregnation is attributed to the silicate gel (polymer) formed by crosslinking with the surface through siloxane bonds to improve the adhesion between earth particles. The water repellent effect of the substrate is due to the formation of a hydrophobic organic polysiloxane thin film which bonds to the substrate. This polysiloxane increases the contact angle of water on the capillary wall surface and greatly reduces the water absorption through capillary depression. The pre-impregnation with soluble sodium silicate greatly enhances the water repellent effect of the treated substrate by improving the molecular weight and the crosslinked structure of the polysiloxane in the capillaries through i) increasing the pH of the substrate which enhances the condensation, ii) reducing the surface area of the capillary wall and iii) increasing the surface chemical functionality.

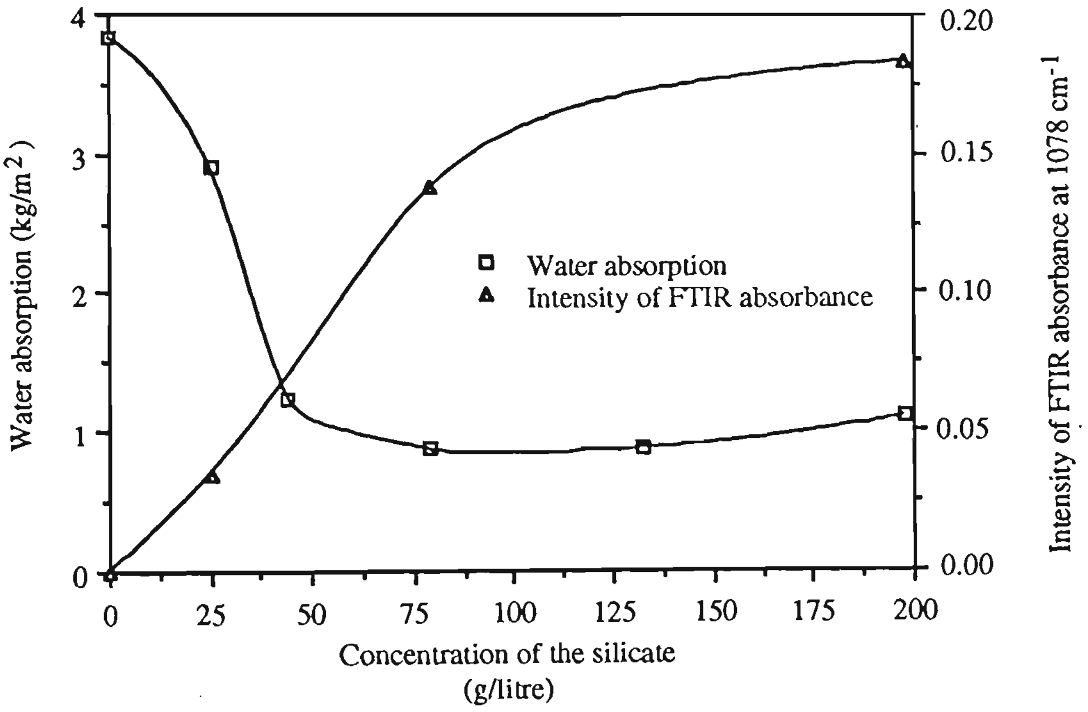


Figure 5.7 Seven day water absorption values and the band intensity at 1078 cm^{-1} as a function of the silicate concentration for the substrates treated with sodium silicate followed by impregnation with 5% OTES/OMMS emulsion

5.3 Improving the water resistance of silicate-treated substrates

A marked water resistant effect has been imparted to masonry substrates by impregnating the substrates with sodium silicate followed by the impregnation with an alkyl quaternary ammonium salt solution. The mechanism of the water resistance developed through the treatments has been discussed. The water resistance and the durability of the treated substrates were examined through various tests. In this research, sodium silicate impregnant was diluted by water (1:1 by weight) to 197.5 g/litre and the alkyl quaternary ammonium salt was diluted with water to various concentrations before impregnation.

5.3.1 Water resistant effect induced by silicate

A test was conducted to determine the water absorption values of permeable concrete paver substrates treated with the sodium silicate impregnant and then with 3% cetyltrimethyl ammonium chloride (Vantoc CC30) solution 24 hours after the first treatment. In comparison, the substrates were treated in the same way but impregnated respectively with various other curing agents (10% aqueous solution) as described by other workers [26, 70, 71, 72, 73] instead of Vantoc CC30 in the second impregnation. Both untreated substrates and the silicate treated substrates were used as the controls. Figure 5.8 shows the water absorption of the treated substrates as a function of time.

