# DEVELOPMENT OF A METHOD TO FIX A BORON-BASED PRESERVATIVE INTO TIMBER

by

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# DECLARATION OF CANDIDATE

I, Kesunathan Govender, declare that unless indicated, this dissertation is my own work and it has not been submitted for a degree at another Technikon or Tertiary Institution.

K. Govender

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# ABSTRACT

Boron, in spite of its exceptional properties as a timber preservative, is not widely used for this purpose. The three key agents that contribute to the destruction of timber are insects, fungi and ultraviolet radiation. Boron is a good fungicide and insecticide and the acrylic/styrene polymer blend resists ultraviolet attack. Treating timber with boron compounds is very easy and, in most instances, does not require sophisticated equipment. The movement of boron into timber is diffusion driven and requires moisture of between 30-50% in the timber. Unfortunately, this superb mobility of boron results in one major disadvantage, namely, the leaching of boron when moisture enters timber. Various methods have been used to impede the movement of boron out of timber (wax coating, paints, varnishes and water-based polymer coatings. None of them have been completely successful. For instance, varnishes, used to prevent boron from leaching out of timber are unsuitable because they also prevent moisture leaving the timber. This results in blistering of the coatings used to contain the boron. In this project, an all-in-one system was developed by systematically varying the nature of the boron compound and the polymer. The successful formulation, which contained disodium octaborate tetrahydrate, as the source of boron and a styrene acrylic polymer blend, has been found to:

- Allow the uninhibited diffusion of boron into timber.
- Form a clear continuous polymer film on curing on the surface of the timber.
- Display good resistance to ultraviolet attack on the polymer and the timber substrate.

The product developed has been formulated with the following concentrations:

- 60 grams per litre of boric acid equivalent
- 150 grams per litre of boric acid equivalent
- 200 grams per litre of boric acid equivalent

The efficiency of the acrylic/styrene polymer barrier was shown by performing qualitative tests for the presence of boron on the surface of the timber treated with the all-in-one formulation. Furthermore, leaching tests were performed by submerging the treated timber in water and thereafter, analyzing the water for leached boron at regular intervals. The results of these tests showed that the new formulation (60 g/L, 150 g/L and 200 g/L) is suitable for treatment of timber that is destined for above - ground applications. The preservative containing a concentration equivalent to 60 g/L of boric acid was sufficient for remedial treatment. The preservative containing an equivalent of 150 g/L and 200 g/L of boric acid was ideal for treating freshly felled timber.

The patent application for this preservative has been accepted.

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# List of Abbreviations

| | |
|---|---|
| BAE: - | Boric acid equivalent |
| DOT: - | Disodium octaborate tetrahydrate |
| Ppm: - | Parts per million |
| PCP: - | Pentachlorophenol |
| TBTO: - | Tributyl tin oxide |
| CCA: - | Chromated Copper Arsenate |
| SABS: - | South African Bureau of Standards |
| ICP: - | Inductively Coupled Plasma Spectroscopy |
| ICP-AES: - | Inductively coupled plasma atomic emission spectroscopy |
| ICP – MS: - | Inductively coupled plasma - mass spectroscopy |

# Glossary

| | |
|---|---|
| Acrylic polymer: - | Polymers or co polymer s of acrylic acid. Resulting polymers have a range of properties from being brittle to elastomeric. |
| Boric acid: - | A compound of boron ($H_3BO_3$) that is used as a reference to relate all boron – based preservatives. |
| Boric acid equivalent (BAE): - | Reference that is used to standardize all boron-based preservatives. All compounds of boron are expressed as an equivalent quantity of boric acid. |
| Chromated-copper-arsenate: - | Also referred to as CCA widely used preservative that is pressure–impregnated into timber. |
| Creosote: - | A coal tar preservative used in the treatment of timber, particularly those in ground contact. A long chain hydrocarbon preservative. This preservative is regarded as an environmental toxin. |
| Curcumin indicator: - | A boron specific reagent that indicates the presences of boron by a red colour. |
| Disodium octaborate | |

| | |
|---|---|
| Tetrahydrate: - | A spray dried mixture of boric acid and borax. Which equates to $Na_2B_8O_{13}.4H_2O$. |
| Fungicides: - | Chemical agents that destroy fungi e.g. Copper. |
| Heartwood: - | The inner zone in a tree. Dead parenchyma cells forms the heartwood. Generally the dead part of the tree and varies for different species. Contains no reserve material. |
| Insecticides: - | Chemical agents that destroy insects e.g. arsenic. |
| In-situ: - | A method of treating timber without removing it from the environment that it is being used. |
| Leachates: - | The contents from the leaching solution that are removed from the substrates. |
| Lumen: - | The controls of the cell wall that fall within the warty membrane. Also referred to as cell cavity. |
| Mass Spectroscopy: - | Chemical analysis based on separating irons according to their masses, using electromagnetic fields. |
| Methylmethacrylate: - | Acrylic resin monomer. Used to form the methacrylamide polymer. |
| Monomer: - | A single unit of a polymer e.g. strene. |
| Nuclear Magnetic Resonance spectroscopy: - | A type of radio frequency spectroscopy based on a magnetic field generated by spinning of electrically charged nucleus of certain atoms. |

| | |
|---|---|
| Paraflint wax paper: - | A covering that keeps evaporation to a minimum |
| Pentachlorophenol: - | Has been shown to have fungicidal properties. Used as a timber preservative. |
| Polymerisation: - | The chemical process by which monomers combine to form a polymer. |
| Sapwood: - | Portion of wood in living trees containing living cells and reserve materials (e.g. starch). |
| Tributyl tin oxide TBTO: - | Used as both a fungicide and an insecticide. Pigment-less timber preservative. |

# CHAPTER ONE

## Introduction

### 1.1 Background and motivation

Boron compounds exhibit two characteristics that make them exceptional timber preservatives i.e. they act as:

- fungicides
- insecticides.

In spite of these desirable characteristics, the use of these boron-based compounds (as timber preservatives) over other more toxic and environmentally damaging preservatives (See Chapter Two for a review of current preservatives), boron-based preservatives account for a small percentage of the timber preserving market.

Why has the use of these boron compounds (hereafter referred to as boron) been limited in the timber preserving market? In a nutshell, the answer is as follows:

In the presence of moisture, boron is able to diffuse into timber. Due to the highly mobile nature of boron, it is however, able to diffuse out of timber at an equally significant rate. This back-diffusion of boron presents a problem because the accumulation of boron on the surface of timber makes it extremely easy for the boron to leach out of the timber and leave the timber vulnerable to attack by:

- Insects (Wood boring insects)
- Fungi (Wet and dry rot fungi)

The advantages of using boron-based preservatives over other preservatives are:

- Boron is environmentally friendly and safe to use (Lloyd, 1998)
- Boron has a low mammalian toxicity (Lloyd, 1998)
- The use of boron does not require sophisticated equipment
- Boron, being relatively cheap and easy to use, has a wide range of applications in rural areas.

In the light of these advantages that mitigate in favour of boron being used as a timber preservative, it appears to be worthwhile to try to overcome the obstacles that prevent the widespread use of boron in timber preserving formulations. The main challenge was to try and contain the boron within the timber and hence increase the active lifespan of the timber. Systems that are currently being used to prevent the leaching of boron out of timber are:

- Paints
- Waxes
- Polymers

(See Chapter Three for deficiencies related to the above systems)

The challenges that face wood scientists as well as preservative formulators are to:

1. Either find an alternative to the current preservatives that are causing damage to the environment or,
2. To find a method of fixing a boron-based preservative into timber, without adversely affecting the bioactivity of the boron.

In view of the above, the aim of this research is to evaluate the effectiveness of a styrene-acrylic polymer blend as a leach resistant barrier in a preservative formulation.

If successful, then some of the spin-offs would be -:

- Fewer trees would be cut down, because the timber in service would be effectively preserved.
- An environmentally friendly preservative would now enjoy wider application.
- Rural areas that do not have electricity to power timber preserving plants would still be in a position to preserve their timber.
- The preservation of timber would not necessarily have to be a costly affair.
- Boron treated timber will not be confined to use in low hazard environments, but may be used in exposed environments.

This brief introduction to the project is concluded with an assessment of boron – based preservatives. The following assessments highlight the properties of boron, which makes its preservatives extremely effective while being very environmentally friendly.

Boron has unique properties that can be used in preservation of timber. Boron is widely recognised for its broad range of activity towards both fungi and insects and for its low mammalian toxicity, cannot provide long term protection to treated timber due to its strong propensity to leach out of timber (Thévenon *et al.*, 1998). Boron does not occur naturally as boron but is present in deposits, broadly referred to as borates. In the jargon of industry boron – based preservatives containing borates are described as "Boron". To standardise the treatment of timber with boron-based compounds, the concentration of boron is expressed as boric acid equivalent (BAE). For the purposes of this research, a spray dried mixture of boric acid and borax, which equates to disodium octaborate tetrahydrate (DOT), was used for all timber preserving trials. In this thesis, "boron" will be used to refer to a preservative prepared from disodium octaborate tetrahydrate.

Boron is an ideal preservative because of its activity against fungi and insects. It has an extremely low mammalian toxicity and it is regarded as an essential trace element for plants (Lloyd, 1998). Boron is regarded as an essential trace element because it is critical in promoting growth in plants and because it cannot be replaced by any other element. The element has also been used in trace amounts in agriculture to improve the yield of avocado crops. At these levels boron is not considered to be toxic to animals and humans. Studies in the United States have shown that between 18-24 mg of elemental boron can be taken per kilogram of body weight (Lloyd, 1998). Since boron occurs in nature in the form of borates, it is not regarded as an environmental pollutant if used in moderate quantities. The other advantage that boron has against its competitors is that it is relatively cheap and it has natural fire retardant properties (Yalinkilic *et al.*, 1999). Borax is currently used in after-shave creams to relieve skin irritations. The use of boric acid for its antiseptic properties, in surgical procedures by Sir Joseph Lister in the mid 19th century, is well documented (Lloyd, 1998). When a boron preservative is applied to timber, it is able to treat the sapwood as well as the heartwood, provided there is sufficient moisture. Unlike most of the preservatives on the market today, boron does not need specialised treatment vessels when treating timber. In the case of freshly felled timber, the boron can diffuse into the timber along the path of moisture and penetrate the timber. With respect to timber that is bone dry, the boron can be pressure-impregnated into the timber.

Boron used for timber treatment is clear, so it does not result in a colour change. Therefore the natural colour and texture of the timber is maintained. Boron has been used in many parts of the world to treat timber for non-exposed application. Australia and New Zealand use boron treatment for timber preservation as well as for pest control.

Boron does not accumulate in the human body because it is readily excreted through the kidneys and therefore, it would be advisable to replace existing insecticides with boron. Borates have been used for the control of cockroaches. The public needs to be educated about the preservation of wood. Though boron treatment has government approval for 'above-ground', non-exposed environments, boron treatments are not widely accepted by the public. The users of timber are only educated about two preservatives, namely, Chromated-Copper-Arsenate (CCA) and Creosote. It will take a number of years before the South African market makes a significant shift towards more environmentally friendly preservatives. Increased exposure to the world market will gradually force local timber preservers to use boron-based preservatives, in order to supply overseas markets with treated timber that is safe and environmentally friendly.

It is hoped that the results of this project would help lead to a more widespread use of boron preservatives in South Africa and in other countries.

## 1.2 Problem statement (Hypothesis)

Can a compatible homogenous mixture of a boron compound and a sun -screen containing polymer be used without sophisticated equipment to preserve timber?

## 1.3 Objective:

To measure the amount of Boron leached after dip treatment of timber over a 10 day period.

# CHAPTER TWO

## Causes of timber destruction and current methods of prevention

### 2.1. Uses of timber?

The low cost of timber, coupled with the fact that timber is readily available in an array of different shapes, sizes and forms as well as its great strength to weight ratio and the low thermal conductivity have made timber an outstanding building material (Hunt and Garret, 1967). In South Africa, there is a desperate need for housing and treated timber can be used to house a larger number of people relatively cheaply. Furthermore, timber is far more aesthetically appealing than metal and concrete. On account of its low thermal conductivity, timber can keep one warm in winter and cool in summer. It is therefore surprising that timber is extremely under-utilised in South Africa. This is due to the fact that timber is very vulnerable to attack and can be destroyed by various factors.

### 2.2. Background to timber destruction

The three principal destroyers of wood are fungi, insects and the weather.

### 2.2.1. Destruction of wood by fungi

Fungi infect trees, logs that are in transit, logs in storage, timber during seasoning and timber in service (Wilkinson, 1979). Fungi cannot manufacture their own food by photosynthesis and therefore live off other plants and animals. The three types of fungi responsible for the destruction of wood are dry rot, wet rot and white rot fungi (Wilkinson, 1979).

Wood destroying fungi differ from other fungi on account of their ability to digest the lignified walls of the wood cells. The dry rot fungus is called *Serpula Lacrymans* (Coggins, 1980). Wet rot decay is a broad term used to describe the destruction of wood by all fungus except *Serpula Lacrymans*. Wet rot fungus is found in situations where, there is above average moisture content in the wood. *'Coniophora Puteana'*, also known as the 'Cellar Fungus', is the most common wet rot fungus. The optimum moisture content for the growth of this fungus is approximately 50% - 60% (Coggins, 1980). Fungal attack leads to certain fundamental changes in properties of the wood, such as colour, texture, continuity, strength and dimensional stability (Hunt and Garrat, 1967).

Attack by fungus affects the integrity of the wood and reduces its life span. Further, wood destroying fungi create favourable conditions for the wood destroying insects to invade the timber. This condition is more common with harder wood species. Fungal rot is more prevalent in European countries, where the moisture content is much higher than in South Africa. White rot causing fungi thrive readily on all the important constituents of wood (e.g. cellulose and hemicellulose), provided there is sufficient oxygen present for the fungi to grow (Wilkinson, 1979). Heartwood shows a greater vulnerability to be attacked by fungi. Wood that has been attacked by 'white rot' fungi shows no loss in its dimensional stability but the wood looks unattractive, with a 'snowy' appearance (Wilkinson, 1979).

### 2.2.2. Destruction of wood by insects

With regard to the destruction of wood by insects, it is noted that there is often little distinction made between the various attacking species. Insect attack is specific to the age of the timber, species of timber and climate in which the timber is found.

Temperature does not appear to limit insect activity as shown by the fact that insects destroy timber in the Arctic as well as in hot desert conditions (Wilkinson, 1979). Insects pose a great competition to man for the vegetation. Trees are a major source of food for the large insect population. Unfortunately, insects do not distinguish between decaying wood and processed timber that may be priceless. Insects attack different parts of the tree. Some insects bore into the softwood (also known as the sapwood) whilst others attack the heartwood (also known as the hardwood). Insects use timber to satisfy their nutritional requirements as well as to provide them with a habitat in which to lay their eggs and ensure the continuation of the species.
In South Africa, damage to wood by insects is greater than that by fungi. For purposes of discussion, it may be better to separate insect attack into two distinct classes:

- Termite attack
- Beetle attack

Termites live mainly in the tropical region of Africa, Asia, America and Australia (Wilkinson, 1979). There are various species of termites and they live on dead or decaying timber and young trees. A single colony of termites can contain several thousands termites which are capable of razing a timber framed house to the ground. The four main types of termites responsible for the destruction of timber are:

- Subterranean termites
- Dry wood termites
- Damp wood termites
- Harvester termites (Wilkinson, 1979).

Whilst dry wood and damp wood termites attack above ground timber, subterranean termites attack timber that is in ground contact and this can either be a dead or decaying tree or a fence post.

It is extremely difficult to visibly detect wood destruction by termites because they leave an outer casing of the timber untouched, while devouring the inside of the timber. The hollowing out of the timber is only noticed at a very late stage, when the entire structure of the timber starts to crumble. Termites form an important part of the fauna of warmer climates (Harris, 1964). The damage that termites cause to a country's economy is two fold because they attack young trees as well as timber in service. Plantations of wattle have fallen prey to termite attack and this has cost the economy dearly (Harris, 1964). Termites that damage plantations are usually of the subterranean type i.e. living beneath the ground surface. Dead and decaying wood forms an integral part of the diet of common termites (Harris, 1964). The degree of resistance that is offered to termites by wood varies with the species of the timber. More dense timber (Hardwoods) (e.g. Bald Cypress and Sassafras) has a greater degree of resistance as compared to softwoods, which have to be made resistant by chemical intervention (Wilkinson, 1979). Hardwoods, which are regarded as exotic wood, has a higher percentage of lignin compared to softwoods, which contains more starches and sugars (Harris, 1964). This is a favourable condition for termite attack and explains why the sapwood is attacked more readily than the heartwood. Some wood species are more readily attacked than others (e.g. Pine would be more readily attacked than Cypress wood). Unfortunately this is rare and we have to rely on chemical intervention to protect timber against termite attack.

Beetles are another class of insects that are responsible for destroying wood. They are capable of living in varying environments and their diets are equally diverse. The damage that is caused by beetles, vary from one country to another. Beetles, which attack timber, are commonly referred to as 'woodworm' (Wilkinson, 1979). Although there are in excess of 250-000 species of beetles that are present in the world today, the following five families of wood destroying beetles need to be considered here:

- *Lyctidae* (powder post beetle)
- *Anobiidae* (death watch beetle)
- *Cerambycidae* (long horn beetle)
- *Bostrichidae* (also referred to as the 'powder post beetle')
- *Platypodidae* and *Scolytidae*

The larvae of *Lyctidae* attack wood that has vessels in which the female can lay its eggs (Wilkinson, 1979). Wood with high starch content such as obeche, mahogany and lumba are most susceptible (Wilkinson, 1979). Obeche is currently imported by South Africa for use in the manufacture of mouldings, coffins and picture frames.

*Anobiidae,* is mainly responsible for the destruction of timber in service i.e. timber in buildings and furniture (Wilkinson, 1979). In this family, there are only two groups that can be identified as large-scale destroyers of timber and these are, *Anobium punctatum* (the furniture beetle) and *Xestobium rufovillosium* (the death watch beetle). The furniture beetle is found mainly in temperate climates. The larvae of this beetle attack both the sapwood and heartwood of both softwoods and hardwood. In South Africa, damage is mainly found in wooden flooring and wooden ornaments. The 'death-watch beetle is known to cause severe damage to old timber and, in England, historic buildings were damaged by the 'death watch beetle' (Wilkinson, 1979).

The *Cerambycidae* family attack timber in plantations. South African pine plantations are particularly susceptible to attack by this family.

Both the lavae and adult beetles of these 'powder post beetles' (*Bostrichidae*) usually attack the sapwood of hard, exotic timber (Wilkinson, 1979).

*Platypodidae* and *Scolytidae* are found in temperate regions and no timber is immune to attack by this family. *Scolytidae* are bark beetles because they bore holes through the phloem and cambium of living tissue (Wilkinson, 1979). Apart from boring holes into the bark, this family, carry with them, highly destructive fungi that can infect vast plantations.

### 2.2.3. Destruction of Wood by Weathering

Exposure to ultraviolet radiation from the sun, cause the wood to slowly deteriorate. Ultraviolet radiation destroys the fibres of the wood and this leads to the gradual break down of the wood. Ultraviolet radiation causes the resins in the timber to migrate to the surface, from where they are lost. This in turn causes the timber to become brittle. It was also found that lignin from wood strongly absorbs ultraviolet radiation and eventually leads to radical-induced depolymerisation of lignin and cellulose at the surface of the wood (Kiguchi *et al.*, 2001). Indoors, wood can maintain its appearance for many years, but outdoors this soon changes (Wilkinson, 1979).

In addition to ultraviolet radiation, rain, wind and combinations of these factors can also destroy timber. Weathering is evident in change to colour, texture and dimensional stability. Wetting and drying, cause swelling and shrinking. This, together with the erosion, causes grain raise, which increases the hazard of fungal decay because the fungal spores have a secure area to adhere to.

## 2.3. Common wood preservatives and their composition

In order to understand the effect that current wood preservatives have on the environment, it is necessary to evaluate their chemical composition and their mode of action. Preservatives may be classified as ones with a long or short residual life.

The short life-span preservatives are generally used to kill the "culprits" and their effectiveness is measured by their 'knock-down' effect. They are not intended to leave any residue for future protection. Generally, they are organic solvent based preservatives which possess either fungicidal or insecticidal properties and in some cases, both.

### 2.3.1. Pentachlorophenol (PCP)

Pentachlorophenol (PCP) has been shown to have fungicidal properties (Wilkinson, 1979). On account of its toxicity to humans it has already been phased out in Europe and is in the process of being phased out in South Africa. PCP has been associated with skin cancer and other dermal conditions and there was a need to find other less harmful alternatives. PCP has been used as a pigment-less alternative in the eighties and early nineties but the availability of PCP has dropped significantly in recent years. High pressure was used to introduce PCP deep into the cell cavities of timber, or alternatively, the preservative is painted on to give an envelope treatment of the timber. The use of PCP as a fungicide alone, as opposed to the requirements for properties as a fungicide and an insecticide has led to its demise as a timber preservative.

### 2.3.2. Tributyl tin oxide (TBTO)

Currently, tributyl tin oxide (TBTO) is being used as both a fungicide and an insecticide. It has proved useful in situations where the wood is required to retain its original colour, because TBTO does not impart any colour to the wood, once treated. TBTO treated timber cannot be used for exterior applications. TBTO is currently mixed with Lindane, to enhance the insecticidal properties and sold as a treatment for in-situ applications. Lindane, an organo-chloride, has often been associated with breast cancer and is banned in many parts of the world. This preservative cannot be fixed into timber. It is usually painted onto timber, to provide an envelope protection to the timber. TBTO/Lindane has a short residual lifespan on timber.

### 2.3.3. Chromated Copper Arsenate (CCA)

Chromated copper arsenate (CCA) is a widely used preservative, which is sold under various brand names. CCA has been used in South Africa since the sixties and the South African Bureau of Standards (SABS) has specifications governing the treatment of timber with this preservative. The constituents of CCA have the following roles:

- Copper acts as a fungicide and is accepted as an effective fungicide.
- Arsenic acts as an insecticide and is responsible for repelling or killing the insects that are responsible for timber destruction.
- Chromium is responsible for fixing the preservative onto the wood fibres.

The quantity of preservative that is pumped into the timber varies, according to hazard class of the application. The higher the hazard classification for the desired application, the higher the concentration of CCA required. CCA is generally mixed in a range of concentrations, depending on the retention required. CCA is a waterborne treatment and the treated product is safe to use after 48 hrs.

The hazards that are associated with CCA relate more to spillage of the preservative solution and the concentrate during transit or at the treatment site. If CCA is spilled, it can be toxic to both wildlife and marine organisms. It also causes long-term ecological imbalances and can be costly to clean up. Timber treatment plants therefore have been pressurised into meeting safety requirements when dealing with CCA. Other problems associated with CCA are disposal of the sludge remaining in the treatment vessel. The latter has prompted wood scientists to perform lifecycle analyses on the treated timber. The idea behind this was to ascertain whether more preservative than necessary was being deposited into timber, given the life expectancy of the timber. The impact of such studies will require the standards set to be completely re-examined so that new standards and norms can be established. Unfortunately this approach has already met with resistance from preservative manufacturers because a reduction in the quantities of preservatives deposited in timber will imply that lower volumes of preservatives will be sold and this would invariably affect their profits. However it is worth noting that some countries have closed down their CCA producing plants, while others like Germany have opted for a 'cradle to grave' policy regarding all treated timber. The 'cradle to grave' policy requires the company responsible for producing the preservative to dispose of the treated timber once it is no longer required by the end user. This policy applies to timber treated with any preservative.

Owing to the nature of CCA, any sludge that is generated is also treated with the same caution as the CCA itself. There are essentially two sources of sludge and the most common source is the sawdust. Timber that is not cleaned prior to treatment is the most common source of sludge. The CCA fixes onto the sawdust and settles at the bottom of the chemical storage tanks. Over a period of time, this CCA that is fixed onto the sawdust forms a sludge that accumulates and hence starts to occupy a sizable volume of the storage tank. The tanks have to be de-sludged in order to maintain correct preservative levels. Other sources of sludge are trace elements that may be present in the CCA. This sludge has to be treated and, only then can it be disposed off in a landfill site.

In Australia, all CCA sludge that has been generated at a timber preserving plant is mixed with concrete so that it is immobilised and the waste is thereafter put into a landfill site (Butler, 1993). In South Africa, the CCA sludge is rendered insoluble by adding a mixture of slaked lime and sodium dithionite to the sludge and thereafter, disposing of the sludge in a landfill site. The disposal of toxic wastes in landfill sites may soon attract the attention of environmental pressure groups.

### 2.3.4. Creosote

Creosote has been used for the treatment of timber, particularly those in ground contact. Creosote is a broad term use to describe the by-product of the carbonisation of bituminous coal (Wilkinson, 1979). It is also obtained from distilling of coal tar and is collected between the temperatures 200 - 400°C. Creosote is generally characterised as heavy oil or light oil, depending on the fraction of the high boiling component present in the distillate. The heavy component of creosote is responsible for its long lasting presence in timber (Wilkinson, 1979). Creosote has been used for almost two hundred years for the preservation of timber. It has proved its effectiveness against both fungi and insects. A creosote treated pole has a black appearance and is widely used by farmers. Creosote is water insoluble and the oils in it prevent the timber from cracking. Unfortunately, in temperate climates, the creosote tends to bleed out of timber and leaves the timber vulnerable to attack by insects and fungi. The bleeding of creosote is also a major environmental hazard. It has drawn the attention of environmental watchdog groupings because it is believed that creosote makes its way to the water table and pollutes the water and causes harm to the environment. Germany has closed down all its creosote plants and is clamping down on the use of creosote treated timber. The other drawback associated with the use of creosote is that the oil base of creosote does not allow for the adhesion of paint to treated timber and this limits its applicability. Timber treated with creosote will only have one colour, namely, black.

It is for these reasons that environmentalist as well as wood scientists have been looking for safer alternatives to the present list of preservatives. In the light of these factors that cause the destruction of timber, the properties of an ideal and desirable preservative begin to emerge. An ideal preservative should be a good fungicide with a broad spectrum of anti-fungal activity. Since fungal attack occurs on the surface of timber, the preservative should not be deactivated when it comes into contact with sunlight or other elements. In addition, the preservative should offer anti-fungal activity against a wide range of fungi. Furthermore, the preservative should not be insect- specific in its activity. Timber is of nutritional value to insects, during all stages of its life. Whether it is for the cellulose of the timber or the cell cavities, which can play host to the larvae of the insects, timber is vulnerable. Permanence is therefore a critical feature of a good preservative. As far as possible, the preservative should not leach out of the timber and enter the natural ecology of the surroundings.

The preservative should be able to protect the timber against harmful ultraviolet radiation that caused damage to the fibres of the timber and ultimately undermines the dimensional stability of the timber. These various properties have to be combined into one so that the preservative ultimately preserves the timber against all these factors.

While it is necessary for a preservative to be toxic to insect and fungi attack, there are limitations to this toxicity because human contact with the preservative or the handling of preserved timber is difficult to avoid and the extreme toxicity will render the preservative un-usable. The aspect of human contact with preserved timber has received a great deal of attention from press agencies in the USA. The spotlight has been cast on CCA and there is a strong lobby in favour of the total ban of CCA. Toxicity is of vital importance to the functioning of a good preservative. However there are also limitations in this regard because the preservative cannot be toxic to the extent that it becomes unsafe to handle or use.

In the recent past the press has been giving much attention to the use of toxic preservatives on playground furniture but this has remained more of an emotive issue. There has also been much negative publicity to the effect of insecticides on both wildlife and bird life. It is sometimes unavoidable that animals and certain species of birds may gnaw on timber that is used to construct their enclosures. Some of these priceless animals and birds are endangered. Thus the preservatives used to treat the timber in these enclosures should not have a high toxicity.

The preservative must be relatively inexpensive so that the seller can make a sizeable profit. The profit margin must be good enough so that the supplier of treated timber will be attracted to the idea of selling treated timber, rather than untreated timber. The other factor that is associated with the profits is the ease with which the timber is treated. If the process is time consuming then the supplier will have to include handling cost to the eventual price and the labour costs also escalate. In addition economic factors need to be taken into account when producing an effective preservative. Therefore, a preservative that is easy to use and relatively inexpensive will be attractive to timber suppliers. Cost can influence which preservative is used in some countries (Wilkinson, 1979). It will therefore make business sense to invest in a product that will take these factors into account.

In addition to cost of the preservative, environmental impact considerations must also be taken into account. "Wood preservatives are somewhat of an anathema because they must be toxic to the target organism, yet they must also be safe to use and safe to the environment" (Rainer, 1993). In an age where more attention is being paid to the environment, the preservative has to satisfy the criterion of being environmentally friendly. It has now become necessary to undertake environmental impact studies to ascertain whether a timber preservative is suitable for commercial purposes. The effect that a preservative will have on both the marine and land ecology must be considered before a preservative can be approved for use. There are preservatives that tend to leach with the passage of time and even though the levels of these toxic preservatives may be low, the fact that leaching does take place is a source of concern. It has always been the practice to use water-soluble fixed preservatives together with water repellent coatings to minimise the loss of these 'so called' fixed toxic preservatives to the ground. However, it has not been common to use water repellent coatings to try and limit the mobility of preservatives that leach (Murphy *et al.*, 1995).

