BORON MODIFICATIONS OF COPPER CHROME ARSENATE WOOD PRESERVATIVES

A thesis submitted for the degree of
Doctor of Philosophy of the University of London
and for the Diploma of Imperial College

by

SCARLETTE MARION GRAY B.Sc., A.R.C.S.

Department of Pure and Applied Biology,
Imperial College of Science and Technology,
London SW7.

November 1983

Abstract

The work described in this thesis can be divided into two parts. The first part deals with the biological testing of wood treated with a selection of waterborne formulations designed for soft-rot protection and the second part looks for a chemical or physical explanation for the biological test results.

Small birch and Scots pine sapwood blocks were treated by the Bethell process with a number of preservatives containing copper, chromium, arsenic and or boron. In some cases two treatments were carried out but in all cases the quantities of the various elements used were the same. Blocks treated with a range of concentrations were cold water leached prior to exposure to soil burial and to monocultures of fungi representing brown, white and soft rots. Larger wood blocks and small stakes similarly treated were exposed in the fill of a water cooling tower and in a soil-bed respectively. Decay was assessed by weight loss and where appropriate by loss in static bending strength.

In all cases, a double treatment where copper chrome boron was followed by arsenic gave a good performance. In birch, where soft-rot was the hazard, this treatment was significantly more effective at many concentrations than all of the other treatments, and was more effective than a treatment where boron was followed by copper chrome arsenic at all concentrations although the same amounts of each of the toxicants were applied.

Several techniques were employed to investigate the results. They included: chemical analysis of the leached woodblocks, comparison of pH changes during fixation and comparison of the relative degree of fixation of each of the preservative elements with time. It was found that the most important difference between the formulations was the extent to which copper became adsorbed to the wood. A hypothesis is put forward to explain the results.

ACKNOWLEDGEMENTS

I would like to thank my supervisor, Dr. D.J. Dickinson, for his enthusiasm and guidance throughout my research and Professor J.F. Levy for his helpful discussions and advice.

I would like to express special thanks to Mr. J.G. Savory (Princes Risborough Laboratory, retired) for many valuable discussions concerning soft-rot testing. Thanks are also due to the Director and staff of the Princes Risborough Laboratory for their assistance and encouragement.

I am grateful to many of the technical staff of the Pure and Applied Biology Department particularly Mr. R. Baker for his skillful preparation af wood samples and Mr. R. Vickery for constructing the deflection apparatus. I would also like to thank Mr. B. Bennett of the Nuclear Technology Section for his valuable gamma irradiation service.

I acknowledge the cooperation of Mr. Selby and his staff at Little Barford Power Station.

In addition, I would like to express my gratitude to my contemporaries in the Timber Technology Section for their valuable comments on this work.

I am most grateful to Borax Holdings Limited for their financial support and in particular to Miss Barbara Kimber for organising contacts, Miss Mary Morrison for typing the manuscript and Mr. J.J. Reid for assistance with the chemical analyses.

Finally, I would like to thank my parents for their continuing interest and encouragement.

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SECTION I: INTRODUCTION

1. SECTION I. Introduction

1.1 Timber Decay

Timber is a natural product and as such is subject to the activities of various decomposer organisms. These organisms are vital in the biological recycling of carbon and nutrients. It is this essential cycle which must be interrupted when man seeks to use timber effectively in buildings, boats, fencing, power distribution networks and the many other uses which utilise the structural properties of timber and timber products.

A wide range of organisms including various bacteria, fungi, actinomycetes and animals (including insects, e.g. wood boring beetles and termites; and molluscs, e.g. Teredo spp. and crustaceans, e.g. Limnoria sp. in the marine environment) (Anon, 1981), is known to be associated with the breakdown of timber. In terrestial temperate situations fungi are the main cause of timber decay whereas in tropical climates insects, particularly termites, can present the more severe problem. This has been recently well illustrated by the findings of the International Research Group on Wood Preservation (IRG) collaborative ground contact field trial where a number of untreated and preservative treated wood stakes have been destroyed by termites in tropical countries (e.g. Australia) whereas fungi have been responsible for the decay in the temperate countries, (Dickinson and J.F. Levy, 1982).

In order for timber to be susceptible to attack by decomposer organisms certain environmental conditions are required which vary

depending on the organisms involved. In the case of fungal attack the timber must have a suitable moisture content (generally above 25%) and be at an appropriate oxygen tension. Insects may attack timber which is air dry (Hickin, 1963). On the other hand, bacterial attack has been observed in saturated wooden piles at low oxygen tensions (Boutelje and Bravery, 1968). Other factors which influence the decay of timber include temperature, the presence of a large population of decay organisms and frequently the level of nutrients (especially nitrogen) in the wood or from an external nutrient source e.g. from soil.

As these factors will vary it will be apparent from the above that in certain situations timber will be more susceptible to decay than in others. For example, protected joinery will generally be at a relatively low risk of microbial attack, whereas timber exposed to soil will be at a high risk. In view of the severe hazard in soil contact, many investigations have been carried out to examine such factors as the natural durability of various timbers in soil, the ecological events leading to the decay of the timber, and various soil parameters such as moisture, organic matter and inorganic nutrient content which may influence timber decay (inter alia Anon 1975, 1977; Banerjee and Levy, 1970; Butcher, 1971; Clubbe, 1980 a, b; Savory and Bravery, 1971; Walchli , 1972 a, b; King et al, 1980; Gersonde and Kerner-Gang, 1976; Leightley, 1980). As a result of these and other studies the principal reasons for soil representing such a severe decay hazard to timber may be summarised as:

(i) timber is frequently maintained at a suitable moisture content to support the activities of decay organisms;

(ii) soil supports a wide range of microorganisms capable of colonising and decomposing timber;

(iii) soil may provide a source of additional nutrients taken up into the wood by "wick action" (Baines and Levy, 1979) and by microbial transfer (King, Mowe, Smith and Bruce, 1981).

As described above, fungi are amongst the most important agents of timber decay and a considerable number of investigations have been carried out to determine the range and nature of their activities. It has been recognised for many years that basidiomycetes are significant amongst the fungi for their wood decaying abilities (e.g. Rabanus, 1931). Basidiomycete decay can be divided into two types: white rot and brown rot. In the case of white rot, the typical morphology of decay involves the production of bore holes and erosion troughs in the wood cell walls surrounding the fungal hyphae. The degradation of the wood results from the production of enzymes which act on both the cellulose and lignin components of the cell walls. With brown rot, a more generalised decay of the wood cell wall takes place which is not restricted to the immediate vicinity of the hyphae. These fungi only utilise the cellulose component of wood, the lignin fraction remaining largely intact. As in all artificial biological groupings there are many intermediate cases but the general rule is that white rot is a localised degrade of both the cellulose and lignin, and brown rot involves a more distant degrade of the cellulose alone within the wall. The morphology of decay and the enzyme systems involved have been considered in detail by Green, 1982; Liese, 1970; Crossley, 1979, and described recently by R. Montgomery (1982).

While the role of basidiomycetes in wood decay has long been recognised, the importance of another group of wood destroying fungi has only been fully appreciated comparatively recently. Findlay and Savory (1954) used the term "soft-rot" to describe the type of decay caused by various ascomycetes and fungi imperfecti. Soft-rot has since been recognised as being of considerable significance in situations which are largely unsuitable for basidiomycete attack to occur due to such factors as high moisture content, elevated temperatures, a high natural durability of the timber species, or the presence of wood preservatives. In particular the ability of soft-rot organisms to attack preservative treated timber, especially in the case of hardwoods, is of major ooncern to wood preservationists (inter alia C.R. Levy, 1982; Hulme and Butcher, 1977 a, b, c). The morphology of soft-rot attack differs considerably from that of basidiomycete attack. In the case of soft-rot the fungal hyphae form discrete chains of cylindrical cavities within the S_2 layer of the cell wall, these cavities enlarging until almost complete decomposition of this wall layer occurs. Soft-rot cavity formation has been extensively studied (Hale and Eaton, 1981; Crossley, 1979; Lundstrom, 1972; Nilsson, 1982) and has been termed Type I attack by Corbett (1963, 1965) in order to distinguish it from a second type of attack involving progressive erosion of the wood cell wall termed Type II. Cavity formation (Type I) is perhaps the major diagnostic feature of soft-rot decay.

Some recent reports have identified forms of timber decay associated with bacteria and actinomycetes (Leightley, 1982 a; Eaton and Dickinson, 1976; Nilsson and Daniel, 1983; Bæcker and King, 1981). Leightley has observed bacterial decay of copper-chrome-arsenic (CCA)

and pentachlorophenol (PCP) treated eucalypt poles in soil and Baecker and King have reported soft-rot attack caused by actinomycetes in untreated wood. Nilsson et al (1983) have observed tunnelling bacteria in preservative treated wood under conditions unsuitable for soft-rot attack. However, further work will be required to establish the significance and mechanisms of decay associated with these microorganisms as to date relatively few studies have been carried out (Boutelje and Bravery, 1968; Greaves and Levy, 1965).

In order for timber to be used efficiently and economically, the activities of the microorganisms described above and those of other wood destroying organisms must be prevented. While good design and handling can often minimise decay problems, timber in a very wide range of end uses will at some time or other be at risk from decay. In the past naturally durable timber species were used but the present demand for timber is so great that perishable timbers must be utilised. Such timber acquires an induced durability by the application of toxicants in the form of wood preservatives. In contrast to the naturally durable species, the sapwood of preservative treated wood is often more durable than the heartwood. The application of preservative chemicals to wood to prevent decay frequently offers an easily available means of increasing its durability and prolonging its service life. A large number of preservatives and methods of application are now available (Wilkinson, 1979; Cartwright and Findlay, 1958). The present study was concerned with inorganic, waterborne preservative formulations applied by vacuum pressure impregnation and based on copper and chromium salts. These are described in detail below. General information regarding other preservative systems is available in the literature cited above.

1.2 Waterborne Preservatives

1.2.1 Multisalt Preservatives

Early waterborne preservatives such as copper sulphate were undesirably prone to leaching, as well as being effective against only a limited number of wood destroying organisms. However, in the early 1900's, Brüning (Wilkinson, 1979) discovered that by the addition of chromium, metal salts could be fixed in wood and were therefore resistant to leaching (i.e. removal by water). Later, Gunn (1926) developed a fixed copper chrome preservative called "Celcure". This was followed by the formulation of the first copper chrome arsenic (CCA) preservative (Kamesan, 1933) termed "Ascu" by Kamesan in 1933. By the early 1960's the brand names "Tanalith C", "Celcure A", "Boliden K33" and "Greensalt" had emerged and are still widely used today. More than 20,000 tonnes of CCA preservatives are consumed worldwide annually (Wilkinson, 1979). At first CCAs were used in the U.K. as an alternative to creosote but later they spread to other areas such as Australasia where they are mostly used to treat hardwoods. The notable exception is New Zealand where they are used to preserve Pinus radiata. As an indication of their importance there are currently standard specifications governing the use of CCAs in the U.K., (e.g. B.S. 1282, 1975; B.S. 4072, 1974), Scandinavia (NWPC 1.2.1., 1970; DS/R 1071.4.1., 1966; DS/R 1071.4.2., 1966), the U.S.A. (e.g. ASTM D 1625), Japan (JIS K1554, 1975), South Africa (SABS 673, 1976), New Zealand (NZ TPA Spec. F2, 1969) and Eire (IS 131, 1964).

The CCA formulations currently in use were designed to give high fixation and incorporate increased amounts of copper. The reason for the high proportion of copper is that this element has been shown to be the active ingredient in controlling soft-rot organisms and many basidiomycete fungi (Findlay and Savory, 1950, 1954; Savory, 1954 a; Duncan, 1960; Theden, 1961; Da Costa and Kerruish, 1963; Hulme and Butcher, 1977 c; Henningsson and Nilsson, 1976 a), whereas the arsenic is effective against a wide range of insects and provides additional protection against a number of copper tolerant fungi (Tamblyn and C.R. Levy, 1981; Tillott and Coggins, 1981).

The mechanism of action of CCA preservatives has been studied by Levi (1969) and more recently by Butcher and Nilsson (1982) and Nilsson (1982) with reference to soft-rot organisms. Two main approaches have been taken to investigating the fixation of CCA in wood:

(i) by chemical analysis of treated wood and leachates from treated wood (Morgan, 1975; Dunbar, 1962; Wilson, 1971; Eadie and Wallace, 1962; Irvine, Eaton and Jones, 1972; D.N.R. Smith and Williams, 1973 a, b);

(ii) by following the chemical reactions that take place during fixation in situ (Dahlgren and Hartford, 1972 a, b, c; Dahlgren, 1972, 1974, 1975 a, b; Pizzi, 1981, 1982 a, b, c; Pizzi and Kubel, 1982).

These studies have contributed substantially to an understanding of the processes leading to fixation, although there still remain many unsolved problems. However, all of the investigations cited above indicate that CCA in treated wood is normally highly resistant to leaching after the conditioning and slow drying periods following treatment (B.S. 4072, 1974).

The main advantages of CCA as a wood preservative, then, are its resistance to leaching and wide spectrum of activity against wood destroying organisms. Other desirable properties include its relatively low cost, safety in handling after fixation has taken place and the clean, non-oily finish to the timber after drying enabling the treated wood to be glued or painted (Tillott and Coggins, 1981). These features mean that CCA is a suitable preservative for timber of many end uses particularly in ground contact or severe leaching situations such as the internal timbers of a water cooling tower.

1.2.2 Boron Preservatives

Waterborne boron compounds have been used widely as wood preservatives and are of proven effectiveness in many service situations. Comprehensive bibliographies on the application of boron compounds in wood preservation have been prepared by Bunn (1974) and Cockcroft and J.F. Levy (1973), thus only the main features of these preservatives will be described here.

The treatment of timber with boron (originally boric acid or borax) against wood destroying insects was initially developed in Australia during the 1940 s for the protection of certain hardwoods against the Lyctus beetle (inter alia Cummins 1938, 1939; Gregory, 1942). Later it was shown that boron compounds were effective against Hylotrupes bajalus, Anobium spp. (e.g. Kaltwasser, 1941) and termites (e.g. Hunt and Snyder, 1948). In the case of fungi, early work with boron was concerned with blue stain in America (e.g. Scheffer and Lindgren, 1940), but later boron was shown to be effective against

basidiomycetes and other fungi (inter alia Findlay, 1939, 1953, 1956, 1959; Blew, 1947, 1948; Carr, 1952, 1957 a, b, 1959, 1961, 1964; Harrow, 1950; Bunn, 1974).

The most common method of treating wood with boron is by a diffusion process (inter alia Harrow, 1952, 1954; Carr, 1955, 1961; McQuire and Goudie, 1972; BWPA Standard number 105; Bunn, 1974). This involves immersing "green" (i.e. unseasoned) timber in a concentrated solution of the boron preservative for a short time then removing and close stacking it to delay drying. This process results in the through and through penetration of the preservative. At first boric acid as well as borax was used as the treating solution, then mixtures of the two, and finally a highly soluble borate - disodium octoborate tetrahydrate which is known as Timbor, the treatment process being known as Timborising. This process has been widely used in New Zealand, Australia, Canada, Scandinavia and the U.K. The advantages of using boron as a preservative are:

(i) it has a wide spectrum of activity against wood destroying organisms;

(ii) it has a low mammalian toxicity and is therefore safe to use;

(iii) it is inexpensive;

(iv) timber species which are relatively resistant to impregnation by the vacuum pressure process can be effectively treated;

(v) freshly felled timber can be treated directly c f. vacuum pressure impregnation with CCA s where the timber must first be dried (seasoned);

(vi) no special treatment plant is needed.

The properties of the boron preservatives which render them suitable for use in diffusion treatments also contribute to their leachability. The leaching of timber following a waterborne boron treatment results in almost total removal of the active ingredient (Tillott and Coggins, 1981) leaving the timber susceptible to decay. The use of boron compounds, therefore, has been confined to environments protected from leaching effects such as interior joinery and painted weatherboards where their performance to date has been good.

The problem of boron leachability has resulted in a number of investigations into the fixation of boron (Borax Holdings Limited, 1979), the most significant of which is the work on copper complexing to produce copper borates (Borax Holdings Limited, 1979). * Failure to fix boron has resulted in an apparent decline in interest in the preservative despite all of its other advantageous properties and the fact that it may not actually require fixation of boron for it to be of use in multisalt preservatives.

1.2.3 Multisalt Preservatives Incorporating Boron

In addition to CCA, several other preservatives based on the copper/chrome composition are currently in use; amongst them is copper chrome boron (CCB) marketed under the names "Celcure M" and "Wolmanit CB". In many countries the use of CCB as a replacement

* Footnote: Cockcroft and J.F. Levy (1973) suggested that in the case of timber species that are impermeable after seasoning, aspiration of the pits on drying following boron diffusion treatment could be an effective means of restricting leaching of the preservative.

for CCA is widespread, often because arsenic is unavailable or its use has been banned or is undesirable (e.g. Germany (Cockcroft and J.F. Levy, 1973), Brazil (Cavalcante, Geraldo and Freitas, 1982), and Sweden (Dickinson, 1982)). In Sweden in recent years CCB has been used in preference to CCA in sensitive areas such as playground furniture (Dickinson, 1982).