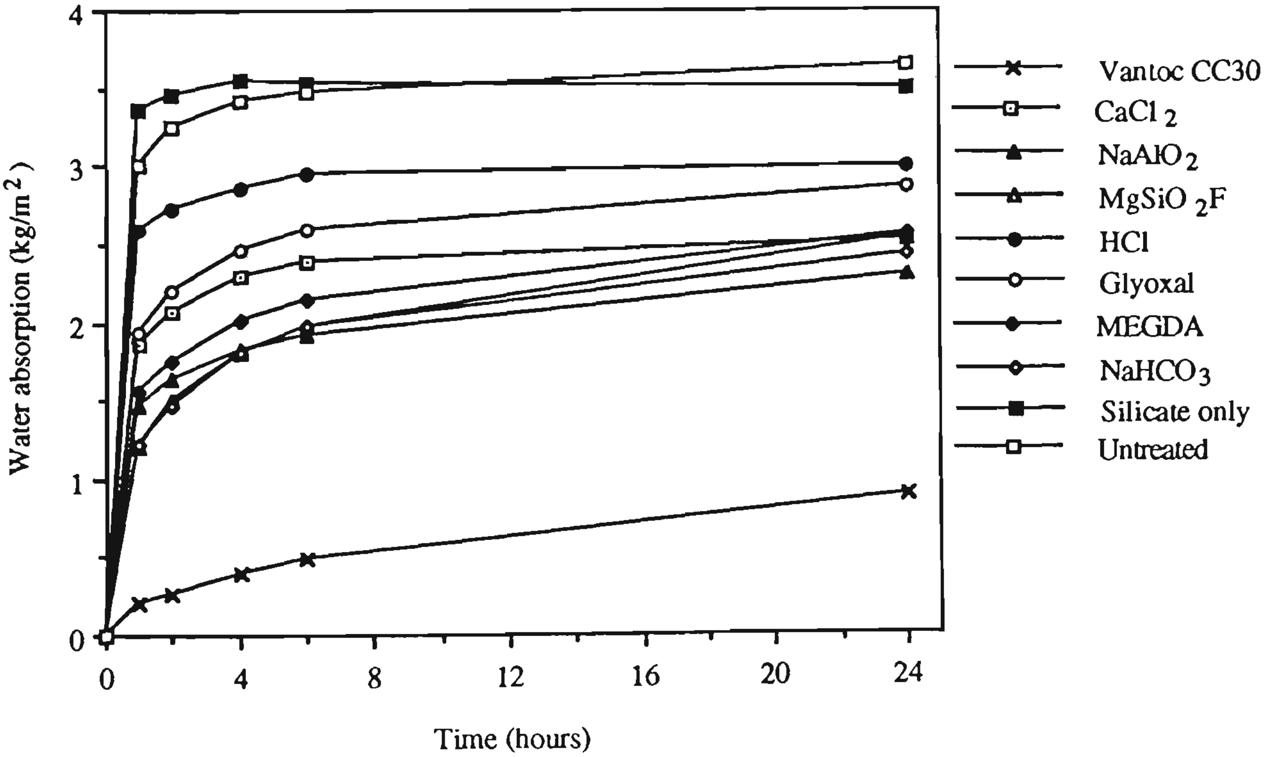
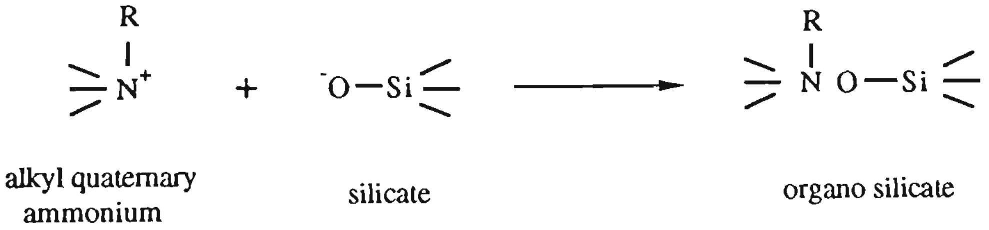


Figure 5.8 Water absorption of permeable concrete pavers treated with silicate followed by impregnation with Vantoc CC30 and various other curing agents