# CHAPTER THREE

## Review of methods being used to prevent the leaching of boron – based preservatives

Prior to reviewing the various methods being used to limit or prevent the leaching of boron-based preservatives from timber, it is necessary to define the term boric acid equivalent (BAE) and the BAE specifications of the SABS.

Since the treatment of timber with boron based compounds can vary, depending on the boron compound that is used, it has become necessary to adopt a format or a reference that makes the different compounds comparable. As a reference, BAE has been used to express all 'boron-based' treatments. Therefore, it is necessary to convert the boron contents in the various preparations to boric acid equivalents. This is an internationally acceptable method.

The standards that are laid down in different countries vary due to the different climatic and environmental conditions, which undoubtedly influence the pool of insect and fungal species. Tests that were done in the fifties, established a toxic threshold for wood destroying fungi to be between 0.6 kg to 2.5 kg of BAE per cubic meter of timber (Drysdale, 1994). It is interesting to note that all standards that are used accept that boron based treatments can only be used for above ground applications. Borate use has gone through major revisions because of public emotions and this has led to inconsistent standards for borate treatments in essentially similar hazard environments (Lloyd, 2000). The indirect advantage for using an internationally acceptable standard for boron treatment is two fold; one is that it would promote a more effective use of treated timber on an international scale and secondly, free trade between the various countries is also promoted (Schoeman *et al.*, 1998). If stringent specifications are enforced in one country whilst relaxed conditions apply to another country, then the chances of treated timber making its way from one country to another becomes less likely.

Borates were found to be effective against the Formosan termite in the USA and subsequently, the USA and Hawaii performed studies to establish a threshold value for treatment against the Formosan termite. The value arrived at was 8 kgs BAE per cubic meter of timber (Schoeman *et al.*, 1998). The adoption of retention specifications is largely dependant on field trials that are carried out on the various fungi and insects

The SABS is responsible for drafting and ensuring conformance to specifications for boron use in timber preserving. The current specifications for boron – based treatment in South Africa stipulates that a minimum of 5 kgs BAE must be deposited per cubic meter of timber, in order for the timber to enjoy thorough protection against wood destroying organisms. It is useful to note that this specification was set on the basis that there was no means of fixing the boron into timber and hence boron treated timber must only be used in above ground, non-exposed environments. The review of the specifications will be dependant on the introduction of boron-based preservatives with greater permanence in timber.

The calculations below can be used to explain the conversion factors that appear in the table below:

The molecular mass of boric acid is 61.8 grams per mole

The molecular mass of disodium octaborate (DOT) is 413 grams per mole but there being 8 atoms of boron per mole, the molecular mass is therefore 413/ 8. This equals to 51.6 grams per mole. Therefore, to convert sodium octaborate to boric acid:

61.8 grams boric acid is equivalent to 51.6 grams of disodium octaborate tetrahydrate.

Converting a mass X of DOT to boric acid = Mass of DOT multiplied by 61.8/51.6

Therefore mass of DOT multiplied by **1.20** gives equivalent mass of boric acid

The conversion of boron to boric acid can be done in a similar manner:

Molecular mass of boron is 10.8 grams per mole

Molecular mass of boric acid is 61.8 grams per mole

Therefore, 61.8 grams of boric acid is equivalent to 10.8 grams of boron

Hence Y grams of boron is equivalent to 61.8/ 10.8 grams of boric acid.

Y grams of boron multiplied by **5.72** gives the equivalent mass of boric acid.

A table of conversion for the various boron-based compounds to Boric Acid Equivalent is given below:

Table 3.1 Conversion factors for the various boron-based compounds

| From | To boric acid<br>$H_3BO_3$<br>Molar mass: 61.8 g/mol. |
|---|---|
| $B_2O_3$<br>Molar mass:<br>69.6 g/mol. | 1.78 |
| $Na_2B_4O_7$<br>Molar mass: 201 g/mol. | 1.23 |
| $Na_2B_8O_{13}.4H_2O$<br>Molar mass:<br>412 g/mol. | 1.20 |
| $Na_2B_4O_7.10H_2O$<br>Molar mass:<br>381 g/mol. | 0.65 |

With the overwhelming evidence that boron-based compounds have the potential to make good timber preservatives, the challenge is therefore to find a method of preventing the loss of boron from timber through leaching. In order to develop a leach-proof method, it is necessary to review work that has already been done. It is also worth noting that the majority of the attempts made focused on the use of boron treated timber for non-ground contact applications. This is, partially due to the high hazard zone that is found approximately 30 cm below the ground surface.

### 3.1. Typical applications of boron, in spite of its mobile nature

Some researchers have claimed that borates were effective against subterranean termites but that the effectiveness was limited to above ground applications (Tsunoda *et al.*, 1998). This supports the view that borates should be confined to use in the preservation of timber for above ground applications.

The studies of Tsunoda and co-workers, showed that boron treated samples underwent weight losses at less than 1% and that the attack did not affect the appearance of the timber significantly. The finding has relevance for South African applications. This is because termites are a severe problem in our country. Furthermore, a significant proportion of houses do not have foundations and the design requires timber to be in contact with the ground. The use of borates in the preservation of timber, since 1934, as well as their effectiveness in the 'hazard class two' application (above ground and non exposed environments) have been well documented (Drysdale, 1994). Research in borates as a preservative has been ongoing in both Australia and New Zealand and borate treatment is being used on a commercial scale.

The mobility of boron has limited the use of boron-treated timber to hazard class two environments, namely for above ground and non-exposed environments. It has been reported that boron is effective against both brown and white rot fungi (Drysdale, 1994). Borate treated timber has found wide use in timber-framed houses and in structural beams of roofs. Borate preservatives continue to be favoured, in spite of the propensity of boron to leach out of treated wood. The timber-framed housing market utilizes boron preserved timber for two reasons. Boron preservatives preserve the natural colour of timber, while protecting it from attack by fungi and insects.

The mobile nature of boron based timber preservatives also has its advantages (Schoeman *et al.*, 1998). The most important advantage of the mobile nature of boron is that it is free to diffuse to a site where moisture has entered and fungal attack is imminent. This application is analogous to the workings of anti-biotic medication. The ideal situation would be to develop a method that will not allow the boron to exit the timber but will allow unhindered movement inside the timber. The presence of moisture is of paramount importance for the thorough penetration of boron into the timber and it is for this reason that boron-based preservatives are ideally suited for use on freshly felled, or green timber.

### 3.2. Coatings and their role in preventing the leaching of boron

The role of borates in the remedial treatment of timber has not been thoroughly explored. It has been proposed that for proper penetration of boron to occur, there had to be some free water in the voids of the cell walls of wood (Schoeman *et al.*, 1998). It was found that higher moisture contents led to greater depths of diffusion. However, after a period of 14 to 35 months, the depth steadily diminished because of 'back diffusion', which was caused by drying out of the timber (Morrell and Freitag, 1995). The presence and subsequent loss of moisture sets some pre-conditions for a coating that will encapsulate boron. The coating must:

-

- Allow the moisture from the freshly felled or green timber, to exit without causing blistering or bubbling.
- Not allow pockets of moisture to accumulate beneath it because this would let the boron diffuse into these pockets and by so doing, the coating will be prized away from the timber.
- The coating must not allow for the rapid loss of moisture, as this will cause the timber to bow and distort due to the non-uniform loss of moisture.

Wide ranges of coatings have been used to prevent the leaching of boron from timber. Some of these coatings consisted of polyvinyl acrylate wall paint whilst others longer lasting oil based paints. These coatings were vulnerable to ultraviolet radiation, which caused the coatings to peel off. Thus the timber was exposed to rain and other weathering elements that aided the leaching of boron. There were also instances where coatings allowed the ultraviolet radiation to pass through the coatings and attack underlying timber (Kiguchi *et al.*, 2001). The role of a coating was to provide a barrier against leaching of boron out of treated timber. Furthermore a coating was intended to act as a screen for ultraviolet radiation. An ideal coating should be stable to ultraviolet radiation while preventing leaching of boron out of the timber.

Waxes and wax emulsions were also used as barriers against leaching.

The use of water repellent emulsions in conjunction with a timber preservative was regarded as one of the most cost-effective methods of preserving uncoated timber in service (Cui and Archer, 1997). Water repellents tend to reduce the rate at which moisture migrates into and out of timber and in so doing, they tend to reduce the amount of deformity that timber undergoes, especially during drying out. Irregular, but especially rapid loss of moisture causes the timber to bend and split. Therefore, coatings not only play a role in delaying or preventing leaching, but they also play a critical role in providing stability during the pre-treating and post-treating phases of timber preservation.

Emulsions that are used for the purposes of water repellency consist of the 'oil in water' system (Cui and Archer, 1997). An important point worth noting is that there is no chemical relationship between the wax emulsion and the timber. The aim of using the wax emulsion is to provide a physical barrier that will prevent boron from leaching out of the timber. Therefore, the possibility exists that the coating can be washed off, eroded or weathered away with the passage of time.

A commercial product that uses the wax-emulsion/preservative system is sold as Totim 'B'. This is an "all in one" dip treatment that has a concentration of approximately 300 g of BAE per litre of product. Difficulties were experienced during the use of this product. Firstly, it did not meet the SABS specification of 5 kg of BAE per cubic meter of the timber. A possible reason for this was that the wax might have impeded the diffusion of boron into the timber. Secondly it attracted dust particles. Thirdly, it promoted the growth of moulds. Inspite of these draw backs there is still a demand for this product. People who are environmentally conscious are willing to pardon the grimy appearance of the timber, in order to make a contribution to environmental protection. The other reason for people still using Totim 'B' is that there are no other viable boron-based products available on the market.

In contrast to waxes, varnishes do not have problems associated with dust adhesion and mould growth. Other advantages of varnishes are the relative ease of application and their transparency after curing. A disadvantage of varnish arises from its property of curing to a fixed dimension. Since temperature invariably alters the dimensions of the timber and the fixed dimension of the varnish cannot accommodate these changes. The result is that the varnish tends to rupture and eventually peel off, once water enters the cracks and voids. Ultimately, the timber is left exposed and boron can leach out unhindered. Over-coating with new layers of varnish partly addressed this problem. However it leaves the timber unsightly while adding to the cost of preservation. For long term and cost effective solutions to the problem of boron leaching, varnishes have proved to be unsuitable.

Ideally, a coating should have the following properties-:

- A moderate ability to repel water
- Sufficient resistance to ultraviolet radiation
- Good adhesion to timber and durability.

It would be a bonus if a coating could function as a one-way membrane i.e. allows water to leave the timber, but prevent the water from entering it. Poor coatings may allow exposure to high levels of moisture. Under such conditions the possibility of fungal decay becomes more likely (Petric *et a*l., 2001). Since the coating is the last line of defence against leaching, the coating will have to be very durable.

Leaching trials were done on wooden beams that were treated with boric acid. As a control, some beams were sealed with a polyurethane varnish to retard leaching. The experiment revealed that approximately 47% of the boron left the "test" beams in the first six months of a 'three year' trial (Peylo and Willeitner, 1997). It was suggested that in order for boron-based preservatives to achieve a greater share of the preservative market, there must be a completely new approach to the chemistry involved in boron treatments (Nicholas *et al.*, 1990). One such approach might be to try and render the boron insoluble in the timber after being treated with the preservative or alternatively, use a water repellent in conjunction with the boron so that the leaching of boron is retarded (Nicholas *et al.*, 1990). Another possible approach is to concentrate on the boron molecule, with the intention of:

- Coupling boron with a chain compound or,
- Coupling boron with another molecule that does not have the same mobility as boron.

An amine /boric acid system was integrated in order to determine the extent of leaching of this boron complex (Petric *et al.*, 2001). Petric and co-workers found that timber that was treated with this complex lost 94% of the biocides that were intended to preserve the timber. This alkanolamine-boric acid preservative was compared with an ethanol soluble boric acid preservative. After having concluded that the alkanolamine preservative did not reduce the rate at which boron leached out of the timber, they used the following coatings to reduce the leaching of the biocides from the timber:

- A transparent low-built acrylate coating with a water-soluble stain.
- A transparent low built alkyd coating with a stain.
- A transparent high built acrylate coating with a stain.
- A transparent high built alkyd coating with a stain.
- An opaque white alkyd paint was used as a coating.

From the five systems that were used, they found that the opaque white paint reduced the loss of biocide by 68%. This opaque white paint was investigated further and the water vapour permeability of the various coatings was investigated. The trials of (Petric *et al*,.2001) led to some important findings-:

- Water vapour permeability was directly related to the loss of biocide.
- The coatings with the lowest water vapour permeability reduced the loss of biocide by the most significant amount.

The water vapour permeability of a coating would make it easy to decide if a particular coating was suitable or not. There are two inferences can be drawn from this finding:

- That opaqueness had a direct effect in limiting ultraviolet attack
- That water vapour permeability is an important factor in determining the suitability of a coating.

## 3.3. The use of water-based polymers as anti-leaching agents:

Water-based polymer emulsions can be classified as coatings that are able to act as relatively good barriers against leaching of boron but yet, do not suffer drawbacks such as poor elasticity and poor adhesion.

Acrylic and styrene polymers have memory associated with their chemical structure and therefore, are able to expand and contract, yet return to their original shape and size. These polymers cure to a water-repellent film. A complete film of sufficient thickness that can expand and contract and display water repellence is a desired characteristic. The effect that polymers have on timber and their effect on preventing photo-degradation of timber was investigated (Kiguchi *et al.*, 2001). In this study two different coatings were used: one was polyethylene glycol (PEG) and the other was UVA grafting (2-hydroxy - 4 (2,3 - epoxypropoxy) benzophenone (Kiguchi *et al.*, 2001). The clear finish durability of these coatings was thereafter evaluated. The timber was observed for signs of cracking and peeling of its coatings, according to a grid sheet test (Kiguchi *et* al., 2001).

In cases of incompatibility between the polymer coating and boron preparations, the boron preparations were first impregnated into the timber, and thereafter, the polymer coating was applied. There were also attempts to prepare ‘all in one’ systems.

Polyethylene glycol was also used as a means to limit the mobility of boron out of timber. One such trial focused on the use of polyethylene glycol with a molecular mass of 400 g/mol being reacted with boric acid so that a polyester borate was formed. The polyester borate was thereafter fixed onto the wood with the aid of methylenediphenyl isocyanate, as a coupling agent (Cui and Kamdem, 1999). The resulting treatment was then put on trial against both brown and white rot fungi. The study also focused on the effects of high concentrations on fungal activity. A good indicator of fungal activity is weight loss from the timber. Greater fungal activity is characterised by higher weight loss. It was found that, at a retention level of approximately 7.9 kgs BAE per cubic meter of timber, the preservative demonstrated adequate protection against the fungi, particularly the brown rot fungus. The limitation of this particular study was that it dealt with timber decay by fungi and no trials were done to evaluate the preservative against insect attack and the durability of the preservative to ultraviolet radiation. In South Africa, as in other temperate parts of the world, insects contribute significantly to the destruction of timber and it is therefore important to also evaluate the preservative against insect attack. The specification for borate treatment in South Africa is a retention of 5 kgs of boric acid or boric acid equivalent per cubic meter of timber. This study showed that 7.9 kgs BAE per cubic meter was far more resistant to fungal decay than 4.9 kgs (Cui and Kamdem ,1999). The mere fact that, at a retention level of 4.9 kilograms of BAE per cubic meter of timber, resistance to fungi is satisfactory, means that:

- A significant proportion of the boric acid or the boron had been de-activated by the polymer network.
- There is some other mechanism by which the availability of the boric acid is being diminished in the timber.

Another study, aimed at an 'all in one' system, involved the reaction of boric acid with albumin of egg to yield an albumin borate complex. The latter was impregnated into timber and the temperature of the system was raised to induce coagulation (Thévenon *et al.*, 1998). The intention of this research was to render boron immobile, so that the leaching of boron was reduced, while still maintaining a sufficiently large reservoir of boron within the timber to prevent insect and fungal attack.

Techniques such as Nuclear Magnetic Resonance Spectroscopy, Mass Spectroscopy, Potentiometric Titrations and Acid-Base Titrations were used to elucidate the structure and also to explain the relationship between the boron and the protein complex (Thévenon *et al.*, 1998).

The complex was in fact a salt of boric acid and protein. While the above system extended the period over which boron remained in the timber, boron did leach out at a phenomenal rate.

At this point it is also worth noting that any system that attempts to control leaching, rather than preventing it, will have one major difficulty and that is, to work against a diffusion gradient. The process that feeds boron compounds to the surface for leaching is a diffusion driven one.

Polymer emulsion systems were also used to prevent boron from leaching by blocking the cell walls and hence preventing the contact between boron and water. It was found that unless the movement of water through the available flow paths (i.e. lumen, pits and void spaces) is impeded, the diffusion of boron out of timber is virtually unavoidable (Yalinkilic *et al.*, 1999). Therefore the focus of the study by Yalinkilic and co-workers, was to immobilise the boron by encapsulating the boron in the cell walls with a water repellent vinyl monomer. A monomer was used to fill the gaps in the cell walls so that contact between the boron and the water was not possible. By delaying the contact between the boron and the water, the diffusion of boron was delayed. It was found that attempting to fill the large lumen voids with monomer was impractical and therefore an alternate method of bulking should be found (Yalinkilic *et al.*, 1999). Also, the monomer shrinkage (25% for methylmethacrylate) would invariably create voids and allow contact between boron and water. Yalinkilic and co-workers, devised a novel way of preventing these voids from forming.

Timber was initially treated with boric acid and, thereafter, they used a method of introducing the monomer into the lumen, but delayed polymerisation. Polymerisation was only initiated once a gradual compression force was applied in a hot press. This resulted in the monomer being forced to penetrate the cell walls while the polymer in the lumen filled the voids. As a control, some samples were compressed prior to monomer loading (pre-compressed). They found that some voids reappeared due to shrinkage of the monomer (Yalinkilic *et al.*, 1999). In summarising the performance of the compressed wood polymer composites, the authors admit that the uncompressed samples did not immobilise the boron as well as the compressed samples. However, the compressed samples did not completely immobilise the boron. This, in itself indicates that the monomers in the cell cavities only succeeded in prolonging the leaching of boron, by increasing the depth of penetration of the monomer into the voids of the cells through compression. The research of Yalinkilic *et al.,* (1999) is extremely useful in that it elucidates the activities involved in the movement of boron at a cellular level. It may be summarised as follows:

- The movement of boron is diffusion driven.
- The concentration of boron will tend to an equilibrium position in a closed system.
- In an open system, (typically timber in the ground) the boron will continually diffuse out of the timber until there is little to no boron in the timber.

A practical problem associated with Yalinkilic and co-workers technique is that the deposition of polymer in the lumen is not a process that can be strictly monitored for quality control purposes. Heterogeneity in the monomer distribution will sometimes account for the appearance of voids in both the compressed and the pre-compressed timber samples and unlike a surface coating that can be visually inspected, a plug in the lumen of the cell will not permit convenient quality control. Whilst it was possible to use a stepwise heating process to polymerise the monomer without undermining the dimensional stability of the wood, a process of this nature would be vulnerable to inconsistent quality control methods; hence the quantity of polymer can vary from one piece of wood to another.

Water -based polymer emulsions of the acrylic and styrene type have one distinct advantage over the varnishes and other polyurethane coatings because the acrylic and styrene coatings cure to a less brittle state and therefore, offer a greater degree of flexibility. Surface coatings like varnishes, paints and waxes helped to delay the leaching of boron but ultimately, the effects of weathering caused the loss of boron from the timber to the environment (Peylo Willeitner, 1997).

The preservation of timber using coatings, in conjunction with fixed water borne preservatives has been adequately investigated  (Murphy *et al.*, 1995). Unfortunately, the same cannot be said in the case of unfixed water borne preservatives like boron. Practical knowledge concerning the use of boron in exterior applications has already been well documented in countries like New Zealand and Australia (Murphy *et al.*, 1995). Acrylic polymer coatings of the Rhom and Haas Rhoplex type, together with water shedding additives (aluminium chlorohydrate) were used to create an impervious barrier against boron leaching (Murphy *et al.*, 1995). Southern pine (*Pinus species*) was treated with these preparations and then evaluated against fungal attack as below (Murphy *et al.*, 1995). Samples of Southern pine were treated with:

- Disodium Octaborate tetrahydrate (Trial one) with BAE of 0.07; 0.18; and 0.74% (m/m).
- Disodium octaborate tetrahydrate in an acrylic polymer background (Trial two) with BAE of 0.07; 0.18 and 0.74% (m/m).
- A plain acrylic polymer (Trial three).

The polymer/boron preservative treatment was conducted as an all-in-one application. This therefore required the disodium octaborate tetrahydrate to be blended into the polymer. The polymer content in the preservative was 3% m/m of solids. After having prepared the preservative the timber was treated in the following manner:

- Timber was placed in a vacuum chest and subjected to a vacuum of –86 kPa. This vacuum served to open the cell cavities of the timber.
- The preservative was then flooded into the evacuated vacuum chest with timber.
- A pressure of 1241 kPa was then applied to pump the preservative into the cell cavities of timber.

After the treatment process was complete, the preserved timber samples were divided into two batches. One batch was subjected to leaching trials and thereafter evaluated against attack from white and brown rot (basitiomycetes). The other batch was evaluated against attack without prior leaching trials.

The concentration of BAE chosen suggests that this preservative is only suitable for protection against fungi. The results indicate that fungal decay occurred even though there was polymer present (Murphy *et al.*, 1995). There were three different trends that became apparent from the trials:

- The fungal activity was low in the plain polymer and polymer/boron systems.
- The polymer/boron system that had the highest concentration of boron showed the highest weight loss of all samples that made use of the polymer/boron systems.
- There were similar decay results for the two separate boron formulations that were used.

The first trend was by far the most significant. It showed that fungal decay did not proceed rapidly even though the boron levels had been reduced prior to exposure to fungi (due to leaching). This suggests that the boron is not the only factor instrumental in limiting fungal activity (Murphy *et al.*, 1995). The authors suggest a few possible mechanisms by which the polymer coating may prevent the fungi from causing decay to the timber. These are:

- The polymer coating may prevent the uptake of significant quantities of moisture and hence favourable conditions for fungal growth do not prevail.
- The polymer may have a toxic action on the fungi.
- The polymer may provide a masking effect on receptor sites on the wood and therefore, the fungal enzymes may not be able to act on the wood.
- The polymer may act as an alternate receptor site for the fungal enzyme to act.

The actual mechanism is still not known but the authors suggest that more work should be done with other polymers, to ensure that the actual mechanism by which the polymer acts is fully understood.

The second interesting trend observed was that the wood sample that was treated with the highest concentration of BAE with polymer showed the greatest extent of decay from all the boron/polymer systems that were evaluated. The possible reason for this is that the incompatibility between of boron and the polymer was increased at higher concentrations of BAE. At these high concentrations, neither the effect of the polymer, nor the effect of the boron, in retarding leaching, could be observed.

The third trend showed that the nature of boron compound did not impact on the extent of fungal activity. Both boric acid/borax formulations, and disodium octaborate formulations experienced the same extent of weight loss in a polymer free preparation (Murphy *et al.*, 1995).

Therefore, the paper concluded that the boron polymer system showed greater resistance to fungal attack not because of:

- The reduction in the depletion of the boron from the timber or,
- The reduction of the overall moisture content of the treated wood, but

  directly due to the polymer treatment on the timber (Murphy *et al.*, 1995).

The authors also made some other conclusions from their research, and these were:

- Impregnating wood with waterborne acrylic polymer/ water repelling systems, alone, or as a combined system, with borates, has tremendous potential to temporarily enhance the durability of timber.
- No dramatic effect to the timber could be observed from the depletion of borates from the wood, even in pro-fungal environments due to the presence of the acrylic polymer coating.

Thus far, the literature that was reviewed, mentions the exceptional properties of boron as an insecticide but all work centred on the efficacy of the formulations as fungicides. There were no attempts made to produce a formulation that protected timber from insect attack using coatings. There are two plausible reasons for this; the one is that there were no facilities available where there was a high enough concentration of insects that would feed on test samples or the second reason was that for timber to be insect resistant there needed to be a sufficiently high concentration of boron present, but this was not possible due to boron-polymer incompatibility at high concentrations of boron. It is also useful to appreciate the fact that a thin film of polymer may not provide a barrier that will be impenetrable to boron and moisture. The polymer will have to be of sufficient thickness to serve as a barrier that can withstand mechanical wear. However, there is a limitation in that if the polymer layer is too thick then the polymer will become tacky and dust will adhere to the polymer. This problem has been observed with a disodium octaborate/wax emulsion product. The dust particles tend to accumulate on the surface of the sticky wax and this has an unsightly appearance. A suitable polymer should display the following characteristics:

- Cure to a film of sufficient thickness (at least 0.5 mm thick).
- Form a continuous film over the wood surface.
- Exhibit water - repelling properties.
- Be as elastic as possible to accommodate expansion and contraction of timber.

A study (Mohareb *et al.*, 2002) was done to assess the effect of protective coatings on the extent of leaching, as well as the efficacy of boron treated timber. This piece of research had two useful components to it; one was that the leaching patterns of boron in treated timber were monitored and the other was that the samples of timber that were preserved with the boron preservative were then exposed to two specific fungal colonies. Two species of timber were used for the purposes of these trials; one was Scots Pine (*Pinus Sylvestris*) and the other was Poplar (*Populus Trichocarpa deltoides*). Sixteen samples of each species were treated with each of the preservatives listed below:

- 1% BAE (prepared from disodium octaborate)
- 1% BAE + 10% glyoxal + 10% glycerol
- 1% BAE + 3.5% polyvinylpyrrolidone
- 1% BAE + 10% commercial resin (alkyd resin)
- 1% BAE + 5% commercial water repellent

Of the sixteen samples that were treated, eight samples were subjected to leaching trials and the other eight of each preparation were coated with a nitrocellulose lacquer and then subjected to leaching trials. Thereafter the efficacy of resistance to fungal colonies was evaluated.

The findings were amplified in the case of the poplar timber, where the positive impact of the coating could be seen. The following is a summary of the leaching trial and the table indicates the percentage of original quantity of boron that remained after 14 days-:

Table 3.2. Boron leaching in nitrocellulose lacquer coated timber vs uncoated timber

| Species | % BAE remaining in uncoated timber | % BAE remaining in coated timber (with nitrocellulose lacquer) |
|---|---|---|
| PINE | 0 | 26.5 |
| POPLAR | 0 | 7.00 |

The effect of additives to the boron can be seen below, particularly in the case of samples that have not been coated with the nitrocellulose lacquer.

A summary of the percentage of the original levels of BAE left in the timber after fourteen days is given in the table below-:

Table 3.3. Boron leaching in Scots pine with nitrocellulose coating and additives

| Type of additive | % BAE remaining in uncoated timber | % BAE remaining in coated timber (with nitrocellolose lacquer) |
|---|---|---|
| 10%Glycerol + 10%glyoxal | 25.8 | 44.9 |
| 3.5% polyvinylpyrrolidone | 7.44 | 39.2 |
| Commercial resin (alkyd) | 15.5 | 40.0 |
| Commercial water repellent | 18.8 | 35.5 |

Table 3.4. Boron leaching in Poplar timber with nitrocellulose coating and additives

| Type of additive | % BAE remaining in uncoated timber | % BAE remaining in coated timber (with nitrocellolose lacquer) |
|---|---|---|
| 10%Glycerol + 10%glyoxal | 18.5 | 33.7 |
| 3.5% polyvinylpyrrolidone | 3.22 | 31.8 |
| Commercial resin (alkyd) | 13.5 | 43.7 |
| Commercial water repellent | 2.63 | 25.0 |

From Table 3.2, it is evident that the coating itself played a critical role in reducing the depletion of BAE from the timber and this was more evident for Pine rather than for Poplar timber. The huge differences in the retained BAE in coated Pine and coated Poplar is probably due to the anatomical structure of the Poplar wood (Mohareb *et al.*, 2002).

From Table 3.3 and 3.4, it is apparent that the additives made a meaningful change to the rate at which the boron leached out of the timber. One additive in particular (glycerol + glyoxal mixed with the 1% BAE) was able to reduce the loss of boron, in spite of the nitrocellulose lacquer being absent. In all cases where the additive and the coating were used, the minimum concentration of the boron that remained in timber was greater than 25%. In all cases where the additives were used, with or without coating, the boron depletion in fourteen days still left sufficient boron to remain above the toxic level of 1 kg of BAE per cubic meter of the timber (Mohareb *et al.*, 2002). In the trials against fungal colonies, the two species of timber that were used were *Pinus Sylvestris* and Beech wood. The resistance of boron treated timber was evident, even after six weeks of exposure to fungi. Pine was exposed to *Poria placenta*, while beech was exposed to *Coriolus* versicolor. There were only two samples that showed unexpected mass loss i.e. 15% mass loss for a pine sample and 10% mass loss for a beech sample (Mohareb *et al.*, 2002). This study contributed a new dimension to the ongoing research of boron fixation in timber. It gave concrete evidence that not only coatings, but additives as well, can play a role in preventing the depletion of boron from timber through leaching.