In the CCB formulations boron is regarded as being unfixed (Wilkinson, 1979; Becker and Buchmann, 1966; Tillott and Coggins, 1981) and subject to leaching in wet conditions. Despite this, C.M. Montgomery (1979) (reported in Gray and Dickinson, 1982) in laboratory decay tests on small, leached woodblocks, found that CCB was more effective than CCA against soft-rot in birch although both Scots pine and birch treated with CCB failed to copper tolerant basidiomycetes. Similarly, Tamblyn and C.R. Levy (1981), in a field trial of treated Pinus radiata and Eucalyptus regnans in Papua New Guinea, found that CCB treated stakes failed to copper tolerant brown rot organisms. Tillott and Coggins (1981), reporting on field trials after seven years' exposure, chose two sites: East Grinstead, Sussex and Dehra Dun, India to illustrate the performance of various waterborne preservatives including copper chrome (CC), CCA and CCB. They found that CCB performed better than CCA in the hardwood tested and attributed this to the greater mobility of boron in the treated timber. They concluded that, since high proportions of the active boron components are rapidly lost during leaching, CCB treated timber would be unsuitable where timber is subjected to severe leaching cf. ground contact which they claimed was not a total leaching situation in this trial.

1.3 Performance of CCA Preservatives

The treatment of permeable softwoods (e.g. pine species) with CCA preservatives has proved to be an outstanding success story in wood preservation, although satisfactory treatment of impermeable softwoods such as spruce still presents problems (Saunders, 1982; Fowlie, 1981). In contrast, the treatment of many hardwood species, including those which are relatively permeable to fluids, has been less effective (in comparison with permeable softwoods) and premature failures have been noted by many authors (Greaves and Savory, 1965; J.F. Levy, 1971; Greaves, 1972, 1977; Tamblyn, 1973, 1975; International Research Group on Wood Preservation, 1974, 1975; Henningsson, 1974; Butcher, 1979, 1980; Aston and Watson, 1976; Hulme and Butcher, 1977 b; Dickinson, 1974 a; Sorkhoh and Dickinson, 1976; J.F. Levy *et al*, 1976; Dickinson *et al*, 1976; C.R. Levy, 1978). The particular problem with hardwoods became evident as a direct result of the development of the CCA market from Europe into the Tropics. The application of vacuum pressure techniques using CCA preservatives (i.e. northern hemisphere technology) to tropical hardwoods (i.e. southern hemisphere) has recently been the subject of a review by C.R. Levy (1982). He stated: "Taken over all, wood preservation has yet to have a significant effect on improvement in the utilisation of tropical forest resources."

The problem of premature failure is so great that in Sweden, Bergman (1977) recommended that salt-treated hardwoods should not be used in ground contact and, in New Zealand, the Timber Preservation Authority (1977) prohibited the treatment of hardwoods in ground contact. Greaves (1972, 1977), Tamblyn (1973, 1975), Aston and

Watson (1976), Henningsson (1976) and C.R. Levy (1978) have attributed the failure of CCA treated hardwoods in service to soft-rot attack. This has been confirmed by many workers (inter alia Dickinson et al, 1976; Fougerousse, 1976; Nilsson, 1976; Clubbe, 1980 a, b).

1.4. The Soft-Rot Problem in CCA Treated Wood

The premature failure of CCA treated hardwoods to soft-rot organisms is a current problem of vast proportions. Greaves (1977) has reported: "In the state of Queensland alone, some 300,000 to 400,000 vacuum pressure impregnated transmission poles are currently affected to varying degrees by a deep form of soft-rot". A conservative estimate of replacement costs runs into tens of millions of Australian dollars. Similarly, in Sweden, Henningsson and Nilsson (1976b) estimated that there were 4 - 5 million zinc salt-treated softwood poles being seriously degraded. The problem is clearly of major economic significance.

In response to the urgency of the soft-rot problem, a considerable amount of research has been undertaken to identify the causes of the poor performance of CCA treated hardwoods and to find practical solutions to extending the use of ground contact preservatives. The following have been considered among the causes of the difference in performance between hardwoods and softwoods treated with CCA preservatives:

(i) tolerance to CCA preservatives (Henningsson and Nilsson, 1976 a; Clubbe, 1978)

(ii) substrate susceptibility (Hulme and Butcher, 1977 b, c)

(iii) macrodistribution of the CCA preservatives in the wood tissues (Dickinson, 1974 a; Greaves, 1974; Dickinson et al, 1976; J.F. Levy and Greaves, 1978; Greaves and J.F. Levy, 1978)

(iv) microdistribution of the CCA preservatives in the wood cell wall (Greaves, 1972, 1974; Dickinson, 1974 a; Dickinson et al, 1976; Drysdale, 1979; Drysdale et al, 1980; Kennmar-Gledhill, 1983)

(v) Variation in the fixation and disproportionation of the CCA preservatives (Greaves, 1974; Drysdale, 1979; D.N.R. Smith and Williams, 1973 a, b).

These aspects are interrelated and have been ably reviewed by Drysdale (1979), Ofori (1980) and J.F. Levy et al (1982). They will not be repeated here although those points relevant to the present work will be dealt with in the discussion.

In addition, there have been several approaches to the problem of practically extending the use of ground contact preservatives including:

(1) remedial treatment of poles

(2) increased loadings of CCA

(3) alternative methods of treatment

(4) alternative solvent systems

(5) new preservatives

and these will be dealt with in detail below.

1.4.1 Remedial Treatment of Poles

Although soft-rot protection of timber for use in the future is of vital importance, perhaps a more immediate problem is that of the vast number of treated hardwood poles (many eucalypts) currently in service (Greaves, 1977, 1979; C.R. Levy, 1978, 1982).

A variety of remedial treatments is available for the supplementary protection of poles and posts at or near the ground line (De Groot, 1981;). De Groot (1981), in a study of groundline treatments of "green" southern pine posts exposed in soil for 22 years, noted that "application of polythene or Kraft paper wraps that hold the preservative against the post also appears to contribute to treatment efficiency". The development and use of pole bandage treatments has been studied extensively in Australia (Greaves, 1977; Chin et al, 1982). Bandage treatments basically consist of applying a diffusible preservative in a highly concentrated form (e.g. paste) to the area of pole/post requiring additional protection and then applying a plastic/paper or bitumen paper wrap around this region to hold the preservative against the post. The preservative subsequently diffuses into the wood protecting it against further decay. The C.S.I.R.O. bandage is a refinement of this basic system and consists of a heat shrink plastic wrap and a matrix impregnated with a fungicide as one unit (Chin et al, 1982).

1.4.2 Increased Loadings of CCA

As a result of investigations into substrate susceptibility, Hulme and Butcher (1977 a, b, c) and Butcher and Drysdale (1978) have concluded that soft-rot control could be achieved in hardwoods

if adequate and often high preservative loadings were used. The actual loading would be determined by the susceptibility of the individual timber species to soft-rot attack. They have demonstrated this in laboratory experiments. However, the high CCA loadings that are required by some hardwood species (e.g.more than 36 kg m^{-3} in Eucalyptus spp.) raises questions over the economic desirability of treating such timbers in preference to importing or planting pine species, and the effect of such high loadings on their strength properties.

1.4.3 Alternative Methods of Treatment

C.R. Levy (1982) has stressed that diffusion treatments of green timber work with every species (c f. vacuum pressure) although they are largely neglected by the wood preservation industry. The problem with diffusion treatments is that the preservative currently in use in single diffusion processes (e.g. boron compounds) are not fixed in the timber and are subject to leaching in wet conditions. With this in mind, Ofori (1980) and Vinden (1983) have experimented with double diffusion processes in which the second treatment serves to fix the elements of the first treatment. Vinden's (1983) results are, as yet, unpublished. Ofori (1980), however, compared the effectiveness of different treatment methods in Scots pine, birch, celtis, obeche and antiaris using a standard bioassay. He found that sap displacement and diffusion treatments of the unseasoned green timbers were more effective than a full-cell Bethel treatment with CCA at the same copper loadings (w/w).

Another approach to treatment methods has been to modify existing processes, in particular, increasing the pressure during the vacuum pressure process (e.g. from 200 to 300 p.s.i.) has been shown to be beneficial (C.R. Levy, 1982) and increasing the vacuum from 25" to over 28" Hg. is believed to result in a more effective treatment (C.R. Levy, 1982).

1.4.4 Alternative Solvent Systems

A further attempt to attain an improved performance against soft-rot organisms has been to use solvent systems other than water, e.g. ammonia, ethanolamine (cell wall swelling agents). Ammonia-based preservatives e.g. ammoniacal-copper-arsenate (ACA) have been developed in Canada for the treatment of relatively impermeable timber species such as white spruce (Rak and Clarke, 1974; Rak, 1976). Here, the fixation of copper and arsenic is mediated by ammonia as opposed to chromium in CCA. Hulme (1979) has reviewed data on the performance of ammoniacal wood preservatives. The adequate fixation and opportunities for delayed drying time allowing for preservative diffusion prompted a study by Henningsson, Hager and Nilsson (1980) of the potential of such a preservative system for the protection of hardwoods in ground contact. Their initial results suggest that ACAs, when allowed a drying period of 3 weeks, provide a superior control of soft-rot than do CCAs applied by vacuum pressure. In addition, Johnson and Gutzmer (1978) have claimed that ammoniacal copper borates (ACB) could replace ACAs for use in ground contact.

Recent work by Greaves, Adams and McCarthy (1982) has suggested that the use of ethanolamine and copper used as a metal soap of either synthetic acid mixes or nonanoic acids gives a better microdistribution of copper in the cell-walls of Eucalyptus sp. in comparison with CCA. This work is still in its early stages but serves to illustrate the potential for modifications to treatment processes and formulations that remains to be explored.

1.4.5 New Preservatives

Before a new preservative can be accepted, rigorous performance trials (see section 2.2.2.1) and tests of mammalian toxicity have to be carried out. In addition, an assessment must be made of the effects of leaching and ageing for many end-uses, compatibility and problem of pollution. These tests are time-consuming and expensive and have probably led to additional research into existing preservatives. An example is the formulation of a copper chrome arsenic boron (CCAB) mixture by Lewis (1980) as a result of the findings of Montgomery (1979) (see section 1.2.3). He substituted 50% of the arsenic compounds of CCA with boric acid. In a soft-rot trial this CCAB formulation was found to be less effective than CCA. The same result was found in the investigation of Tamblyn and C.R. Levy (1981) referred to in section 1.2.3, both CCA and CCB being much more effective than CCAB. The poor performance of the CCAB treated stakes was attributed to a lack of fixation, but the copper content reported was much lower than that of either CCA or CCB.

In addition to research into existing preservatives, new preservatives are being developed. A recent example of a successful development and launching has been that of the alkylammonium compounds

(AACs) (Butcher, 1980; Butcher and Drysdale, 1977; Butcher and Greaves, 1982). These preservatives are currently used in New Zealand for the protection of timber in slight to moderate decay hazards (e.g. fence battens, interior joinery) in preference to CCAs due to lower mammalian toxicities and greater environmental acceptability. To date AACs have given a poor performance in situations where there is a severe decay hazard, (e.g. ground contact), and variable results in Canada (Ruddick, 1981) and the United Kingdom (Tillott and Coggins, 1981) have limited their wider application. However, further work is in progress to examine the effects of modifying AAC formulations with copper to enhance their range of uses (Nilsson, 1983; Butcher, Preston and Drysdale, 1979).

1.5 Aims and Objectives

The aim of the present study was to make an additional contribution to the solution of the soft-rot problem in hardwoods, that of modifying existing preservative treatments of known effectiveness with the objective of improving their performance.

In the light of previous work undertaken in the Timber Technology Section of Imperial College (Montgomery, 1979), the preservatives selected for study were CCA and CCB. The modifications made to the preservatives and to the method of treatment were to be kept to a minimum. The treatments would be applied to a permeable, perishable softwood (Scots pine sapwood) and a permeable, perishable hardwood (birch) where their effectiveness against wood destroying

fungi would be assessed using a range of bioassay techniques. Performance against wood destroying insects and animals was beyond the scope of this study. Following biological assessment it was planned to look at some of the chemical aspects influencing the more important results.

SECTION II: MATERIALS AND METHODS

2. Section II. Materials and Methods.

2.1 Introduction

A range of formulations containing copper, chromium, arsenic and or boron was selected for study. The treatments were straightforward but there were many problems associated with the biological assessments. The formulations tested and method of evaluation were derived simultaneously but the development of the biological assay will be dealt with first. The adoption of a particular test method for each type of assessment was the result of a survey of the relevant literature and the findings of preliminary tests where appropriate. This sequence will also be used to describe the test methods in the following sections.

2.2 Development of the Biological Assay - Method of Test

2.2.1 Introduction

The evaluation of a preservative involves determining its activity against the decay hazards that the wood will encounter in service, and estimating the permanence of this activity. Service tests take far too long to be of use in development and consequently other tests have been developed both in the field and the laboratory. But laboratory tests are not without their problems. Because an effective preservative is designed to protect timber for many years in practice, a laboratory test must be accelerated greatly in order to help predict performance. In addition, the range and complexity of the interacting environmental hazards that the wood will be subjected to in service cannot possibly be simulated in the laboratory. Therefore, the tests applied in evaluating a preservative have to be selected carefully as being those most suitable for the intended end use of the treated timber.

In the present study the preservative treatments were designed for the protection of hardwoods against soft-rot attack, which occurs most commonly in ground contact. Therefore there was a particular need for evaluating the effectiveness of the treatments with respect to soft-rot organisms. However, no standard laboratory soft-rot test has yet been accepted. The European Committee for Standardization (EN 160 draft, 1981) has attributed this to inadequate knowledge of the subject. The main problem is not one of finding a test organism which is easy to handle in the laboratory but of finding one whose

activity is representative of the soft-rot type. This is probably due to the fact that a considerable range of microorganisms are able to cause soft-rot decay.

To permit the comparison of test results both between trials and between different organisations the tests must be carried out under the same conditions, which in turn must be precisely defined and closely followed. Agar block tests with basidiomycetes have accommodated these rigid controls (EN 113, 1982) but no equivalent soft-rot tests have been evolved. Attempts have been made to develop unsterile soil burial tests as a realistic soft-rot assay but, because of the complex nature of both soil and its microflora, these tests cannot be precisely defined and are therefore neither comparable within organisations nor between them (Savory and Carey, 1975). Part of the problem seems to lie in the moisture relations of the soil and buried wood blocks. A more recent development, the soil-bed, may have overcome some of these problems as stakes are not totally buried and more closely resemble the field situation.

Because of the uncertainties in the field of soft-rot testing, it was felt that as many different tests as were feasible should be carried out in the evaluation of the preservatives against soft-rot in hardwoods.

In view of previous data regarding the failure of copper chrome boron (CCB) and copper chrome arsenic boron (CCAB) treated timber to

copper tolerant basidiomycetes (Tamblyn and C. R. Levy, 1981), the boron containing formulations selected were tested against white and brown rot fungi as an indication of their spectra of activity. The availability of standard test methods meant that this was simple in comparison to soft-rot testing but, even so, care was taken to select not only standard test organisms but also those with a notable tolerance to copper.

A further consideration in the evaluation of the preservatives was that of leaching since this is characteristic of the soft-rot environment (e.g. ground contact) to which the treated timber is exposed in service. As a routine the samples were subjected to an accelerated leaching procedure prior to biological assessment (EN 84, B.S. 5761. Part 2). In addition, the preservative treatments were evaluated in the severest of leaching conditions and high soft-rot hazards of a water cooling tower.

An attempt was made to establish the toxic values of the preservatives in each of the tests. The toxic value is defined as the preservative concentration below which the wood is no longer adequately protected and the concentration above which a product ensures protection.

PLATE 1

BASIDIOMYCETE MONOCULTURE TEST SET UP WITH GLOEOPHYLLUM TRABEUM AND SCOTS PINE

2.2.2 Basidiomycete Monoculture Tests

2.2.2.1 Introduction

There are many laboratory tests involving basidiomycete fungi in monoculture, of which three main types are relevant to preservative testing. The ultimate test involves the interaction of wood, fungus, preservative and the method of application. An example of this is the thin cross-section test (Sutter, 1979) where a known effective level of toxicant is used and the method of application is assessed. The simplest test is a test of the fungal toxicity of the compound. in the absence of wood. Examples of this are the filter paper test (Dickinson, 1974b) and incorporation of the compounds into the agar medium (Humphrey and Fleming, 1915; Richards, 1923). Although toxic values can be obtained from these tests no account is taken of the interaction of a wood substrate. The third and most commonly used type of test is one of the toxicity of the preservative in wood which is known to be completely treated. Among the best known are the agar-block tests (e.g. EN113, 1982) and the soil-block tests (e.g. ASTM 1413, 1961). The agar-block method involves exposing sterile wood blocks to monocultures of fungi growing on an agar medium. The soil-block method replaces the agar with moist, sterile soil and the wood blocks are infected via an inoculated "feeder" block which rests on the soil surface. Both of these methods are time consuming and require a large volume of glassware. More recently, several alternative smaller scale techniques have been put forward. Among these is a miniaturised wood block test (Bravery, 1979, 1983). This is similar to the test described in the European Standard (EN 113, 1982) except that smaller wood blocks are exposed in smaller culture vessels for a shorter time period.