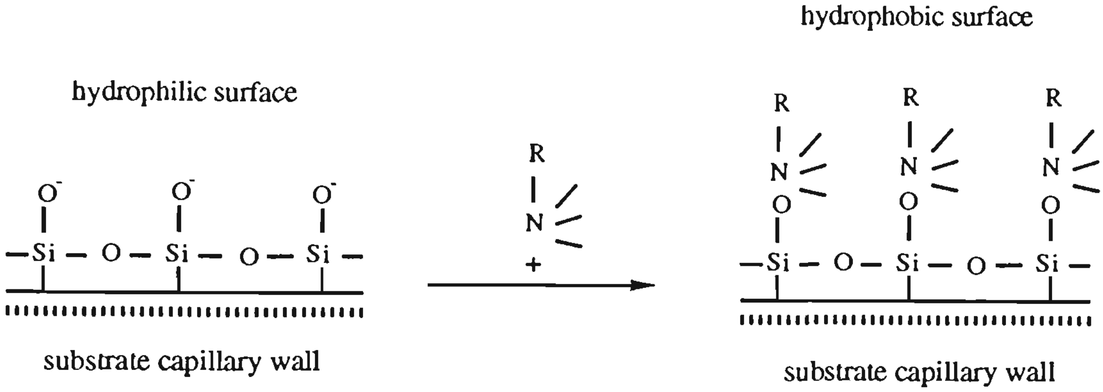
The test results show that the water absorption of the substrates treated with silicate followed by 3% Vantoc CC30 solution treatment was significantly lower than that of the controls and those of the substrates treated with other curing agents. In addition, the depth of impregnation of the treated concrete substrate was found to be 7 mm. Within this 7 mm layer, the substrate was less able to be wetted with water. The water resistant effect of the treated substrates may be mainly attributed to this water resistant layer.

The water resistant layer may be due to the deposition of organo-silicate on the capillary surfaces of the substrates. Once the substrates are impregnated with sodium silicate, the sodium silicate starts to condense with itself and the substrate in the presence of ambient carbon dioxide to form silicate oligomer or polymer product on the capillary surface. This product strengthens the concrete and may impart a water resistant effect to the concrete if the capillaries are completely blocked by the silicate reaction product [68, 69]. However, a completely water resistant effect could not be claimed as the concrete capillaries could not be fully blocked by this simple impregnation. If such treated substrates were impregnated with Vantoc CC30 solution, the quaternary ammonium moiety may react with the silicate structure to form an organo-silicate which could be deposited on the capillary wall surfaces of the substrates (see Scheme 5.1). Comparable reactions between silicate and quaternary ammonium compounds outside of concrete substrates have been reported in the literature. Rieck et al.[201] have successfully prepared an organo-silicate product from soluble sodium silicate and distearyldimethyl ammonium chloride. This product was found to be not soluble in aqueous solution and was used as an oil absorbent to absorb oil from water. Dwyer and Jenkins [202] have also made an organo-silicate compound from colloidal silica, sodium hydroxide and tetrapropyl ammonium bromide.



(Scheme 5.1)

It was further found in this investigation that spontaneous precipitation can be observed by adding quaternary ammonium salts to silicate solutions. Such an organo-silicate in the masonry could change the hydrophilic surfaces of the capillaries into hydrophobic surfaces due to the large hydrocarbon in the silicate structure and may also reduce the capillary size of the concrete by this structure to impart sufficient water repellent effect to the substrates (see Scheme 5.2). The water resistant effects induced in substrates which were treated with other curing agents instead of quaternary ammonium salt solutions were found to be much less, probably because no hydrocarbon had been introduced into the silicate structure. These curing agents only accelerated the curing of the silicate in the pores as detailed in the literature [26, 70, 71, 72, 73].



(Scheme 5.2)

It is known that cationic surfactants such as alkyl quaternary ammonium salts can be adsorbed on a solid substrate surface [112, 160, 183, 187, 204] to leave their hydrocarbon groups facing outside from the substrate surfaces resulting in a water repellent effect. This adsorption may achieve a hydrophobic surface on the masonry substrate impregnated with a cationic surfactant. A test was conducted to determine whether the water resistant effect of the substrate was due to the quaternary ammonium adsorption on the surface or due to the formation of an organo-silicate deposited on the capillary surface of the substrates. The water absorption of the permeable concrete pavers treated with 1.2% myristyltrimethyl ammonium bromide (Vantoc N40) was examined. The substrate which was first treated with the sodium silicate impregnant and then treated again with the same solution of Vantoc

N40 after 24 hours was used as a comparison. The controls were untreated substrates and substrates treated only with silicate. The results are shown in Figure 5.9.