# CHAPTER FOUR

## Experimental

The procedure for fixing boron and testing for leaching comprised of the following steps:

- Selecting of suitable timber for the test and control preservative to be applied to
- Preparation of preservatives at three different concentrations
- Preparation of timber for the treating process
- Monitoring the curing of the polymer over a period of six weeks
- Applying a curcumin indicator as a means of quality control, to ensure that the boron had been successfully encapsulated inside the timber.
- Leaching of the timber in a leaching vessel using de-ionised water as a leaching medium, with timber completely submerged
- Leaching trials and a detailed sequence of leaching
- Analysing of the leachate at regular intervals

### 4.1. Selection of timber

For a preservative to be economically viable its potential user base must be as large as possible. It was therefore necessary to select a timber that was popular in the South African market. One such species of timber is South African pine, which is also relatively cheap and readily available. South African pine is used extensively in the manufacture of roof trusses, Wendy houses and sun decks. This timber is relatively soft and vulnerable to attack by both fungi and insects. This implies that there is tremendous potential to use large volumes of a boron - based preservative on South African pine timber.

The timber for the test was obtained from Tekwani Sawmills located in the Eastern Cape. The timber is widely used in the construction of picket fencing.

### 4.1.1. Factors that determined the selection of timber samples-:

- The sapwood to heartwood ratio in the individual pieces had to be comparable and similar in all the timber selected.
- The timber had to have identical, known and comparable dimensions.
- The timber had to be of a size that allowed laboratory-scale dipping and leaching trials to be done i.e. to fit into a vessel with a cross sectional diameter of 110 mm and a height of 400 mm.
- The timber had to be free of fungal or insect attack.

The timber had low moisture levels because the timber was kiln dried before being machined. This presented problems because the preservative is dependant on moisture for sufficient diffusion into the timber.

### 4.1.2. Preparation of timber for dip treating

The timber was soaked in hot water, overnight, to overcome the problem associated with low moisture levels in the timber. The following procedure was followed-:

> Each piece of timber (1 cm X 4.5 cm X 28 cm) was individually weighed, and the weight was recorded. The timber was then soaked in hot water overnight. The new mass of the timber was thereafter recorded. The timber was then ready for dip treatment with the relevant preservative formulation.

## 4.2. Preparation and application of timber preservatives:

### 4.2.1. Preparation of "test" and "control" preservative

Two sets of preservative were prepared; one was the preservative under test and the other was the control. The difference between the "test" and the "control" sets was that the polymer was omitted from the "control" set. Three different concentrations (one litre of each) of the test and control preservative were produced:

- 60 g/L of boric acid equivalent (BAE).

- 150 g/L of boric acid equivalent (BAE).
- 200 g/L of boric acid equivalent (BAE).

(Due to constraints imposed by the patent process, the exact method of blending and preparation will not be divulged). A homogenous boron-polymer mixture that was made up of polymer and disodium octaborate (DOT), was such that concentrations listed above could be produced. The mixing process takes approximately 6 hrs to complete and there was no settling out of the disodium octaborate tetrahydrate powder. The exact masses of the powdered DOT are given in Table 6.1 and 6.2. Industrial grade of disodium octaborate tetrahydrate was used to prepare the preservatives. The company that manufactures the raw material is Borax from the USA.

### 4.2.2. Dip treating of timber with the preservative formulations

For the purposes of dipping the timber, a dip trough was constructed using a design, which minimises the chance of contamination of timber during the dipping process. The dip trough was constructed of sheet metal and the trough was coated with an oil-based paint. The trough was deep enough to accommodate a single piece of timber and a litre of preservative.

Each pre-soaked and pre-labelled piece of timber was dipped in its pre-selected preservative formulation and allowed to drip dry over a drip tray. The excess preservative that drained off the timber was collected in the tray. The "controls" were also treated in the same way. During the dipping process, the following conditions were met:

- The dip time was set as five minutes and this was carefully controlled for both the test samples and the "controls".
- Each piece of timber was completely submerged during the dipping process. This was to ensure that the preservative covered all sides of the timber.
- The excess preservative was allowed to drain off the timber without forming blobs or droplets that could be regarded as boron reservoirs on the surface of the timber.
- The timber was kept away from sunlight, so that air - drying of the treated samples could take place. (Accelerated drying can cause the moisture to provide a path for the

redistribution of boron on the outside of the timber and blistering of the polymer coating is then likely).

- Since a single dip tray was used, the tray was carefully cleaned, before a solution of different concentration was added to the timber.
- The timber samples had to be rotated, during drying, so that the polymer treated samples did not adhere to the drying racks. Removal of the timber from the drying racks could cause some of the polymer film to be left behind on the racks and this could leave the timber vulnerable to leaching of the boron.
- After the timber was dry, the mass of the timber was recorded again. The difference between this mass and the initial mass was the mass taken up by the timber.
- The test samples consisted of the following samples, Sample 1 and 2 (dipped in 60 grams per litre preservative with polymer), Sample 3 (dipped in 60 grams per litre control – no polymer), Sample 4 and 5 (dipped in 150 grams per litre preservative with polymer), Sample 6 (dipped in 150 grams per litre control-no polymer), Sample 7 and 8 (dipped in 200 grams per litre preservative with polymer) and Sample 9 (dipped in 200 grams per litre control – no polymer).

Records of the masses as well as the preservative uptake are given in Tables 6.14. to 6.16.

## 4.3. Qualitative test on treated timber

### 4.3.1 A boron specific reagent was prepared for testing treated timber

A reagent was prepared consisting of two portions, one is a 10% alcoholic extract of tumeric and the second consists of a salicylic acid mixture (6 grams of salicylic acid in 20 mL of hydrochloric acid and 80 mL of ethyl alcohol. The alcoholic extract was first sprayed onto the timber to be tested; once this was dry, the salicylic acid mixture was sprayed on. The presence of boron is indicated by a red colour.

### 4.3.2 Surface testing for the presence of boron

Samples of timber that was treated with each of the three concentrations of preservative as well as the “controls” were sprayed on the surface to detect the presence of boron.

4.3.3 A surface layer of the timber was removed mechanically, and the depth of diffusion of boron was assessed using the reagent.

## 4.4. Leaching of preservatives out of the timber

### 4.4.1. Introduction

Various methods are available for the leaching of preservatives from treated timber; examples include the shower test method and leaching vessel method (Havermans *et al.*, 1993).

Timber that is treated with the preservative that was developed is intended for Hazard class 3 applications as defined by SABS timber is intended for use in aboveground and exposed environments (Hazard class three as defined by the South African Bureau of Standards). It is therefore more than sufficient for the scope of this research to submerge the timber in water and ensure that there is sufficient agitation so that boron can leave the timber without hindrance. In reality, timber that is intended for hazard class three environments will not experience such harsh conditions. Continuous agitation ensures that there is a current in the leaching system, so that if boron had to diffuse out of the timber, it would not accumulate on the surface of the timber but it would be continuously driven away, allowing continued diffusion to take place. An accumulation of boron on the surface of the timber will prevent further free and uninhibited movement of boron out of the timber.

Boron is expected to leach under these conditions but the leaching rate will be compared to that of a control, which has no polymer barrier to prevent or delay the leaching. By comparison with a control sample, the role of the polymer will become apparent.

### 4.4.2. Leaching systems used in this work

Leaching vessels had to be specially manufactured by a glass blower. The dimensions of the timber had to be taken into account so that there would be an adequate quantity of water that surrounds the timber. A total volume of 1200 mL of purified water was used to completely submerge the timber samples. Allowance had to be made to accommodate a magnetic stirrer that could agitate the water freely. The timber was prevented from floating to the top by a glass rod held in place by a retort stand. The top of the leaching vessel was covered by paraflint wax paper, so that evaporation was kept to a minimum. The leaching vessels were placed on the magnetic stirrer units. Each sample of timber was leached for a period of ten days and samples of the leachate (95 mL) were drawn at intervals of 24 hrs. The volume of sample removed was made up with double de-ionised water.

The samples, which were withdrawn, were treated in the following way-:

- The samples were pipetted into 100 mL volumetric flasks.
- The samples were brought to mark using freshly prepared 10% nitric acid.
- The samples were then filtered through a 25-micron filter prior to analysis using the inductively coupled plasma atomic emission spectroscopy (ICP-AES).

The standard solutions were prepared from a certified standard of boron, containing 1000 ppm of boron. Each standard solution was prepared using serial dilution of a 100 ppm stock solution. All standard solutions were prepared in 100 ml volumetric flasks. Double de-ionised water was used to make up the standard solutions.

In cases where the concentration of analyte was higher than that of the highest standard, the sample was diluted using purified water and brought into range.

Due to time constraints, the samples were not all analysed after being withdrawn from the leaching vessel. Samples were sometimes retained for a period of up to three days before analyses could be performed. In these cases, special methods were developed to minimise the memory effects that are normally experienced with boron.

## 4.5. Analytical - determination of boron

### 4.5.1. Introduction

Boron can be determined using (ICP - AES). However it has been reported (Matilainen, 1995) that in some cases, it has been extremely difficult to determine boron at its most sensitive wavelength because of spectral interference. It was found that the presence of iron could cause significant background shifts (Pougnet and Orren, 1986). In some instances, it is not possible to determine the boron at its most sensitive wavelength of 249.773 nm, but instead, the boron has to be determined at 208.96 nm. For the determination of boron in a background that consists of distilled water, there is no need for matrix modifiers or the investigation of interference effects. In a study to determine the levels of boron in fly ash, Pougnet and Orren

(1986) were able to successfully determine the levels of boron in lake water without interference by other trace impurities and this was done at the most sensitive wavelength for boron (249.773 nm. However, the study focussed on attaining the maximum sensitivity possible at a low analyte concentration and this meant that the instrument had to be carefully optimised (Pougnet *et al.*, 1986).

The use of borosilicate glassware during the determination of boron has been shown to contaminate samples and lead to erroneous results. Borosilicate glassware (e.g. Pyrex or Kimax) should be avoided at all costs in both sample and standard preparation (Brenner and Cheatham, 1998). With ICP instrumentation, the sample introduction systems (spray chambers and nebulisers) contain a significant proportion of borosilicate material and this becomes a source of contamination. This happens even when low concentrations of hydrofluoric acid or other caustic material come into contact with this type of sample introduction system. The acids and caustic materials form volatile compounds such as $BF_3$ as a by-product of the decomposition of the glass (Brenner and Cheatham , 1998). Another report (Brenner and Cheatham, 1998) suggests that the decomposition can go on after the glass has been soaked and washed with HCl or $HNO_3$. It was also found from previous studies that the levels of boron in de-ionised water from a fresh ion exchange bed, were 0.1pg per mL. This level rapidly increased to 1pg per mL after additional use and this was followed by a stable value at a higher concentration, until eventually, the boron breaks through the ion exchange resin (Brenner and Cheatham, 1998). This series of concentration changes represents three different plateaus in the levels of boron and this is thought to represent three different species of boron. Water purification systems that were used could not remove all the boron present and left significantly high levels of boron in the water. The levels of boron left in the water gives an appreciable signal for boron and this brings into question, the validity of analysis for trace level of boron. One way of monitoring this is to analyse quality control standards, periodically during an analysis.

Memory effects are also a serious problem when the detection of trace levels of boron is involved (Brenner and Cheatham, 1998). This becomes significant if the analysis that preceded the current one, contained boron in the sample that was aspirated or, if corrosive or caustic liquid was aspirated through the sample introduction system. The net result is that boron will affect the subsequent analyses. Even the values for "blank" analyses are rendered unreliable.

Four analytical wavelengths are available for routine boron determination by ICP - AES, namely, 249.773, 249.678, 208.959 and 208.893 nm (Matilainen *et al.*, 1995). The two most sensitive ones are at, 249.773 nm and 249.678 nm. ICP - AES is regarded as one of the most suitable methods for the determination of boron, due to its high sensitivity, good precision and an extremely wide calibration range (Matilainen *et al.*, 1995). Other analytical methods like atomic absorption spectrometry (AAS) and X - Ray Flourescence (XRF) have poor sensitivity for boron (Matilainen *et al.*, 1995). ICP -Mass Spectrometry appears to be sensitive and precise for boron analysis (Sun *et al.*, 1998). However, the improvement in sensitivity from ICP - MS to ICP -AES has not been significant enough to warrant choosing ICP - MS over ICP- AES. Furthermore, ICP- AES is also much cheaper (Sun *et al.*, 1998).

Several techniques can be used for the separation of the boron as a complex prior to its analysis. One such species is a boric acid - mannitol complex (Brenner and Cheatham, 1998). Solvent extraction techniques are useful at extremely low concentrations, particularly when routine analyses on the ICP –AES are unable to detect boron.

## 4.6. Modifications and method development:

The instrument that was used was a Perken Elmer P40, with a photo multiplier tube and a glass nebuliser. All analyses were sequentially done.

During the course of this research, tremendous insight was gained into the need to eliminate the interference effects of boron from the analysis. The calibration of the ICP for the determination of an element, required the use of the highest standard for wavelength calibration. This caused immense problem during the calibration of the blank, which was de-ionised water. It was expected that the intensity of the blank would be zero, but an intensity of 3000 units was sometimes obtained. The literature that was reviewed above suggested that there would be problems experience in two different areas. One was the memory effect and the other was the effect of iron on the determination of boron at its most sensitive wavelength, 249.773 nm. Hence care had to be taken to avoid these factors from influencing the determination of boron. It appeared as though the boron adhered to the surfaces of the sample introduction system. During the course of the analysis, a method was developed to overcome this problem and hence reduce the intensity of the blank to values that were lower than 200 units.

A solution of 10% of nitric acid was used to decontaminate the sample introduction system as described in the steps below:

- The mixture of 10% nitric acid was first aspirated to ensure that the sample introduction system was clean. The nitric acid was aspirated for a period of 5 min.
- This was followed by the aspiration of the 50 parts per million (ppm) standard, using the fast aspiration mode on the peristaltic pump (the pump had a fast and normal mode), to introduce the sample close to the plasma and thereafter switching to the normal aspiration mode before analysis. This was done to minimise the time that the boron standard spent in the sample introduction system.
- Once the wavelength was calibrated, the 10% nitric acid mixture was aspirated again, using the fast setting on the peristaltic pump. This was done for a period of 2 min.
- The blank was then aspirated and a low intensity obtained.
- Thereafter the lowest standard was aspirated using the fast/normal mode on the peristaltic pump and this was followed, by aspirating the 10% nitric acid mixture.
- After each standard solution was aspirated using the fast/normal mode, the 10% nitric acid mixture was aspirated. This step was also followed when the remaining standards, as well as the samples were analysed.

When the procedure was effected as described above, an intensity reading of zero units was obtained for the blank. When time was limiting and the cleaning stage was more briskly performed, intensity readings of approximately 200 c/s were obtained. An important aspect of this cleaning cycle was that the sample introduction system had to be thoroughly cleaned at the end of a set of analyses. The 10% nitric acid had to be aspirated through the system for a period of approximately 10 mins. The peristaltic pump tubing had to be changed during multiple sample runs, to avoid contamination.

The possibility that iron interferes in boron analysis was not ruled out and care was taken to ensure that iron was not present in the system. The source of boron for the timber preservative was disodium octaborate. In the preparation of disodium octaborate, iron is not present in the reaction. In the preparation of the timber preservative, iron is not used in any form, whatsoever. Even when the samples are prepared for analysis, iron was not used.

The following is a summary of the parameters within which the instrument was operated -: The wavelength that was used to determine boron was 249.773 nm. The time delay setting was 20 s. The samples were analysed in triplicate. The instrument was run under manual mode. The blank that was used was double de-ionised water. There were three standards that were used, namely, 10 ppm, 25 ppm and 50 ppm. The concentration of the quality control standard that was used was 10 ppm.

## 4.7. Interference and their effects on the results obtained

A special system was devised to compensate for the memory effects normally encountered when boron is analysed. One of the first areas that was focused on to reduce the memory effect during the analysis of boron was to ensure that the sample delivery tubing was kept as clean as possible. This required the use of an acidic solution, in which the sample delivery tubing was soaked, in between analyses. There were situations where up twenty-seven samples of leachate were to be analysed continuously. This required some forethought because memory effects can be severely amplified, especially if higher concentrations are analysed before the less concentrated samples. The greatest possibility of depositing high concentrations of boron into the sample delivery system was during the analysis of the control samples that allowed huge levels of boron to diffuse out of the timber and accumulate in the leaching solution. The analysis of these control samples had to be strategically positioning in a multiple sample run. There were also three different concentrations of boron in the preservative formulations that were used to preserve the timber samples. These three different concentrations also influenced the rate of boron leaching differently. These analyses had to also be strategically positions. For the samples to be best positioned, scouting analyses had to be performed on the ICP to get a good gauge of the approximate concentrations of boron and the extent of leaching of boron in the various concentrations of the preservatives that were prepared. After having performed various scouting runs, a system was developed to structure the analysis:

## 4.8. Structuring the analysis

On a sequential run of approximately 27 samples, being withdrawn from vessels that had timber treated with three different concentrations of preservative, the following order was used:

4.8.1. Two different batches treated with preservative containing 60 g/l of BAE, withdrawn over a period of three days – (six samples).

4.8.2. One batch of control samples treated with a concentration of 60 g/l of BAE, withdrawn over a period of three days – second (three samples).

4.8.3. Two batches treated with a preservative containing 150 g/l of BAE, withdrawn over a period of three days – third (six samples).

4.8.4. One batch of control samples, treated with a concentration of 150 g/l of BAE, withdrawn over a period of three days – fourth (three samples).

4.8.5. Two batches treated with a preservative containing 200 g/l of BAE, withdrawn over a period of three days – fifth (six samples).

4.8.6. One batch of control samples, containing 200 g/l of BAE, withdrawn over a period of three days - (three samples).

Of these control samples, the samples that leached the highest concentration of boron were the samples that had been treated with the highest concentration of boron (200 g/L BAE). To minimise the effect of these high concentrations on 60 g/l on the other analyses, these samples were analysed last. These samples were preceded by the other control samples, starting with the control that had the lowest concentration of boric acid equivalent and progressing to the sample with the highest concentration of boric acid equivalence.

The next factor that influenced the placement of samples in the sequence was the concentration of the boron in the water-based polymer preservative. Sample could not be analysed in the order in which they were withdrawn from the leaching vessels. All the samples, from three separate days, were grouped. Therefore, the leachate from samples treated with the lowest concentration of boric acid equivalent, were analysed first. Thereafter, the leachates were analysed in order of increasing boron concentration. Scouting runs from previous leaching trials helped to predict the extent of leaching.

# CHAPTER FIVE

## Product Development

It is noted that the three variables involved in the formulation are: source and concentration of boron and the type of polymer. In the course of developing this boron-based timber preservative, many problems similar to those reported by other researchers were encountered. This Chapter will describe how these were systematically overcome.

The following three sources were investigated for compatibility with water-based polymer emulsions, boric acid, borax and disodium octaborate tetrahydrate.

The details of the trials to identify the most suitable source of boron are described in Appendix 1. It was found that disodium octaborate was the most compatible because it did not settle out. However, it was also the most expensive of the three sources investigated.

As shown in Appendix 1, the choice of 20 grams per litre implies that 250 litres of preservative has to be deposited into 1 cubic meter of timber. This is neither feasible nor cost effective. It was therefore decided that 60 grams per litre of BAE would be produced. This concentration was found to meet the SABS specifications at extremely high costs. However, it was found to be suitable for remedial *in situ* applications. In contrast to primary treatments, which absorb high quantities of preservative, remedial treatments require relatively small amounts of preservative to afford protection to micro-organisms.

Since the product had to meet two needs; namely, primary treatment and remedial treatment, two formulations were required. The suitable formulation for primary treatments was found by changing the ingredients and concentrations systematically.

Further trials were concerned with increasing the concentration of the boric acid and assessing the ability of the product to provide a successful barrier against leaching. Since the polymer had been identified as one of the variables that could be changed, a basic understanding of emulsion polymers was necessary in order to make informed decisions. The latter is described in the following three paragraphs.

Some of the features of emulsion polymers are that they are composed of discrete polymer particles (approximately 0.05 - 1.0 microns) in a continuous medium, which is usually made up of water. There are absorbed surfactants at the water/polymer interface that prevent coalescence of the fine polymer particles. Most of the polymers consist of vinyl monomers, water, surfactants and initiators. Other additives, which are regarded as non - essential components, are buffers and protective colloids. It should be noted that properties of the polymer are influenced by the choice of monomer. Film casts from emulsion polymers can range from hard and resinous to soft and rubbery. Hard monomers are generally styrene, methyl metacrylate or acrylonitrile.

The glass transition temperature (Tg) is a fundamental polymer characteristic, which is a useful measurement of the hardness or softness of a polymer. Polymers with a high Tg, are resinous at room temperature, while those with a low Tg are more rubbery in nature. Poly methyl metacrylate has a Tg of $105^0$C while polystyrene has a Tg of $100^0$C. Emulsion polymers are mixtures of polymers with low and high Tg's. The properties desired will dictate the ratios of the mixture. However, it is not simply a question of final properties that are taken into account. Some of the other factors that are important are that the monomers must be reactive by free radical mechanisms in an aqueous environment and, the monomers must be co-reactive with each other. The most important consideration is that these co-polymers must polymerise to form polymers that are not 'water soluble'.

Surfactants are another extremely important component of polymerisation. They are responsible for determining the size of the particles in the latex dispersion as well as for maintaining the particles in a discrete form. The surfactants are also used to provide stability to mechanical shear, stability to chemicals and pigments used and freeze-thaw stability.

The first polymer that was singled out for trial was a styrene polymer, manufactured by Rhom and Hass (commercial name-Selfguard). Sixty grams of BAE was blended with the Rhom and Hass polymer and the product was evaluated for stability. The stability was good, with no blistering or peeling of the film. The product also formed a continuous film on timber substrates. Appendix 2 captured the essence of the trials with the 60 g/l BAE preparation. The conclusions pointed the direction in which the product should be developed. The most important development that had to be made was to increase the concentration of the boron in the product. A concentration of 60 g/L BAE would be ideal for remedial treatment.

Attempts to produce preservatives in the range of 100 g/l to 300 g/l using the styrene polymer were unsuccessful. The highest concentration that could be achieved was 100 g/L. The failures were captured in Appendix 3. The details of these trials are described in Appendix 3.

The effect of modifying the polymer, by blending the styrenated polymer with a commercial undercoat (a styrenated polymer with lower suspended solids) was investigated as detailed in Appendix 4. Blending the two polymers allowed high concentration of the preservative to be achieved with ease. Timber was dipped into the preservatives and the polymer was assessed after curing. Unfortunately, it was at this stage that the polymer failed. The timber did not appear to have a coating. Whilst the existence of a coating was not disputed, the polymer film was too thin to detect. Leaching trials were not performed on the preserved timber because there was a strong possibility that boron would leach. An indicator was used to assess the penetration patterns of boron and it was found that the boron had a peripheral distribution of one millimetre.

A methacrylamide polymer with a tendency to form thick coatings was used to remedy the problem associated with thin films. Specifications of the polymer are contained in Appendix 5. High concentrations were obtained with ease but the viscosity of the polymer caused large quantities of the preservative to be deposited on the surface of the timber. Large droplets of the polymer cured on the surface of the timber and spoilt the appearance of the timber. Attempts to remove these droplets also resulted in the film being damaged. The viscosity of the polymer was reduced so that the spread rate of the preservative increased. Water was used to dilute the acrylic polymer by 50%. This resulted in an improved depth of diffusion of the boron but, the film thickness was adversely affected and this was apparent by a patchy appearance. The high water content in the polymer caused 'grain raise' in the timber. The details of this trial are given in Appendix 6. The dilution rate was reduced to one part water to three parts of polymer. All three concentrations (60, 150 and 200 g/L) were produced with ease. The film thickness did not improve drastically. The polymer did not cure to a glossy finish. Appendix 7 contains details of the preparation as well as the evaluation of the timber that was dipped into the product.

In order to increase the film thickness and gloss of the polymer coating, the ratio of water to polymer was reduced to 1 part to 9 parts respectively. However, the preservative was still too viscous but it was tried on Saligna logs. It was thought that the high viscosity would be an advantage for ground contact. The trial revealed that the pure acrylic polymer did not enjoy a high degree of flexibility. The Saligna poles cracked on drying and the polymer coating was unable to expand through the span of the crack. Details of these trials are contained in Appendix 8 (A) and (B).

To introduce flexibility and reduce the viscosity of the pure acrylic polymer, the acrylic polymer was blended with the original styrene polymer that was tried at the outset. A 1:1 dilution rate was followed. The overall results were very favourable because the desired concentrations (60, 150 and 200 grams per litre) were produced. The viscosity of the polymer product was reduced significantly and the trials with timber revealed that a glossy and visible film encapsulated the timber. This formulation appeared to be the basis of the product that was being sought. Leaching trials were then performed in order to investigate the efficiency of the polymer barrier. The details of the leaching trials are contained in Appendix 9. The leaching trials did not give the anticipated results because high levels of boron diffused out of the timber within 31 hrs. The levels of boron that leached were proportional to the concentrations of the preservative. Literature suggests that water vapour permeability is the factor that determines the effectiveness of the coating (Yalinkilic *et al.*, 1999). In order to prevent the leaching of boron, the entire project was revisited. Every attempt was made to retain the current polymer blend because the product was stable over a long period.

At this stage of the research, if the polymer were to be changed, then compatibility studies would have had to begin from the outset. To avoid this, attempts were made to modify the existing polymer. Literature by Petric *et al.*, (2001), suggested that water vapour permeability of the coating must be reduced in order to reduce the leaching of boron. A convenient way of reducing the water vapour permeability is by introducing a water repellent. This theory was useful when aspects relating to polymer modification were decided upon.

A suitable additive that would increase the water repellent nature of the coating was sourced. Various wax emulsions from the petroleum industry were tried. A large proportion of the hydrowaxes that were tried caused the preservative to solidify.

Eventually, an additive that was found to improve the water repellent properties of the coating was found. This 'additive' was blended in at concentrations of 2.5% $^{v}/_{v}$. The viscosity of the preservative did not change drastically. Firstly, the polymer coating gave a very smooth finish to the timber. The coating was continuous with no signs of pits or bubbles on the surface. Secondly, the timber could be dipped into water and wiped off to complete dryness. The polymer coating exhibited a degree of water repellency. The effects of the ‘additive’ dramatically influenced the future of the product and it was given a name, Product ‘X’.

Several batches of these preservative at all three concentrations (60,150 and 200 g/l) were produced. Timber, both planned and unplanned were treated with these preservatives. The adhesion of the product to timber was carefully monitored.

The following tests were done to ensure that the quality and the performance of the preservative were acceptable (See Appendix 10 for full details).

- Accelerated weathering trials to assess the ultraviolet resistance of the product. (Courtesy of a paint company)
- Chemical analyses were done to compare the initial weight of boron added to the boron that was determined chemically in the preservative.
- A mould was used to prepare a disc of the preservative. The disc, when cured, was examined for flexibility and memory properties.
- Leaching trials were done, with the timber being completely submerged in de - ionised water and samples were withdrawn periodically to assess the leaching of boron. These are extremely harsh environments that would not normally be experience by boron treated timber.
- Timber that was preserved with Product ‘X’ was also exposed to natural weathering and monthly inspections were done to check the integrity of the polymer and to note any other signs of damage.
- Freeze thaw tests were also done on the product to assess stability in various environments.

# CHAPTER SIX

## Results and Calculations

This Chapter will focus on the results of the qualitative testing that was done on the samples as well as the calculations to determine the extent of leaching of boron. The results of the leaching trials will be presented in tabular form.

### 6.1. Qualitative testing:

6.1.1 Results of qualitative testing on the surface of the polymer treated samples and controls. The test and control samples were sprayed with curcumin indicator as described in section 4.3. None of the three test samples of concentrations (60, 150 and 200 grams per litre) tested with the curcumin showed evidence of boron on the surface but boron was detected beneath the surface. The characteristic red colour that denotes the presence of boron was absent on the surface. The three control samples (60, 150 and 200 grams per litre) gave positive tests for the presence of boron on the surface. (See Fig 6.2)

6.1.2. The test samples and the control samples were mechanically split so as to expose their interiors to tested for the presence of boron, using the curcumin indicator. All samples tested gave positive results for the presence of boron. Boron had diffused into the timber and was deposited across the cross sections of the timber (See Fig 6.1.).