All of the above methods employing wood use weight loss as the criterion of decay but there are also methods which use other criteria such as loss in strength, in particular loss in bending strength (Mateus, 1957), loss in tensile strength (Bravery and Grant, 1971), and work to maximum load (Bravery and Lavers, 1971). In Mateus' method small beams are supported over an agar plate monoculture and are deflected under a constant load at time intervals. Bravery and Lavers' method is similar but destructive since the beams are loaded to failure. Another method based on fracture is the thin shavings test (Richardson, 1979). Here thin shavings are dip treated and exposed to monocultures on agar plates. Decay is assessed by pulling the shavings apart longitudinally between the fingers and examining the resulting fracture. There are also methods based on change in specific gravity (Lindgren and Eslyn, 1961) and respirometry (R.S. Smith, 1969).

2.2.2.2 Selection of Test Method

In this investigation it was not the method of treatment but the interaction of wood and preservatives which was of most interest. Therefore a test method was selected from the third group. After careful consideration the miniaturised wood block test was selected as the most appropriate for the current purposes. The main reasons for this choice were:

(i) treated woodblocks are the substrate

(ii) the test is rapid and reliable

(iii) the test yields quantitative data

(iv) weight loss is measured as the criterion of decay

(v) no special equipment is required

(vi) previous results have been comparable to those obtained by BS 838 (EN 113) and there is a variety of published data for comparison.

2.2.2.3 Test Procedure (see Plate 1)

A 4% malt agar medium was sterilised by autoclaving at 15 p.s.i. for 20 minutes. Sterile 9 cm Petri dishes (Sterilin Ltd.) were charged with 20 ml medium using a tilt measure. The depth of the agar was such that waterlogging of the test blocks by condensation from the lid did not occur. The plates were inoculated with an active culture of the test fungus and incubated at $22\pm2^{o}C$ until the fungus had completely covered the agar. Sterile discs of plastic mesh with holes 5-7 mm (Transatlantic Plastics Ltd.) measuring 80 mm diameter with a 25 mm central hole were placed on the cultures. The meshes were there to act as supports for the wood blocks to prevent waterlogging.

2.2.2.4 Test Specimens

The wood blocks were prepared, treated, leached and sterilised as described in 2.4. They measured 30x15x5 mm compared to those of 30x10x5 mm recommended by Bravery (1979, 1983). The reason for this was

that 30x15x5 mm was the size proposed for the International Research Group on Wood Preservation collaborative soft-rot trial (Savory and Carey, 1973) and these were needed for the main soft-rot tests in this study. Consequently it was convenient to use the same size for both types of test. Bravery (1979) showed that during a 6 week trial there was no significant difference between toxic thresholds for the two block sizes. Six replicate blocks were used at each treatment concentration for each fungus and, additionally, 6 replicates at each treatment concentration were incubated above sterile agar and termed "sterile controls". Three replicate blocks were placed equidistant from the centres of each agar plate. The plates were then incubated in plastic boxes (Stewart Plastics Ltd.) at $22\pm2^{o}C$ for 6 weeks. After incubation the blocks were scraped clean of fungus and weighed to establish their final moisture contents. The final moisture content could give an indication of waterlogging as an explanation for an unexpectedly low weight loss.

2.2.3 Monoculture Tests with Soft-rot Organisms

2.2.3.1 Introduction

Many methods have been proposed for testing wood preservatives against monocultures of soft-rot fungi (BS 838 Part 2, 1961; Schulz and Riewendt, 1962; Duncan, 1965; Bravery, 1968 a,b). As yet none of these methods has gained general acceptance as a standard method of test due to its lack of reproducability. In devising a test method it is first essential to find conditions suitable for inducing soft-rot attack in the laboratory and then to find a convenient method of exposing treated wood samples to the soft-rot hazard. The factors influencing soft-rot attack will be considered before an attempt is made to derive a suitable method of test.

2.2.3.2 Factors Influencing the Development of Soft-rot

There are numerous reports of observations in this field but only those considered to be of direct relevance will be discussed here.

2.2.3.2.1 Nutrients

Savory (1955) reported that without additional mineral nutrients decay of wood by soft-rot fungi was slow. Oliver (1959) found that decay caused by Chaetomium globosum in beech increased with added nitrogen and phosphate. Savory (1954 a) obtained similar results for C. globosum, Trichurus terrophilus and 2 species of Stysanus in beech

and recommended the use of Abrams' medium (1948) for investigating degradation of cellulosic materials. In addition Savory (1954 a,b 1955) and Duncan (1960, 1965) achieved greatest decay using double strength Abrams' medium. A similar optimum nitrogen concentration was obtained by Kaune (1970). Also, Lundstrom (1972, 1973) found that decay in veneers increased when they were impregnated with a solution containing nitrogen. Sharp (1974) found that soft-rot development could be prevented by a reduction in wood nitrogen. In contrast, Butcher and Drysdale (1974) in a series of tests using Pinus radiata found that the greatest level of decay in the softwood was achieved with the smallest addition of nitrogen, giving a C:N ratio of 250:1. Higher levels of nitrogen resulted in decreased soft-rot attack. Similarly, Lundstrom (1973) found that C:N ratios of 140:1 and 250:1 were optimum for decay in birch. In collaborative soft-rot trials (Savory and Bravery, 1970) there was no correlation between nitrogen level and degree of attack. This was probably masked by the alteration of other test variables. Gersonde and Kerner-Gang (1975, 1976) found that the highest rates of decay of beech and pine in vermiculture were achieved when a nutrient medium with 3g/l nitrate was added. Da Costa and Be zemer (1979) compared low phosphate Abrams agar with malt agar using a range of soft-rot organisms on radiata pine and 2 Eucalyptus spp. and found that the Abrams agar consistently gave the highest rates of decay.

Duncan (1965) tested a range of nitrogen sources with a range of soft-rot fungi and found that all utilised ammonium nitrate relatively well. At equal nitrogen concentrations it was utilised as much as asparagine and urea in agar and more than sodium nitrate and ammonium sulphate for soft-rot production. Savory (1954 b) and Zycha (1964)

also found ammonium nitrate to be the best nitrogen source whereas Lundstrom (1973) obtained better results with a mixture of ammonium nitrate and ammonium tartrate. Urea was found to be a superior source of nitrogen by Chalal and Gray (1968) and Butcher and Drysdale (1974).

The addition of alternative carbon sources such as glucose tends to decrease soft-rot decay (Banerjee and Levy, 1970; Bravery, 1968 a,b). This is probably due to preferential utilisation of the simpler carbon compound (Siu, 1951) resulting in a lower induction of cellulases (Jensen, 1971). In contrast, Duncan (1965) reported that the addition of up to 0.25% glucose to Abrams' medium resulted in an increase in decay, although higher concentrations of glucose inhibited decay. Butcher (1975) found no increase in decay with added glucose. Similarly, Banerjee and Levy, (1970), Kaune (1970) and Da Costa and Bezemer (1979) found that addition of malt extract considerably reduced decay. Duncan (1965) recommended the use of a filter paper feeder strip which was incorporated by many other investigators (e.g. Bravery, 1972). Duncan (1960, 1965) also recommended the addition of microelements and vitamins to Abrams' medium for increased soft-rot decay. Thiamine has been shown to have an effect on decay by fungi (Highley, 1970). Butcher and Drysdale (1975), in tests with Pinus radiata in vermiculite burial, varied the levels of each of the nutrients of Abrams' medium. They found that C. globosum gave the highest rate of decay with the lowest phosphate concentration, the highest magnesium sulphate concentration and was unresponsive to the addition of glucose and Duncan's (1965) micronutrient/vitamin concentrate.

2.2.3.2.2 Temperature

The optimum temperature for linear growth on agar of a majority of soft-rot fungi investigated by Duncan (1960, 1965) and Kerner-Gang (1966) was found to be between 28°C and 34°C. Both Thomson (1968) and Lundström (1972, 1974) commented that optimum temperatures for growth and decay may not be the same. The optimum temperature for decay by soft-rot fungi was found by Duncan (1965) to be 32°C and by Kerner-Gang (1970) to be near the optimum for growth. Gersonde and Kerner-Gang (1976) found that a majority of the soft-rot fungi they investigated decayed beech most heavily at 32°C in vermiculite whereas the optima for pine sapwood were 24°C and 28°C. Most investigations have been carried out at temperatures between 25°C and 30°C (Rosch and Liese, 1968).

2.2.3.2.3 pH

Duncan (1960) investigated the effect of pH on the growth of 32 soft-rot fungi on agar. Maximum growth of the majority occurred in a pH range of 6.0-7.0. Sharp and Eggins (1970) obtained similar results but reported lower pH optima for decay than growth on agar.

In soil burial tests Walchli (1969) recommended a soil pH of 6.5-7.0. Sharp and Eggins (1970) found that decay in unsterile soil was not markedly different over a pH range of 3.7-8.6. More recently, Butcher (1975) testing softwood decay in unsterile soil found that pH changes of 4.5 to 6.5 had no effect but in soil inoculated with C. globosum there was an effect. Sharp and Eggins (1970) showed that some fungi were favoured by a low pH and others

by a higher pH. This could explain the apparent tolerance of unsterile soil to changes in pH.

2.2.3.2.4 Aeration

Aeration requirements of soft-rot fungi have been examined by Duncan (1961), Follstad (1967) and Griffin (1966). Duncan (1961) found that soft-rot fungi were more tolerant of low oxygen tensions than were the basidiomycetes she tested. Savory (1955) states that the small amount of oxygen present in well aerated water is sufficient to permit the growth of microfungi in totally immersed wood, but that soft-rot may be prevented if the water is not well aerated.

2.2.3.2.5 Moisture

Savory (1955) stated that the microfungi could attack wood which was too wet or too dry for basidiomycete decay. Kerner-Gang (1970) found that the most active soft-rot fungi required high wood moisture contents. Duncan (1965) recommended impregnation of blocks with water prior to testing or placing thin test blocks directly on wet agar or soil. In their investigation, Becker and Kaune (1966) found that the lower limit for decay of beech and pine sapwood was in the region of 30-35% while the upper limit for pine was 60-80% and beech was 80-120%. Gersonde and Kerner-Gang (1976) also found that beech specimens needed to have a higher moisture content than pine to give optimum decay. More recently, Byrne and R.S. Smith (1982) found an optimum addition of nutrient solution to the test medium in red alder but were unable to distinguish the effects of moisture and nutrients as was Kaune (1970) in a similar investigation.

The limitation of decay by high wood moisture levels as reported by Becker and Kaune (1966) may well be associated with aeration of the wood.

2.2.3.2.6 Block Size

Duncan (1960), Da Costa and Kerruish (1963), Baker, Savory and D.N.R. Smith (1969) and Bravery (1968 a,b) have shown that soft-rot decay is more rapid in smaller blocks than those recommended for basidiomycete testing and these are specified in BS 838 (1961). The reason for the apparent acceleration in decay is that soft-rot attack is commonly a surface phenomenon.

Taking all of these factors into consideration, a summary can be made:

2.2.3.3 Summary of Conditions Desirable for Soft-rot Production in the Laboratory

(1) a supply of mineral nutrients

(2) an elevated temperature

(3) a suitable pH

(4) a high wood moisture content

(5) a small test block of high surface area to volume ratio

(6) a suitable inoculum.

2.2.3.4 Effect of Test Conditions on Preservative Testing

The conditions required for the induction of soft-rot in the laboratory may adversely affect the preservative chemicals under test and the toxic values to be established.

The addition of supplementary mineral salts, especially high levels of phosphate, has been shown to affect the toxicity of some preservatives, notably those containing fluorine (Schulz and Riewendt, 1962) and those containing arsenate or arsenite (Da Costa, 1972). In addition, pH shifts of only one unit have been shown to change the activity of some preservatives by 100-fold (Wessels and Adema, 1968).

Duncan (1960) and others have concluded that the use of small wood blocks, especially veneers, promotes leaching of the preservative under test. In an investigation of the effect of altering the length of the incubation time on the toxic values of a CCA preservative, Bravery (1968 a) found that toxic thresholds were raised with increase in incubation time. He suggested that this was due to increased decay following a period of "physiological adjustment", and referred to the juvenile, dynamic and mature phases in the fungal decay of wood. Kerner-Gang and Gersonde (1981) have found that the toxic limits also vary (as do the weight losses) with the number of test specimens in the test vessel. The more test specimens the lower the weight losses and toxic limits.

2.2.3.5 Methods of Test

The available data on the conditions required for soft-rot production in the laboratory have been interpreted by numerous workers in the development of their test methods. These methods fall into two categories: those utilising an agar medium and those based on a sterile matrix such as sterile soil, sand and vermiculite.

In the first group, the nutrients and moisture required are supplied by the agar medium, which is inoculated with the fungus. Agar-block testing is preferred (Kirk, 1969) to simple agar plate testing. The agar medium usually incorporates the selection of mineral salts recommended by Abrams (1948) either at Abrams' original concentration (BS 838, 1961; Schulz and Riewendt, 1962; Savory and Bravery, 1970) or at double the concentration (Savory, 1954 a,b; Duncan, 1965; Savory and Bravery, 1970; Bravery, 1968 a,b). Sometimes alternative carbon sources are supplied in the form of a filter paper (BS 838, 1961; Savory and Bravery, 1970), malt extract (Savory and Bravery, 1970), glucose (Duncan, 1965) or cellulose (Savory and Bravery, 1970). Microelements and vitamins may also be added (Duncan, 1965). The culture vessel varies from a Petri dish (Savory and Bravery, 1970) to a large glass jar (BS 838, 1961). The block sizes range from 30x20x1.4 mm (Savory, 1955) to 50x25X5 mm (BS 838, 1961) and the incubation period from 6 weeks (Schulz and Riewendt, 1962) to 16 weeks (Savory and Bravery, 1970), usually at a temperature of 30°C (Schulz and Riewendt, 1962). The fungus is usually Chaetomium globosum.

Into the second category fall two rather unusual test methods (Eggins, H.O.W., Malik, K.A. and Sharp, R.F., 1968; Armstrong and Savory, 1959) and a host of burial techniques. Eggins et al (1968) devised a system for supplying nutrients using glass fibre wicks. One such wick linked the test specimen to the nutrient solution and another the specimen to air. By evaporation of water from the second wick a flow of nutrients was brought about. Armstrong and Savory (1959), on the other hand, impregnated test specimens with triple strength Abrams solution, inoculated them with a spore suspension and suspended them in moist air above water.

It is more usual for test blocks to be buried in sterile vermiculite (Kaune, 1970; Gersonde and Kerner-Gang, 1976), soil (Duncan, 1965; Savory and Bravery, 1971) or sand (Butcher, 1975) which is then inoculated with a spore suspension and often a nutrient solution. For example, Butcher (1975) recommends the use of fine sand at a moisture content of 75% field capacity and pH 6.5, with added mineral nutrients to give a veneer C:N ratio of 200:1 to 250:1 incubated at 30°C. In contrast, Duncan (1965) recommends soil of pH 5-7 and minimum water holding capacity 40%, wetted to water holding capacity with a solution of mineral salts, glucose, micronutrients and vitamins, with a filter paper feeder strip incubated at 32°C for 12 weeks. With vermiculite as the matrix material, Gersonde and Kerner-Gang (1976) used cubes of wood buried for 12 weeks if beech and 16 weeks if pine at 28°C, the vermiculite being wetted with a mineral salt solution with a similar source and quantity of nitrogen as in that of Abrams (1948).

2.2.3.6 Selection of Test Method

Bravery (1968 a), in a comparison of test methods, concluded that agar pure culture tests may be too severe and too specialised to give a realistic evaluation of preservative performance. However, he conceded that these tests may be useful in comparative evaluations. Since the requirements of the present study were for a comparative evaluation of preservatives when exposed to soft-rot organisms in monoculture under defined conditions, this test method was found to be the most suitable. The choice was made bearing in mind the problems of achieving optimum moisture contents in buried blocks (e.g. Bravery, 1972) and the need for an experimental design which could be repeated and where little incubation space was required. For this reason the Petri dish was selected as the culture vessel. Considering the variation in published experimental design, several small-scale tests were carried out to establish some of the parameters of the method before the main tests were undertaken.

2.2.3.7 Pilot Tests

The basic test was carried out as follows: untreated beech (*Fagus sylvatica*) veneers measuring 25x15x2 mm and sometimes birch miniblocks (see section 2.4.1) were exposed to a monoculture of a soft-rot organism growing on 20 ml agar medium in a Petri dish. Decay was assessed by weight loss. Sterile controls were included.