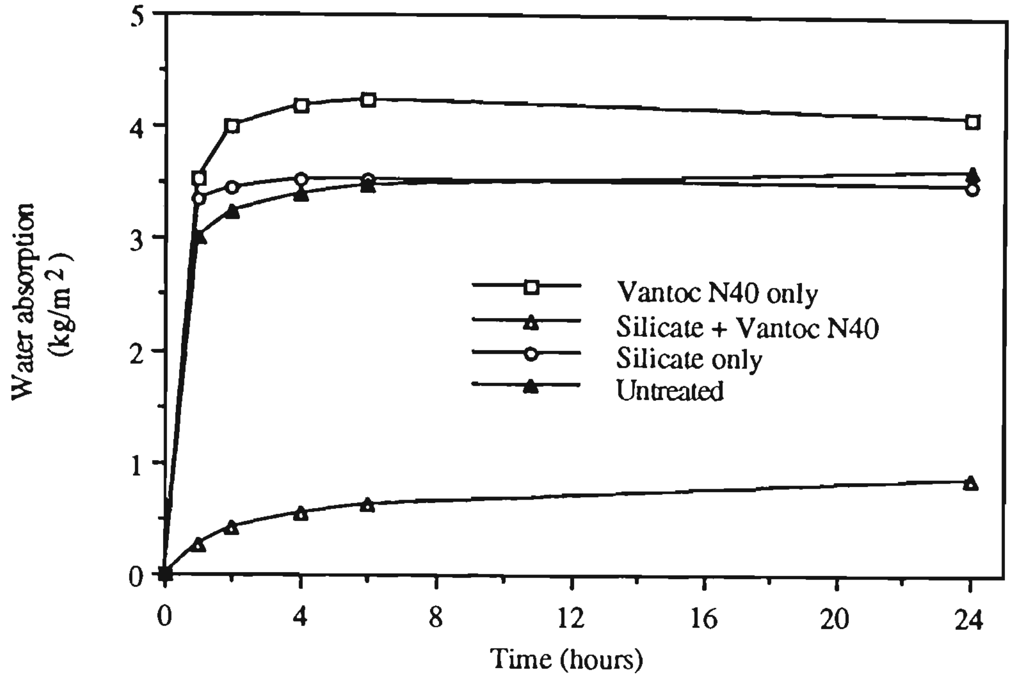
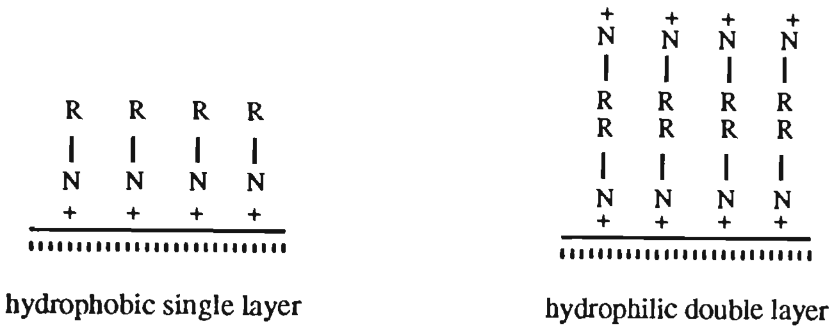


Figure 5.9 Water absorption of permeable concrete paver substrates

The test results clearly show that the water resistance of the substrates could not be attributed to the adsorption of cationic surfactant on the substrate surface because the water absorption value of the substrate treated with the quaternary ammonium solution showed the highest water absorption value compared to that of untreated substrates and that of the substrates treated only with silicate. The substrates treated with the silicate followed by the same quaternary ammonium solution treatment showed a significantly lower water absorption value. To a polar substrate such as a concrete surface, the adsorption between positively charged nitrogen of the quaternary ammonium salt and the negatively charged oxygen of the concrete surface may be strong [112, 160, 183, 187, 204]. However, it is possible that such adsorption could allow the substrate surface to become more hydrophilic by forming a double layer [165] (see Figure 5.10). This double layer formed by the quaternary ammonium salt could further lower the critical surface tension of the substrate and make the substrates become more hydrophilic because the quaternary ammonium salt has a surfactant structure. Therefore, this would explain the water absorption of the substrates treated only with this quaternary ammonium bromide.



hydrophobic single layer

hydrophilic double layer

Figure 5.10 Formation of cationic surfactant layer (or double layers) on the masonry substrate surface

A water vapour transmission test of the permeable concrete paver substrates treated with the silicate followed by impregnation with 3% Vantoc CC30 solution was carried out. The controls were substrates which were treated only with the silicate impregnant, and the untreated substrates. The water vapour transmission values as a function of time are shown in Figure 5.11. The test results show that the water vapour transmission rate of the substrates treated with diluted silicate solution was slightly lower than that of the untreated substrates. In addition, the vapour transfer rate of the substrates treated with silicate followed by the impregnation with quaternary ammonium salt solution was lower than that of the untreated substrates in the first 24 hours. However, the water vapour transmission rates in the three cases were almost the same after the 24 hour test. The initially higher rates in the untreated and silicate-only cases may be attributed to the same reason as discussed in ξ 3.4.4. The test results imply that the capillaries were not fully blocked by the simple impregnations either with diluted silicate or the silicate followed by quaternary ammonium salt. Some pore volume may be reduced by the silicate or organo-silicate formed in the capillaries. However, vapour transfer rates were not significantly affected. It is further confirmed that the water resistant effect of the treated substrates was attributed to the organo-silicate which formed a water repellent organic layer on the capillary surface rather than fully blocking the capillaries.