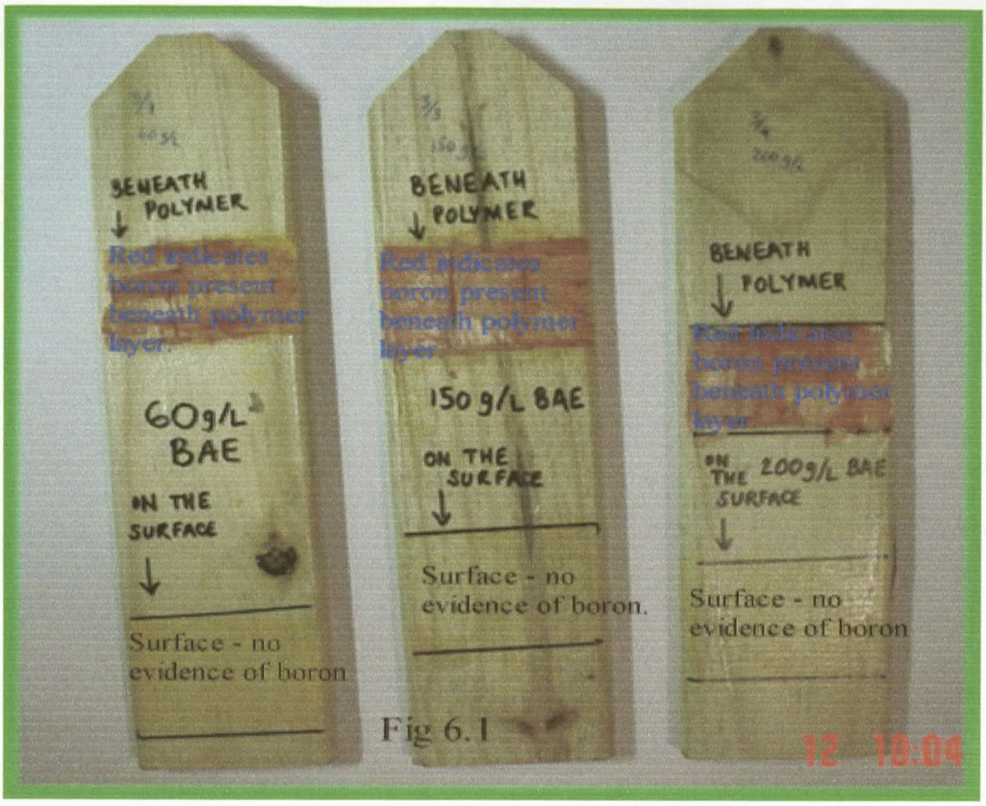


Fig 6.1

Photograph of qualitative testing for boron on surface of boron treated timber

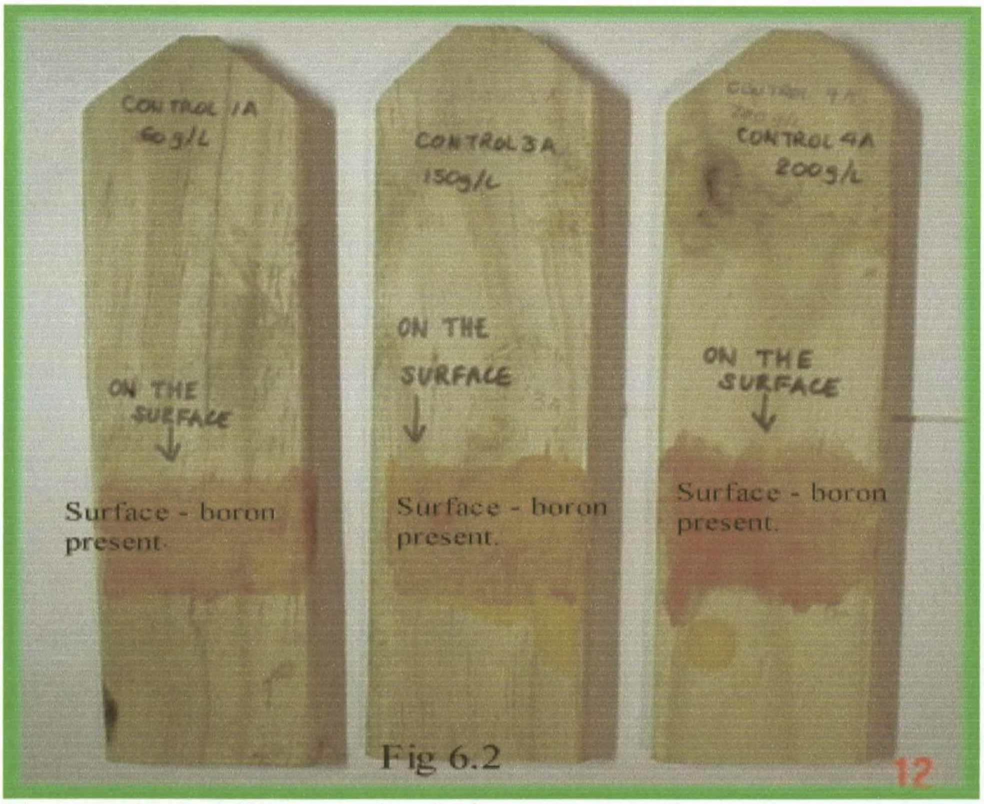


Fig 6.2

Photograph of qualitative testing for boron on control sample

## 6.2. Calculations of exact amounts of BAE in preservatives.

Three different 'test' preservatives were prepared. They contained the following approximate concentrations:

- 60 grams per litre of BAE
- 150 grams per litre of BAE
- 200 grams per litre of BAE

It is noted that for the purposes of calculation, the exact masses of the preservatives had to be recorded. The source of boron was disodium octaborate tetrahydrate (DOT). These masses were converted to the equivalent mass of BAE. Details for the calculations of exact masses are contained in (Section 11.1) Appendix 11.

The exact masses of each test preservative calculated, are shown in (Section 11.1) Appendix 11.

Table 6.1 Exact masses to BAE for the test preservatives

| CONCENTRATION in grams per litre | Mass of disodium octaborate tetrahydrate in grams | Equivalent mass of boric acid (BAE) in grams |
|---|---|---|
| 60 | 51 | 61 |
| 150 | 126 | 151 |
| 200 | 168 | 202 |

Similarly, for the control samples, the exact masses of the BAE had to be calculated. The details of the calculations are contained in Appendix 11 (Section 11.1)

Table 6.2 Exact masses to BAE for the control samples

| CONCENTRATION in grams per litre | Mass of disodium octaborate tetrahydrate in grams | Equivalent mass of boric acid BAE in grams |
|---|---|---|
| 60 | 50 | 60 |
| 150 | 126 | 152 |
| 200 | 170 | 204 |

## 6.3 Evaluation of the percentage of BAE in the cured polymer for each of the three concentrations of 'test' preservatives.

Exact volumes of preservative were pipetted out in triplicate. The mass of these known volumes of preservative was then recorded. Three samples of each preservative (60, 150, and 200g/L) were then placed into a previously heated oven at 80 $^{0}$C for 14 hrs, so that the polymer could cure. By using the volume of the preservative, the exact mass of BAE in the preservative and the mass of the cured polymer, the percentage of BAE in the cured polymer was found. Details of the calculation can be found in Appendix 11 (Section 11.2) The summary of the calculations is given in Table 6.3 below.

Table 6.3 Percentage BAE in the cured preservative

| PRESERVATIVE g/l | % BAE in the cured preservative |
|---|---|
| 60 | 13.5 |
| 150 | 29.0 |
| 200 | 37.4 |

## 6.4 Calculation of the amount of boron, as BAE that leached out of timber samples

Samples of 95 millilitres were withdrawn daily from each leaching vessel containing a total volume of 1200 millilitres of de-ionised water. The concentration of BAE in the 95 millilitres was recorded and added to the following days results because this quantity of boron was discarded after each analysis. Results were obtained in parts per million and they were eventually converted to grams of BAE.

A typical set of data is shown for Sample 1

Mass of timber sample = 89.7 grams

Mass of timber and preservative = 93.0 grams

Therefore mass of cured pres. = 3.26 grams

But the % BAE in the cured pres. = 13.5

Therefore, mass of BAE = 3.26 X 0.135

= 0.44 grams

Once the initial amount of BAE in each sample was obtained, the amount of BAE leached on a daily basis was being calculated from daily analysis results (see table 6.4. for daily analysis results for sample 1).

Table 6.4 Daily analysis results for Sample 1

| DAY | 1 | 2 | 3 | 4 | 5 | 6 | 7 | 8 | 9 | 10 |
|---|---|---|---|---|---|---|---|---|---|---|
| Boron conc. in ppm | 3.18 | 4.97 | 6.59 | 8.16 | 10.0 | 8.35 | 11.4 | 13. 6 | 15.4 | 15.9 |

The calculations for the amount leached was done as follows:

For day 1, the boron levels were determined to be 3.18 ppm. Given that 1000 ppm has 1 mg per mL, 3.18 ppm contains 3.18 X $10^{-3}$ mg per mL, or 3.18 X $10^{-6}$ g/mL. Since the leaching vessel had a total volume of 1200 mL, the total mass of boron in the vessel was 3.18 X $10^{-6}$ g/mL X 1200 mL giving a total mass of 3.82 X $10^{-3}$ grams of boron. The boric acid equivalent is obtained by multiplying this mass by 5.72 (Conversion factor from page 17) giving 0.0218 grams of BAE in the leaching vessel. The mass of BAE in the 95 mL aliquot, which was used to make up the analyte solution, must be calculated and added onto the following day's determination because boron in this aliquot was consumed in the analysis. Mass of BAE in the 95 mL aliquot is (95/1200) X 0.0218 grams and this gives 0.00170 grams.

For Sample 1, Table 6.5 summarises the mass of BAE for each analysis in column 5. Column 6 reflects the daily increases in leached boron. The daily increases in leached boron can be obtained by the difference in boron levels over two consecutive days. On days when no boron leached, boron concentrations from one day to the next reduces, due to 95 mL of having been withdrawn and replaced by 95 mL of purified water. When boron leaches out, then the difference in concentration of boron the current day to the previous day indicates the quantity of boron that leached.

Similarly the calculations for the other 8 samples were done.

The results for all 9 samples are given in Tables 6.1 to 6.9.

Sample 1 – 60 g/L

Table 6.5. Summary of the levels of boron that leached for Sample 1

| Day | Conc. of Leached boron (ppm) | Conc. of Leached boron in grams of BAE | Grams of BAE consumed in daily sampling | Total grams of BAE Leachate per day | Daily incremental increases in grams BAE |
|---|---|---|---|---|---|
| 1 | 3.18 | 0.0218 | 0.00170 | 0.0218 | 0.0218 |
| 2 | 4.97 | 0.0341 | 0.00270 | 0.0358 | 0.0140 |
| 3 | 6.59 | 0.0452 | 0.00358 | 0.0479 | 0.0121 |
| 4 | 8.16 | 0.0560 | 0.00443 | 0.0596 | 0.0117 |
| 5 | 10.0 | 0.0688 | 0.00544 | 0.0732 | 0.0136 |
| 6 | 8.35 | 0.0573 | 0.00452 | 0.0628 | 0 |
| 7 | 11.4 | 0.0785 | 0.0062 | 0.0831 | 0.0203 |
| 8 | 13.6 | 0.0931 | 0.00740 | 0.0993 | 0.0162 |
| 9 | 15.4 | 0.106 | 0.00830 | 0.113 | 0.0137 |
| 10 | 15.9 | 0.109 | 0.00860 | 0.118 | 0.00460 |
| Total | | | | | 0.128 |

Sample 2 – 60 g/L

Table 6.6. Summary of the levels of boron that leached for Sample 2

| Day | Conc. of Leached boron (ppm) | Conc. of Leached boron in grams of BAE | Grams of BAE consumed in daily sampling | Total grams of BAE Leachate per day | Daily incremental increases in grams BAE |
|---|---|---|---|---|---|
| 1 | 6.57 | 0.0451 | 0.00360 | 0.0451 | 0.0451 |
| 2 | 11.4 | 0.0781 | 0.00620 | 0.0817 | 0.0366 |
| 3 | 12.1 | 0.0831 | 0.00660 | 0.0893 | 0.00754 |
| 4 | 15.6 | 0.107 | 0.00850 | 0.114 | 0.0246 |
| 5 | 16.8 | 0.116 | 0.00920 | 0.124 | 0.0106 |
| 6 | 17.2 | 0.118 | 0.00930 | 0.127 | 0.00280 |
| 7 | 18.2 | 0.125 | 0.00989 | 0.131 | 0.00380 |
| 8 | 18.5 | 0.127 | 0.0100 | 0.137 | 0.00560 |
| 9 | 19.2 | 0.132 | 0.0104 | 0.142 | 0.00530 |
| 10 | 20.4 | 0.140 | 0.0111 | 0.151 | 0.00880 |
| Total | | | | | 0.151 |

Sample 3 – 60 g/L controls

Table 6.7. Summary of the levels of boron that leached for Sample 3 (Control)

| Day | Conc. of Leached boron (ppm) | Conc. of Leached boron in grams of BAE | Grams of BAE consumed in daily sampling | Total grams of BAE Leachate per day | Daily incremental increases in grams BAE |
|---|---|---|---|---|---|
| 1 | 26.1 | 0.179 | 0.0142 | 0.179 | 0.179 |
| 2 | 27.5 | 0.189 | 0.0150 | 0.203 | 0.0245 |
| 3 | 28.0 | 0.192 | 0.0152 | 0.207 | 0.00400 |
| 4 | 28.1 | 0.193 | 0.0153 | 0.208 | 0.00120 |
| 5 | 27.4 | 0.188 | 0.0150 | 0.204 | 0 |
| 6 | 23.8 | 0.164 | 0.0130 | 0.179 | 0 |
| 7 | 25.9 | 0.178 | 0.0141 | 0.191 | 0.0120 |
| 8 | 23.2 | 0.159 | 0.0126 | 0.173 | 0 |
| 9 | 22.1 | 0.151 | 0.0120 | 0.164 | 0 |
| 10 | 30.4 | 0.209 | 0.0165 | 0.221 | 0.0569 |
| Total | | | | | 0.277 |

Sample 4 – 150 g/L

Table 6.8. Summary of the levels of boron that leached for Sample 4

| Day | Conc. of Leached boron (ppm) | Conc. of Leached boron in grams of BAE | Grams of BAE consumed in daily sampling | Total grams of BAE Leachate per day | Daily incremental increases in grams BAE |
|---|---|---|---|---|---|
| 1 | 11.3 | 0.0778 | 0.00620 | 0.0778 | 0.0778 |
| 2 | 16.5 | 0.113 | 0.00890 | 0.119 | 0.0414 |
| 3 | 23.0 | 0.158 | 0.0125 | 0.167 | 0.0479 |
| 4 | 24.4 | 0.168 | 0.0133 | 0.180 | 0.0132 |
| 5 | 29.0 | 0.199 | 0.0158 | 0.212 | 0.0321 |
| 6 | 29.6 | 0.203 | 0.0161 | 0.219 | 0.00650 |
| 7 | 29.6 | 0.203 | 0.0161 | 0.219 | 0.000200 |
| 8 | 35.3 | 0.242 | 0.0192 | 0.258 | 0.0391 |
| 9 | 34.0 | 0.233 | 0.0185 | 0.252 | 0 |
| 10 | 48.5 | 0.333 | 0.0264 | 0.352 | 0.0993 |
| Total | | | | | 0.357 |

Sample 5 – 150 g/L

Table 6.9. Summary of the levels of boron that leached for Sample 5

| Day | Conc. of Leached boron (ppm) | Conc. of Leached boron in grams of BAE | Grams of BAE consumed in daily sampling | Total grams of BAE Leachate per day | Daily incremental increases in grams BAE |
|---|---|---|---|---|---|
| 1 | 14.0 | 0.096 | 0.00760 | 0.0962 | 0.0962 |
| 2 | 19.4 | 0.133 | 0.0106 | 0.141 | 0.0446 |
| 3 | 26.2 | 0.180 | 0.0143 | 0.191 | 0.0498 |
| 4 | 29.6 | 0.204 | 0.0161 | 0.218 | 0.0271 |
| 5 | 33.3 | 0.228 | 0.0181 | 0.244 | 0.0266 |
| 6 | 30.4 | 0.209 | 0.0165 | 0.227 | 0 |
| 7 | 35.8 | 0.246 | 0.0195 | 0.262 | 0.0179 |
| 8 | 37.1 | 0.255 | 0.0202 | 0.274 | 0.0119 |
| 9 | 39.4 | 0.271 | 0.0214 | 0.291 | 0.0166 |
| 10 | 47.0 | 0.322 | 0.0255 | 0.344 | 0.0532 |
| Total |  |  |  |  | 0.344 |

Sample 6 – 150 g/L controls

Table 6.10. Summary of the levels of boron that leached for Sample 6 (Control)

| Day | Conc. of Leached boron (ppm) | Conc. of Leached boron in grams of BAE | Grams of BAE consumed in daily sampling | Total grams of BAE Leachate per day | Daily incremental increases in grams BAE |
|---|---|---|---|---|---|
| 1 | 55.9 | 0.384 | 0.0304 | 0.384 | 0.384 |
| 2 | 68.5 | 0.467 | 0.0372 | 0.500 | 0.116 |
| 3 | 64.9 | 0.445 | 0.0352 | 0.482 | 0 |
| 4 | 69.5 | 0.477 | 0.0377 | 0.512 | 0.0297 |
| 5 | 67.7 | 0.465 | 0.0368 | 0.502 | 0 |
| 6 | 58.2 | 0.399 | 0.0316 | 0.436 | 0 |
| 7 | 58.7 | 0.403 | 0.0319 | 0.434 | 0 |
| 8 | 62.6 | 0.430 | 0.0340 | 0.462 | 0.0273 |
| 9 | 66.5 | 0.456 | 0.0361 | 0.490 | 0.0289 |
| 10 | 76.7 | 0.526 | 0.0417 | 0.562 | 0.0718 |
| Total | | | | | 0.658 |

Sample 7 – 200 g/L

Table 6.11. Summary of the levels of boron that leached for Sample 7

| Day | Conc. of Leached boron (ppm) | Conc. of Leached boron in grams of BAE | Grams of BAE consumed in daily sampling | Total grams of BAE Leachate per day | Daily incremental increases in grams BAE |
|---|---|---|---|---|---|
| 1 | 12.6 | 0.086 | 0.00680 | 0.0861 | 0.0861 |
| 2 | 20.8 | 0.143 | 0.0113 | 0.150 | 0.0634 |
| 3 | 29.7 | 0.204 | 0.0162 | 0.215 | 0.0659 |
| 4 | 34.1 | 0.234 | 0.185 | 0.250 | 0.0349 |
| 5 | 36.8 | 0.252 | 0.0200 | 0.271 | 0.0205 |
| 6 | 39.0 | 0.267 | 0.0212 | 0.287 | 0.0165 |
| 7 | 36.4 | 0.250 | 0.0198 | 0.271 | 0 |
| 8 | 41.6 | 0.286 | 0.0226 | 0.305 | 0.0341 |
| 9 | 43.6 | 0.299 | 0.0237 | 0.322 | 0.0166 |
| 10 | 62.9 | 0.432 | 0.0342 | 0.456 | 0.134 |
| Total | | | | | 0.472 |

Sample 8 – 200 g/L

Table 6.12. Summary of the levels of boron that leached for Sample 8

| Day | Conc. of Leached boron (ppm) | Conc. of Leached boron in grams of BAE | Grams of BAE consumed in daily sampling | Total grams of BAE Leachate per day | Daily incremental increases in grams BAE |
|---|---|---|---|---|---|
| 1 | 12.6 | 0.0864 | 0.0068 | 0.0864 | 0.0864 |
| 2 | 19.1 | 0.131 | 0.0104 | 0.138 | 0.0516 |
| 3 | 27.8 | 0.191 | 0.0151 | 0.201 | 0.0629 |
| 4 | 32.7 | 0.224 | 0.0178 | 0.240 | 0.0386 |
| 5 | 38.5 | 0.264 | 0.0209 | 0.282 | 0.0424 |
| 6 | 37.8 | 0.260 | 0.0206 | 0.281 | 0 |
| 7 | 39.0 | 0.268 | 0.0212 | 0.288 | 0.00750 |
| 8 | 45.5 | 0.313 | 0.0248 | 0.334 | 0.0457 |
| 9 | 46.7 | 0.321 | 0.0254 | 0.346 | 0.0117 |
| 10 | 71.2 | 0.489 | 0.0387 | 0.514 | 0.169 |
| Total | | | | | 0.515 |

Sample 9 – 200 g/L controls

Table 6.13. Summary of the levels of boron that leached for Sample 9 (Control)

| Day | Conc. of Leached boron (ppm) | Conc. of Leached boron in grams of BAE | Grams of BAE consumed in daily sampling | Total grams of BAE Leachate per day | Daily incremental increases in grams BAE |
|---|---|---|---|---|---|
| 1 | 88.6 | 0.608 | 0.0481 | 0.608 | 0.608 |
| 2 | 99.7 | 0.685 | 0.0542 | 0.733 | 0.125 |
| 3 | 112 | 0.771 | 0.0610 | 0.825 | 0.0927 |
| 4 | 98.2 | 0.674 | 0.0534 | 0.735 | 0 |
| 5 | 94.3 | 0.647 | 0.0512 | 0.701 | 0 |
| 6 | 73.7 | 0.506 | 0.0400 | 0.557 | 0 |
| 7 | 81 | 0.556 | 0.0440 | 0.596 | 0.0389 |
| 8 | 109.0 | 0.748 | 0.0592 | 0.792 | 0.196 |
| 9 | 99.5 | 0.683 | 0.0541 | 0.742 | 0 |
| 10 | 112 | 0.768 | 0.0608 | 0.822 | 0.08 |
| Total | | | | | 1.14 |

The tables below summarise the physical details of each piece of timber, the amount of preservative that was taken up by each piece of timber, the amount of BAE that was deposited in the timber, the amount of boric acid that leached and the percentage of BAE that leached.

Table 6.14. Summary of the recorded masses and BAE leached for Samples 1 to 3

| SAMPLE NUMBER | ONE | TWO | THREE CONTROL |
|---|---|---|---|
| DRY MASS of TIMBER in grams | 89.7 | 85.91 | 89.1 |
| VOL. of TIMBER in $m^3$ | $2.86 \times 10^{-4}$ | $2.86 \times 10^{-4}$ | $2.86 \times 10^{-4}$ |
| CONCENTRATION of BAE in g/L | 60 | 60 | 60 |
| SPECIFIC GRAVITY of PRESER. in $g/cm^3$ | 1.07 | 1.07 | 1.02 |
| MOISTURE CONTENT of TIMBER after SOAKING | >50% | >50% | >50% |
| % BAE in CURED PRESERVATIVE | 13.5 | 13.5 | NO POLYMER COATING |
| MASS of TIMBER + CURED PRESER. in grams | 93.0 | 89.4 | 89.7 |
| PRESERVATIVE UPTAKE in grams | 3.26 | 3.54 | 0.560 |
| MASS of BAE. in TIMBER in grams | 0.439 | 0.476 | 0.560 |
| RETENTION EXPRESSED as $kg/m^3$ | 1.54 | 1.66 | 1.96 |
| DIP TIME in MINUTES | 5.00 | 5.00 | 5.00 |
| QTY of BAE LEACHED in grams | 0.129 | 0.151 | 0.277 |
| % BAE LEACHED | 29.1 | 31.6 | 49.5 |

Table 6.15. Summary of the recorded masses and BAE leached for Samples 4 to 6

| SAMPLE NUMBER | FOUR | FIVE | SIX CONTROL |
|---|---|---|---|
| DRY MASS of TIMBER in grams | 84.1 | 90.5 | 115 |
| VOL. of TIMBER in $m^3$ | $2.86 \times 10^{-4}$ | $2.86 \times 10^{-4}$ | $2.86 \times 10^{-4}$ |
| CONCENTRATION of BAE in g/L | 150 | 150 | 150 |
| SPECIFIC GRAVITY of PRESER. in $g/cm^3$ | 1.10 | 1.10 | 1.06 |
| MOISTURE CONTENT of TIMBER after SOAKING | >50% | >50% | >50% |
| % BAE in CURED PRESERVATIVE | 29.9 | 29.9 | NO POLYMER COATING |
| MASS of TIMBER + CURED PRESER. in grams | 89.3 | 96.5 | 116 |
| PRESERVATIVE UPTAKE in grams | 5.29 | 5.96 | 1.11 |
| MASS of BAE. in TIMBER in grams | 1.58 | 1.78 | 1.11 |
| RETENTION EXPRESSED as $kg/m^3$ | 5.53 | 6.22 | 3.86 |
| DIP TIME IN MINUTES | 5.00 | 5.00 | 5.00 |
| QTY of BAE LEACHED in grams | 0.357 | 0.361 | 0.658 |
| % BAE LEACHED | 22.6 | 20.3 | 57.8 |

Table 6.16. Summary of the recorded masses and BAE leached for Samples 7 to 9

| SAMPLE NUMBER | SEVEN | EIGHT | NINE CONTROL |
|---|---|---|---|
| DRY MASS of TIMBER in grams | 83.1 | 88.5 | 103 |
| VOL. of TIMBER in $m^3$ | $2.86 \times 10^{-4}$ | $2.86 \times 10^{-4}$ | $2.86 \times 10^{-4}$ |
| CONCENTRATION of BAE in g/L | 200 | 200 | 200 |
| SPECIFIC GRAVITY of PRESER. in $g/cm^3$ | 1.117 | 1.117 | 1.08 |
| MOISTURE CONTENT of TIMBER after SOAKING | >50% | >50% | >50% |
| % BAE in CURED PRESERVATIVE | 37.4 | 37.4 | NO POLYMER COATING |
| MASS of TIMBER + CURED PRESER. in grams | 87.4 | 93.5 | 106 |
| PRESERVATIVE UPTAKE in grams | 4.37 | 4.94 | 2.64 |
| MASS of BAE. in TIMBER in grams | 1.64 | 1.85 | 2.64 |
| RETENTION EXPRESSED as $kg/m^3$ | 5.71 | 6.46 | 9.23 |
| DIP TIME in MINUTES | 5.00 | 5.00 | 5.00 |
| QTY of BAE LEACHED in grams | 0.472 | 0.515 | 1.14 |
| % BAE LEACHED | 28.8 | 27.8 | 43.2 |

# CHAPTER SEVEN

## Discussion and Conclusion

### 7. Introduction

For the purposes of assessing the product for normal (above ground) usage and its behaviour under extremely hazardous conditions, the discussion will be done in two parts.

### 7.1 Assessment of the Product for above ground usage:

In terms of SABS specifications, boron based preservatives are acceptable for use in zero, first and second hazard class environments. Further, the specification requires that for hazard class two (the most hazardous of the three environments) the timber may only be used above ground applications and there must be a coating of some sort on the timber. Generally, many of the coatings that have been used generally have very poor ultraviolet resistance. This results in the coatings having limited lifespans. However, the development of this product has adequately addressed these shortcomings. Apart from having suitable flexibility to expand and contract with varying temperature, the coating also has a sun-screen that make it different form the other coating on the market. It should be noted that the coating forms while the boron diffuses into the timber. This particular polymer has a great degree of flexibility, which is attributed to its structure. The durable qualities of the polymer have been demonstrated by the results obtained in the accelerated weathering trials (See Section 10.4 in Appendix 10 for details of these trials). In the light of the above, it can be concluded that the polymer coating which was produced in this project, can be considered as an advancement on current technology. This makes the product highly competitive in the existing boron market.

As a means of quality control, the polymer coating has also been checked for the presence of boron on its surface, as described in Section 4.3 (illustrated in Fig 6.1).An absence of boron from the surfaces of timber, on all three test preservative substrates was found. This serves as proof that the polymer successfully allows the boron to enter the timber, while providing a barrier on the outside. The negative test for boron suggests that the polymer has functioned well in sealing the boron within the timber. The timber has sufficient gloss and will not require the use of additional varnishes to enhance its appearance. There are also limitations associated with the use of varnish because varnish does not allow for the expansion of the timber substrate. Varnish cracks after extended exposure to the sun.

The results represented in Fig 6.2 in Section 6.1.1 shows that, in the absence of polymer, there is qualitative evidence for the presence of boron on the surface of the timber. The surface boron may be transported away, even by small amounts of water that splashes onto the timber. Any area that has experienced a loss of boron, without subsequent replacement will be vulnerable to fungal and insect attack. In this regard, the product which was developed maintains a mobile reservoir of boron within the timber. Any entry of moisture into the timber will be accompanied by diffusion and subsequent accumulation of boron at that spot within the timber.

Hence in summarizing the performance of the preservative for above ground applications, the preservative has adequately demonstrated that-:

- Boron has been successfully been deposited within the confines of the timber.
- The coating has not affected the appearance of the timber adversely.
- The polymer does not disintegrate easily, and will therefore not allow the boron to effuse from the timber.
- The behaviour of the coating during the leaching trials, show that the product will suffice for above ground applications.
- Since approximately 10% of timber in a low cost house is below ground, the product developed in this project can be successfully used to preserve the remaining 90% of the timber in the house.

## 7.2 Assessment of the Product for high hazard environments:

The product has been formulated with three different concentrations of boron. Each concentration is useful for a particular application. In assessing the performance of the product in high hazard environments, the efficacy of each of the three concentrations will be discussed separately.

High hazard environments for timber samples fall into four separate categories. The least hazardous of the four is H3 (Hazard class three) and the most hazardous is H6 (Hazard class six). Hazard classes 5 and 6 are regarded as extreme environments because timber samples in these environments are in constant contact with water. H6 environments are typically marine jetties and seashores.

At the outset, it should be noted that timber, dip-treated with the product developed in this project, was subjected to an extremely hazardous environment. By contrast, had chromated-copper-arsenate (CCA) been used, the minimum preservative content in the timber would have been 16 kg per cubic meter of timber (Specified by SABS). In this study, timber samples containing 5 kg of BAE per cubic meter were placed in water, which was in constant motion due to stirring. Under such conditions, any boron that leached out would have been transported away from the surface of the timber. Thus a continuous flow of boron out of the timber would be ensured. Any malfunction on the part of the polymer would result in a substantial loss of boron from the timber. However the results in Tables 6.5 to 6.12 (excluding Tables 6.7, 6.10 which are for controls) show that, relatively low levels of boron had leached out. This serves to establish that the polymer was very effective against large egresses of boron, which was anticipated for these harsh conditions.