2.2.3.7.1 Test 1 Selection of Nutrient Medium

The conventional medium recommended by Abrams (1948) was compared with the medium recommended by Gersonde and Kerner-Gang (1976) since the latter medium is low in phosphate (Butcher, 1975; Da Costa, 1972). The level of the nitrogen source only was doubled in each case and 1 ml of a trace element solution was added per litre of medium. A Phialophora fastigiata (F.P.R.L. S6A) spore suspension was the inoculum. Beech veneers were exposed for 16 and 28 days and birch miniblocks for 28 days at 25°C. Details of the media and results are given in appendix A.

2.2.3.7.2 Test 2 Alternative Carbon Source

The medium selected from test 1 was tested with added glucose at 5 levels and against a 4% malt agar. P. fastigiata (F.P.R.L. S6A) was the test organism. Beech veneers were incubated at 25°C for 14 and 28 days. Details of the media and results are given in appendix A.

2.2.3.7.3 Test 3 Selection of Test Organism and Use of Filter Paper Feeder

The medium selected from test 2 was used with and without a 50 mm square filter paper feeder strip. In addition, half of the wood samples were treated with a 0.75% CCA solution so that the preservative tolerance of the organisms could be tested. Beech veneers were incubated for 28 days at 25°C with a range of fungi, namely: Chaetomium globosum (F.P.R.L. S70), Phialophora fastigiata (F.P.R.L. S6A) and Phialophora hoffmannii (F.P.R.L. S967). Details of the test and results are given in appendix A.

2.2.3.7.4. Results

Test 1

The weight losses in both beech and birch were small but in each case the Gersonde and Kerner-Gang medium resulted in more decay than did the Abrams medium. (from statistical tests).

Test 2

After 14 days, the 0.1% glucose medium gave a significantly greater weight loss than the other media, the 4% malt agar resulting in a lower weight loss than all of the other media. After 28 days the 1.0 and 0.25% glucose media resulted in a significantly lower weight loss than all of the others, of which 0.5% glucose was the most effective.

Test 3

The P. fastigiata cultures were mostly contaminated by mite infestation. The weight losses caused by C. globosum were much greater than those caused by P. hoffmannii. In each case there was more decay without the filter paper, these differences often being statistically significant. The effect of the preservative treatment was to reduce the weight losses, sometimes significantly. With no filter paper the weight losses caused by C. globosum were not significantly different in the treated and untreated veneers, suggesting a degree of preservative tolerance. P. hoffmannii tended to be more sensitive to the treatment when no filter paper was used.

2.2.3.7.5 Conclusions

From the results of the pilot tests the following conclusions were drawn:

(1) a modified mineral nutrient medium based on that recommended by Gersonde and Kerner-Gang (1976) is preferable to that of Abrams (1948) under present conditions

(2) a 0.1% addition of glucose is advantageous

(3) there is no requirement for a filter paper feeder strip

(4) the most suitable test organism of the 3 tested is Chaetomium globosum (F.P.R.L. S70).

2.2.3.8 Test Procedure

As a result of the pilot tests, the following procedure was derived from the available data.

A mineral nutrient agar medium was used. The composition was as follows:

6.00 g	NH_4NO_3	ammonium nitrate
2.56 g	K_2HPO_4	di-potassium hydrogen phosphate
1.02 g	$MgSO_4$	magnesium sulphate
0.25 g	KCl	potassium chloride
0.005 g	NaCl	sodium chloride
0.001 g	$FeSO_4$	ferrous sulphate
0.001 g	$MnSO_4$	manganese sulphate
1.00 g	glucose	
1 ml	trace element solution	
20 g	agar	

per litre distilled water

Trace element solution - per ml.

570 µg	boric acid
310 µg	zinc chloride
145 µg	ferric chloride
40 µg	cobalt chloride
60 µg	copper sulphate
30 µg	magnesium chloride
20 µg	ammonium molybdate

The medium was sterilised by autoclaving at 15 p.s.i. for 20 minutes. Petri dishes were charged with 20 ml medium and inoculated with the test fungus using a spore suspension. A spore suspension was the most suitable inoculum because:

(1) P. fastigiata (see section 3.3) grows very slowly on nutrient agar and takes several weeks to cover the plate if inoculated at a single point.

(2) P. fastigiata (S6A) tends to sector and most genetic material will be present in a spore suspension.

(3) fruiting structures hindered decay especially in C. globosum (see below).

For P. fastigiata the spores were suspended in sterile distilled water but in the case of C. globosum a more even spore distribution was found in a 1% gelatin solution mixed on a "whirlimixer". The plates were incubated at 25°C for P. fastigiata and 30°C for C. globosum for several days prior to planting of the test specimens. This was carried out before fruiting structures had formed since these tend to lift the blocks clear of the agar and hinder the onset of decay (B.S. 838, Part 2, 1961).

2.2.3.9 Test Specimens

The wood blocks were prepared, treated, leached and sterilised as described in section 2.4. They measured 30x15x5 mm, the size recommended for the International Research Group on Wood Preservation collaborative soft-rot tests (Savory and Carey, 1973) and were convenient for use in petri dishes.

Six replicate blocks were used at each treatment for each fungus and, additionally, 6 replicates at each treatment concentration were incubated on sterile agar as controls. Two replicate blocks were placed equidistant from the centre of each plate. The reason

for the exact quantity of medium in each plate, the exact positioning of the blocks and the particular number of specimens per plate was as follows: Savory and Carey (1980), in a test of the effect of nitrogen concentration on weight loss caused by Chaetomium globosum on beech blocks buried in vermiculite, found that the weight loss increased with increasing nitrogen concentration.

For a potential weight loss of 45% the required nitrogen level was about 14 mg per g wood substrate. 20 ml medium contains 42 mg elemental nitrogen. Assuming that the test blocks weigh 1.5 g or less, each agar plate should supply enough nitrogen for 45% weight loss in each of 2 blocks. If the test blocks weigh less they will receive proportionally more nitrogen. The assumption is made that all of the nitrogen is available to the fungus attacking the wood, hence the careful positioning of the blocks.

The lids of the dishes were aligned and marked with the block identifications in case of severe staining which would obscure the labels. The plates were incubated in plastic boxes, over water to prevent drying out, at 25°C and 30°C for P. fastigiata and C. globosum respectively (Seehann, Liese and Kess, 1975).

After incubation the blocks were cleaned of fungus and weighed to establish their final moisture contents. These could give an indication of drying out as an explanation for an unexpectedly low weight loss.

2.2.4 Soil Burial

2.2.4.1 Introduction

Some of the literature relevant to soil burial testing has already been referred to in section 2.2.3 and only a brief consideration will be given here.

Mixed culture soft-rot tests are commonly carried out by burial of blocks in vermiculite or unsterile soil (Gersonde and Kerner-Gang, 1976; Bravery, 1968 a, b; Savory and Bravery, 1970, 1971; Savory and Carey, 1980; N.W.P.C. 1.4.1.2./70). Vermiculite must be inoculated with a mixed culture (Savory and Carey, 1980) or a soil extract (Kaune, 1967) whereas the natural soil flora can sometimes be relied upon to effect decay (Theden, 1961; Becker and Kaune, 1966; Bravery, 1975). Another advantage of soil over vermiculite is that a wide range of soil types contain sufficient nutrients for decay (Theden, 1961; Becker and Kaune, 1966; Leutritz, 1946) but vermiculite must be supplied with a nutrient solution. For these reasons soil was selected as the burial medium in the present study.

2.2.4.2 Selection of Test Method

There are many different test methods in use (Bravery, 1968 a, b; Savory and Bravery, 1970) but most of them differ only in detail. The method selected was that used in the International Research Group on Wood Preservation collaborative soft-rot tests (Savory and Carey, 1973).

2.2.4.3 Test Procedure

Soil was dug from Silwood Park (Imperial College Field Site, Ascot), partly dried and sieved into plastic trays. An analysis of the soil is given in table 1. The water holding capacity (w.h.c.) was determined by the method described in paragraph 2.2.5.3.1. The wood blocks were prepared, treated and leached as described in 2.4. The blocks, measuring 30x15x5 mm, were buried horizontal in a random pattern 1 cm below the soil surface.

The moisture content of the soil was adjusted to 100% w.h.c. and maintained at this level by addition of water as a fine spray during the incubation. The trays were wrapped in polythene and incubated at 25°C for 20 weeks. After incubation the blocks were recovered, wiped clean and weighed to establish their moisture contents (paragraph 2.2.2.3).

Table 1 -

Physical Characteristics of
Silwood Park Soil (after Clubbe, 1980 a)

Soil Type: Sandy Loam

Humus Content: 6.06 ± 0.14%

pH: 6.38 ± 0.06

Elemental composition of total soil using radiofrequency argon plasma spectroscopy.

Element	Concentration (ppm)	Standard Deviation
Aluminium (Al)	8233	621
Barium (Ba)	33.00	1.22
Boron (B)	20.56	11.94
Cadmium (Cd)	-	-
Calcium (Ca)	2668	203
Chromium (Cr)	53.73	8.14
Cobalt (Co)	-	-
Copper (Cu)	16.30	1.28
Iron (Fe)	11217	763
Lead (Pb)	48.00	15.12
Magnesium (Mg)	747	57.35
Manganese (Mn)	161.25	11.01
Nickel (Ni)	7.67	1.04
Phosphorus (P)	365	35.94
Strontium (Sr)	28.38	1.57
Vanadium (V)	31.23	2.13
Zinc (Zn)	50.50	3.07

Cation exchange capacity: 13.46 ± 1.36 milli equivalents Na^+/100 g soil.

PLATE 2

A SOIL-BED IN THE PRINCES RISBOROUGH LABORATORY FUNGAL CELLAR

2.2.5 Soil-Bed

2.2.5.1 Introduction

Until recently, the usual procedure for testing potential wood preservatives for use in ground contact has been to carry out a range of accelerated tests in the laboratory (ASTM 1413; 1961; EN 113, 1982; Bravery, 1968 a,b) and then to carry out a full scale field trial (European Standard (in preparation); Anon, 1972, NWPC 1971). Although the laboratory tests are rapid and suitable for establishing relative performance of preservatives against certain fungi they are limited in their usefulness for predicting probable field performance (Forest Research Institute, 1978). Since an adequate field testing of a preservative formulation can require 20 or more years (Johnson, Thornton and Greaves, 1982), field trials offer little for short term research and development studies. For this reason alternatives have been developed. Soil burial tests, discussed in sections 2.2.3 and 2.2.4, have been used to bridge the gap between agar-block tests and field trials but have been found to be unreliable. At a recent meeting of the International Research Group on Wood Preservation (Cockcroft, 1980) collaborative work using the soil burial technique, (Savory and Carey, 1973) was stopped and the decision was taken to look for other methods. Such a method has been developed in New Zealand and Australia and is known as the soil-bed. The major difference between soil burial and the soil-bed is that samples are not totally buried in the soil-bed. The use of small stakes has been found to give reliable reproducible results (Baines, 1982). Soil-bed is a term used for a trough of unsterile soil kept at an elevated temperature and relative humidity. The soil-bed is distinct from the fungus cellar in that a soil-bed contains unsterile soil and a fungus cellar contains inoculated sterilised soil (Gersonde, 1967).

The soil-bed is considered to represent an intermediate stage between accelerated laboratory tests and field trials. Thus it was found to be a most suitable test system in the current study.

2.2.5.2 Soil-bed Design

Currently soil-bed testing is being carried out in Australia (Thornton, Johnson and Saunders, 1981; Johnson, Thornton and Greaves, 1982), New Zealand (Forest Research Institute, 1978; Hedley, 1980; Butcher, 1981a; Murphy, Schasching and Dalley, 1982), Sweden (Henningsson, Käärik, Lundström and Nilsson, 1981) and in the U.K. (Baines, 1982; Vinden, Savory, Dickinson and Levy, 1982). The designs of the various soil-beds differ slightly in that some use ungraded soil (Hedley, 1980; Johnson, Thornton and Greaves, 1982) and some use graded soil (Johnson, Thornton and Greaves, 1982; Vinden, Savory, Dickinson and Levy, 1982) but they all use unsterile soil at elevated temperatures (26-30^{o}C) and relative humidities (75-90%) (Murphy, Schasching and Dalley, 1982).

The design used in this study was based entirely on that developed by Vinden (Vinden et al, 1982) at the Princes Risborough Laboratory. (see Plates 2 and 3)

2.2.5.3 Soil-bed Preparation

Topsoil was dug from a site of known biological activity (D.N.R. Smith, 1980) in the grounds of the Building Research Establishment, Princes Risborough Laboratory. An analysis of the soil is given in table 2. The soil was spread out on plastic sheeting in a well ventilated, heated, building to dry. Occasionally the soil was raked and turned until it was dry enough to sieve. (moisture content at time of sieving, 17%). Two sieves were used, one with a mesh size of 3 mm and the other 7 mm. Soil retained by the 7 mm sieve was termed "coarse", that which would pass through the 7 mm mesh but was retained

by the 3 mm sieve was termed "medium" and that which would pass through the 3 mm sieve was termed "fine". A 114 litre (25 gallon) household plastic water tank with 16 13 mm drainage holes drilled at intervals 5 cm up from the base was positioned in a fibre-glass tray of sudol* solution (to prevent the spread of soil organisms to other rooms) before being filled with soil. A 10 cm layer of 2.5 cm stones was covered by a layer of washed glass fibre insulation. Then a 7.5 cm layer of coarse soil was covered with a 7.5 cm layer of medium soil and finally a 20 cm layer of fine soil (see figure 1). The soil was compacted, watered and left for 3 weeks to settle. The room was maintained at a temperature of 28^{o}C and a relative humidity of 80%.

2.2.5.3.1 Water Holding Capacity

The water holding capacity (w.h.c.) of the fine soil was determined using the method of Carey and Grant (1975) as follows: about 200 g soil was placed in a Buchner funnel over a Whatman No. 4 filter paper. The soil was flooded with water, levelled and a vacuum drawn for 10 minutes. The % moisture content of the evacuated soil was determined by oven drying and taken as the water holding capacity. Three such determinations each gave a result of 29.4%.

2.2.5.4 Test Specimens

After three weeks the test stakes (measuring 150x10x5 mm, section 2.4.1.1.3) were saturated with water and buried vertically to a depth of 140 mm in regular rows in the soil. There were 10 replicates of each of the birch treatments and 7 of the Scots pine. The layout of the stakes was such that rows of Scots pine and birch alternated with each other.

* supplied by Teneco Ltd. Avonmouth.

2.2.5.5 Soil-bed Maintenance

The moisture content of the soil was regulated by applying a fine spray of deionised water periodically. Soil moisture determinations were carried out by oven drying soil from different depths. Occasionally, lengths of 6 mm birch and Scots pine dowel were partially buried in the soil, retrieved after 3 or 4 days, cut into lengths and oven dried to establish the moisture contents at different depths.