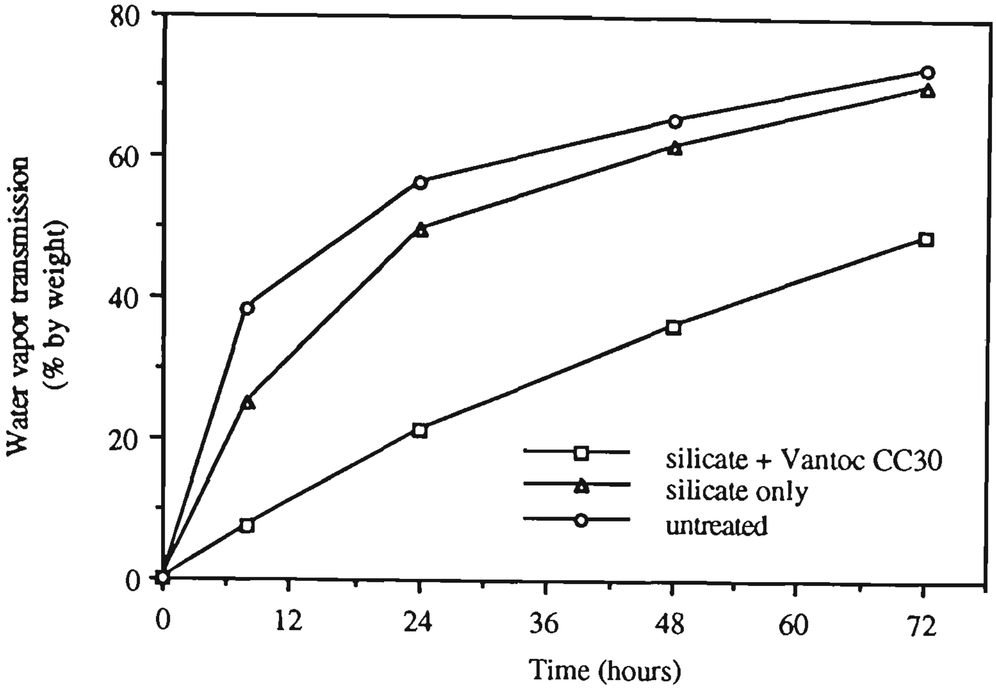


Figure 5.11 Water vapour transmission of permeable concrete pavers

5.3.2 Factors affecting the water resistant effect of the treated substrates

Table 5.2 shows the effects on the water resistant effect of the treated permeable concrete pavers by different quaternary ammonium salts at various concentrations. The substrates were treated with the sodium silicate impregnant first and then impregnated with the quaternary ammonium salts after 24 hours.

Table 5.2 Effects on water absorption of the treated substrates

Quaternary ammonium salts	Concentration (%)	Water absorption (24 hours, kg/m^2)
Cetyltrimethyl ammonium chloride (Vantoc CC30)	0.3%	1.1
Cetyltrimethyl ammonium chloride (Vantoc CC30)	1.5%	1.03
Cetyltrimethyl ammonium chloride (Vantoc CC30)	3.0%	0.88
Benzyllauryltrimethyl ammonium chloride (Vantoc CL80)	0.9%	0.98
Myristyltrimethyl ammonium bromide (Vantoc N40)	0.9%	1.02
Untreated	-	3.64

The test results show that the water absorption value slightly decreased with an increase in the concentration of cetyltrimethyl ammonium chloride (Vantoc CC30) solution. However, in the tested concentration range, the water absorption values of the treated substrates were all significantly lower than that of the controls. In addition, the test results also indicate that all three alkyl quaternary ammonium salt solutions impart a similar water resistant effect to the treated substrates. The common property of the three quaternary ammonium salts was that they all had a long hydrocarbon chain (e.g. a R_{16} for Vantoc CC30 , a R_{12} for Vantoc CL80 and a R_{14} for Vantoc N40) which together with the sodium silicate provided the satisfactory water resistance for the treated substrates.

Two-step impregnations were involved in these water resistant treatments. Curing conditions were found to affect the final water resistance of the treated substrates. Table 5.3 shows the effects of curing time of the first impregnation on water absorption of the treated substrates. The substrates were first treated with the silicate impregnant and cured under ambient conditions for 3 hours, 24 hours and 96 hours respectively. Then the substrates were impregnated with 1.2% Vantoc N40 solution. The test results show that the curing time of the first treatment slightly affected the final water absorption value. The water absorption value decreased with a decrease in the curing time after first treatment but was similar when the curing time was 24 hours or less. This may be explained by the silicate starting to condense and react with substrates after impregnation into the substrate. After a certain period, the silicate could form a fully crosslinked structure and leave less ability to react with the alkyl quaternary ammonium to form the organo-silicate product. Therefore, the water absorption value increased with the increase of curing time after the first impregnation. However, it is necessary to allow the substrate to cure and dry for a certain period and then apply the second impregnant. If the quaternary ammonium solution was applied immediately after the silicate impregnation, the silicate could be redissolved into the second impregnant solution to precipitate the quaternary ammonium salt in the impregnation solution. Further, the second impregnant would not impregnate the substrates as the capillaries may be filled with the aqueous silicate solution at the time of the second impregnation. It was found that between 3 and 24 hours of curing after the silicate impregnation of the concrete was satisfactory.