Whilst the application of this product is not envisaged for ground contact, the leaching trials were performed under extremely harsh conditions. This is particularly useful because if the product does not malfunction under these conditions, it is very likely that the product would be successfully used for less hazardous environments.

In summarizing, it can be said of the product that-:

- The product will be able to cope adequately when exposed to moisture in the form of rain.
- Although there is no intention of using this product for ground contact, the leaching trials show that timber treated with this product can be used for ground contact in low hazard (termite-free) environments.

### 7.2.1 Assessment and discussion of the 60 grams per litre BAE samples

As noted in Section 4.2.2 the leachates for two test samples and a control sample were analysed for boron. The control sample (timber treated with DOT but no polymer coating) will be compared to the preservative treated samples of the same concentration. It is also necessary to assess each concentration, with a clear understanding of the end use of the product.

Table 6.1.4 contains the values of BAE, as a percentage of the amount of BAE that leached out of the timber. It is seen that there is a considerable difference between the levels of BAE that leached from the control sample (49.5), as compared to Sample 1(29.1%). This difference was calculated over a ten-day period. A slightly different picture emerges when the leaching is examined at on a daily basis. It is seen from Figs 7.1 (a), 7.2 (a) and 7.3 (a) the increases in the boron levels over the ten-day period are gradual for Samples 1 and 2. It is noted that no boron leached out of Sample 1 on day 6.

In the case of the Control sample, a very different pattern emerged; boron loss was not gradual. Approximately 32% of the BAE was lost in the first 24 hrs. Boron does not completely diffuse out of the timber. Its movement is dependant on sensitive equilibriums between the water-timber interface and also between the internal-peripheral interfaces of the timber. When a large difference between the boron concentration in the periphery of the timber and the leaching solution exists, then this gradient becomes the driving force behind the movement of boron out of the timber. This in turn offsets the equilibrium inside the timber and if a sufficient gradient exists, then boron will diffuse towards the periphery of the timber until equilibrium returns. Leaching may sometimes come to a complete stop. Continued dilution of the concentration of boron in the leaching vessel, by daily withdrawal of sample (95 mL) and subsequent re-addition of purified water, can re-introduce a gradient that can cause boron to start diffusing again until a new equilibrium is established.

This would explain the slight increases of BAE leaching on the seventh day. The quantity of BAE in the timber was not sufficient to create a sufficient diffusion gradient. As movements of boron in the timber changed, in the presence of the leaching solution, there is a possibility that a small gradient developed by the seventh day. A small quantity of BAE diffused out (Illustrated on Fig 7.3 (a).

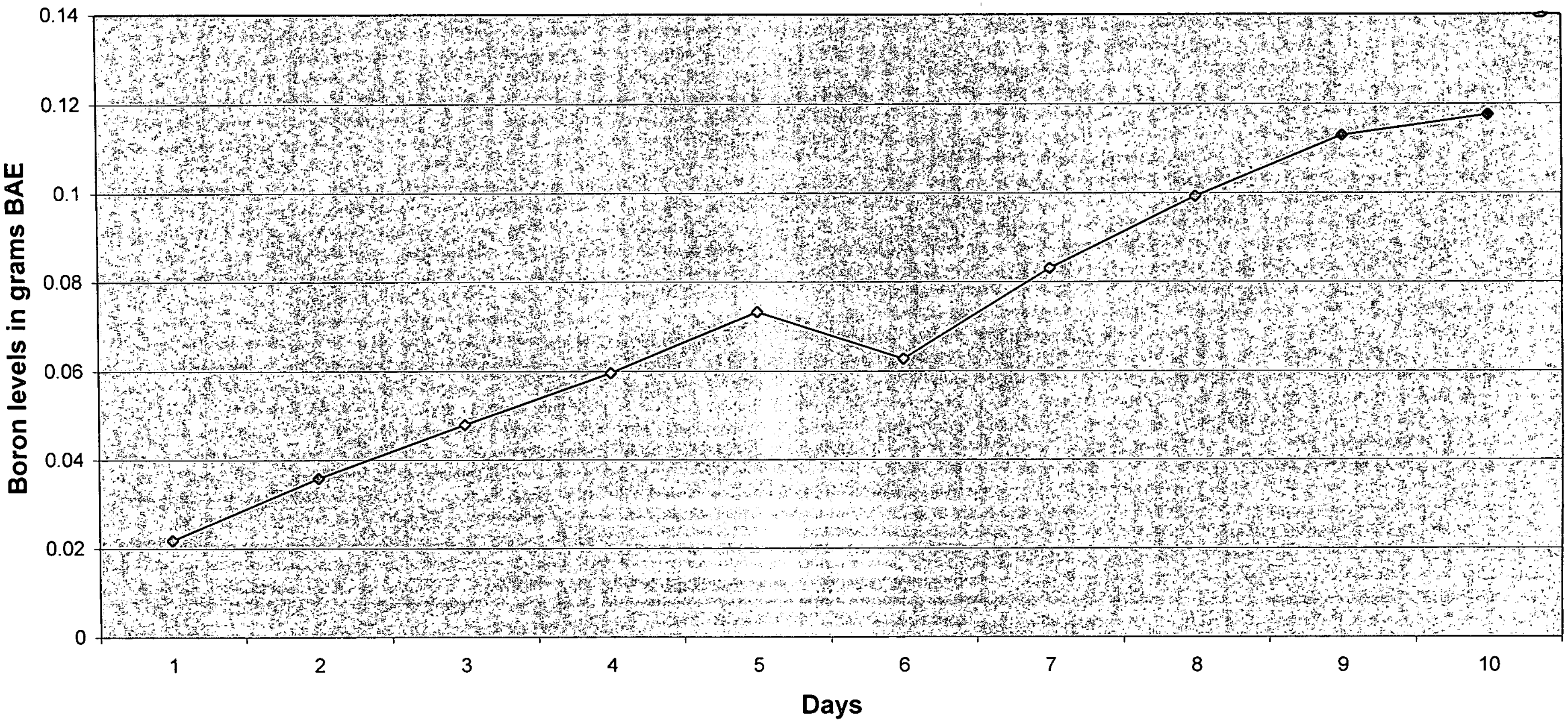
On the ninth day, Sample 2 and the Control showed a marked increase in the concentration of boron in the leaching vessel. This is probably due to the concentration of BAE in the periphery of the timber being so low that a diffusion gradient was created and this was accompanied by a sudden increase in the leaching of boron (As illustrated in Figs 7.2 (b) and 7.3 (b).

The amounts of BAE retained in the timber are shown in Table 6.14 after leaching for 10 days which also has results of the original retention of BAE in the timber. It is evident that this concentration (60 g/L) is not sufficient for primary treatment. The SABS specification of 5 kilograms of BAE per cubic meter was not met. As shown in Table 6.14 samples 1, 2 and 3 had retentions of 1.54, 1.66 and 1.96 kilograms of BAE per cubic meter, respectively.

Since the 60 g/L solution is mainly intended for remedial treatment of timber, it is highly unlikely that preservatives with the concentration of BAE will be used for exterior applications. It might appear that use of the polymer is superfluous, because leaching of boron is unlikely in the concentration of non-exposed timber. On the contrary, the polymer will ensure that that the boron will remain in the timber during the entire lifespan of the timber.

The possible reason for a comparable difference between the control and the test samples can be attributed to the fact that 60g/L BAE concentrations do not create a sufficient gradient to drive boron into great depths of the timber. A band of boron on the periphery of the piece of timber creates a sufficient gradient to force boron out when there is no boron in the leaching solution.

Although it is unsuitable for primary treatment the product with a concentration of 60 grams per litre appears ideal for remedial application. Only minimal diffusion is expected because the " aged" timber that will be treated will not be expected to have any moisture in it. Typical cases for which this preservative, (containing60 grams per litre BAE would be suited), include in-situ applications on antique furniture and very old buildings. The concentration would be more suited for the domestic market, rather than for industrial applications. The preservative solution would be suited for treatment of fungal colonies that may appear in forms of patches. This is generally as a result of exposure to moisture.



A graph of boron concentrate in the leachate as grams BAE vs days for Sample 1 - 60 g/L

Fig 7.1 (a)

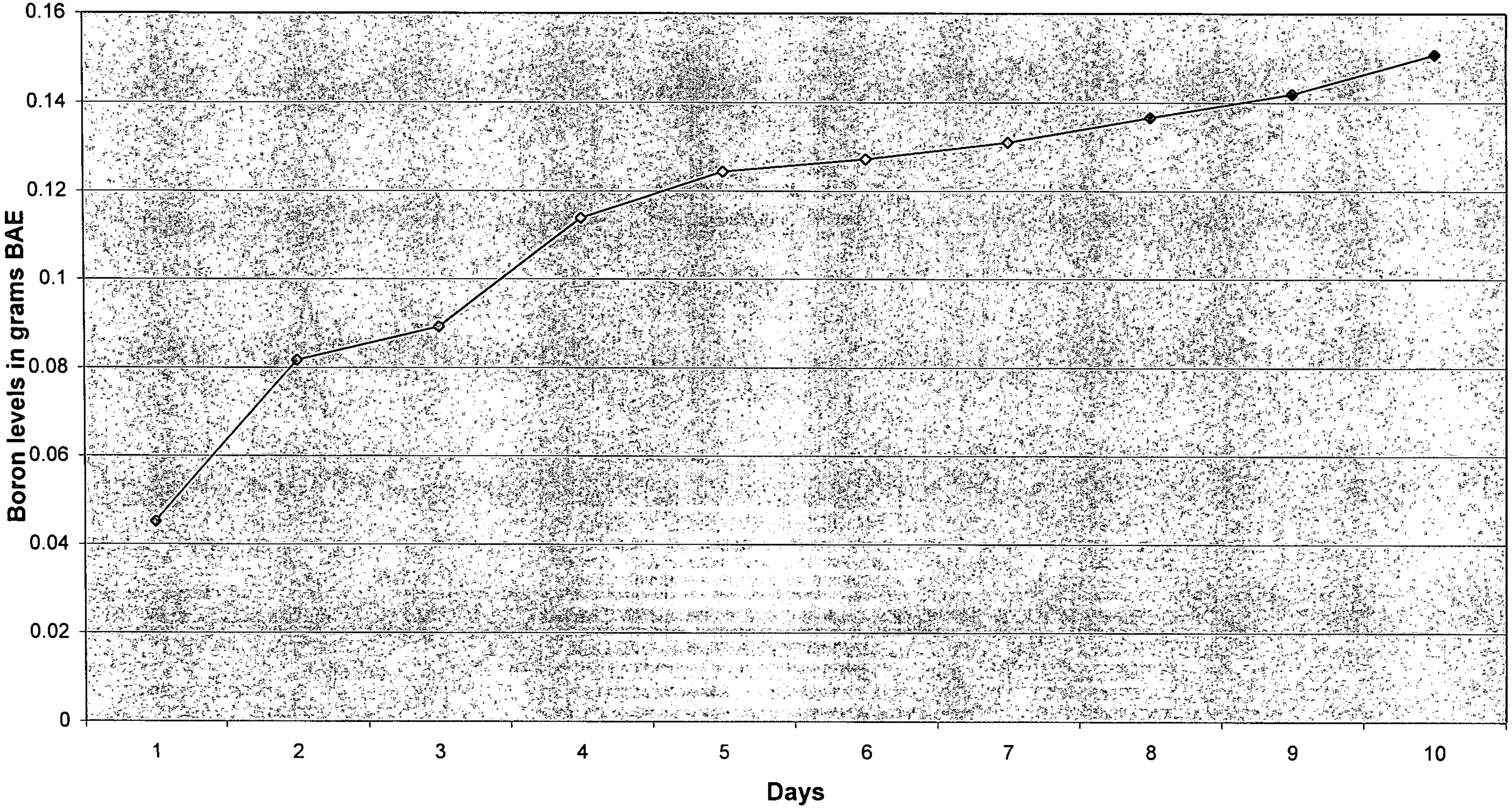


Fig 7.2 (a)

A graph of boron concentrate in the leachate as grams BAE vs days for Sample 2 - 60 g/L

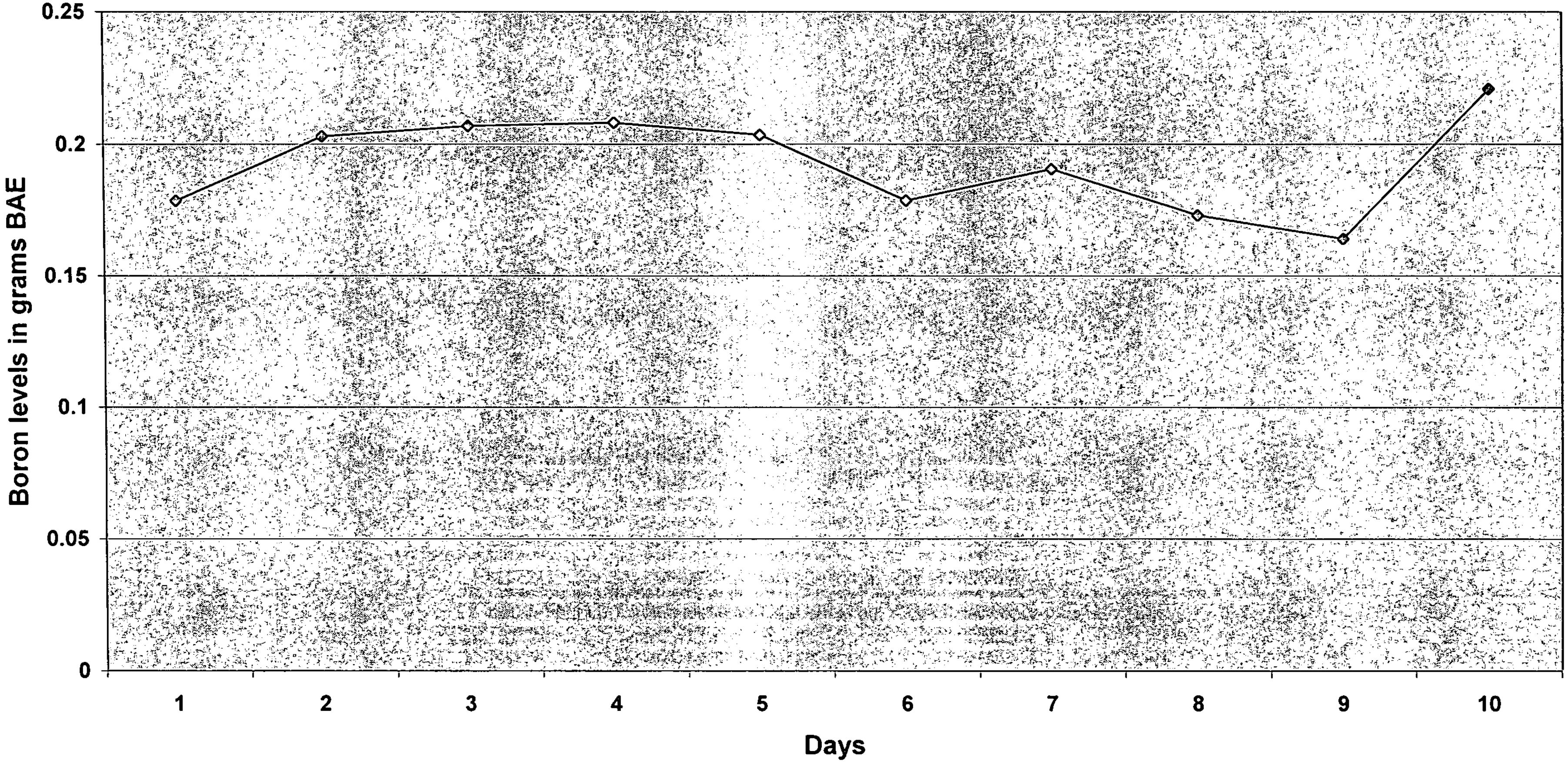


Fig 7.3 (a) A graph of boron concentrate in the leachate as grams BAE vs days for Sample 3 - 60 g/L control

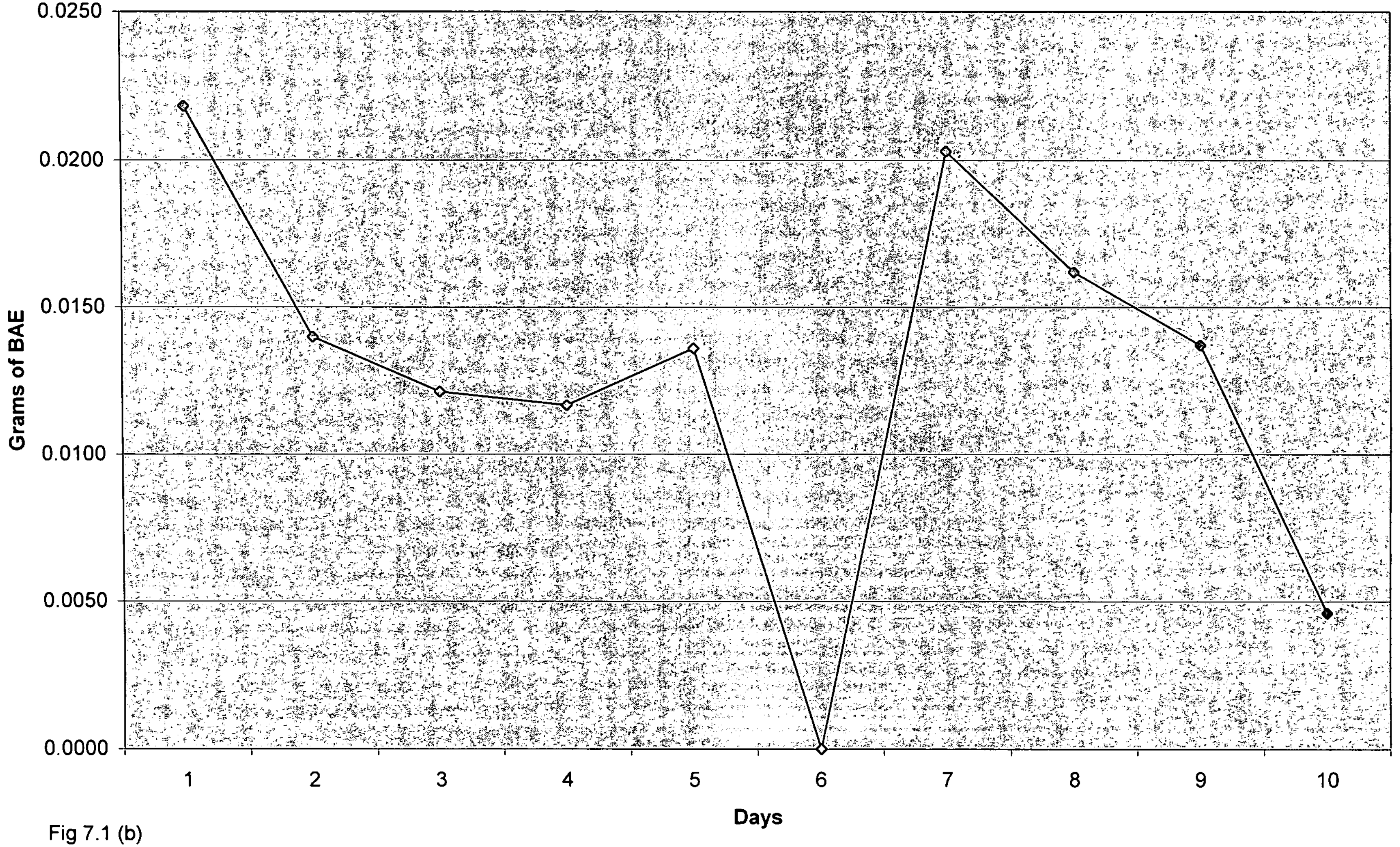


Fig 7.1 (b)

A graph of daily boron leaching as grams BAE for Sample 1 - 60 g/L

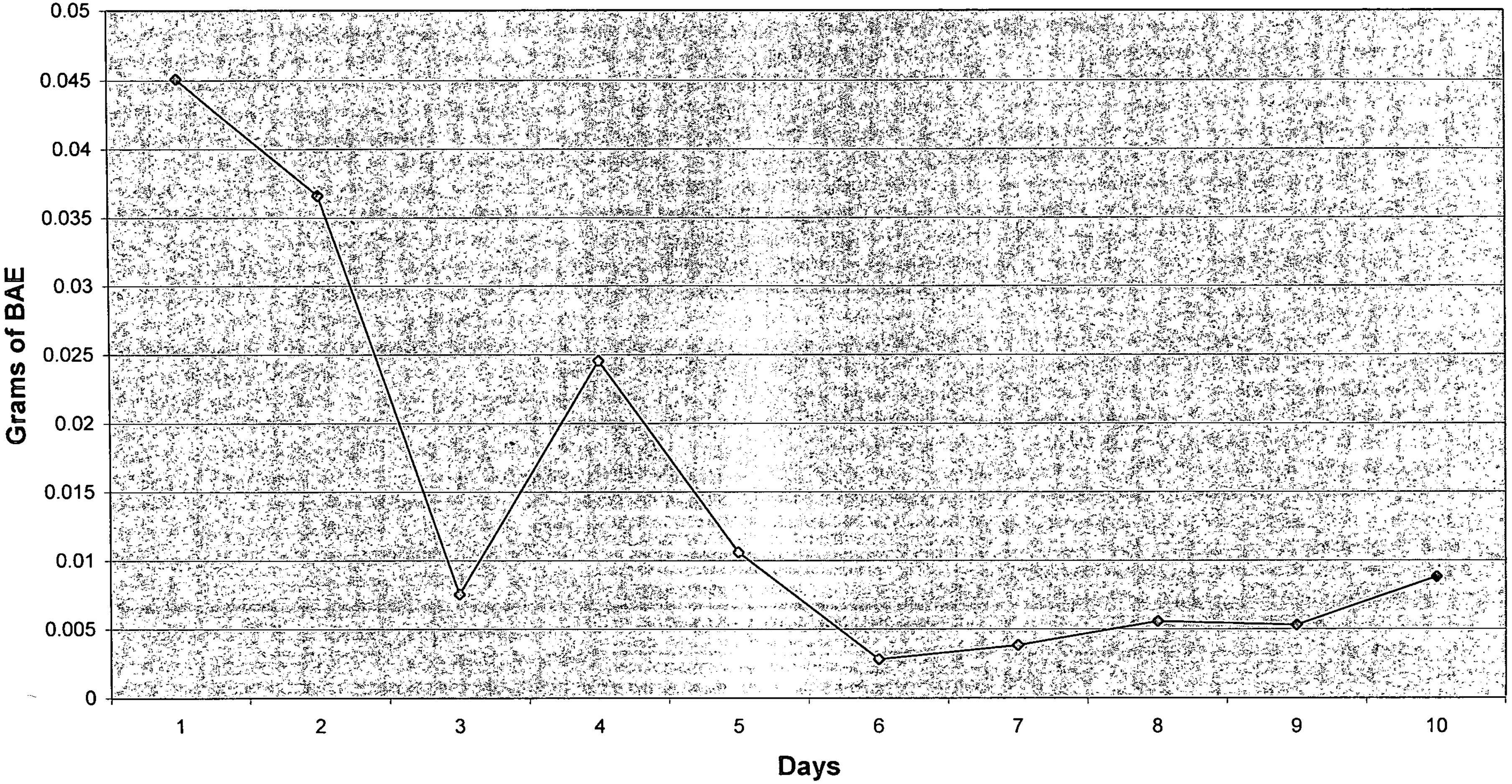


Fig 7.2 (b)

A graph of daily boron leaching as grams BAE for Sample 2 - 60 g/L

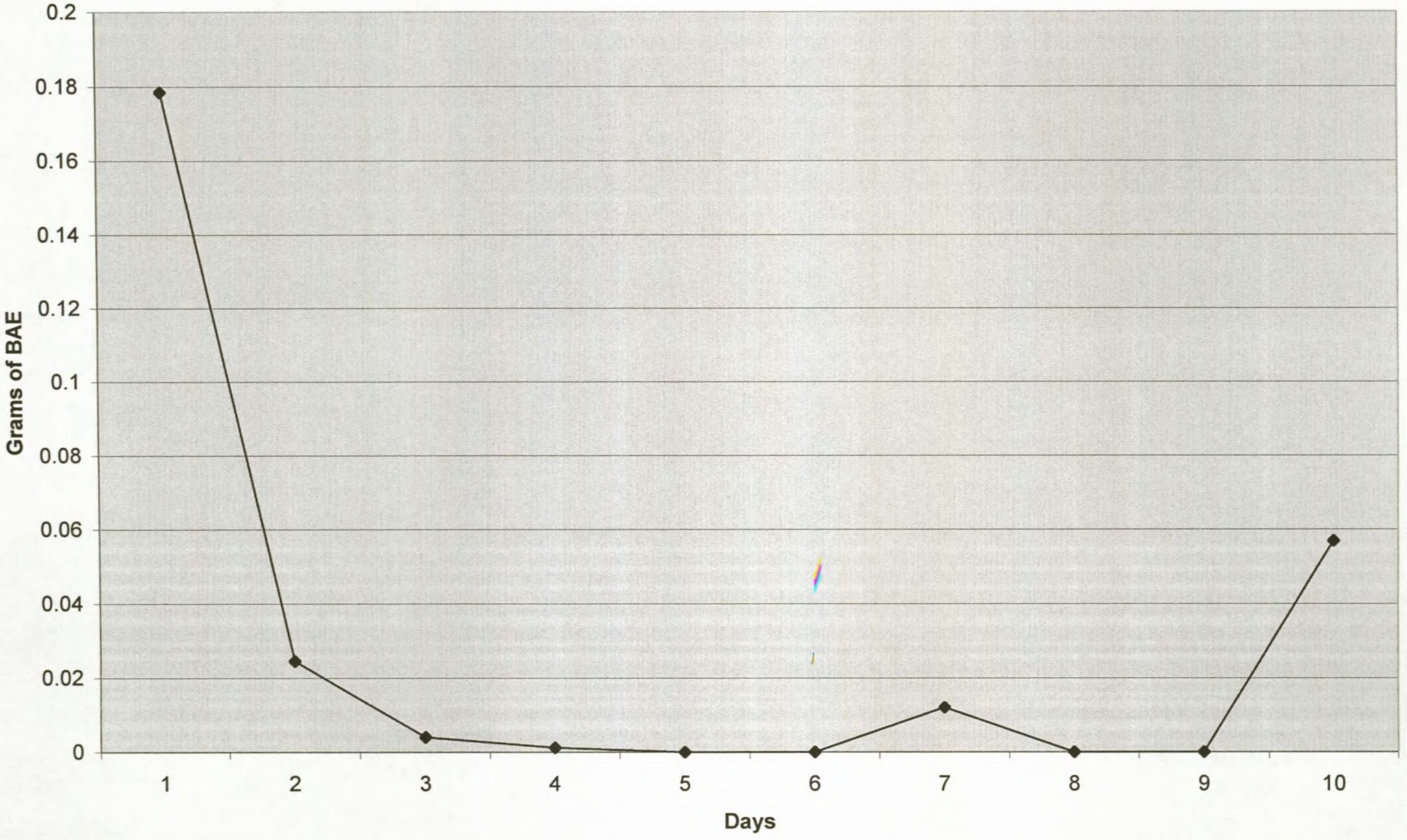


Fig 7.3 (b)

A graph of daily boron leaching as grams BAE for Sample 3 - 60 g/L control

### 7.2.2 Assessment and discussion of the 150 grams per litre BAE samples:

This particular concentration is in a unique position because it can be used as a remedial preservative, as well as primary applications. Over the ten days of leaching, Samples 4 and 5 lost 22.6% and 20.3% of the BAE respectively. A very big difference exists between these two samples and the Control, which lost 57.9% of its BAE. There can be no doubt that the polymer has played a significant role in containing the boron inside the timber.

This set of samples showed the best results comparatively. There was only 4.9% of leaching from Sample 4, in the first 24 hours of leaching. Fig 7.4(b) is very erratic with reduced leaching, followed by increased leaching. This is would normally happen if there is a very small conducting pathway which allows some moisture to enter the timber. The shape of the graph, suggest that boron follows a slow release mechanism when leaching out of the timber. The graph in Fig 7.5(b) also shows a similar trend. Initially, 5.4% of boron leached out of the timber and thereafter there was erratic movements of boron, albeit very small quantities. The control allowed 34.7% of boron to leach out in the first 24 hours. By the third day, the movement of boron had stabilised and the virtually no boron moved out of the timber (As illustrated in Fig 7.6 (b)).

Sample 4 and 5 only lost 13.4% and 13.7% of the boron respectively in the first five days of leaching. The results show that the 150 g/L test samples stood up well to the leaching conditions.