Table 2 -

Composition of Princes Risborough Soil (C.R. Levy, 1975)

pH	7.3
specific conductivity	0.381
total soluble salts	0.11
calcium (Ca)	41.2
magnesium (Mg)	1.08
potassium (K)	0.87
sodium (Na)	1.22
sum	44.4
carbon (C) (W&B) %	4.6
nitrogen (N) %	0.34

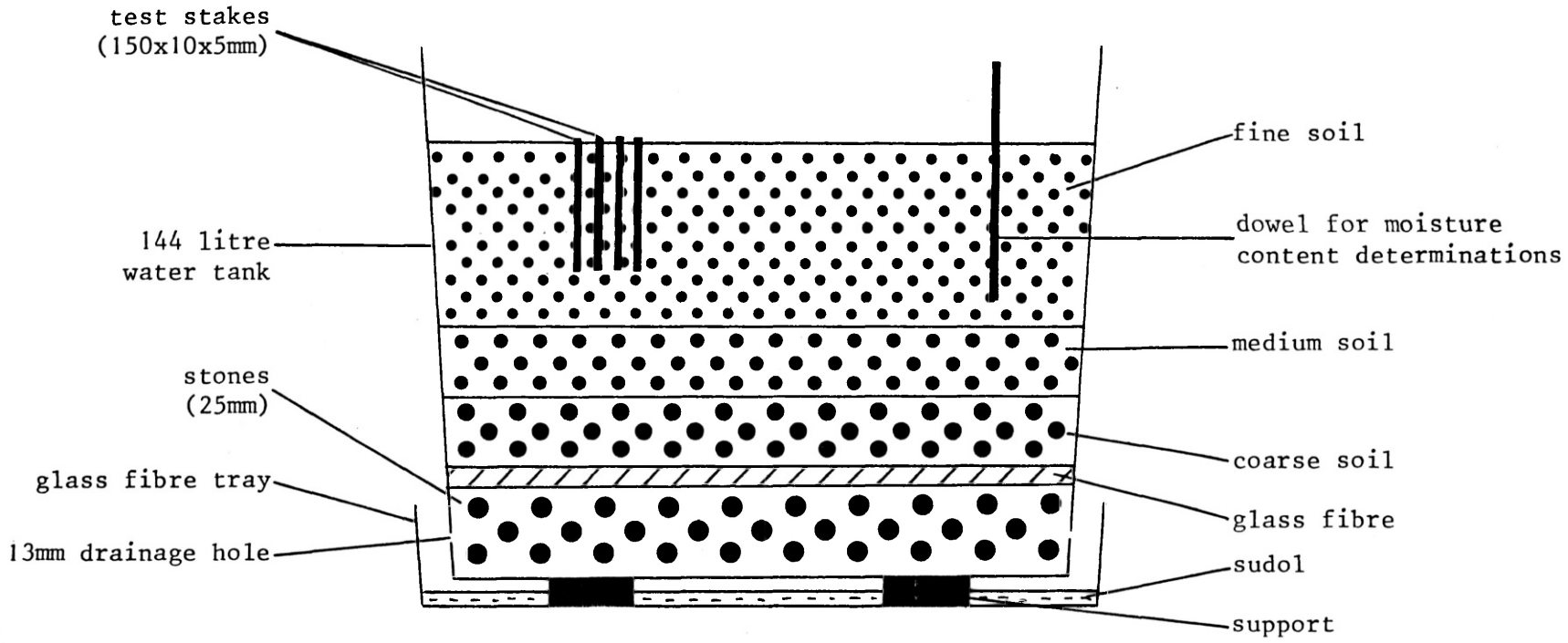


FIGURE 1 Diagram to show preparation of a soil bin

PLATE 3

CLOSE-UP OF TEST STAKES IN THE SOIL-BED

PLATE 4

WATER COOLING TOWERS AT LITTLE BARFORD POWER STATION

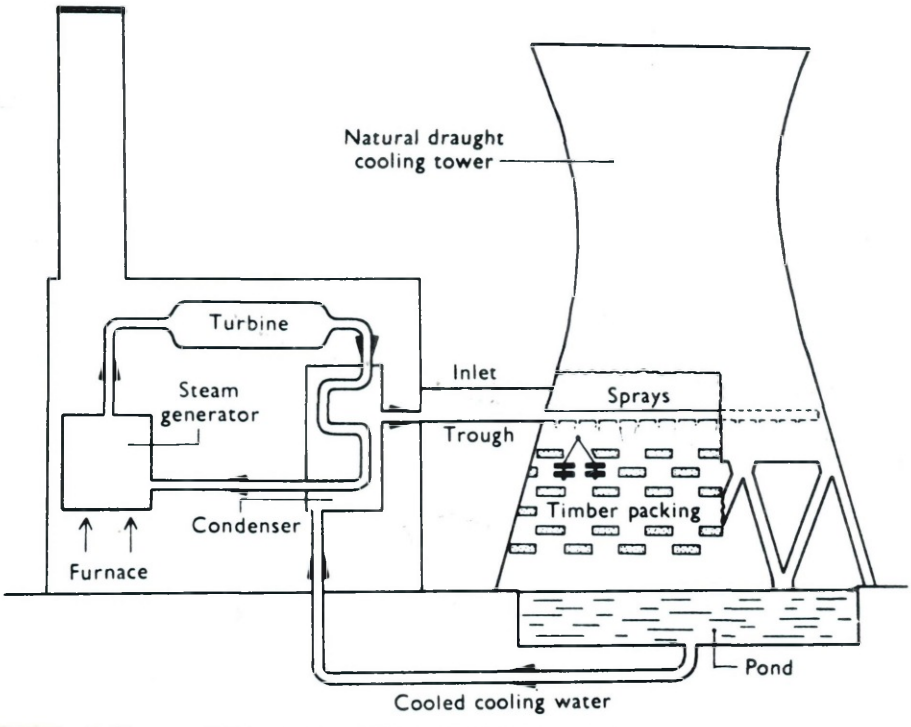


PLATE 5

SECTION THROUGH A WATER COOLING TOWER (AFTER EATON, 1972)

2.2.6 Water Cooling Tower

2.2.6.1. Introduction

Many observations on the decay of preservative treated wood in water cooling towers have been made on wood which is part of the internal stack.(Ross and Wood, 1957; Dunbar, 1962; Wilson, 1979; Vermaak, 1980). However, some investigations have been made on small samples exposed in water cooling towers for set periods. Schulz and Riewendt (1962) used pine sapwood samples measuring 150x25x13 mm exposed for 11 and 22 months. Price (1957) exposed pine sapwood specimens for 24 months. Irvine, Eaton and Jones (1972), using specimens measuring 50x25x5 mm, observed weight losses in untreated beech and Scots pine sapwood of 21.6-31.8% and 3.1-30.8% respectively after 40 weeks' exposure. They also made observations after 12, 24 and 36 weeks and found that the 12 week time period frequently gave the greatest weight losses of CCA preservative treated Scots pine (Irvine, Eaton and Jones, 1972).

Since there was little time available for this trial, the size of test specimen and test method of Irvine, Eaton and Jones (1972) was adopted.

2.2.6.2 Selection of the Cooling Tower

From Irvine, Eaton and Jones' (1972) experiments it can be seen that the choice of water cooling tower can greatly affect the weight losses obtained in untreated test specimens. In this trial the No. 6 tower at Little Barford Power Station, St. Neots, was selected as the test site for the following reasons:

(1) neither chlorine, hypochlorite nor any other chemical was added to the circulating water for cleaning purposes.

(2) the cooling tower contained some treated and untreated decayed timber from 1959 in its stack.

(3) the cooling tower was not due for its annual 6 week overhaul during the test period.

(4) the cooling tower was the nearest one in operation to London.

(5) the station manager and his staff were interested in the trial.

The conditions in the water cooling tower are given in table 3.

Table 3 - Water Cooling Tower Details

Water cooling tower type:	natural draft, concrete envelope
Source of water:	River Ouse
Cleaning agent:	sponge sphere passing through pipes
Rate of water flow:	22,000 gallons per minute
Water temperature:	19-28^{o}C
Total no. running hours:	884
Mean no. running hours per day:	7.9

2.2.6.3 Test Procedure

Scots pine and birch sapwood blocks measuring 50x25x15 mm were prepared, treated and leached as described in 2.4. 5 mm thick slices were cut from each outer (50x25 mm) face of 3 blocks at each treatment concentration to give 3 pairs of blocks, 50x25x5 mm in size. One block from each pair was exposed in the cooling tower, the other retained for later experiments. In addition to the 3 blocks described, 3 full sized (50x25x15 mm) blocks at each treatment concentration were used as test specimens. 1 mm holes were drilled near the top of each of the test specimens which were then threaded on to nylon strings in groups of 6. The blocks were separated from one another and from plastic labels bearing their identifications by short lengths of PVC tubing. The blocks themselves were labelled by stamp and with waterproof ink. The individual strings were attached to a length of nylon rope and positioned in the packing of the cooling tower. This was carried out while the tower was in operation so that the samples could be placed near effective spray nozzles. (see Plates 4 and 5)

The intended period of incubation was 12 weeks. After incubation the blocks were retrieved, washed, soxhlet extracted and oven dried to establish their final oven dry weights. Similar unexposed blocks (control blocks) were also soxhlet extracted and oven dried so that the weight changes of the test blocks could be corrected for weight gain due to preservative treatment and weight loss due to the laboratory leaching procedure. Thus any change in weight was solely caused by exposure in the cooling tower.

2.3 Development of the Biological Assay - Method of Assessment

2.3.1 Introduction

The assessment of decayed wood, be it in the field or in a laboratory test, involves the measurement of a parameter which is altered in the course of decay. At present, in Britain, the standard test methods all utilise weight loss as the criterion of decay. The advantages of weight loss are that it is simple to measure and requires no specialised equipment. On the other hand, long incubation periods may be required to obtain suitable weight losses (that is, it is insensitive in some cases); the original weight of the sample must be known; its determination is destructive in effectively sterilising the wood; and only one determination can be made, marking the end of the trial. In addition, to be accurate, weight changes due to other factors such as preservative treatments or leaching need to be taken into account. Similarly, specific gravity (C.R. Levy, 1973; Lindgren and Eslyn, 1961; Rothrock, Smith and Lindgren, 1961; Hoffmeyer, 1976) has been shown to more than halve in decayed wood (Hoffmeyer, 1976) but has no real advantage over weight loss as a criterion of decay.

Significant losses in certain strength properties of wood can develop more rapidly than losses in weight (Hartley, 1958). Loss in tensile strength has been investigated in relation to decay by Hopkins and Coldwell, 1944; Theden, 1953; Kennedy and Ifju, 1962; Brown, 1963; Wilson and Ifju, 1965; Richardson, 1968; D.N.R. Smith, 1970; Bravery and Grant, 1971, and Hoffmeyer, 1976. Hoffmeyer (1976), looking at salt-treated poles, found that a 5% weight reduction resulted in a 50% reduction in tensile strength whilst the modulus of elasticity decreased by only 15-25%. In the same study a 5% weight/weight reduction resulted in a 15-25% decrease in compression strength. More commonly, strength has been measured by static bending and impact bending tests

(Gohre, 1955; Trendelenburg, 1940; Zycha, 1964, Sharp and Eggins, 1968; Armstrong and Savory, 1959; Liese and Ammer, 1964; Kirk and Schulz-Dewitz, 1968; Scheffer, 1936; Henningsson, 1967; Walchli, 1969; Bravery and Lavers, 1971; Cartwright, Campbell and Armstrong, 1936). Using impact bending tests on small samples of beech exposed to soft-rot organisms in monoculture, Liese and Ammer (1964) found that impact bending strength (toughness) decreased with increasing weight loss and was especially sensitive up to 5% loss in weight. For the same weight loss Paecilomyces caused a greater loss in strength than did Chaetomium globosum. Similarly, Henningsson, (1967), investigating changes in impact bending strength in birch following fungal attack, found that samples with a negligible weight loss suffered substantial losses in strength. For high weight losses, brown rot fungi caused more strength loss than did white rot fungi, but at low weight losses the reduction in strength was similar. Chaetomium globosum also caused a marked reduction in toughness with little weight loss.

Armstrong and Savory (1959) are among those who have used both static bending tests and impact bending tests to compare loss in bending strength with loss in toughness. They examined the effects of a white rot (Coriolus versicolor), a brown rot (Coniophora cerebella) and a soft-rot organism (Chaetomium globosum) on beech. All 3 fungi caused a rapid loss in toughness for a comparatively small loss in weight. In fact the toughness of beech infected with C. globosum was reduced by 50% for a 2% loss in weight. They found that loss in bending strength was more gradual and was not significant until definite losses in weight were evident.
More recently, Bravery and Lavers (1971) carried out

static bending tests on miniature test beams exposed to basidiomycete monocultures. From their data they calculated the modulus of rupture, modulus of elasticity, work to maximum load (a measure of toughness) and total work. Only work to maximum load was found to be more sensitive to decay than weight loss, modulus of elasticity being the least sensitive.

Some of these strength tests are advantageous in that they are more sensitive to decay than is loss in weight. The obvious disadvantages of all of them are the requirement for sophisticated equipment, the need for high quality samples and the fact that they are destructive - once tested samples cannot be re-incubated and re-tested. Perhaps the biggest drawback is the fact that all of the tests rely on undecayed samples as their estimate of 100% strength. This inevitably results in errors and the need for well-matched samples and many replicates. To overcome this, use has been made of a modified static bending test (Mateus, 1954, 1957). This differs from conventional tests in that the beams are not loaded to failure but deflected under a constant load. Mateus (1957) used such a system to record deflection with time during the course of decay by basidiomycete monocultures. He claimed that deflection (essentially modulus of elasticity) was more sensitive to decay than was weight loss. However, in comparative tests Bravery and Lavers (1971) found that significant weight losses developed much earlier than losses in modulus of elasticity with Coniophora cerebella and, considering the greater number of replicates and more careful measurement required, found that Mateus' method was not advantageous. However, they were only testing beams once and conceded that if repeated deflection

measurements were made on individual beams increased deflection would indicate fungal attack of the wood. Bravery and Lavers (1971) also compared the accuracy of the simple Mateus static bending test with that of a more sensitive and accurate universal strength testing machine. They found that under the conditions of the test there was no significant difference between the two machines. More recently, Baines (1982) and Vinden et al (1982) have used this type of test to observe decay of stakes in the soil bed.

Another method of assessment which can be used in the laboratory is that of respirometry. Methods measuring carbon dioxide evolution (Klingstrom, 1965; R.S. Smith, 1967; R.S. Smith and Wilson, 1967) or oxygen consumption (Damaschke and Becker, 1965; Halabisky and Ifju, 1968) permit rapid, repeatable evaluation of fungal attack but are restricted in their use by their requirement for sophisticated apparatus.

A totally destructive assessment technique is one used by Henningsson (1967) in a comparison of methods. He measured the solubility of decayed samples in dilute sodium hydroxide and found that although the alkali solubility of brown rotted birch increased steeply during decay, the solubility of the white and soft rotted wood tested increased only slightly or not at all. With a similar sort of approach, Zycha (1964) made visual observations on macerated fibres.

Visual assessment is a common method of assessing decay in the field (Anon, 1972, ASTM D 1758-74) and in the laboratory (Duncan, 1965). Although various systems differ they all endeavour to classify the stages of decay. A number is given to each class and average values can be found in the usual way.

A similar system is that of soft-rot degree (S.R.D.) (Hoffmeyer, 1976). The appearance of a cross section of wood under the microscope is classified according to the severity of soft-rot attack. This method has been used extensively in the examination of soft-rot in salt-treated poles in Scandinavia, and has been shown to correlate well with specific gravity and strength measurements (Hoffmeyer, 1976). One advantage over weight loss is that the original weight of the specimen is not required.

Other methods for looking at decay in poles are the poking method (Sorsa, 1973), knife method (Henningsson and Nilsson, 1976 b). Shigometer (Shigo, 1974) and use of the Pilodyn (Friis-Hansen, (1980). Measurements with the Pilodyn have been shown to give a close correlation to density and therefore decay (Leightley, 1982 b) and not to require corrections for moisture content (Friis-Hansen, 1980). In contrast, the knife and poking methods are affected by the moisture content of the pole (Friis-Hansen, 1976; Henningsson and Nilsson, 1976). The use of the Pilodyn in the assessment of graveyard stakes, however, has been shown to be very sensitive to stake moisture content (Hedley, 1982). It is thought that this effect is masked in pole examination by use of a more powerful Pilodyn.

2.3.2 Selection of Method of Assessment

2.3.2.1 Introduction

As has been pointed out before, the selection of the method of assessment and the method of test goes hand in hand, and this is in fact how the selections were made in the work described here. The choices were governed by the type of information required from each test category (basidiomycete monoculture, soft-rot monoculture, soil burial, soil-bed, cooling tower), and this will be dealt with briefly here.

2.3.2.2 Monoculture and Soil Burial Tests

The objective of these tests was to establish rapidly comparative toxicity data on the formulations which were in line with current standard techniques (EN 113, 1982). Since toxic values have been found to change with incubation time (Bravery, 1979; Butcher and Nilsson, 1982) an exact interval is specified after which the test is no longer comparable with standard techniques, nor with other similar tests of shorter duration. The method of assessment, therefore, does not need to be non-destructive. Suitable quantitative techniques include weight loss and the various strength tests. Mateus' method (1957) has been found to be no more sensitive to basidiomycete decay than weight loss (Bravery and Lavers, 1971) and the extra sample preparation and measurement is therefore unnecessary. Another advantage of this technique lies in its non-destructive quality which would be of no advantage in these tests. The other strength tests (e.g. impact bending strength) require rigorous sample matching and preparation since strength properties are particularly sensitive to defects and the 100% strength value is based on that of matched, unexposed samples. Taking all these factors into consideration, loss in weight was selected as the most appropriate, simple, reliable criterion of decay. In addition, visual and microscopical observations were made whenever possible.

2.3.2.3 Soil-bed

The soil-bed is a comparatively recent addition to methods of testing preservative treated wood (Forest Research Institute, 1978) and, as yet, there are no standard tests with defined conditions and exposure

periods. It is used as a sort of "accelerated field simulator" (Johnson, Thornton and Greaves, 1982) and the wood samples very much resemble those used in field trials (Forest Research Institute, 1978). To resemble the field situation the methods used for assessing the stakes should be non-destructive and cause as little disturbance to the soil microflora as possible. Visual assessment is the obvious choice here and has been used by Hedley (1980). But for the inexperienced, a more objective quantitative assessment is required, such as that of Mateus (1957). The advantages of this method for soil-bed studies are:

(1) miniature stakes are suitable
(2) comparative measurements can be made over an extended period of time
(3) little disturbance of the soil is required
(4) the method is more sensitive than weight loss to decay by soft-rot fungi (Baines, 1982) and can give an earlier indication of decay
(5) it is insensitive to stake moisture content above fibre saturation point (Findlay, 1975)
(6) the test yields quantitative data
(7) stake preparation is not as critical as for other strength tests (Bravery and Lavers, 1971)
(8) measurements are rapid
(9) the apparatus is inexpensive
(10) loss in strength is relevant to the trials.