Table 5.3 Effect of curing time on water absorption of the treated substrates

Curing time (hours)	3 hours	24 hours	96 hours
24 hours water absorption (kg/m^2)	0.94	1.00	1.58

It was further found that increasing the curing temperature of the second impregnation decreased the water resistant effect. Table 5.4 shows the effect. Substrates were treated with the silicate and then with 3% Vantoc CC30 solution after 24 hours. After 7 days of curing under ambient conditions, the substrates were then placed into an oven at 70°C for 12 hours. The test results indicate that the water absorption value of the treated substrate with heating was slightly higher than that of the substrates without heating. This could be due to some loss of some organo-silicate through evaporation from the pores of the substrates with an increase in temperature.

Table 5.4 Effect of heating on water absorption of the treated substrates

Conditions	With no heating	With heating
24 hours water absorption (kg/m^2)	0.93	1.56

In order to investigate the durability of the substrate treated by the silicate followed by the quaternary ammonium salt treatment, a long term water absorption and a UV and condensation weathering test was conducted on the Indian fired brick substrates. The substrates were first treated with the silicate impregnant and then with 3% Vantoc CC30 solution after 24 hours. The long term water absorption results are shown in Figure 5.12 and the water absorption values before and after the weathering are listed in Table 5.5. The durability of the substrates was found to be significant according to the test results. It appeared that the organo-silicate was insoluble and possibly crosslinked to the substrate, and so was unable to be destroyed by this long term water absorption test and the UV and condensation weathering.

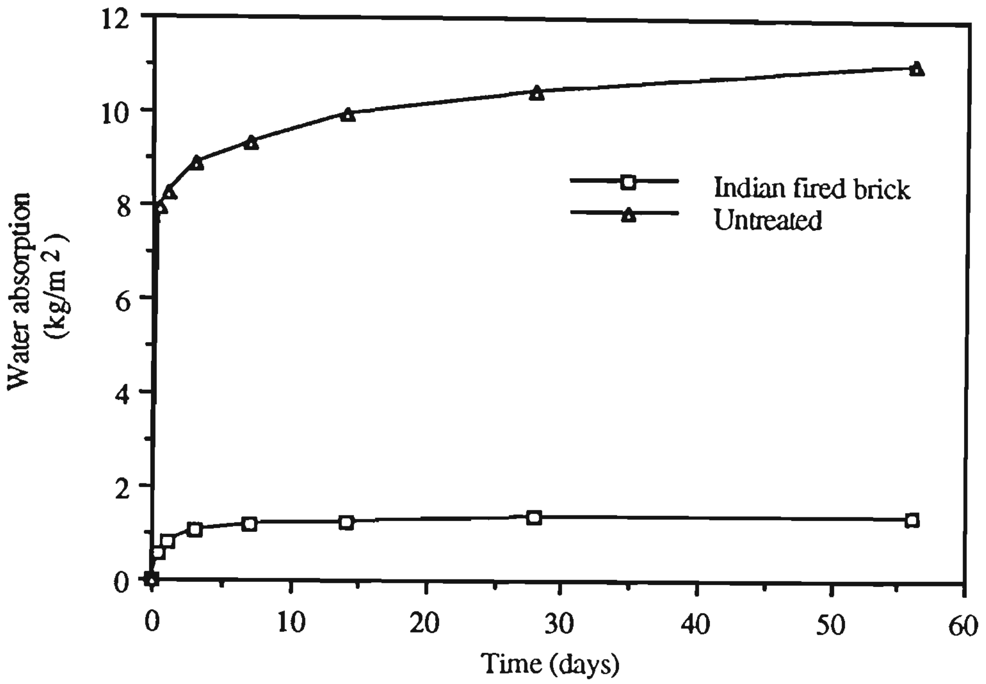


Figure 5.12 Long term water absorption of treated Indian fired bricks

Table 5.5 Water absorption (24 hours) before and after the weathering test

Conditions	Before weathering	After weathering
Water absorption (kg/m^2)	0.67	0.35

However, the effectiveness of this treatment was found to be inferior to silicone water repellent treatment. Table 5.6 lists the beading effect and the water absorption of the treatments on permeable concrete pavers and Indian fired bricks. A full water repellent effect for the substrates may not be obtained by treating the substrates with the silicate followed by impregnation with cationic surfactant. However, the ability of the substrate to resist the water penetration is significantly improved.