Another interesting trend can be seen from Figs 7.4(b), 7.5(b) and 7.6 (b). On the ninth day, there is an increase in the leaching. This is probably due to slight movement of boron inside the timber sample. Negligible amounts of BAE leached-out on the eighth day, for Sample 4, 5 and the Control. There might have been a gradient inside the timber and this could have caused boron to migrate towards the surface of the timber. On the ninth day, the BAE diffused from the inside of the timber to the outside possibly through a small conducting pathway, in the case of Samples 4 and 5. Had there been a breakdown of the polymer coating, there would be largely increases in the levels of boron in the leaching solution. However, analysis results indicate that this is not so. Samples 4 and 5 had retained 77.3% and 80% of the original BAE respectively, after the ten days of leaching. The Control had only 42.2% left after 10 days. The amount of BAE left in Sample 4 and 5 after 10 days of leaching is high enough to approximate to SABS standards for primary treatment namely 5 kilograms of BAE per cubic meter of timber.

Since the overall concentrations of boron that was retained in the timber was high, is suggestive that the erratic movements of boron in the two test pieces (sample 4 and 5) represent very small quantities of boron.

It is also true the conditions used for leaching are much higher than would be experienced by timber in hazardous class 2 and 3 environments (above ground exposed environments). The most important question is, whether this preservative would be able to afford sufficient protection in the intended hazardous class? The answer is surely, yes. Unless the timber is completely submerged in water, there would be no continuous conducting pathway along which boron will effuse out of the timber. The results show that: -

- Boron is only lost in small quantities as compared with the control.
- The polymer the uncontrolled loss of boron.
- The polymer does not breakdown underwater
- Timber will be adequately protected using a 150 g/L BAE preservative that was developed in this project.

This concentration would be ideal for the treatment of freshly felled timber because there is sufficient boron to produce a gradient, which causes boron to diffuse into the sap and heartwood. With regard to field trials, it is noted that this concentration (150 g/L) was used to treat logs of Poplar pine in Cape Town. The treated timber was exposed to sea spray, UV and rain. Qualitative tests showed that no boron was present on the surface of the polymer coating. The treated timber was subsequently used in the construction of expensive log houses in Cape Town. All the feed -back, thus far, has been positive, showing that the coating is serving its purpose.

From a commercial point the product with this concentration is expected to be profitable.

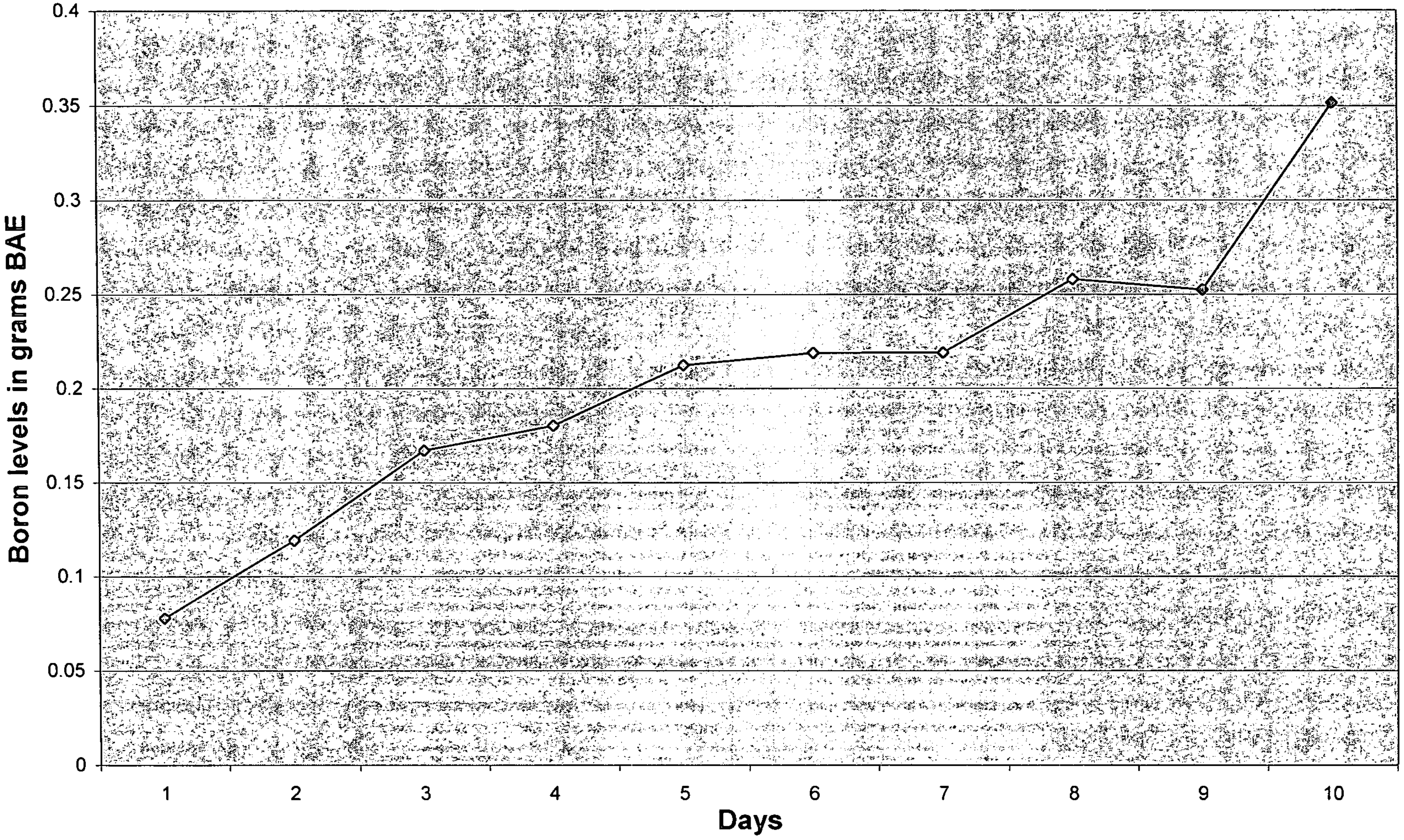


Fig 7.4 (a) **A graph of boron concentration in the leachate as grams BAE vs days for Sample 4 - 150 g/L**

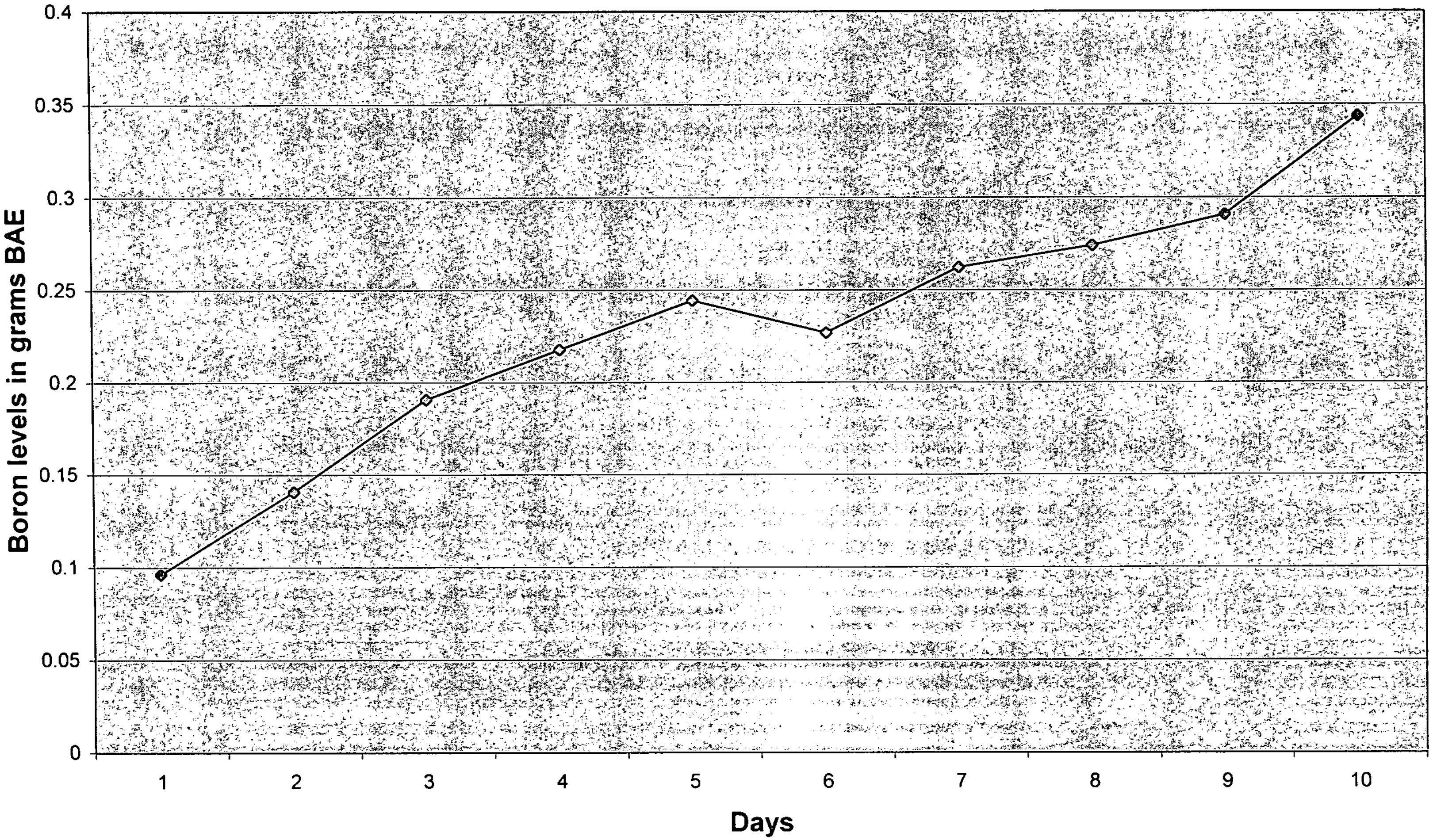


Fig 7.5 (a) **A graph of boron concentration in the leachate as grams BAE vs days for Sample 5 - 150 g/L**

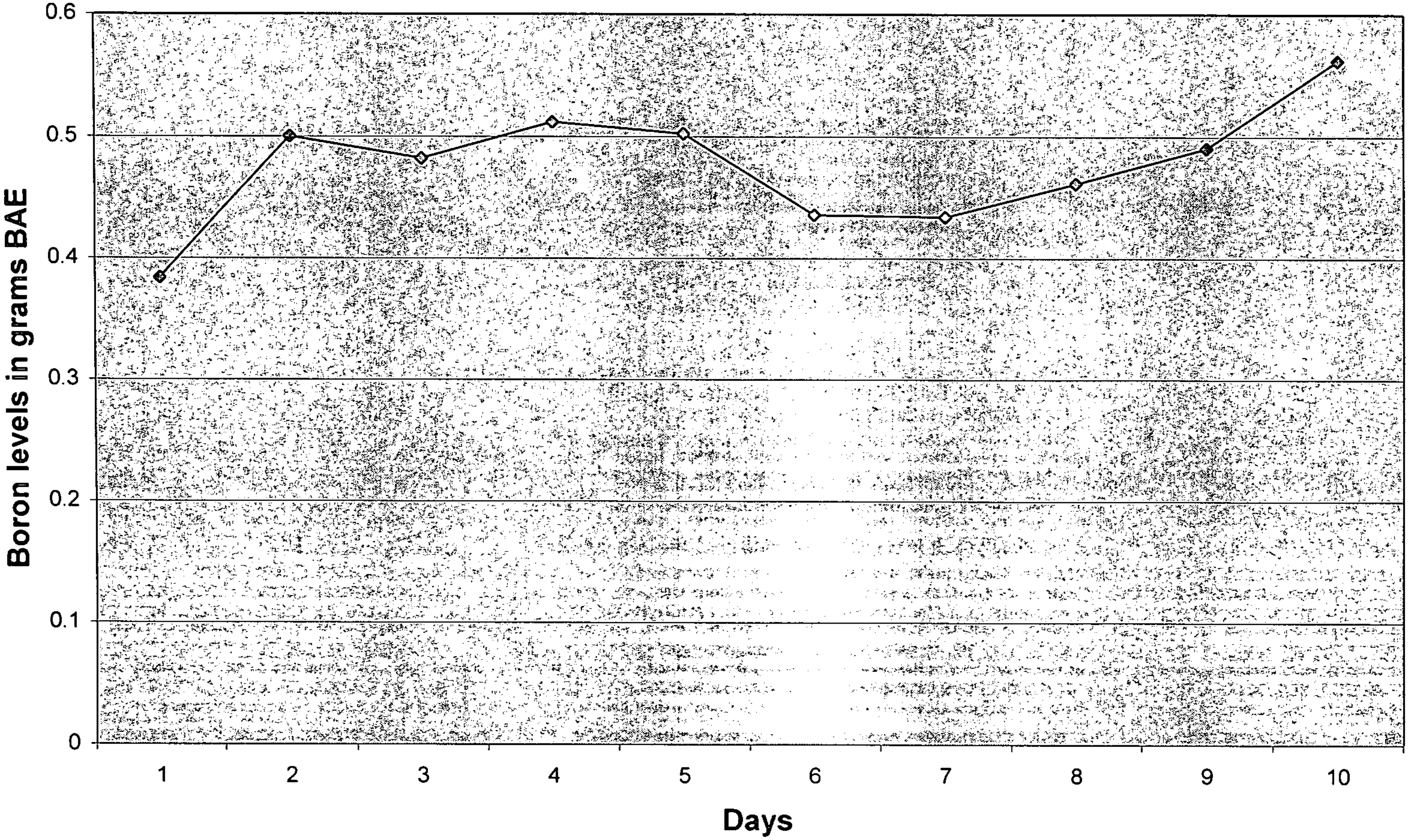


Fig 7.6 (a) **A graph of boron concentration in the leachate as grams BAE vs days for Sample 6 - 150 g/L control**

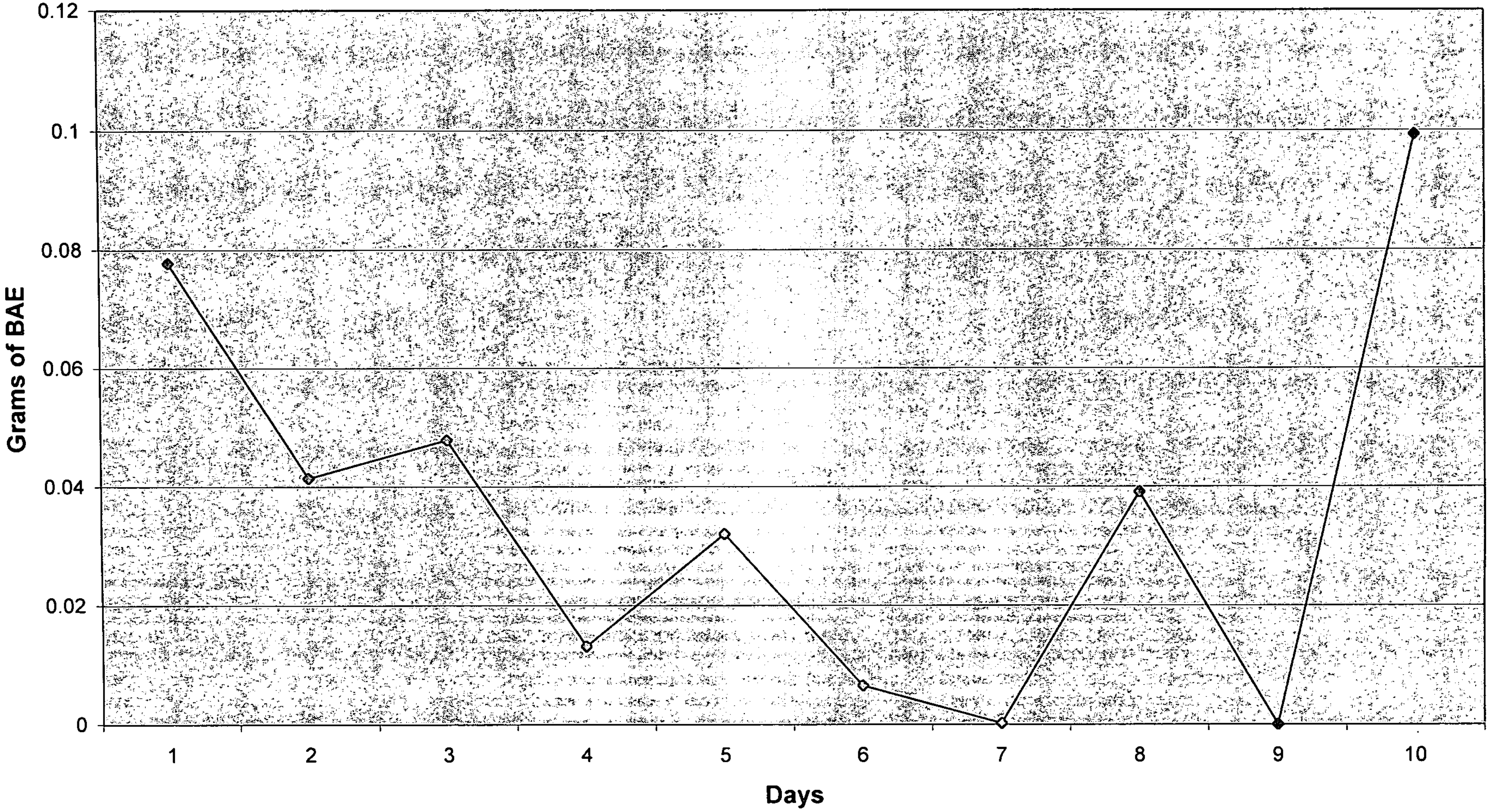


Fig 7.4 (b)

A graph of daily boron leaching as grams BAE for sample four - 150 g/L

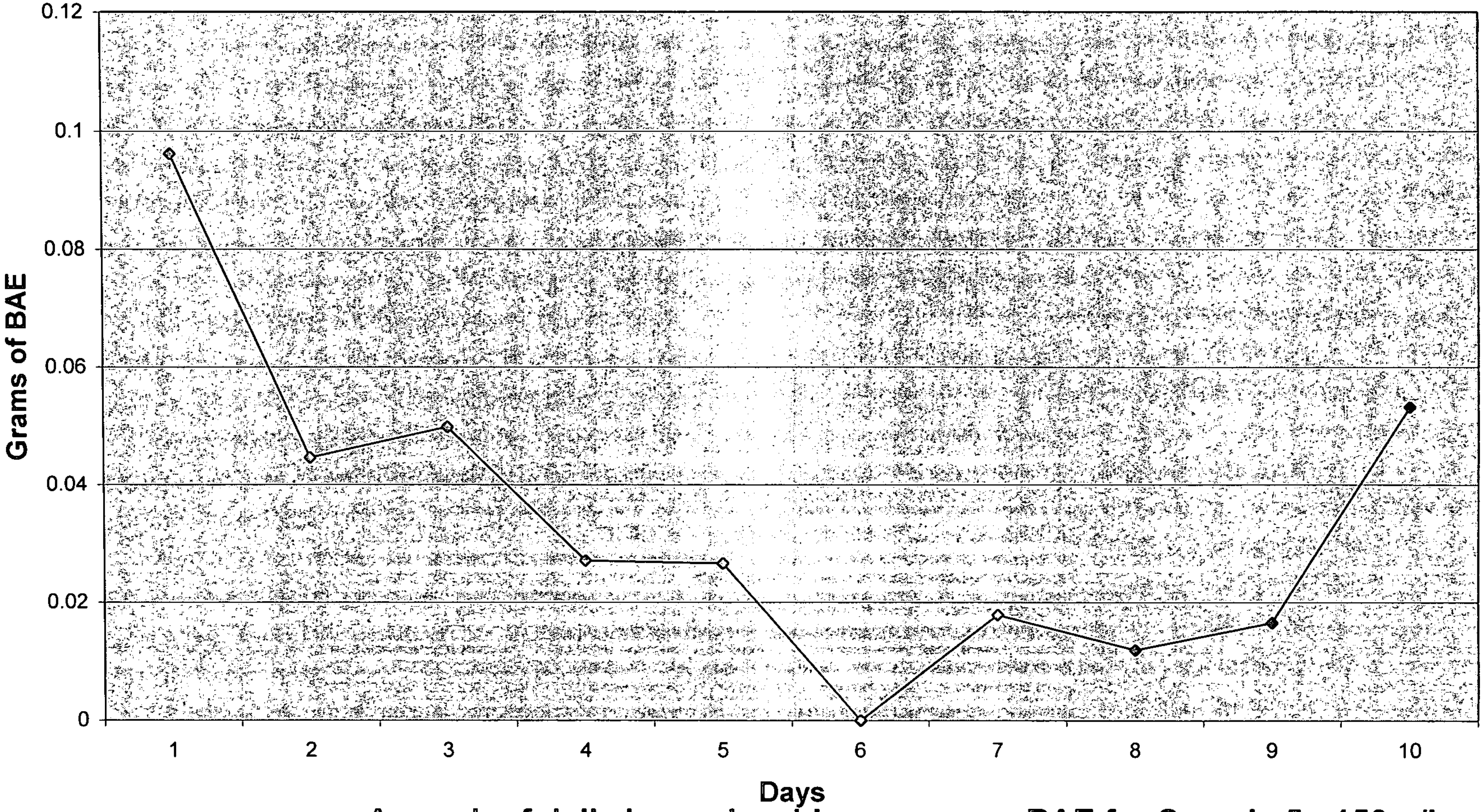
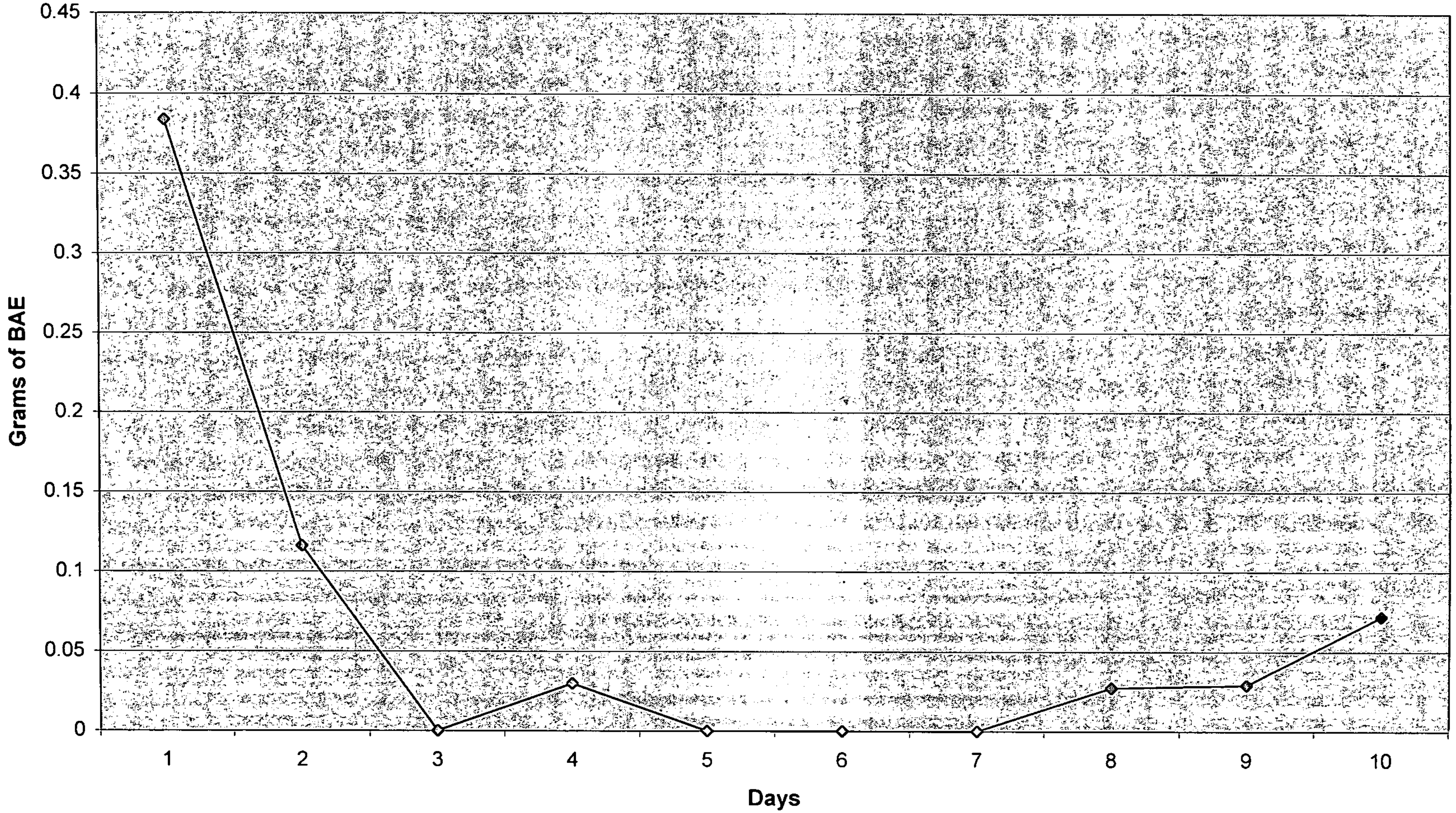


Fig 7.5 (b) **A graph of daily boron leaching as grams BAE for Sample 5 - 150 g/L**



A graph of daily boron leaching as grams BAE for Sample 6 - 150 g/L control

Fig 7.6 (b)

### 7.2.3 Assessment and discussion of the 200 grams per litre BAE samples:

The reason for producing a 200 g/L BAE preservative is to force boron into timber that is relatively thick e.g. logs with a cross-sectional diameter of more than 200 mm. Treating thinner pieces of timber, creates a high concentration band of boron. The results of this is that there is a strong gradient that forces boron out of timber, into the leaching solution, which had a low concentration of boron. This particular concentration (200 g/L BAE) of preservative had the highest propensity to leach boron, by virtue of the concentration of boron inside the timber. If timber treated with this concentration (200 g/L BAE) of preservative does not allow a large percentage of the original boron to leave the timber, then this is valuable proof that the product will perform well in its intended application.

In the first 24 hours of leaching, Samples 7 and 8 lost 5.3 and 4.7% of the boron (as BAE) respectively (See Table 6.12 and 6.13). This is very low considering the fact that this set of samples had the highest concentration of boron. The control had lost 23% of its boron in the same period. Over the 10 day period, Sample 8 showed a more erratic leaching pattern than Sample 7 (as can be seen from Figs 7.8 (b) and 7.7 (b) respectively). Sample 7 shows a very gradual decrease in the amount of boron lost as BAE from the first to the seventh day. This is expected because the high concentration of boron inside the timber will create a very steep gradient, which will force boron out of timber.

Over the first five days, Sample 7 lost 16.6 % of its boron (as BAE) and Sample 8 lost 15.2% but the control lost 31.3%. These results are consistent with the view that the polymer extends the lifespan of the boron inside the timber. At high concentrations of boron, there would be a strong tendency for boron to leach out, but the polymer was able to contain the boron in the timber at relatively high level to ensure continued biocide activity.

Sample 7 lost 8.2 % of the boron (as BAE) on the ninth day. This can be clearly seen in Fig 7.7(b). Sample 8 lost 9.1 % of the boron (as BAE). Losses for both samples are very comparable. Both test samples behaved in a very similar manner. The sudden change in the direction of the graph cannot be attributed to a breakdown of polymer because the control sample, with no polymer shows a similar trend, albeit not to the same extent. The possible reason for increased leaching may be due to changes in the distribution of boron within the timber. The difference in concentration of boron between the inside and outside of the timber, will force boron to diffuse out through any available pathway. However, the levels of boron as BAE that were retained in the timber for Samples 7 and 8 were still high (71.1% and 72.1% respectively) compared to the control, which only retained 56.8% of its original BAE.

Since the majority of the boron in the test samples was retained, shows that the polymer performed its intended function. More than 70% of the original boron was contained in the timber and therefore, the preservative can be successfully used as a primary treatment for freshly felled timber.

In summarizing the performance of the 200 g/L BAE preservative, the following can be concluded-:

- The results show that the polymer did not suffer boron/polymer incompatibilities – there was no evidence of blotching and blistering of polymer.
- The high concentration of boron did not prevent the polymer from functioning as a continuous film – more than 70% of the original boron was retained in the timber.
- The polymer allowed the complete diffusion of boron into the timber – there was no evidence of boron on the surface of the polymer.
- The large concentration gradient did not force boron out of the timber – in spite of having been completely submerged for 10 days, more than 70% of the boron remained encapsulated in the timber.