For these reasons Mateus' method of assessment was selected and, in addition, weight loss and visual and micropical observations were made.

2.3.2.4 Cooling Tower

The objective of the cooling tower exposure was to see how the formulations stood up to the severe leaching conditions and soft-rot hazard encountered in running water. To accelerate this process the block size was reduced. Ideally the trial should have been continued for a longer period of time, being monitored at intervals. Since this was not possible, a simple destructive assessment technique was suitable. Weight loss, as used by Irvine, Eaton and Jones (1972), was selected. It can be argued that there was a need for a microscopical examination but if decay in water cooling towers occurs in the wood surface layers which are later removed by the action of the water then much of the decayed material will be absent, giving a false picture. Loss in weight was therefore selected as the criterion of decay although visual observations were also made.

2.3.3 Determination of Weight Loss

The percentage weight loss of a specimen can be calculated from:

$$\frac{\text{original oven dry weight - final oven dry weight}}{\text{original oven dry weight}} \times \frac{100}{1}$$

The original oven dry weight was found for untreated material simply by drying the specimen in an oven at 105°C for 24 hours, cooling in a dessicator and weighing. However, since oven drying was thought to adversely affect treated wood and boron is lost during oven drying, this method could not be used. Several other methods were tried:

(1) The treated blocks were conditioned and one set was oven dried. The moisture contents were calculated and from these the oven dry weights of the test blocks were worked out. The problem with this method was the need for extra blocks and the conditioning. Blocks from each treatment concentration had different moisture contents.

(2) The oven dry weights were found before treatment. From the preservative uptakes the weight of preservative solids was found and added to the untreated oven dry weight. The disadvantages of this method were the calculations that had to be made for each specimen and the fact that no account was taken of leaching or over-absorption.

(3) The oven dry weights of all of the blocks were found before treatment. The weight changes due to preservative treatment, leaching, agar uptake, etc., were found in "sterile control" blocks. The weight changes in the test blocks were corrected for the mean weight change in the corresponding "sterile controls".

Method 3 was used in the main tests. All blocks were warm water leached in a soxhlet apparatus for 24 hours after exposure to remove any soluble matter and fungus due to diffusion and decay.

2.3.3.1 Toxic Values

A minimum weight loss of 3% (after correction) was taken as being significant (EN 113, 1982).

2.3.4 Deflection Testing

2.3.4.1 Apparatus

The available static bending apparatus (Mateus, 1957) was not suitable for the soil-bed studies since it was designed for testing very small stakes (82x5x5 mm), its use is time consuming and it is subject to great error. Therefore a static bending machine was built for the

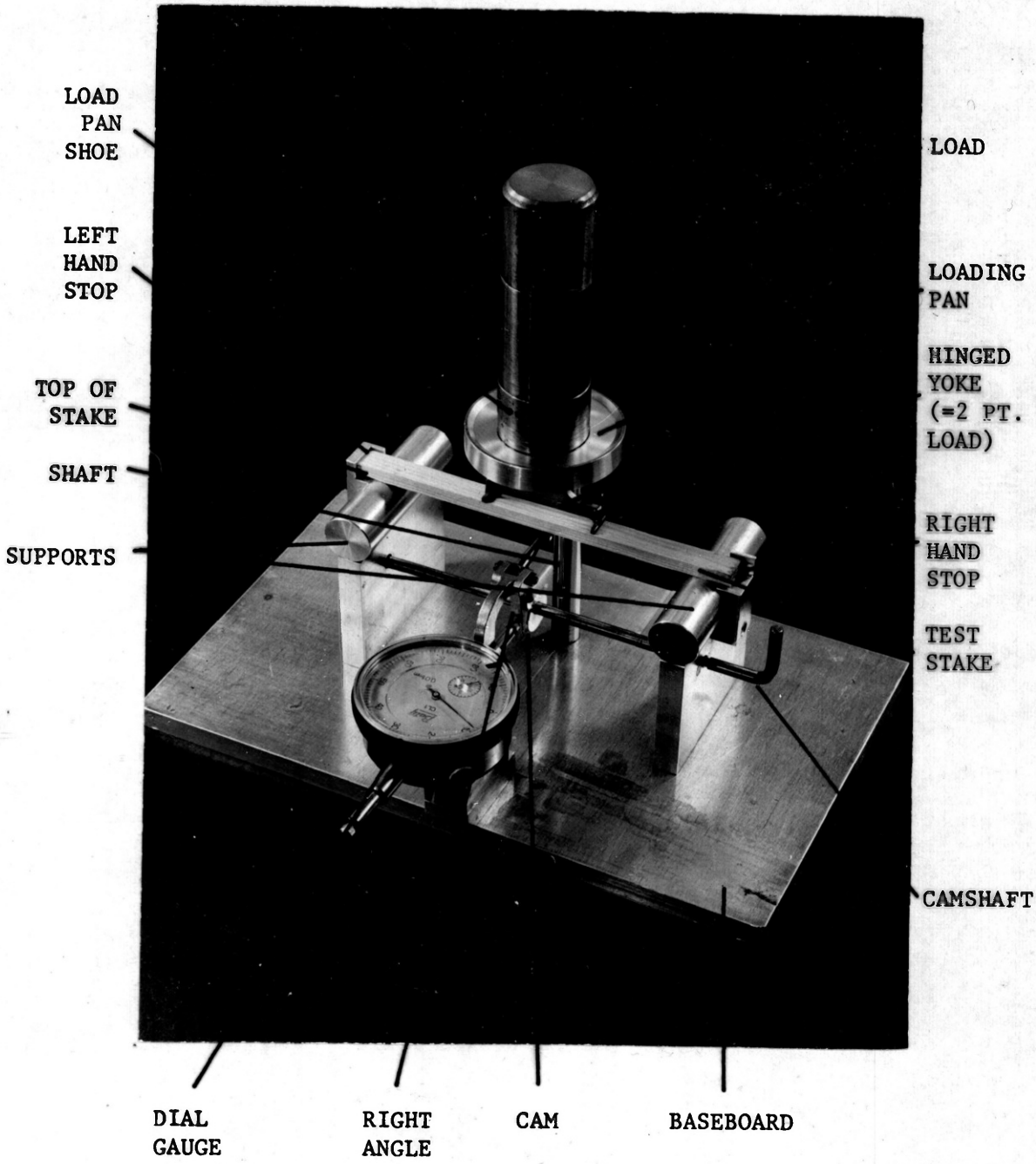


PLATE 6

DEFLECTION APPARATUS - SEE OVERLAY FOR DETAILS

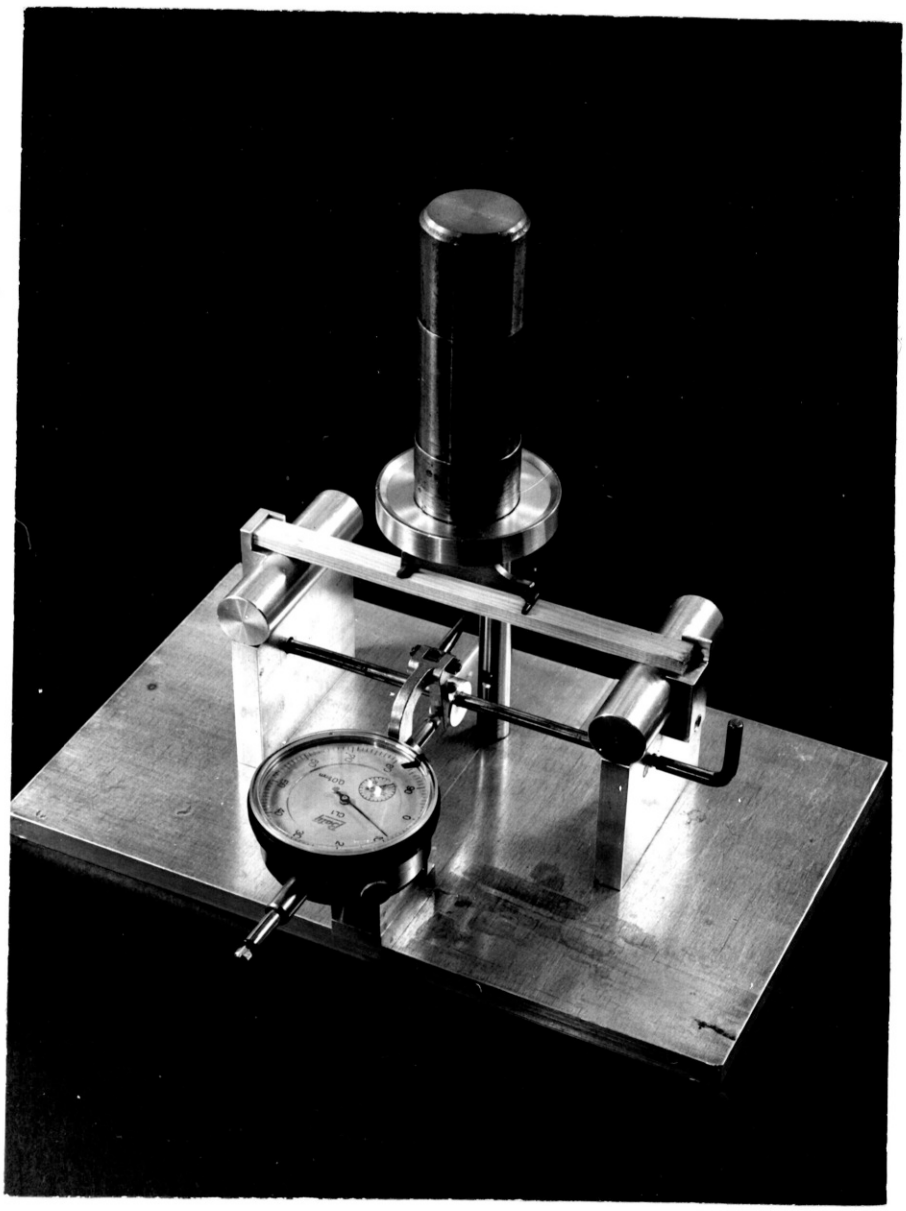


PLATE 6

DEFLECTION APPARATUS - SEE OVERLAY FOR DETAILS

measurement of deflection of soil-bed stakes. This was an opportunity to design the apparatus around a larger stake size which was more suitable for use in the soil-bed. The resulting apparatus is shown in Plate 6. Constructed in "Duraluminium" and brass it consists of:- 2 supports, with a span of 130 mm, which are firmly attached to a baseboard. A shaft supports a moveable loading pan which, through a tongue and groove, can be raised up and turned through 90^{o} out of the way. On the lower side of the loading pan is a hinged yoke which acts as a 2 point load. The distance between the loads is one-third of the span (43.3 mm). Centred between the loads beneath the test beam is a right angle which operates a horizontal dial gauge. The dial gauge reads to 0.01 mm. The right angle can be held away from the beam by means of a cam. (see Plate 6)

2.3.4.2 Procedure

The loading pan was raised up and locked aside. The camshaft was turned to hold back the right angle of the dial gauge. The test beam was placed firmly against the left-hand stop and then the right-hand stop. The loading pan was lowered on to the beam. The cam was turned. The bench was tapped to settle the apparatus. The dial gauge was zeroed. A 1,000 g cylindrical weight was positioned in the shoe of the loading pan. The beam was bent. The bench was tapped. The reading was taken from the dial gauge. The loads were removed and the stake was returned to the soil-bed.

The stakes were always placed with their tops to the right-hand stop and the label facing upwards. There were two reasons for this:

(1) the deflection was always measured at the same point.

(2) if any part of the stake were below fibre saturation point it would have been the top 1 cm. This would have affected the deflection. But in this position the top 1 cm of stake was beyond the span of the supports.
(c f. Baines (1982) where stakes were buried to half their length and deflected over all of it).

2.3.4.3 Testing the Apparatus

To ensure that the machine was operating below the limit of proportionality, i.e. that the deflection was proportional to the load applied, a test was carried out. With a saturated undecayed beam in position several different loads were applied and the corresponding deflections noted. Deflection was plotted against load in figure 2.

2.3.4.4 Calculation of Residual Strength

The modulus of elasticity for a beam under 4 point loading below the proportional limit is given by:

$$E = \frac{Pa\,(3l^2 - 4a^2)}{24y\,\frac{bh^3}{12}}$$

where E = modulus of elasticity, a = distance from support to a load point, l = span, b = width of beam, h = depth of beam, y = deflection and P = load. (Brown, Panshin and Forsaith, 1952).

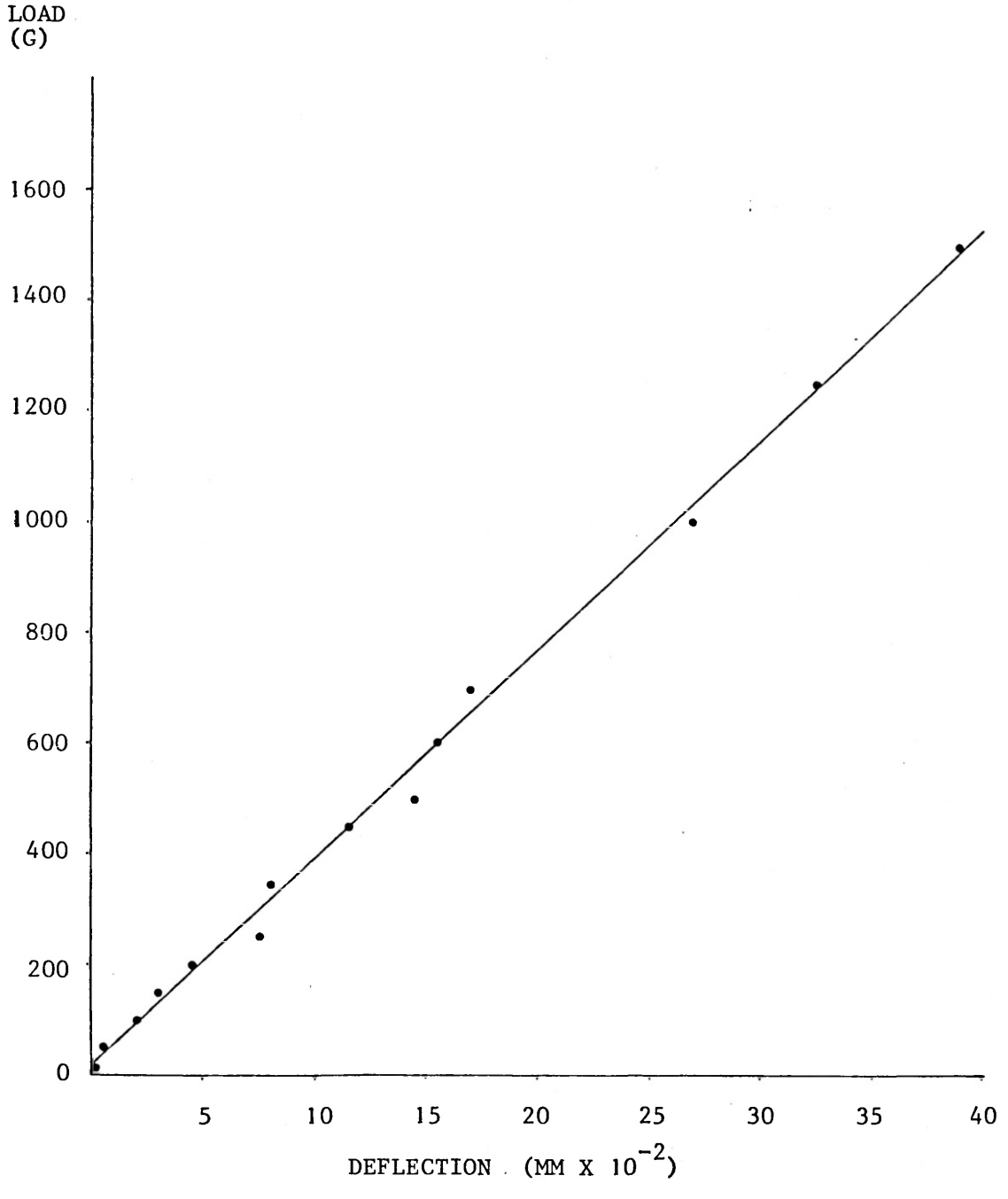
It can be seen that the only variable in the formula for any one stake between measurements is y, the deflection. Thus, without calculating the original modulus of elasticity, a value can be obtained for expressing the % original modulus of elasticity (= % residual strength) after time t from the following:

$$\frac{yo}{yt} \times 100 = \% \text{ residual strength}$$

2.3.4.5 Toxic Values

A minimum loss in strength of 20% (i.e. a residual strength of 80%) was taken as being significant (Bravery and Lavers, 1971).