***Table 5.6** Impregnation performance of permeable concrete pavers and Indian fired bricks*

Substrates	Treatment conditions	Beading effect	Water absorption (24 hours, kg/m^2)
Permeable concrete	Silicate + 3% Vantoc CC30	4-5	0.88
	5% OMMS-Sn in Isopar G	1-2	0.24
	Untreated	7	3.64
Indian fired brick	Silicate + 3% Vantoc CC30	4-5	0.80
	5% OMMS-Sn in Isopar G	2	0.05
	Untreated	7	7.97

5.3.3 Conclusion

The water absorption of masonry substrates such as permeable concrete pavers and Indian fired bricks examined herein can be significantly reduced through impregnation with 197.5 g/litre sodium silicate followed by impregnation with various diluted alkyl quaternary ammonium salt solutions (concentration from 0.3-3%). The water resistant effect was attributed to the deposition of an organo-silicate which contains a long hydrocarbon chain on the capillary walls of the substrates rather than fully blocking the capillaries. Although the performance of such impregnated substrates is not comparable to those treated with silicone water repellents, a more valuable way to improve the water resistant effect for silicate-treated masonry substrates than other silicate curing agents is provided.

6. CONCLUSIONS

6.1 Potassium octyl/methyl siliconate impregnant

A novel potassium octyl/methyl siliconate (POMS) impregnant has been developed in this research. The mechanisms of the surfactant micellar catalysis of alkaline-silane hydrolysis and the stabilisation of higher alkylsiliconates in aqueous solutions by surfactants has been studied and discussed. The POMS was found to be able to form a stable aqueous solution and to impart a significant water repellent effect to very alkaline masonry substrates. The POMS was obtained by hydrolysing octyltriethoxysilane (OTES) in potassium methylsiliconate (PMS) in the presence of an alkylalcohol ethoxylate nonionic surfactant such as Teric G12A12. The hydrolysis was found to be significantly accelerated by the surfactant through surfactant micellar catalysis. The final POMS contained a siliconate mixture including siliconate monomers, dimers, oligomers and co-oligomers.

By studying the stabilisation of the commercial potassium propylsiliconate (PPMS) in aqueous solution, it was found that alkylalcohol ethoxylate nonionic surfactants can stabilise the higher alkylsiliconate solution by surfactant micellar solubilisation and possibly by interaction between the surfactant and the siliconate. This stabilisation method was also applicable to the POMS solution. Therefore, the surfactant not only accelerates the silane hydrolysis in PMS but also stabilises the final POMS product in water to form a stable aqueous siliconate solution.

The novel POMS solution was found to be effective in rendering masonry substrates water repellent particularly for alkaline substrates. The alkali stability of substrates treated with POMS is significantly improved in comparison to those of commercial siliconate products such as PMS and PPMS. Various test results showed that 2% POMS impregnant can impart to very alkaline substrates such as very fresh cement mortar almost the same quality of water repellent effect as organic solvent-based siloxane (OMMS-Sn) impregnant imparts to these substrates. The POMS impregnant may be regarded as an environmentally friendly replacement for its commercial organic solvent counterparts.

The surfactant in the both PPMS and POMS siliconates reduced the water repellent effect particularly in very alkaline substrates if surfactant addition was high or the diluted solution was stored. However, this surfactant effect may be limited to the minimum by carefully controlling the surfactant concentration in the POMS solution and limiting the storage time following the dilution of POMS concentrate before impregnation.

6.2 Silane/siloxane emulsion impregnant

A novel silane/siloxane (OTES/OMMS) emulsion impregnant has been developed in this research. The mechanism of the silane/siloxane emulsion stabilisation has been studied and discussed. The novel silane/siloxane emulsion was obtained by emulsifying an octyltriethoxysilane (OTES) and octyl/methyl methoxysiloxane (OMMS) mixture in the presence of an acidified alkylamine ethoxylate surfactant. The emulsion was stable and can render various masonry substrates including either alkaline substrates or non-alkaline substrates effectively water repellent. The performance of a 5% emulsion impregnant in various substrates is almost equivalent to that of the solvent-based siloxane (OMMS-Sn) impregnant. The test results show that the emulsion may be regarded as an environmentally friendly replacement for commercial organic solvent-based siloxane impregnants.

The high quality of the water repellent effect of the silane/siloxane emulsion was found to be due to the oligomeric siloxane in the emulsion composition. The good depth of impregnation was attributed to the silane as one of the active parts of the oil phase of the emulsion. In addition, the alkylamine ethoxylate surfactant modified by acetic acid was found to impart no wetting effect to the treated substrate surface. General commercial silicone emulsion impregnants cause wetting on the substrate surface and decrease the water repellency of the treated substrates due to the surfactants in the emulsion. Most surfactants apart from the alkylamine ethoxylate or acidified alkylamine ethoxylate surfactants such as Teric 16M2 or some cationic surfactants were found to impart a wetting effect to the substrates treated with the emulsion.