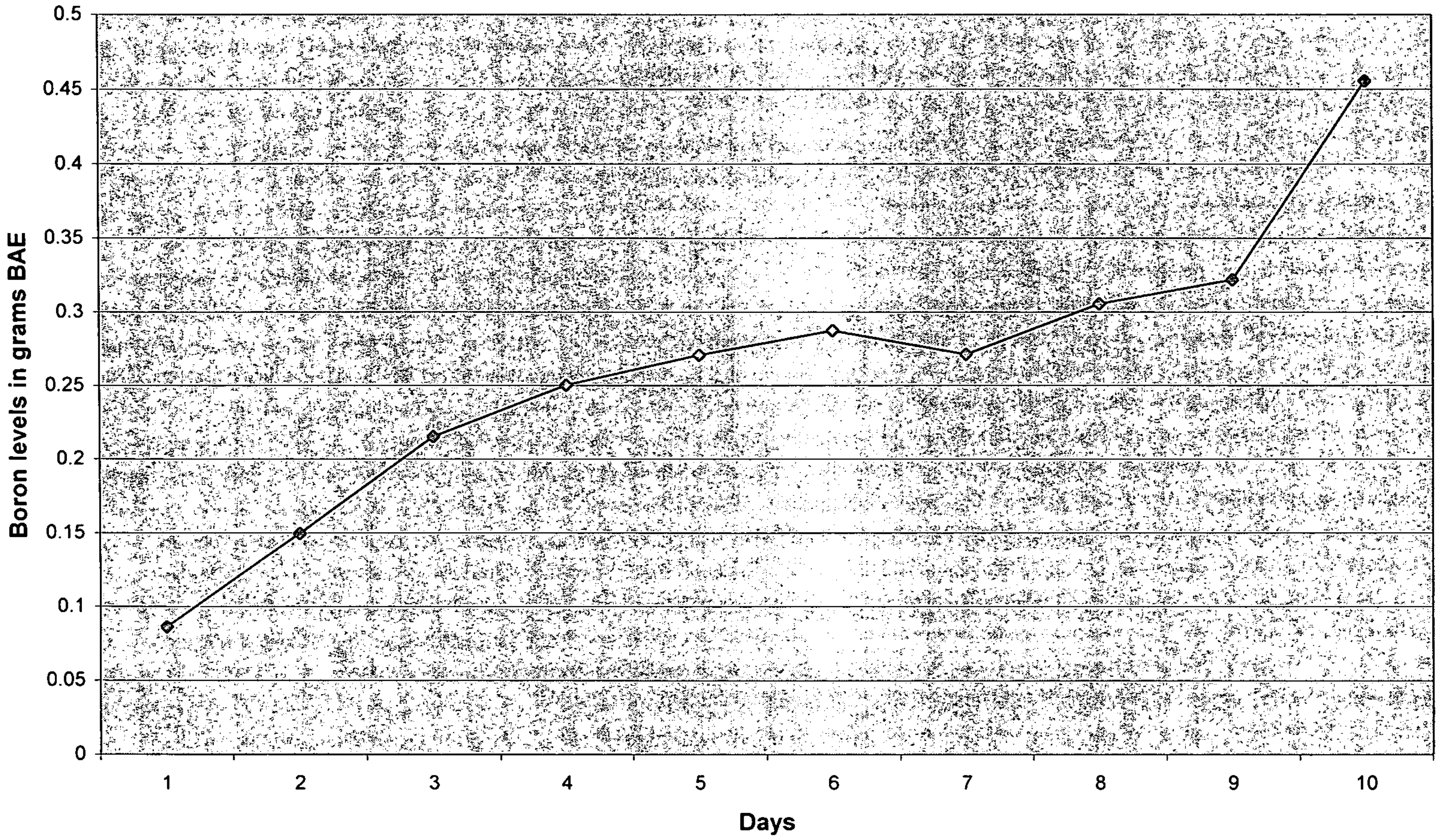
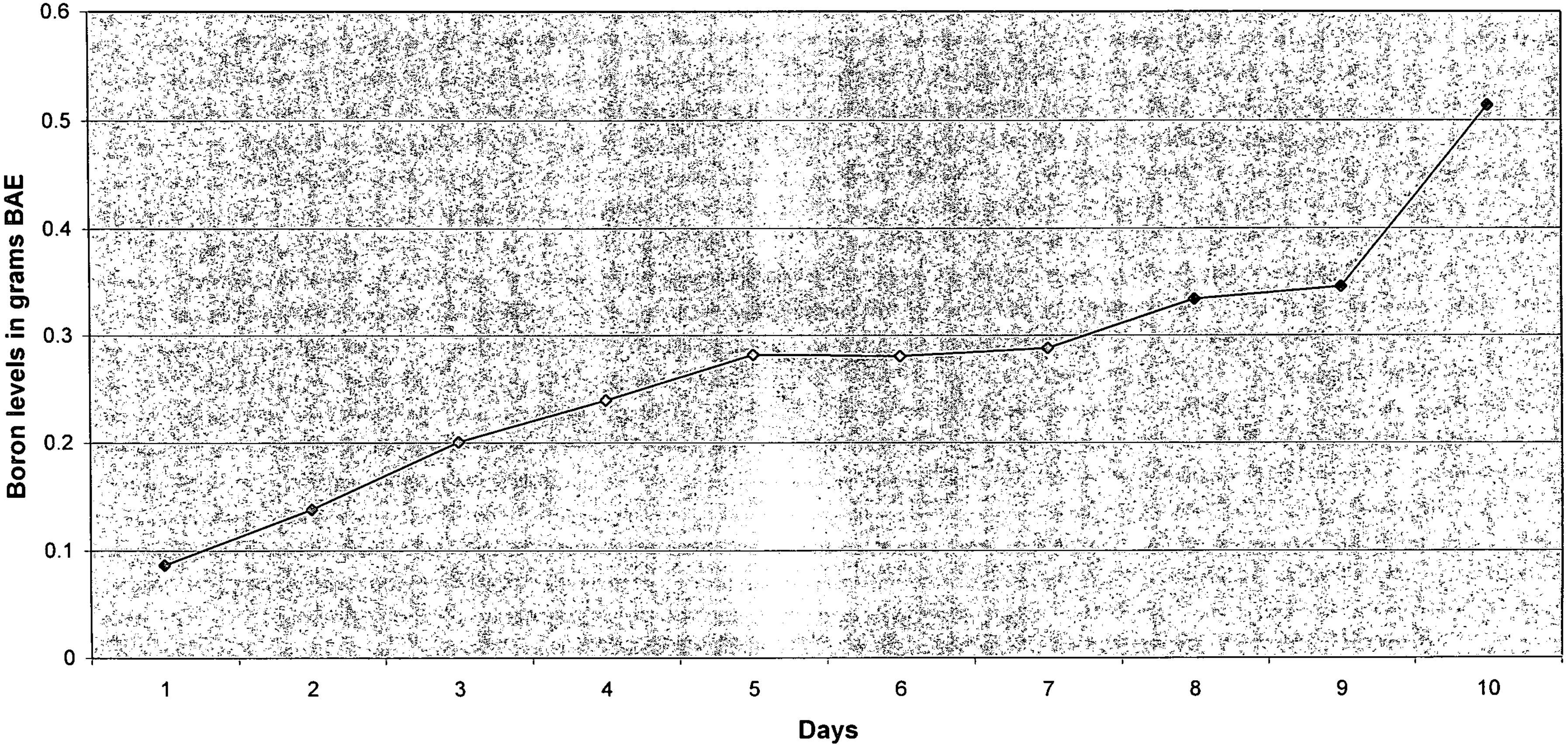


Fig 7.7 (a) **A graph of boron concentration in the leachate as grams BAE vs days for Sample 7 - 200 g/L**



**A graph of boron concentration in the leachate as grams BAE vs days for Sample 8 - 200 g/L**

Fig 7.8 (a)

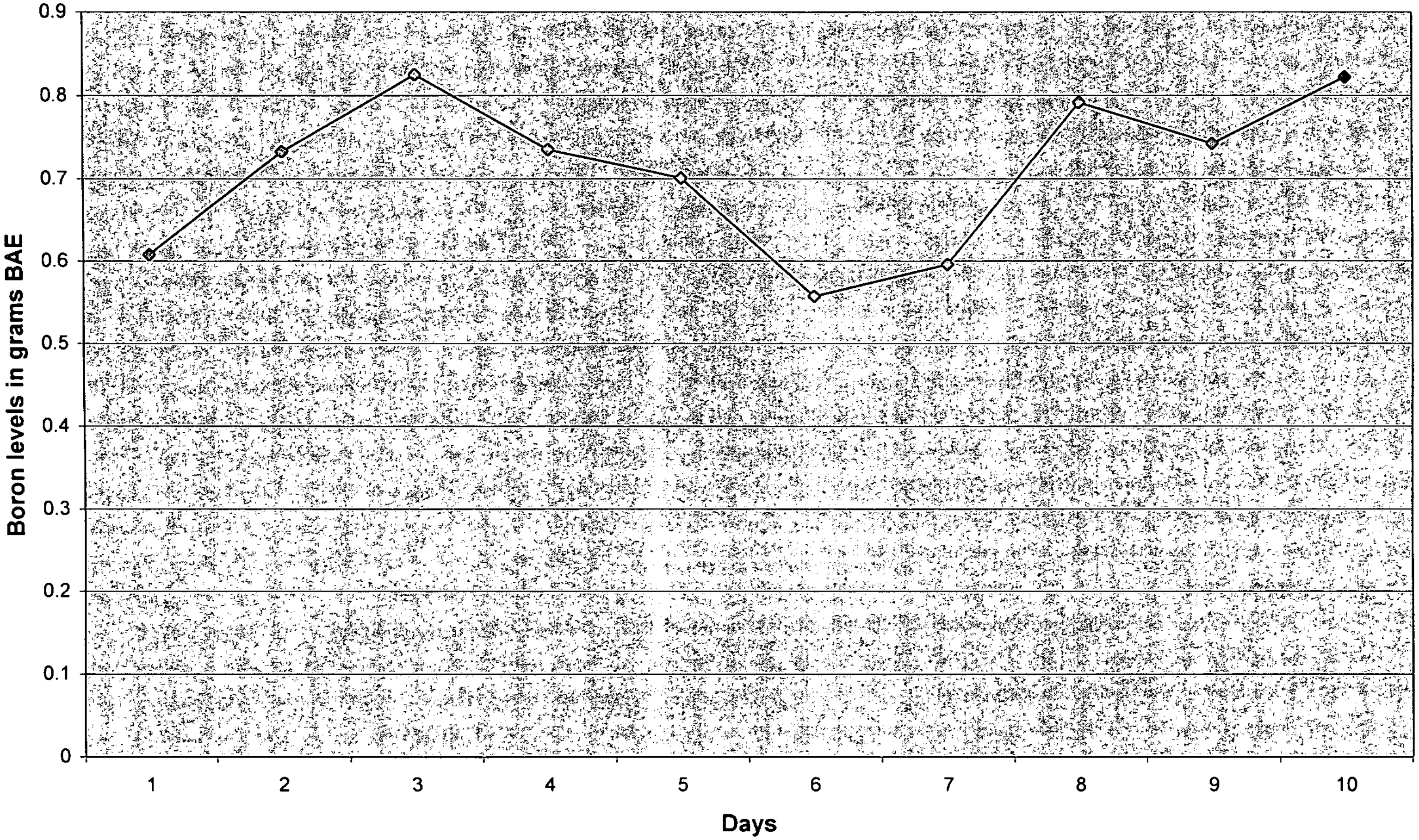


Fig 7.9 (a) **A graph of boron concentration in the leachate as grams BAE vs days for Sample 9 - 200 g/L control**

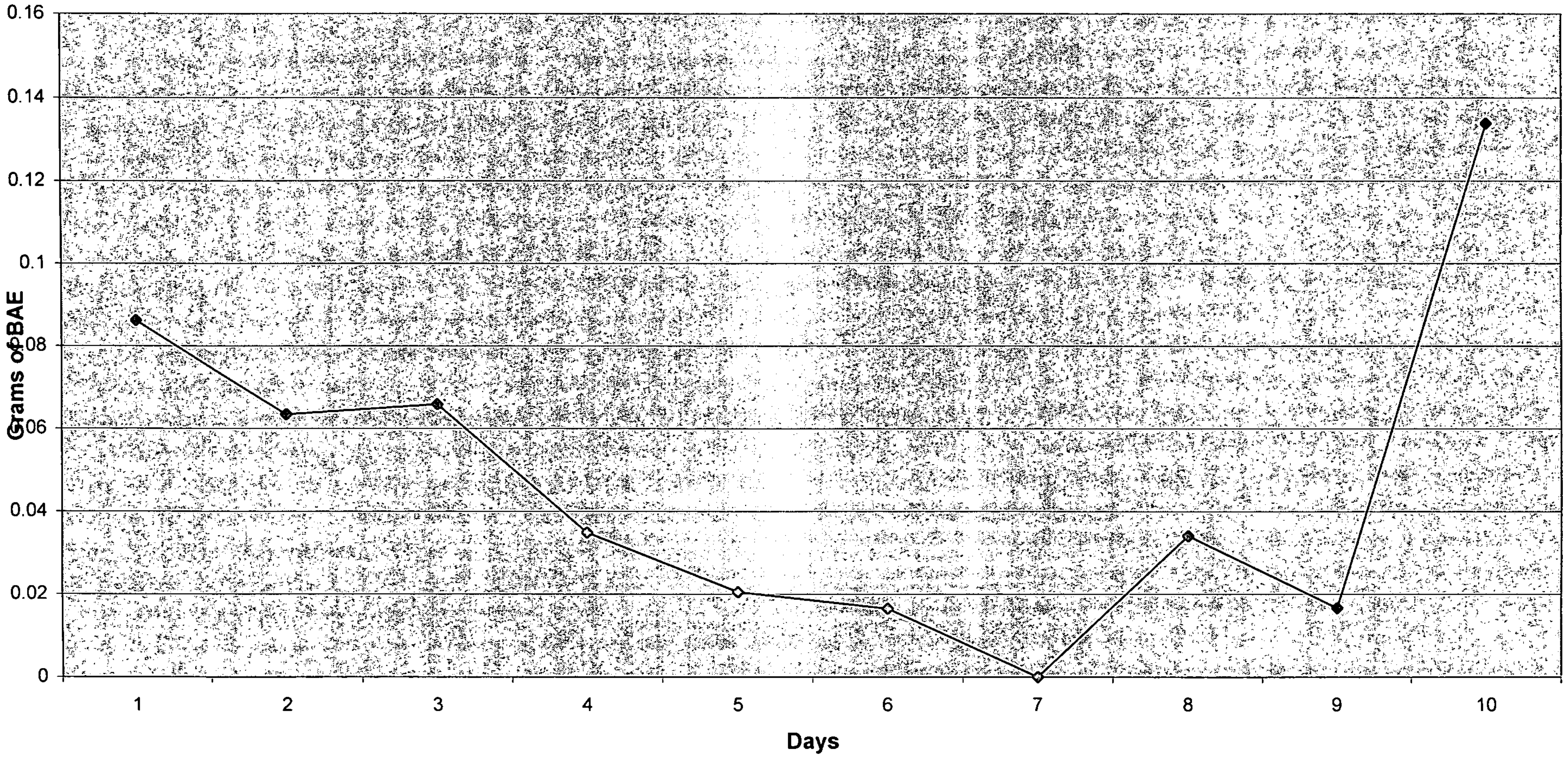


Fig 7.7 (b) A graph of daily boron leaching as grams BAE for Sample 7 - 200 g/L

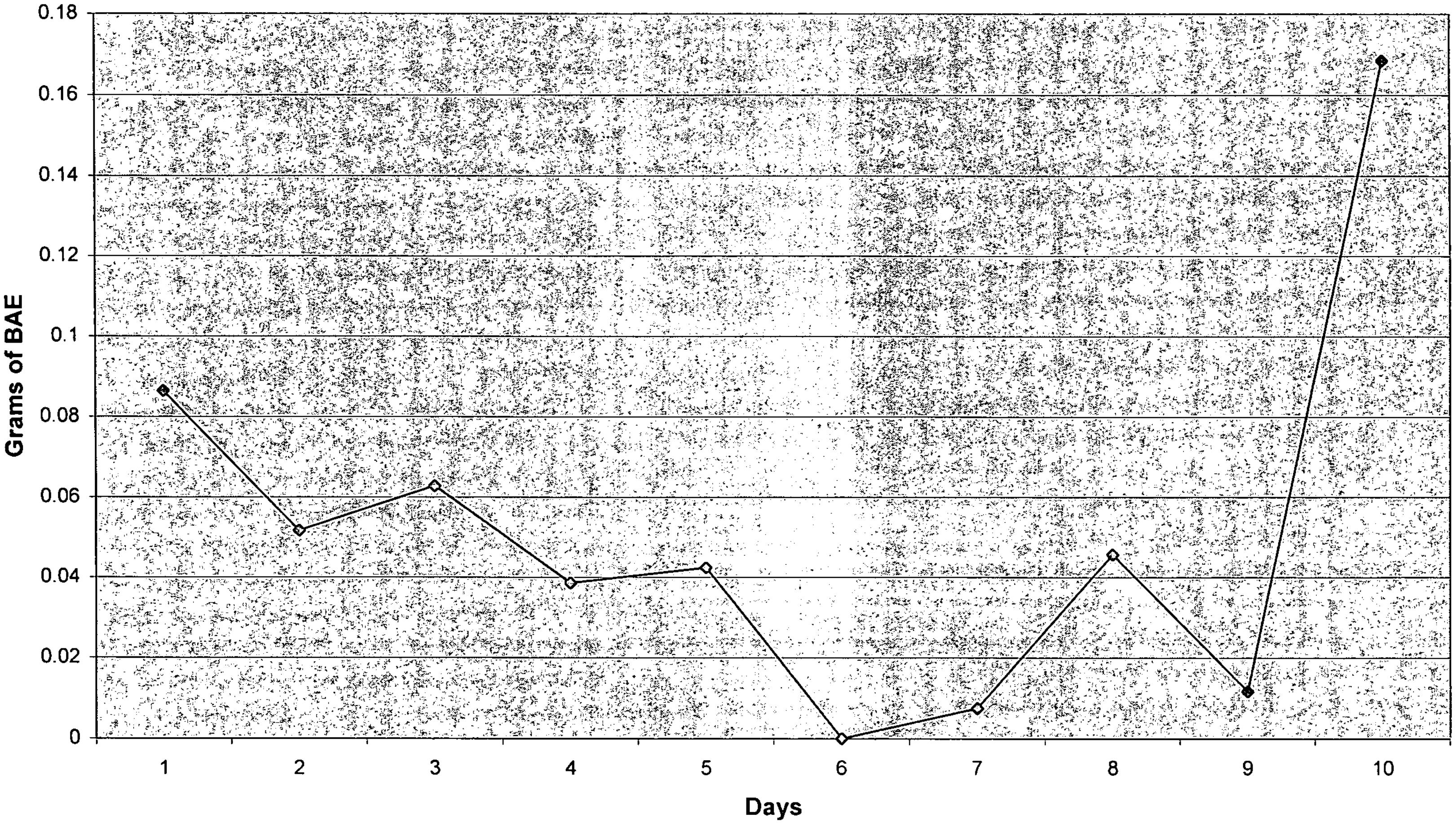


Fig 7.8 (b)

A graph of daily boron leaching as grams BAE for Sample 8 - 200 g/L

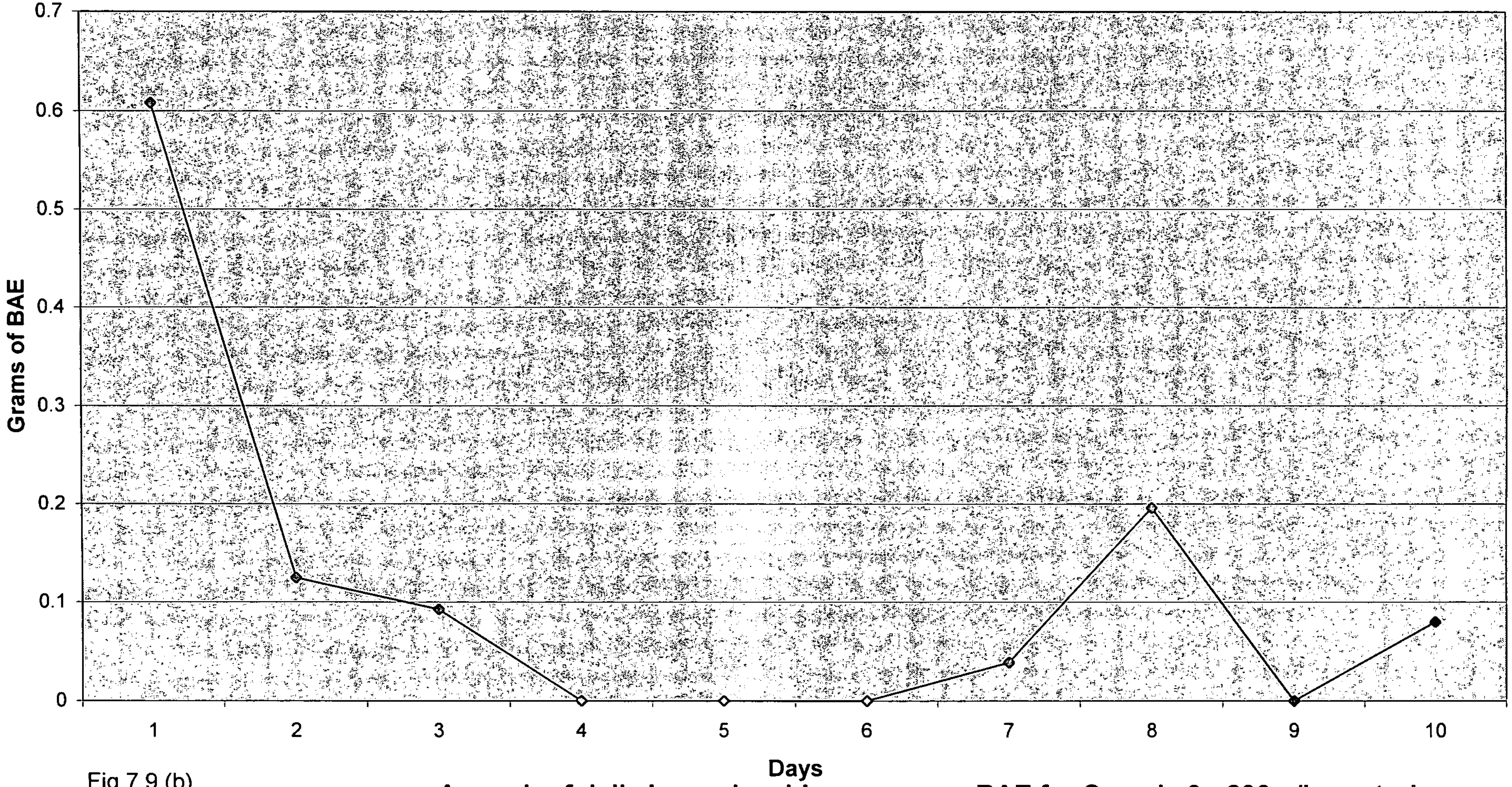


Fig 7.9 (b)

A graph of daily boron leaching as grams BAE for Sample 9 - 200 g/L control

## 7.3 Conclusions:

The fundamental difference between the approach used in this project and that of others is that the formulated preservative may be applied through dip treatment whereas those of others required vacuum/ pressure conditions. Since dip treatment is facilitated by a diffusion gradient, high concentrations of BAE have to be used. Coincidently this also meets with the SABS specifications.

Other researchers notably, Murphy et al, (1995) tried to fix boron into timber using a Rhoplex polymer. Their preservatives were introduced into the timber under the influence of a pressure of 1241 kPa. An important finding of these researchers is that polymer alone helped to reduce the decay of timber by fungi. They also found at the levels of BAE (namely 0.74%), which they used, their polymer was unsuccessful in preventing leaching of boron. They cited polymer/boron incompatibility at high concentrations of boron as the driving force for this leaching.

In the case of this project, it was possible to increase the concentration of boron in the preservative (without encountering boron/polymer incompatibility) to 20% BAE. This is attributed to the nature of the polymer selected and a novel method of blending the polymer and boron. Although this concentration is twenty fold higher than that used by Murphy et al, (1995) no appreciable boron was lost.

The fact that the all-in-one preservative developed as part of this project has been accepted for patent (Patent No 20017130), suggests that this product has novel features, namely, a compatible homogenous mixture of a boron compound and a sun-screen containing polymer. Perhaps the most appealing feature of this system is that it requires no sophisticated equipment for treatment and can therefore be used in both developed and underdeveloped areas of the world for timber preservation.

The product has the potential to take timber preserving to rural areas in South Africa and to make housing more affordable to people. The are no sophisticated pieces of equipment that are needed to treat timber, yet many years can be added to the life of timber in service and the need to cut down more trees can be reduced.

## Appendix 1

**Aim:**

A trial was conducted to use boron compounds as a source of boron for a timber preservative.

Three different sources of boron that were tried: -

| | |
|---|---|
| Disodium Octaborate | ($Na_2BgO_{13}$. $4H_2O$) |
| Boric Acid | ($H_3BO_3$) |
| Borax | ($B_2O_3$) |

Masses of the above corresponding to 20g/L BAE was added to each of the flasks containing one litre of styrene polymer The three different samples were allowed to stand for approximately 16 hrs and stability was assessed.

**Findings:**

The preservative that were prepared from Borax and boric acid settled out
and lumps formed in the preservative mixture. The preservative that was prepared from the DOT, as a source of boron had good stability.

**Trial of preservative on timber:**

The preservative was used on timber with moisture content of approximately 30 %.
The timber was dipped in the preservative for a period of 2 minutes.
The polymer cured in the space of 3 hrs.
An assessment of the treated timber indicated that the polymer cured to a clear finish with a slight gloss. There was no evidence of film being undermined in anyway.

**The limitations of this experiment: -**

The Approximate cost of 1L of this preservative would be in the range of R20.00/L.

To treat 1m$^3$ of timber would require 250 L i.e.
5000g.m$^3$ (SABS spec. 5 Kg /m$^2$)
20g/L
= 250L/m$^3$ which would cost R 5000 per m$^3$

This would not allow the preservation to compete favourably in the market. Further action: Mix a high concentration of DOT

If a 60g/L preservative is prepared,

The volume of preservative that would be required to preserve a cubic meter of timber is:

$$\frac{5000\text{gm}^{-3}}{60\text{-gL}^{-1}}$$

which equates to 84 L per cubic meter at a cost of R20.00 per litre will equate to R1680.00.

# Appendix 2

**Aim:**

To prepare a boron based preservative with Disodium Octaborate as the source of boron; having a concentration of 60g BAE/L

**Polymer:**

A Rhom and Haas polymer (Styrene) with 50% solids content.

**Preservative volume:** 1L

**Results:**

The DOT mixed well with the styrenated polymer

After approximately 8hrs the preservative had a good stability and there was no evidence of any settling of DOT.

Preparation of the preservative took Approximately 1hr.

Trial of the preservative on timber:

The preservative was tested on timber with a moisture content of less than 40% (<40%).

The timber was dipped in the preservative solution for 2 minutes.

The polymer was allowed to cure and a visible inspection of the polymer film was done.

The polymer cured to a clear finish. The polymer film was apparent so there was no suspicion of the film being too thin.

It is possible for the preservative to be prepared with a concentration of 60g BAE/L

After a period of 2 weeks, the timber was split and a curcumin indicator was sprayed on to the timber to assess the diffusion patterns of boron.

It was found that the boron deposited itself in the form of a peripheral band, within a depth of 1mm of the timber.

Evaluation of profitability:

For SABS specification to be satisfied,

5000 g/$m^3$

60g/L

which equates to 83 L of preservative that must be deposited per cubic meter

Whilst the preservative has a good stability it would be difficult to consistently deposit 83L of preservative per hr, particularly if the timber has a higher percentage of heartwood than softwood.

Conclusions:

- Use the 60g/L for the purpose of remedial application of preservatives:
- For the purpose of primary treatment, a higher concentration should be prepared (100,150,200,300g/L)
- Reproduce the 60 g/L and continue with trials for remedial applications.

## Appendix 3

**Aim:**

To prepare boron preservatives using DOT as the source of boron, and concentration of BAE should be in the range 100,300g/L.

CONCENTRATION RANGE: 100, 150, 200, 300g/L

POLYMER: RHOM & HAAS-styrenated polymer

**Preservative volume**: 1L

**Results**:

Difficulty was experienced when trying to produce the 100g/L.
Two initial batches had to be discarded, due to the entire preservative solution solidifying.

**Action:**

The rate at which the boron was added is significantly reduced.
The 100g/L was produced over a period of 3hrs.

There was no success in trying to produce the 150g/L, there were no attempts made to produce the 200 and 300g/L.

**Action:**

A different polymer must be investigated.

## Appendix 4

**Aim:**

To produce a boron-based preservatives with BAE concentrations of 100g/L to 300g/L.

**Polymer:**

A blend of 50% styrenated polymer and 50% of an undercoat (also known as a binder with a solids content of 35%.

**Volume of preservative:** 1L

**Results:**

Preservatives with the following concentrates were successfully prepared
100g/L BAE, 150g/L and 200g/L.

It was also possible to produce a 300g/L (BAE) preservative.

**Observations:**

It is very time consuming to produce preservative of the above concentration. The blending of the polymer mixture (50% styrene+50% binder) and DOT was very critical. A number of batches were discarded due to solidification.

**Trial of preservative on timber:**

The timber that was used had 30% moisture

Dip time: 2 minutes

The polymer was allowed to cure for 3 hours.

**An assessment of the treated timber revealed the following:**

- The timber did not show signs of the existence of a polymer film on the surface. This observation was true for all three concentrations produced i.e. (100g/L, 150g/L and 200g/L).

- The surface of the timber had a powdery feeling. Boron had deposited and recrystallised on the surface of the timber.

- The boron formed a band of +-1mm on the periphery of the timber, with a heavy deposit of boron on the surface of the timber.