FIGURE 2 TEST OF BENDING APPARATUS FOR RESPONSE TO LOAD



2.4 Preservative Treatments

2.4.1 Materials

2.4.1.1 Wood Samples

2.4.1.1.1 Selection of Timber Species

Birch (Betula pendula) and Scots pine (Pinus sylvestris) sapwood was selected for the present investigations. These species were considered to be most suitable for the following reasons:

(i) they represent a hardwood and a softwood respectively.

(ii) they are both naturally perishable.

(iii) both are permeable to fluids and are therefore effectively treated by vacuum-pressure impregnation - this was important as it was the preservatives and not the method of treatment which were under test (section 2.2.2.2).

(iv) they have been widely used in research programmes and there is a variety of relevant data in the literature.

(v) when conventionally treated they represent a good performer (Scots pine) and a poor performer (birch) against the soft-rot hazard.

In the past beech (Fagus sylvatica) has been used as the reference hardwood species and is still included in the European Standard (EN 113, 1982). However, in soft-rot studies it has given variable results on occasion (Ofori, 1977).

Birch is becoming the established research tool for studying the soft-rot problem (Bravery, 1981; Butcher, 1981b; Dickinson, 1980; Dickinson, 1976; Nilsson, 1981) and was preferred to beech for the present purpose.

2.4.1.1.2 Timber Origins

Standing trees were examined by increment borer for sapwood yield, growth ring depth, resin and soundness. Sound, resin-free, slow-grown trees (with 2.5 to 8 annual rings per centimetre in Scots pine and 2 to 6 in birch) were felled, converted and kilned within 3 days to ensure that the timber remained free from bluestain organisms and other pests. In conversion the heart was "boxed" and the timber quarter-sawn to give the maximum sapwood yield. This method of obtaining the timber was essential for ensuring that the test blocks were free from chemical, from anti-stain treatments and biological contamination. The alternative was to purchase sawn timber and to machine off the outer layers to remove any anti-stain treatments. However, since boron is frequently used in such treatments and is readily diffusible, this practice was rejected as any remaining boron would interfere with the formulations to be tested.

2.4.1.1.3 Preparation of Test Blocks

The timber was sawn into strips and planed to thickness before cross-cutting to give test blocks of dimensions: 30x15x5, 50x25x15 and 150x10x5 mm for use in monoculture, cooling tower and soil-bed respectively. The specimens were orientated so that the longest dimension was along the longitudinal axis of the wood, the larger face was in the radial longitudinal plane and the smaller face was in the tangential longitudinal plane.

The sawdust was retained for later experiments. Blocks with knots, wavy grain, resin pockets or any other imperfections were rejected. All blocks were lightly sanded with 120 grade glass paper before use.

2.4.1.2 Preservatives

The basic wood preservative used was a waterborne copper chrome arsenic (CCA) formulation made up according to BS 4072 type 2 (1974). The nominal composition was:

35% $CuSO_4.5H_2O$ (cupric sulphate)

45% $K_2Cr_2O_7$ (potassium dichromate)

20% $AS_2O_5.2H_2O$ (arsenic pentoxide or 17% anhydrous arsenic pentoxide AS_2O_5)

This particular formulation was used because:

(i) it is recognised and used worldwide

(ii) there are data on its toxicity and susceptibility to soft-rot

(iii) there are data on its fixation, permanence and microdistribution.

2.4.1.2.1 Preservative Terminology

The other preservatives used were modifications of this basic CCA composition. Their compositions were expressed in terms of CCA equivalents (CCA eq.) for simplicity.

For example, an arsenic solution with a composition of 2% CCA eq. contained the same quantity of arsenic pentoxide as was used to make up a 2% CCA solution.

The composition of the copper chrome boron (CCB) preservative was:

35%	$CuSO_4.5H_2O$	(cupric sulphate)
45%	$K_2Cr_2O_7$	(potassium dichromate)
20%	H_3BO_3	(boric acid)

A 2% CCA eq. solution of CCB contained the same quantities of copper sulphate and potassium dichromate as did a 2% CCA solution. The boric acid replaced the arsenic pentoxide. In a 2% CCA eq. solution of copper chrome arsenic boron (CCAB) there were the same quantities of copper sulphate, potassium dichromate and arsenic pentoxide as in a 2% CCA solution and the same quantity of boric acid as there was in a 2% CCA eq. CCB solution. Stocks solutions of 10% CCA eq. were made up as below:

	CCA	35 g	$CuSO_4.5H_2O$	per litre distilled water
		45 g	$K_2Cr_2O_7$	
		17 g	As_2O_5	
(copper chrome boron)	CCB	35 g	$CuSO_4.5H_2O$	" " " "
		45 g	$K_2Cr_2O_7$	
		20 g	H_3BO_3	
(copper chrome arsenic boron)	CCAB	35 g	$CuSO_4.5H_2O$	" " " "
		45 g	$K_2Cr_2O_7$	
		17 g	As_2O_5	
		20 g	H_3BO_3	
(boron)	B	20 g	H_3BO_3	" " " "
(arsenic)	A	17 g	As_2O_5	" " " "

Serial dilutions were made to give concentrations of: 0.4, 0.6, 0.8, 1.2, 1.8, 2.6, 3.7 or 0.4, 0.8, 1.6, 2.6, 3.7% w/v CCA equivalent.

In some cases double treatments were used; that is, the treatment schedule was run through twice, with two different solutions. The examples of the double treatments were B + CCA and CCB + A (see table 4). In the case of B + CCA a boron treatment was followed by a CCA treatment and in the case of CCB + A a CCB treatment was followed by an arsenic treatment of the same strength (in terms of CCA equivalents).

2.4.1.2.2 Table 4 - Summary of Preservative Treatments

(see following page)

2.4.1.2.2 Table 4 - Summary of Preservative Treatments

CCA	0.33% Cu, 0.59% Cr, 0.41% As → storage (fixation) → drying
CCB	0.33% Cu, 0.59% Cr, 0.13% B → storage (fixation) → drying
CCAB	0.33% Cu, 0.59% Cr, 0.41% As, 0.13% B → storage (fixation) → drying
B + CCA	0.13% B → storage → drying → 0.33% Cu, 0.59% Cr, 0.41% As → storage (fixation) → drying
CCB + A	0.33% Cu, 0.59% Cr, 0.13% B → storage (fixation) → drying → 0.41% As → storage (fixation) → drying

Note: Figures are % element in the 3.7% CCA equivalent treating solution.

2.4.2 Methods

A vacuum-pressure impregnation treatment was used. This was preferred to the vacuum impregnation described in EN 113 (1982) because the differences caused by the preservatives being tested were thought to be subtle differences in detail (e.g. in micro-distribution) which may be related to the method of treatment (Dickinson, Sorkhoh and Levy, 1976).

The treatment process can be described briefly as follows: the selected wood blocks were oven dried at 105°C for 24 hours, cooled in a desiccator, weighed and labelled using waterproof ink. The blocks were loosely arranged in a beaker, ballasted with plastic mesh and glass blocks and the beaker was put into a desiccator where a vacuum of about 760 mm Hg (depending on atmospheric conditions) was drawn and held for 30 minutes. The treating solution was then drawn into the beaker and the pressure returned to atmospheric pressure. Then the beaker was put into a treatment cylinder where it was subjected to a pressure of 10.2 bar (150 p.s.i.) for one hour followed by a soaking period of one hour at atmospheric pressure. The blocks were removed from the treating solution, blotted and weighed wet to establish their preservative uptakes. Whilst still wet the blocks were stored in sealed polythene bags in the dark at room temperature where they remained for two weeks for fixation and conditioning. At the beginning of the third week the blocks were laid out in enamelled trays, whose lids were removed progressively over 7 days, and completely for the fourth week. The blocks were turned at intervals. (EN 113, 1982).

The reason for the slow drying was to minimise redistribution of the preservative elements in the wood. When available, freeze-drying was used for the same purpose, and was preferred as it was less time-consuming, required less space and did not allow the fungal growth on the woodblocks which occurred during the slow drying.

2.4.2.1. Leaching

All wood blocks were cold water leached after the full preservative treatment period. This was carried out as described in BS 5761 Part 2, 1980 (EN 84).

The blocks were impregnated with water under vacuum. After 2 hours the water was changed, the volume being 5 times that of the wood. This volume of water was changed daily for two weeks. The blocks were then air dried in the laboratory for two weeks.

2.4.2.2 Sterilisation

The blocks were packed in heavy gauge polythene "layflat tubing" (Transatlantic Plastics Ltd.) using a heat sealer and were sterilised by gamma irradiation. Gamma irradiation was used in preference to ethylene-oxide-based sterilants, propylene oxide and steam which are all unsuitable for products containing boron (EN 113, annex C, 1982). The tubing was flushed with nitrogen before sealing to minimise the oxygen content and therefore the production of ozone on irradiation. 2.5 megarad were supplied from a cobalt source.

2.4.3.3 Determination of Volume

Since treatments were compared on a preservative retention basis there was a need to establish the individual volumes of the woodblocks. Although the woodblocks were machined accurately, any slight differences in dimensions of the small blocks would result in proportionally large differences in volumes. This is one of the drawbacks of using small blocks. Because woodblock volumes change with moisture content up to fibre saturation point, a wet volume determination was chosen as the most accurate and simple.

The volume of each block was determined accurately by one of two methods. In the first method the blocks were measured in their three dimensions to 0.1 mm using callipers. The second method made use of Archimedes' principle. A beaker of water was put on the balance which was tared to read 0.000 g. The saturated woodblock was pushed onto a mounted needle and submerged in the water. The block then displaced its own volume of water whose weight in g was numerically equal to its volume in ml. Thus the reading on the balance was the volume of the block in cm^3.

The first method could be carried out directly after treatment when the samples were saturated with preservative. However, the second method required that the blocks were submerged in water and so this determination was conveniently carried out during the leaching procedure.

2.4.2.4 Calculation of Preservative Retention

The preservative retentions in the treated woodblocks were calculated as follows:

$$\text{uptake} = \text{wet weight after treatment} - \text{dry weight before treatment}$$

$$\text{net dry salt retention} = \text{NDSR} = \frac{\text{uptake}}{\text{volume}} \times \frac{\text{treating solution}}{100} \ (\text{kgm}^{-3}).$$

The retention expressed as a percent weight of preservative per weight of wood material was calculated as follows:

$$\frac{\text{net dry salt retention}}{\text{wood density}} \times 100 \quad (\%\ \text{wt./wt.})$$

Since the proportions of Cu, Cr, As and B in the formulations were 8.91%, 15.91%, 11.08% and 3.50% respectively, the elemental contents of the wood were as follows:

$$\%\ \text{w/w Cu} = \frac{8.91}{100} \times \frac{\text{NDSR}}{\text{density}} \times 100$$

$$\%\ \text{w/w Cr} = \frac{15.91}{100} \times \frac{\text{NDSR}}{\text{density}} \times 100$$

$$\%\ \text{w/w As} = \frac{11.08}{100} \times \frac{\text{NDSR}}{\text{density}} \times 100$$

$$\%\ \text{w/w B} = \frac{3.50}{100} \times \frac{\text{NDSR}}{\text{density}} \times 100$$

2.5 Conclusions

The choice of basidiomycete test was relatively simple because of the wealth of experience which has been gained with the use of this long-established technique. Therefore, in this case, a single method was used with confidence. On the other hand, the choice of soft-rot test was much more difficult since many of the parameters influencing soft-rot are as yet unknown. We are still a long way away from an accepted standard method of test. In view of this it was decided to take several approaches from those currently being used to assess soft-rot performance. The methods of test adopted are summarised in table 5.

(see following page)

2.5.1 - Table 5 - Summary of Biological Tests

Test	Timber	Block Size (mm)	Vessel	No. Blocks per Vessel	No. Replicates	Medium	T°C	Incubation	Support	Method of Assessment
Basidiomycete monoculture	Birch SP	30x15x5	Petri dish	3	6	4% malt agar	22°	6 wks.	plastic mesh	weight loss
Soft-rot monoculture	Birch SP	30x15x5	Petri dish	2	6	6g NH_4NO_3, 2.56 K_2HPO_4, 1.02g $MgSO_4$, 0.25g KCl, 0.001g $FeSO_4$, 0.001 $MnSO_4$, 1.00g glucose, 1 ml trace element soln. l^{-1} → per l^{-1} dw.	C.g. 30° P.f. 25°	6 wks. 8 wks. 12 wks.	agar	weight loss
Soil burial	Birch SP	30x15x5	plastic tray	88	11	unsterile soil (Silwood)	25°	20 wks.	-	weight loss
Soil-bed	Birch SP	150x10x5	water tank	up to 150	10 birch 7 SP	unsterile soil (BRE)	28°	0-400 days	-	loss in bending strength
Water-cooling tower	Birch S Pine	50x25x15 50x25x5	-	-	6	-	19-28° when in operation	16 wks.	string	weight loss

SECTION III: BIOLOGICAL ASSESSMENTS

3. Section III - Biological Assessments

3.1 Introduction

Birch and Scots pine wood samples treated with the water-borne formulations described in section 2.4 were biologically assayed using a range of selected tests (see section 2). The background to the procedures of the tests is given in the relevant paragraphs of section 2. Not all of the combinations of timber species and treatment were tested in each trial. This was the result of two factors: firstly, the treatments were derived as the assays proceeded and, secondly, in some cases there was a limit to the number of samples that could be assayed simultaneously, e.g. in the case of the soil-bed testing. However, CCA and CCB were incorporated into each trial of each test to act as internal standards.

The experimental observations will be dealt with in the same order as used in section 2.

3.2 Basidiomycete Monoculture Tests

3.2.1. Introduction

The purpose of this series of tests was to give an indication of the spectrum of activity of the formulations with regard to brown and white rot fungi.

3.2.2 Method

A miniaturised agar wood block test was used as described in section 2.2.2.3.

The test organisms were:

Coniophora puteana (F.P.R.L. 11E) a brown rot.
Coriolus versicolor (F.P.R.L. 28A) a white rot.
Gloeophyllum trabeum (F.P.R.L. 108E) a brown rot.
Poria placenta (F.P.R.L. 280) a brown rot.

These fungi were selected for the following reasons:

(1) they are representative of brown and white rot fungi.

(2) strains of each of these fungi are the obligatory test organisms for products other than creosote in the European Standard (EN 113, 1982). Although EN 113 specifies the use of *C. puteana*, *P. placenta* and *G. trabeum* for softwoods and *C. versicolor* for hardwoods, all of the fungi were used with both birch and Scots pine.

(3) they possess a tolerance to wood preservatives especially C. puteana and P. placenta to copper (Da Costa and Kerruish, 1964) and G. trabeum to arsenic.

(4) they are all active under laboratory conditions.

Trial no. 1

Test organisms: Coniophora puteana, Coriolus versicolor.

Timber species: Scots pine, birch.

Preservatives: CCA, CCB, CCAB.

Treating solutions: 0.4, 0.6, 0.8, 1.2, 1.8, 2.6, 3.7% w/v CCA equivalent.

Trial no. 2

Test organisms: Coniophora puteana, Coriolus versicolor.

Timber species: Scots pine, birch.

Preservatives: CCA, CCB, CCB + A.

Treating solutions: 0.4, 0.8, 1.6, 2.6, 3.7% w/v CCA equivalent.

Trial no. 3

Test organisms: Gloeophyllum trabeum, Poria placenta.

Timber species: Scots pine, birch.

Preservatives: CCA, CCB, CCAB, B + CCA, CCB + A.

Treating solutions: 0.4, 0.8, 1.6, 2.6, 3.7% w/v CCA equivalent.

The tests carried out are summarised in table 6.

Table 6 - Summary of Basidiomycete Monoculture Tests

Timber	Birch				Scots Pine			
Treatment	Coniophora puteana	Coriolus versicolor	Poria placenta	Gloeophyllum trabeum	Coniophora puteana	Coriolus versicolor	Poria placenta	Gloeophyllum trabeum
CCA	**	**	*	*	**	**	*	*
CCB	**	**	*	*	**	**	*	*
CCAB	*	*	*	*	*	*	*	*
B + CCA	-	-	*	*	-	-	*	*
CCB + A	*	*	*	*	*	*	*	*

* = one test
** = two tests
- + no test

3.2.3 Results

A list of the tables and figures corresponding to each trial will be followed by a description of the main findings for each test organism.

3.2.3.1 Trials

Trial 1. The mean weight losses and their standard errors are given in tables 7 - 10. The data are plotted against treating solution concentration in figures 3 - 6.

Trial 2. The mean theoretical copper retentions and weight losses with their corresponding standard errors are given in tables 11 - 14. The data are plotted in figures 7 - 10.

Trial 3. The mean theoretical copper retentions and weight losses with their standard errors are given in tables 15 - 18. The data are plotted in figures 11 -14. A statistical analysis (analysis of variance) was carried out. The f ratios, least significant differences (L.S.D.) and significant results are given in table 19 for birch and table 20 for Scots pine.

The toxic values obtained from all three trials are given in table 21.