Further, the acidified alkylamine ethoxylate surfactant has a satisfactory surface activity to impart a small and evenly distributed emulsion particle size. Due to the possession of both cationic and nonionic surfactant properties, the acidified alkylamine ethoxylate surfactant can impart a significant stabilisation effect to the silane/siloxane emulsion by forming a stable interfacial film in the oil/water interface and imparting positive charge to the emulsion particles. The stabilisation of the emulsion was also found to be related to the siloxane in the oil phase of the emulsion. The siloxane was assumed to take part in formation of the interfacial film of the emulsion. In addition, polysiloxane induced from hydrolysis and condensation of the siloxane may also impart a long term stabilisation effect to the emulsion due to polymeric stabilisation.

6.3 Interactions between the substrates and the impregnants

A successful way to treat mud bricks to effect consolidation and water repellency was developed by impregnating the mud brick with diluted sodium silicate impregnant followed by impregnation with a silane/siloxane emulsion or other silicone water repellent impregnants. By studying the interaction between the substrate and the impregnants by FTIR, GPC and various methods, the roles of the silicate and the silane/siloxane emulsion impregnant in rendering the mud brick water repellent were able to be clarified. The general water repellent effect of impregnated substrate is also better understood as a result of this studies. The water repellent effect may be attributed to the deposition of the hydrophobic polysiloxane on the substrate capillaries, which was formed by the hydrolysis and condensation of the silane/siloxane. The silicate not only consolidates the mud brick substrate but also significantly improves the water repellent effect induced by the second impregnation with the silane/siloxane emulsion.

A new way to improve the water resistance of silicate-treated permeable masonry substrates was also developed in this research. The water resistance was significantly improved by impregnating the substrate with diluted sodium silicate followed by an alkyl quaternary ammonium salt solution. This effect was attributed to the deposition of an organo-silicate on the capillary walls of the substrates rather than the full blocking of the capillaries. This organo-silicate is believed to be the reaction product of sodium silicate and the alkyl quaternary ammonium salt. The water resistance of silicate-treated masonry substrates was significantly improved by this method which did not involve the blocking of the substrate capillaries with silicate polymer or by increasing the crosslinking of the inorganic silicate polymer structure in the pores by addition of silicate curing agents as reported by other workers. However, the performance of treated substrates was not comparable to substrates treated with silicone water repellents.

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CODE NAMES OR ABBREVIATIONS

Silicones:

BTES	Isobutyltriethoxysilane
BTMS	Isobutyltrimethoxysilane
MTMS	Methyltrimethoxysilane
OMES	Octyl/methyl ethoxysiloxane
OMMS	Octyl/methyl methoxysiloxane (VP 1268)
OMMS-Sn	Octyl/methyl methoxysiloxane with tin catalyst (Wacker 290)
OTES	Octyltriethoxysilane
OTMS	Octyltrimethoxysilane
SMS	Sodium methylsiliconate
PMS	Potassium methylsiliconate (Rhodorsil 51T)
POMS	Potassium octyl/methyl siliconate
PPMS	Potassium propylsiliconate (Wacker BS20)

Surfactants:

Gardilene IPA/94	Isopropylamine alkylbenzene sulfonate
Hostapon KA	Sodium fatty acid isethionate
Hostapur SAS 60	Sodium secondary alkane sulfonate
LABSA	Linear alkylbenzene sulfonic acid
SPAN n	Sorbitan ester (n is number)
Teric GmAn	(Fatty) alkylalcohol ethoxylates (m or n is number)
Teric GN n	Nonylphenol ethoxylates (n is number)
Teric 16M n (or 16M n)	(Fatty) alkylamine ethoxylates (n is number)
Teric 16M2-n	Modified alkylamine ethoxylates (n is number)
TWEEN n	Ethoxylated sorbitan ester (n is number)

Vantoc CL80	Benzyllauryldimethyl ammonium chloride
Vantoc CC30	Cetyltrimethyl ammonium chloride
Vantoc N40	Myristyltrimethyl ammonium bromide

Other chemicals:

$CDCl_3$	Deuterated chloroform
D_2O	Deuterium oxide
EtOH	Ethanol
Exxsol D60	Mixture of n-paraffins/iso-paraffins and naphthenes
HAc	Acetic acid
Isopar G	Petroleum hydrocarbons (mostly isoparaffins)
MEGDA	Monoethylene glycol diacetate
MeOH	Methanol
n-PrOH (or PrOH)	n-Propanol
iso-PrOH	iso-Propanol
THF	Tetrahydrofuran

Other abbreviations:

EO	Ethylene oxide unit of polyoxyethylene nonionic surfactant
d	Diameter
h	Hight
HLB	Hydrophilic and lipophilic balance of nonionic surfactant
R (or R_n)	Alkyl group (n is the number of hydrocarbon unit)
T_c	Cloud point of nonionic surfactant solution