**Action:**

There was no point in conducting leaching trials because there was no visible evidence of the existence of a polymer film encapsulating the timber.

**A polymer should satisfy the following requirements:**

- It should be compatible with a boric acid on at a concentration of 60g/L to 200g/L. 300g/L would make the product more economically viable.

- The polymer should allow the passage of boron into the timber and the polymer should cure to reveal a film thickness of minimum 0.5mm

- The polymer film should not compromise the appearance of the timber.

# Appendix 5

**Aim:**

To produce a boron-based preservatives with BAE concentrations of 100g/L to 300g/L.

**Polymer of choice:**

A methacrylamide polymer.

Pure acrylic emulsion Viscosity: 500-1500 cps
Ph = 8.5
Solubility: Water soluble Oil – insoluble.
Solid contents: 45 - 49%

**Results:**

The polymer was used to successfully prepare preservatives of the above concentrations. The time taken to prepare the preservatives was comparable to the time taken to prepare the preservative from the styrenated polymer.

The preservative was very viscous and thus would invariably affect the deposition of preservative on the timber. With a viscous preservative the chances of over treating timber is extremely likely. Therefore, the viscosity of the preservative would have to be reduced in order to keep the cost within acceptable limits.

**Trial of preservative on timber:**

SA Pine timber was dip treated with preservative with concentration ranging from 60g/L BAE to 200g/L BAE.

The timber was extremely difficult to handle and large volumes of preservative was deposited on the surface of the timber.

**Appearance of timber:**

The boron diffused into the timber. There was no evidence of back diffusion of boron into polymer film. However, an extremely thick polymer film coated the timber. The timber had an extremely sticky feel, even after the polymer cured.

**Action:**

The polymer in its current form -(pure acrylic) with 45% - 49% solids cannot be used.
One or more of the following actions must reduce the viscosity of the polymer.

- The polymer can be diluted using water,
- The pure acrylic polymer can be blended with another acrylic or styrene polymer.
- A less viscous acrylic polymer can be used in place of the current polymer.

## Appendix 6

**Aim:**

To produce a boron-based preservatives with a blend of an acrylic polymer and water.

**Type of polymer:**

A pure acrylic polymer (with 45% - 49% solids) was diluted by 50% with water
This mixture was then used to prepare a boron-based timber preservative.

**Volume of preservative:** 1L.

**Results of the preparation of the preservative:**

All three concentrations of BAE (60,150,200g/L) that were prepared with preservative preparation were stable. i.e. No setting out occurred after standing for 48hrs.

**Trial of preservative on timber:**

| | |
|---|---|
| Timber species selected: | SA Pine |
| Dip time: | 2 minutes |
| No. Of samples dipped: | 6 |

Appearance of the timber: A very thin polymer film coated the timber. The high % of water in the formulation caused grains in the timber to raise and this was not attractive.
The diffusion pattern was better than in previous trials. The depth of diffusion of boron was > 2mm into the timber.

**Overall assessment of the preservative preparation:**

The high dilution rate influenced the film thickness and the appearance of the timber.

**Further Action:**

The dilution rate can be reduced and an assessment can be made on the polymer film and the appearance of the timber.

**Action:**

The polymer in its current form -(pure acrylic) with 45% - 49% solids cannot be used.

One or more of the following actions should be taken to reduce the viscosity of the polymer:

- The polymer can be diluted using water,
- The pure acrylic polymer can be blended with another acrylic or styrene polymer.
- A less viscous acrylic polymer can be used in place of the current polymer.

# Appendix 7

**Aim:**

To produce a boron-based preservatives with a blend of an acrylic polymer and water.

**Type of polymer:**

A pure acrylic polymer (with 45% - 49% solids)
-Diluted in the following manner
75% acrylic polymer
25% with water

**Volume of preservative**: 1L.

**Results of the preparation of the preservative:**

All three concentrations of BAE (60,150,200g/L) were produced with relative ease. There were no stability problems encountered. The preservative was allowed to stand for 48hrs.

**Trial of preservative on timber:**

| | |
|---|---|
| Timber species selected: | SA Pine |
| Dip time: | 2 minutes |
| No. Of samples dipped: | 6 |
| Appearance of the timber: | The film thickness was not sufficient. It was difficult to detect the existence of a polymer coating on the surface of the timber, except that the timber had a dull matt appearance.<br>Excessive grain raise was not noted.<br>Diffusion patterns of the boron were abandoned to find a better coating. |

**Overall assessment of the preservative preparation:**

The preservative that was produced was not satisfactory. There is a definite need to improve the film thickness of the polymer.

**Some of the options that are available are:**

- Reduce the dilution factor of the existing polymer.
- Blend a different polymer with the existing polymer.
- Find a different monomer that will polymerise to form a better film.

# Appendix 8 A

**Aim:**

To produce a boron-based timber preservatives within the following concentration range (60,150, 200g/L) and comprising of water –based polymer emulsion.

**Polymer:**

Methacrylamide polymer 45% - 49% solids

Diluted with 10% with water i.e.

| | |
|---|---|
| Acrylic polymer - | 900 mls |
| Water - | 100mls |

**Volume of preservative:** 1L.

**Results of the preparation of the preservative:**

All three concentrations of BAE (60,150,200g/L) were prepared and the resulting preservative was stable i.e. No setting out occurred after standing for 48hrs.

**Observation:**

All the concentrations were prepared with ease. There were no problems associated with the stability of the preservative.

To ensure that the preservative would be reproducible, 10 batches of the preservative of each concentration were produced. There were no problems with any of the batches.

**Trial of preservative on timber:**

Fifteen pieces of timber were treated with this preservative. The polymer was still too viscous for easy treatment. The viscosity of the preservative affected the spread rate of the preservative on the timber adversely. The excess preservative did not drain of the timber easily. The result of this was that the droplets of preservative adhered to the timber and cured in the fashion. This affected the appearance of the timber.

The film thickness was good. There was a definite presence of a coating on the surface of the timber. This preservative will be used to treat the Saligna poles and assess the spread rate on rough timber. The droplets that cured on the surface of the timber may not present a problem with rough timber.

## Appendix 8 B

**Aim:**

To assess the effect (visual) of the acrylic polymer (10% dilution with water) on Saligna timber poles.

**Polymer:**

Methacrylamide polymer 45% - 49% solids

Diluted with 10% with water i.e.

| | |
|---|---|
| Acrylic polymer - | 900 mls |
| Water - | 100mls |

| | |
|---|---|
| **Volume of preservative:** | 25 Lt preservative used. |
| Quantity timber used: | 6 X 1.2m Saligna droppers |
| Moisture content: | 35% |
| Dip time: | 2 minutes |
| Curing time | 48hrs |

**Results:**

The polymer left a visible film that also improved the appearance. However, the timber started to split while drying out and this affected the integrity of the continuous polymer film. The film stretched while the timber split and this eventually led to the polymer breaking up.

**Recommendations:**

The pure acrylic polymer cannot be used in its current form, because there are a few drawbacks associated with this product. Namely,

- The polymer has a high viscosity that is not suitable for use
- The property of the polymer does not alter significantly with the addition of water
- The polymer does not display a high degree of flexibility.

The most promising property of this polymer is its ability to form a continuous film of sufficient thickness.

If this polymer is to be used, it should be used with another polymer with greater flexibility and lower viscosity.

## Appendix 9

**Aim:**

To find a polymer formulation that would display the following characteristics especially when blended with disodium octaborate: -

1. A clear continuous film
2. Flexibility that would allow expansion and contraction with the timber substrate.
3. Have a viscosity that would allow dipping of timber without undue retention of preservative on timber. (Possibly 15 seconds through a Ford cup)

**Preparation of the preservative:**

The pure acrylic polymer was blended with a styrenated polymer with an ultraviolet screen. The polymers were blended over a period of six hours. The exact blending of the two polymers cannot be revealed due to patent obligations.

**Assessment of the polymer blend:**

The blend was stable and showed no signs of separating out into two layers.

**Adhesion to timber:** The polymer adhered very well to the timber. There was no evidence of blistering or peeling. A continuous film of sufficient thickness to bond to timber formed. Therefore, the polymer blend can be used to prepare timber preservative with the following concentrations: 60g/L, 150g/L and 200g/L.

The polymer blend was thereafter used to prepare boron – based timber preservative with the above concentrations.

**Volume of preservative:** 1L

**Results of the preparation using polymer blend and disodium octaborate:**

1. All three concentrations were successfully prepared .The preservatives were then assessed after 72 hrs for setting out of DOT. There was no evidence of any instability i.e. (thickening or settling out). The preservative was then prepared again to ensure reproducibility – 5L volume. The preservatives were then prepared in larger quantities i.e. 25L of each concentration.

**Trial of preservative on timber:**

Species of timber that was used: SA Pine (*Pinus Sylvestris*)

There were 10 samples of each preservative that was prepared.

The volume of the timber was $2.86 \times 10^{-4}$ $m^3$.

**Assessment of the preserved timber:**

The preservative cured to give a gloss and the polymer appeared to form a continuous film.

There was no evidence of back diffusion or blistering.

The diffusion patterns of boron were assessed after a week.

The boron did not diffuse as deep as was anticipated. A very high concentration of boron accumulated in the 2mm peripheral zone of the timber.

The effectiveness of the barrier was then evaluated.

This was done by completely submerging the boron treated timber into 1.5L leaching vessels and leaching the boron into 1.2L de-ionised water.

The results of the leaching trials were not favourable because within 24 hrs, there were significant quantities of boron that leached out.

The following is a summary of the levels of boron that leached out: -

| Time in hrs | S1<br>Conc. in ppm | S2<br>Conc. in ppm | S3<br>Conc. in ppm | S4<br>Conc. in ppm |
|---|---|---|---|---|
| 8 | 12.3 | 81.9 | 90.3 | 107 |
| 24 | 4.60 | 6.32 | 6.62 | 10.3 |
| 31 | 1.60 | 1.26 | 1.51 | 2.08 |

| | |
|---|---|
| S1- | Treated with 60g/L preservative. |
| S2- | Treated with 100g/L preservative. |
| S3- | Treated with 150g/L preservative. |
| S4- | Treated with 200g/L preservative. |

**Calculations:**

95mls sample

12.319 ppm in 95mls

1000 ppm = 1mg per ml

12.319 ppm = Xmg per ml

Therefore, X is equal to 0.0124

0.0123 mg per ml X 1200 mls (Total volume of leaching vessel)

14.8 mg in the entire leaching vessel

0.0148 g in the leaching vessel and this converts to 0.0845 gram BAE. Similarly it can be shown that the concentration of BAE that leached at 24 hours and 31 hours are 0.0315 grams and 0.0109 grams respectively. The table below summarises the leaching in the remaining samples, using the above method to calculate these values.

Quantity of BAE leached

| Time in hrs | 100g/L sample | 150g/L sample | 200g/L sample |
|---|---|---|---|
| 8 | 0.562 g BAE | 0.619 g BAE | 0.736 g BAE |
| 24 | 0.0433 g BAE | 0.0454 g BAE | 0.071 g BAE |
| 31 | 0.00860 g BAE | 0.0100 g BAE | 0.0142 g BAE |
| Total | 0.614g BAE | 0.674 g BAE | 0.824 g BAE |

The quantity of BAE that was put into the pieces of timber:

| Preservative concentration | BAE + Polymer | BAE put into timber |
|---|---|---|
| 60 | 4.95 g x 0.135 g | 0.666 g |
| 100 | 5.75 g x 0.178 g | 1.03 g |
| 150 | 4.43 g x 0.290 g | 1.28 g |
| 200 | 4.89 g x 37.4 g | 1.83 g |

## Appendix 10

**Aim:**

To prepare a boron based preservative using a blend of styrene and acrylic polymer and an additive that will ensure the polymer coating behaves as a water repellent. The preservative should consist of the following concentrations of BAE.

60g/L
150g/L
200g/L

**Volume of preservative:** 1L

**Ratio of polymer blend:** 1 part styrene polymer to 1 part acrylic polymer.

**Volume of additives:** 25% $^{v}/_{v}$

The polymer blend (styrene 50% and acrylic 50%) was initially mixed with the additive and assessed for stability and miscibility. Then the DOT was mixed in. All four concentrations of preservative that were produced were stable. There was no evidence of settling out.

### 10.1. Assessment of the stability of the preservative

The preservative was allowed to stand for a lengthy period and the product was then assessed for sediment.

There was however, no evidence of sediment in the preservative.

### 10.2. Stability of the preservative during the freeze and thaw test.

The product was not stable at low temperatures. The product settled out in two layers. Therefore, low storage temperatures must be avoided. Upon thawing, the two layers still remained.

### 10.3 Paint on trial with preservative with timber

The preservative was tested for grain raise, adhesion and gloss on timber.

Findings:

10.3.1. It was found that the preservative adhered well to the timber. There was no sign of blistering or peeling.

10.3.2. There was no evidence of grain raise on the timber. The timber had a smooth appearance.

10.3.3. There were no droplets adhering to the timber.

### 10.4. Accelerated weathering:

The polymer was exposed to mist and ultraviolet light. This was done using specialised equipment that is used by paint manufacturers. A large paint company agreed to conduct these trials on timber that was treated with this product. The timber was exposed for a period equivalent to 18 months. The polymer showed no sign of deterioration. The mist and moisture did not affect the adhesion of the polymer to the timber substrate.

Findings:

10.4.1. The ultraviolet radiation did not attack the polymer. There were no signs of flaking off, of the polymer coating and the integrity of the coating was unaffected.

10.4.2. Moisture did not accumulate between the polymer and the wood substrate. There was evidence that the polymer had a sufficient amount of water repellency.

10.4.3. The polymer did not show any signs of whitening. Whitening is normally attributed to the ultraviolet attack and is followed by the coating turning brittle.

### 10.5 Qualitative test for the presence of boron on the surface and beneath the surface of treated timber:

10.5.1 The surfaces of timber that were previously dipped into preservative, were checked for the presence of boron. The control samples for all three concentrations (60, 150 and 200 g/L) gave positive results for the presence of boron, using a curcumin indicator (10% alcoholic extract of turmeric). The polymer-boron system gave negative results for the presence of boron.

10.5.2 The penetration of boron into the timber was monitored. Both the control samples (60, 150, 200 grams per litre) and the test preservatives (60, 150, 200 grams per litre) gave positive tests for the presence of boron. Hence boron diffused successfully into the timber.

### 10.6. Analytical Determination of the boron available in the preservative:

The recovered boron was compared to the quantity of boron that was originally put into the preservative. The results of these trials are as follows:

A sample of 100g/L BAE was given to an external laboratory for analysis of the boron content and the results were then expressed as boric acid content.

The concentrations of BAE that were obtained after separating the polymer from the boron were:

| | Samples prepared as g/L BAE | Analytically determined levels of BAE in grams per litre |
|---|---|---|
| Sample A | 100 | 104 |
| Sample B | 200 | 193 |
| Sample C | 100 | 110 |
| Sample D | 200 | 188 |

### 10.7. Assessment of the product through natural weathering and exposure:

The treated timber was placed outdoors and assessed for signs of deterioration through used, fungal and UV attack.

Findings:

10.7.1. There was no evidence of attack by fungi.

No spotting or any discolouration could re – determined on the surface of the timber. The timber retained the original post – treatment colour.

10.7.2. Insects did not attack the timber. It is worthy noting that insect attack seldom occurs on timber that is put out on trial. It is difficult to bait insects.

10.7.3. The polymer was assessed for degradation and deterioration.

There were no signs of deterioration. A continuous film of polymer encapsulated the timber.

### 10.8. Leaching trials of the preservative

Leaching trials were conducted to assess the movement of boron out of the timber. This is an important facet of the research and the results are presented and discussed in chapter 6 and 7.

# Appendix 11

## 11.1 Calculation of the exact masses of BAE in 'test' samples and control samples of preservatives.

### 11.1.1 Exact masses for the 60 grams per litre of preservative.

Mass of weighing boat = 28.3 grams

Mass of weighing boat + Mass of DOT = 78.9 grams

Therefore, exact mass of DOT = 50.6 grams

The preservative was made up to 1 litre with a polymer blend.

The concentration of the preservative = 1.20 X 50.6 grams

(1.20 for converting DOT to BAE)

Hence the concentration is **60.7 grams BAE per litre**.

### 11.1.2 Exact masses for the 150 grams per litre of preservative.

Mass of weighing boat = 28.3 grams

Mass of weighing boat + Mass of DOT = 154 grams

Therefore, exact mass of DOT = 126 grams

The preservative was made up to 1 litre with a polymer blend.

The concentration of the preservative = 1.20 X 126 grams

(1.20 for converting DOT to BAE)

Hence the concentration is **151 grams BAE per litre**.

### 11.1.3 Exact masses for the 200 grams per litre of preservative.

Mass of weighing boat = 28.4 grams

Mass of weighing boat + Mass of DOT = 197 grams

Therefore, exact mass of DOT = 168 grams

The preservative was made up to 1 litre with a polymer blend.

The concentration of the preservative = 1.20 X 168 grams

(1.20 for converting DOT to BAE)

Hence the concentration is **202 grams BAE per litre**.

### 11.1.4 Exact masses for the 60 grams per litre of control sample.

Mass of weighing boat = 28.3 grams

Mass of weighing boat + Mass of DOT = 78.3 grams

Therefore, exact mass of DOT = 50.0 grams

The preservative was made up to 1 litre with purified water.

The concentration of the preservative = 1.20 X 50.0 grams

(1.20 for converting DOT to BAE)

Hence the concentration of the control sample is **60.0grams BAE per litre**.

### 11.1.5 Exact masses for the 150 grams per litre of control sample.

Mass of weighing boat = 31.0 grams

Mass of weighing boat + Mass of DOT = 157 grams

Therefore, exact mass of DOT = 126 grams

The preservative was made up to 1 litre with purified water.

The concentration of the preservative = 1.20 X 126 grams

(1.20 for converting DOT to BAE)

Hence the concentration of the control sample is **152 grams BAE per litre**.

### 11.1.6 Exact masses for the 200 grams per litre of control sample.

Mass of weighing boat = 31.0 grams

Mass of weighing boat + Mass of DOT = 201 grams

Therefore, exact mass of DOT = 170 grams

The preservative was made up to 1 litre with purified water.

The concentration of the preservative = 1.20 X 170 grams

(1.20 for converting DOT to BAE)

Hence the concentration of the control sample is **204 grams BAE per litre**.

## 11.2 Evaluation of the percentage of BAE in 20mls of cured test preservative samples.

### 11.2.1 Evaluation of % BAE in the 60 grams per litre test preservative.

Mass of weighing boat = 1.62 grams

Mass of weighing boat + 20 mls of test pres. = 22.2 grams

Mass of weighing vessel + cured pres. = 10.8 grams

Therefore, Mass$_1$of cured preservative = 9.13 grams
(Pres. is abbreviation for preservative)
Curing took 14 hours at 80 degrees Celcius

Evaluation of % BAE in the 60 grams per litre test preservative.
Mass of weighing boat = 1.51 grams
Mass of weighing boat + 20mls of test pres. = 22.1 grams
Mass of weighing vessel + cured pres. = 10. 5 grams
Therefore, Mass$_2$ of cured preservative = 8.94 grams
(Pres. is abbreviation for preservative)
Curing took 14 hours at 80 degrees Celcius

Evaluation of % BAE in the 60 grams per litre test preservative.
Mass of weighing boat = 1.60 grams
Mass of weighing boat + 20mls of test pres. = 22.1 grams
Mass of weighing vessel + cured pres. = 10.5
grams
Therefore, Mass$_3$ of cured preservative = 8.92 grams
(Pres. is abbreviation for preservative)
Curing took 14 hours at 80 degrees Celcius

Therefore, average mass of cured preservative is (Mass1 + Mass 2 + Mass 3) /3
This is 9.13 + 8.94 + 8.92 grams / 3 = 8.99 grams

Since there are exactly 60.7 grams of BAE in 1000 millilitres of preservative, there are 1.21 grams of BAE in 20 millilitres of pipetted sample. Therefore, the percentage of BAE in the cured polymer is 1.21 grams / 8.99 grams X 100. **This equals 13.5 % for the 60 grams per litre polymer preservative.**

11.2.2 Evaluation of % BAE in the 150 grams per litre test preservative.
Mass of weighing boat = 1.53 grams
Mass of weighing boat + 20 mls of test pres. = 23.0 grams
Mass of weighing vessel + cured pres. = 11.7 grams
Therefore, Mass$_1$of cured preservative = 10.2 grams

(Pres. is abbreviation for preservative)

Curing took 14 hours at 80 degrees Celcius

Evaluation of % BAE in the 150 grams per litre test preservative.

Mass of weighing boat = 1.50 grams

Mass of weighing boat + 20mls of test pres. = 22.9 grams

Mass of weighing vessel + cured pres. = 11.8 grams

Therefore, Mass$_2$ of cured preservative = 10.3 grams

(Pres. is abbreviation for preservative)

Curing took 14 hours at 80 degrees Celcius

Evaluation of % BAE in the 150 grams per litre test preservative.

Mass of weighing boat = 1.50 grams

Mass of weighing boat + 20mls of test pres. = 23.1 grams

Mass of weighing vessel + cured pres. = 12.2 grams

Therefore, Mass$_3$ of cured preservative = 10.7 grams

(Pres. is abbreviation for preservative)

Curing took 14 hours at 80 degrees Celcius

Therefore, average mass of cured preservative is (Mass1 + Mass 2 + Mass 3) /3

This is 10.2 + 10.3 + 10.7 grams / 3 = 10.4 grams

Since there are exactly 151 grams of BAE in 1000 millilitres of preservative, there are 3.11 grams of BAE in 20 millilitres of pipetted sample. Therefore, the percentage of BAE in the cured polymer is 3.11 grams / 10.4 grams X 100. **This equals 29.9 % for the 150 grams per litre polymer preservative.**

11.2.3 Evaluation of % BAE in the 200 grams per litre test preservative.

Mass of weighing boat = 1.61 grams

Mass of weighing boat + 20 mls of test pres. = 23.5 grams

Mass of weighing vessel + cured pres. = 12.6 grams

Therefore, Mass$_1$ of cured preservative = 11.0 grams

(Pres. is abbreviation for preservative)
Curing took 14 hours at 80 degrees Celcius

Evaluation of % BAE in the 200 grams per litre test preservative.
Mass of weighing boat = 1.57 grams
Mass of weighing boat + 20mls of test pres. = 23.3 grams
Mass of weighing vessel + cured pres. = 12.3 grams
Therefore, Mass$_2$ of cured preservative = 10.7 grams
(Pres. is abbreviation for preservative)
Curing took 14 hours at 80 degrees Celcius

Evaluation of % BAE in the 200 grams per litre test preservative.
Mass of weighing boat = 1.56 grams
Mass of weighing boat + 20mls of test pres. = 23.3 grams
Mass of weighing vessel + cured pres. =12.2 grams
Therefore, Mass$_3$ of cured preservative = 10.7 grams
(Pres. is abbreviation for preservative)
Curing took 14 hours at 80 degrees Celcius

Therefore, average mass of cured preservative is (Mass1 + Mass 2 + Mass 3) /3
This is 11.0 + 10.78 + 10.87 grams / 3 = 10.8 grams

Since there are exactly 202 grams of BAE in 1000 millilitres of preservative, there are 4.04 grams of BAE in 20 millilitres of pipetted sample. Therefore, the percentage of BAE in the cured polymer is 4.04 grams / 10.8 grams X 100. **This equals 37.4% for the 200 grams per litre polymer preservative.**

# List of References

Brenner, I.B and Cheatham, M.M (1998), **Determination of Boron: Aspects of Contamination and Vaporization**. ICP information Newsletter No. 24, University of Masschusetts.

Butler, A.J.B (1993), **Development of a Commercial – Scale CCA Chemical Sludge Recycling System**. Proceedings of the 2nd International symposium – Wood Preservation, Cannes- Mandelieu, France.

Coggins, C.R (1980), **Decay of Timber in Buildings Dry rot, wet rot and other fungi**. pp. 45 and 60. Rentokil Ltd, Felcourt, East Great Britain.

Cui, F and Archer, K (1997), **Treatment of lumber with preservatives/water repellent emulsions- The significance of shear stability on penetration.** Proceedings of the 28th Annual Meeting, Whistler, Canada, IRG/WP 97-20124.

Cui, W and Kamdem, D.P (1999), **Bioefficacy of Boric Acid Grafted onto Wood.** Proceedings of the 30th Annual Meeting, Rosenheim, Germany, IRG/WP 99-30202.

Drysdale, J.A (1994), **Boron treatments for the preservation of wood – A review of efficacy data for Fungi and Termites.** Proceedings of the 25th Annual Meeting Bali, Indonesia, IRG/WP 94-30037.

Harris, W.V (1964), **Termites – Their recognition and control** (Second impression), pp. X1, 109-119. Longmans, Green and Co Ltd, London.

Havermans, J.B.G.A, Homan, W.J and Boonstra, M.J (1993), **The slower test method- A leaching test for assessing preservative losses from treated timber under simulation open storage conditions**. Proceedings of the 2nd International symposium – Wood Preservation, Cannes-Mandelieu, France.

Hunt, G.M and Garratt, G.A (1967), **Wood Preservation** (Third Edition). pp. 1 and 25. McGraw- Hill Book Company, New York.

Kiguchi, M, Karaoke, Y, Evans, P.D, Kadegaru, Y and Imamura, Y (2001), **Pre-treatments of wood Surfaces for Improving Weatherability of Clear finishing.** Proceedings of the 32nd Annual Meeting, Nara, Japan, IRG/WP 01-40196.

Lloyd, J D (1998), **Borates and their biological application**. Proceedings of the 29th Annual Meeting, Maastricht, Netherlands, IRG/WP 98-30178.

Lloyd, J D (2000), **Borate Preservatives for Exterior Situations.** Proceedings of the Annual General Meeting of The South African Wood Preservers Association, Johannesburg, RSA.

Matilainen, R, Tummavuori, J (1995), **Determination of boron in fertilizers by inductively coupled plasma – atomic emission spectrometry: studies of some spectral interferences at different wavelengths**. Journal of AOAC, pp. International 78, pp. 599-605.

Mohareb, A, Van Acker, J, Stevens, M (2002), **Effect of protective additives on leachability and efficacy of borate treated wood**. Proceedings of the 33rd Annual Meeting, Cardiff, South Wales, UK, IRG/WP 20-30290.

Morrell, J.J and Freitag, C.M (1995), **Effect of wood moisture content on diffusion of boron-based biocides through Douglas-Fir and western Hemlock lumber**. Forest Products Journal, 45, pp. 51-55.

Murphy, R.J, Barnes, H.M and Gray, S.M (1995), **Decay and soil depletion studies with polymer/boron preservative systems**. Forest Products Journal, 45, pp. 77-81.

Nicholas, D.D, Jin, L and Preston, A.F (1990), **Immediate research needs for diffusible boron preservative.** Proceedings of the First International Conference on Wood Protection with Diffusible Preservatives, Nashville, Tennessee.

Petric, M, Pavlic, M and Cadez, F (2001), **Leaching of the New Boron Based Biocide from Coated Wood.** Proceedings of the 32nd Annual Meeting, Nara, Japan, IRG/WP 02-30267.

Peylo, A and Willeitner, H (1997), **Leaching of Boron- more than 3 years of field exposure**. Proceedings of the 28th Annual Meeting, Whistler, Canada, IRG/WP 97-30142.

Pougnet, M.A.B and Orren, M.J (1985), **Determination of boron by inductively coupled plasma atomic emission spectrometry. Part 2. Applications to South African Environment Samples**. International Journal of Analytical Chemistry, 24, pp. 267-282.

Rainer, J.B (1993), **Borates as Wood Preservatives – an Enviromental, Health and Safety Perspective**. Proceedings of the 2nd International symposium – Wood Preservation, Cannes- Mandelieu, France.

Schoeman, M.W, Lloyd, J.D and Manning, M.J (1998), **Movement of borates in a range of timber species at various moisture contents.** Proceedings of the 29th Annual Meeting, Maastricht, Netherlands, IRG/WP 98-30181.

Sun, D, Waters, J.K and Mawhinney, T.P (1998), **Determination of total boron in soils by inductively coupled plasma atomic emission spectrometry using microwave-assisted digestion**. Communications in soil science and plant analysis, No. 29 pp. 2493-2503.

Thévenon, M.F, Pizzi, A, Haluk, J.P (1998), **Albumin borate: A new non-toxic, wide-spectrum, long-term wood preservative**. Proceedings of the 29th Annual Meeting, Maastricht, Netherlands, IRG/WP 98-30167.

Tsunoda, K, Adachi, A, Yoshimura, T, Byrne, T, Morris, P.I and Grace, J.K (1998), **Resistance of borate- treated lumber to subterranean termites in the field**. Proceedings of the 29th Annual Meeting, Maastricht, Netherlands, IRG/WP 98-10255.

Wilkinson, J.G (1979), **Industrial timber preservation.** pp. 89-136. Association Business Press, Great Britain.

Yalinkilic, M.K, Imamura, Y, Takahashi, M and Yalinkilic, A.C (1999), **In Situ polymerization of vinyl monomers during compressive deformation of wood treated with Boric acid to delay boron leaching**. Forest Products Journal,49, pp. 43-55.