3.2.3.2 Test Organisms

Gloeophyllum trabeum and Coriolus versicolor were controlled at very low concentrations by all of the formulations tested both in Scots pine (tables 10, 14, 18) and birch (tables 8, 12, 16). In both timber species Coniophora puteana was controlled at relatively low concentrations by CCA, CCAB and CCB + A, but decay was virtually unaffected by all of the concentrations of CCB tested (figures 3,5, 7,9).

Poria placenta with Scots pine was not controlled by any of the five formulations (figure 13), that is, no toxic values were established. From the statistical analysis (table 20) CCB was found to be significantly less effective than the other formulations at several of the lower concentrations. The ranking of the treatments varied with concentration. At the 2.6% treating solution there was no statistical significant difference between the preservatives. This concentration formed a crossover point and at the highest concentration CCB was one of the more effective treatments.

Similarly, in birch, Poria placenta was not controlled by any concentration of some of the preservatives (figure 11). Toxic values were established for CCB, CCB + A and B + CCA. Once again, in the statistical analysis (table 19), the 2.6% treating solution was a crossover point and there was no significant difference between the treatments. At lower concentrations CCB was often found to be less effective than the other preservatives. Again, as in the case of Scots pine, the ranking of the formulations varied with concentration.

Table 7 -

Mean Weight Losses in Birch Tested Against Coniophora puteana in Trial 1

Treatment	Concentration % CCA Equivalent	Mean Wt. Loss %	Standard Error
U	-	31.48	1.21
CCA	0.4	4.00	1.84
	0.6	-0.78	0.15
	0.8	-0.69	0.12
	1.2	-1.13	0.10
	1.8	-1.26	0.12
	2.6	-1.49	0.15
	3.7	-1.43	0.18
CCB	0.4	32.12	1.16
	0.6	29.70	1.69
	0.8	29.86	0.95
	1.2	32.06	1.55
	1.8	30.25	1.23
	2.6	23.25	2.24
	3.7	23.11	3.77
CCAB	0.4	8.17	4.11
	0.6	1.08	0.21
	0.8	1.28	0.26
	1.2	0.30	0.19
	1.8	0.25	0.11
	2.6	-0.12	0.15
	3.7	0.15	0.12

FIGURE 3 PERFORMANCE OF BIRCH EXPOSED TO CONIOPHORA PUTEANA IN TRIAL 1

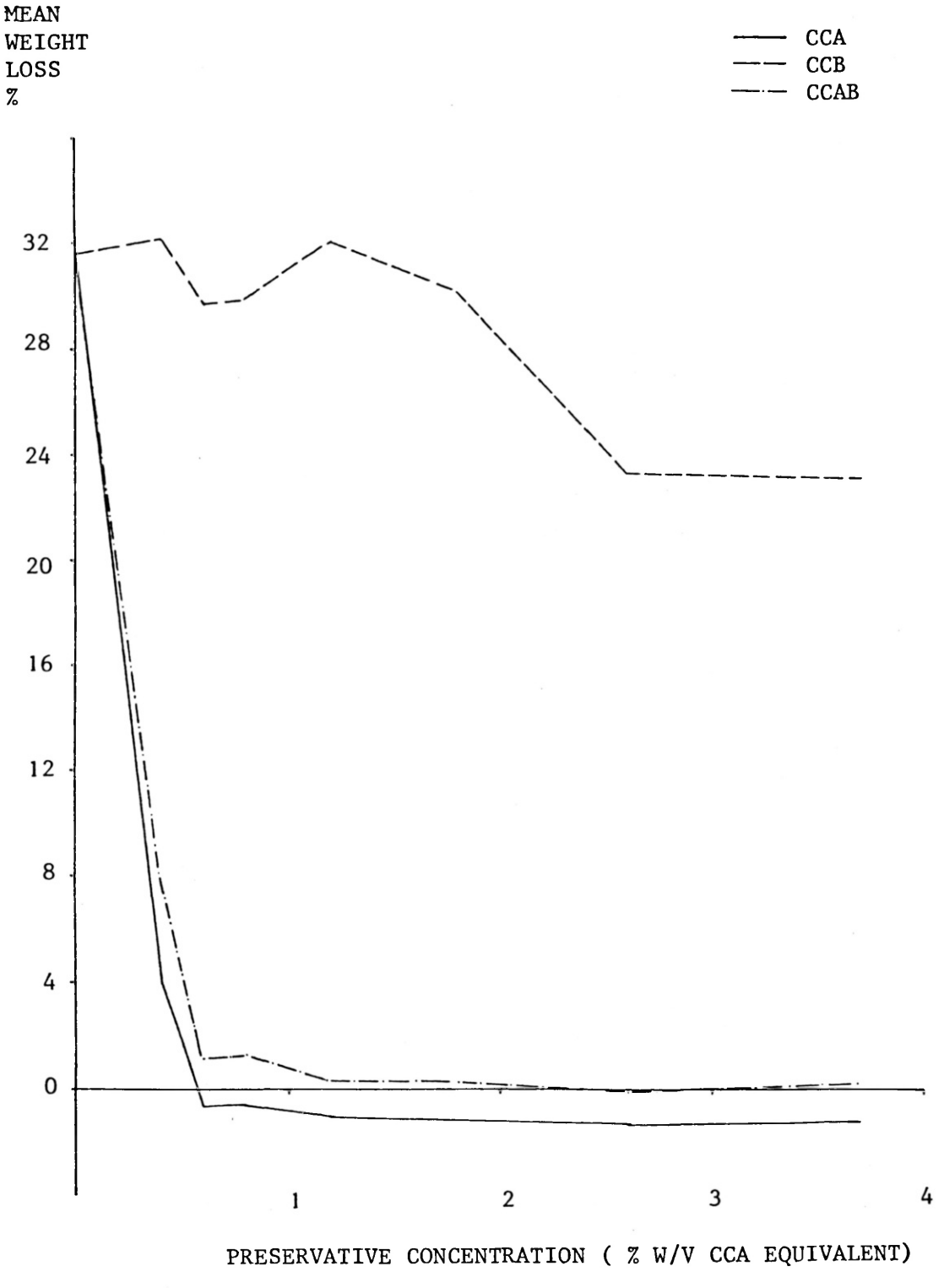


Table 8 -

Mean Weight Losses in Birch Tested Against Coriolus versicolor in Trial 1

Treatment	Concentration % CCA Equivalent	Mean Wt. Loss %	Standard Error
U	-	19.86	1.28
CCA	0.4	5.82	2.24
	0.6	1.15	0.82
	0.8	-0.03	0.39
	1.2	-0.73	0.15
	1.8	-0.81	0.07
	2.6	-0.69	0.13
	3.7	-0.90	0.16
CCB	0.4	6.68	2.23
	0.6	1.30	0.89
	0.8	0.18	0.13
	1.2	0.08	0.28
	1.8	-0.97	0.39
	2.6	-0.11	0.21
	3.7	-0.20	0.15
CCAB	0.4	4.44	1.83
		-0.59	0.17
	0.8	-0.83	0.15
	1.2	-0.47	0.21
	1.8	-1.08	0.10
	2.6	-0.92	0.13
	3.7	-0.89	0.32

FIGURE 4 PERFORMANCE OF BIRCH EXPOSED TO CORIOLUS VERSICOLOR IN TRIAL 1

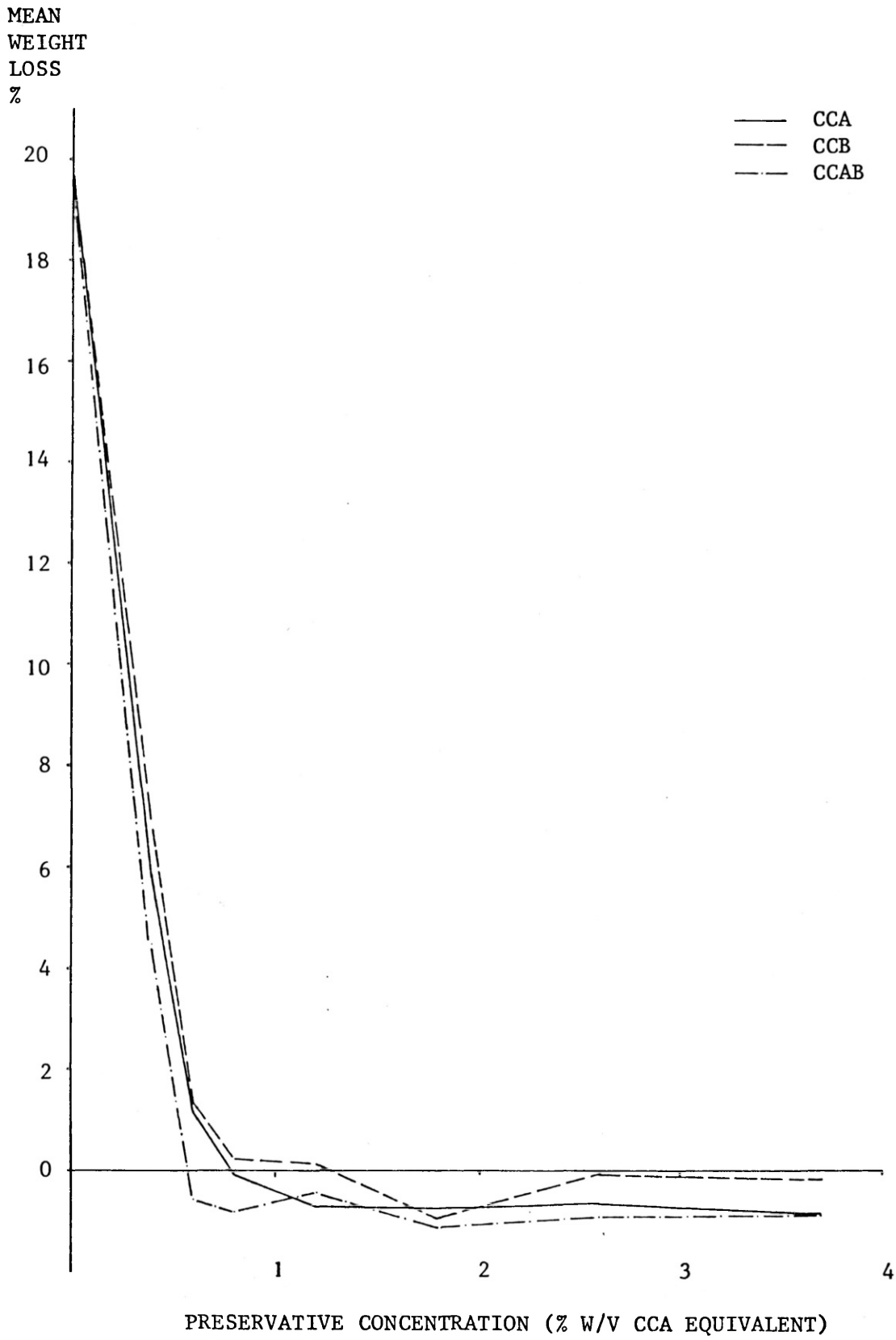


Table 9 -

Mean Weight Losses in Scots Pine
Tested Against Coniophora puteana in Trial 1

Treatment	Concentration % CCA Equivalent	Mean Wt. Loss %	Standard Error
U	-	29.62	1.89
CCA	0.4	0.53	0.17
	0.6	-0.23	0.08
	0.8	-0.33	0.15
	1.2	-0.65	0.06
	1.8	-0.58	0.12
	2.6	-1.22	0.14
	3.7	-1.08	0.08
CCB	0.4	23.46	1.12
	0.6	26.74	1.66
	0.8	25.71	1.07
	1.2	27.03	1.85
	1.8	30.88	1.37
	2.6	26.29	1.34
	3.7	24.53	0.62
CCAB	0.4	1.23	0.38
	0.6	0.77	0.14
	0.8	0.40	0.39
	1.2	-0.22	0.22
	1.8	-0.72	0.30
	2.6	-0.04	0.22
	3.7	-0.55	0.16

FIGURE 5 PERFORMANCE OF SCOTS PINE EXPOSED TO CONIOPHORA PUTEANA IN TRIAL 1

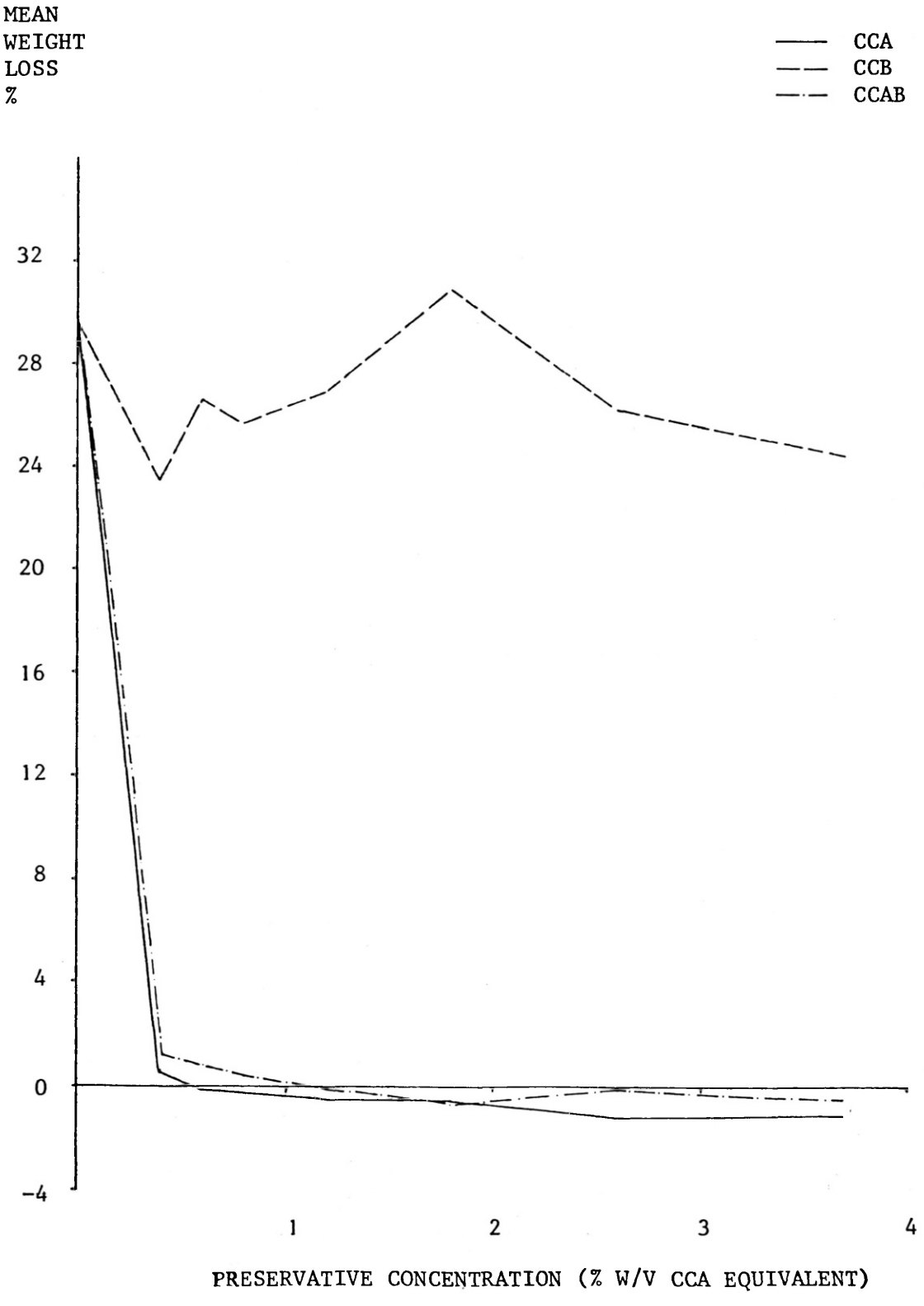


Table 10 -

Mean Weight Losses in Scots Pine
Tested Against Coriolus versicolor in Trial 1

Treatment	Concentration % CCA Equivalent	Mean Wt. Loss %	Standard Error
U	-	12.16	1.70
CCA	0.4	0.55	0.20
	0.6	-0.16	0.12
	0.8	0.33	0.18
	1.2	0.07	0.22
	1.8	0.07	0.13
	2.6	-0.09	0.17
	3.7	-0.01	0.14
CCB	0.4	-0.02	0.28
	0.6	-0.92	0.13
	0.8	-0.79	1.41
	1.2	-0.37	0.56
	1.8	-0.94	0.10
	2.6	-1.44	0.17
	3.7	0.00	0.26
CCAB	0.4	0.46	0.34
	0.6	-0.32	0.30
	0.8	-0.26	0.26
	1.2	-0.64	0.64
	1.8	-0.55	0.55
	2.6	-0.94	0.94
	3.7	-0.52	0.52

FIGURE 6 PERFORMANCE OF SCOTS PINE EXPOSED TO CORIOLUS VERSICOLOR IN TRIAL 1

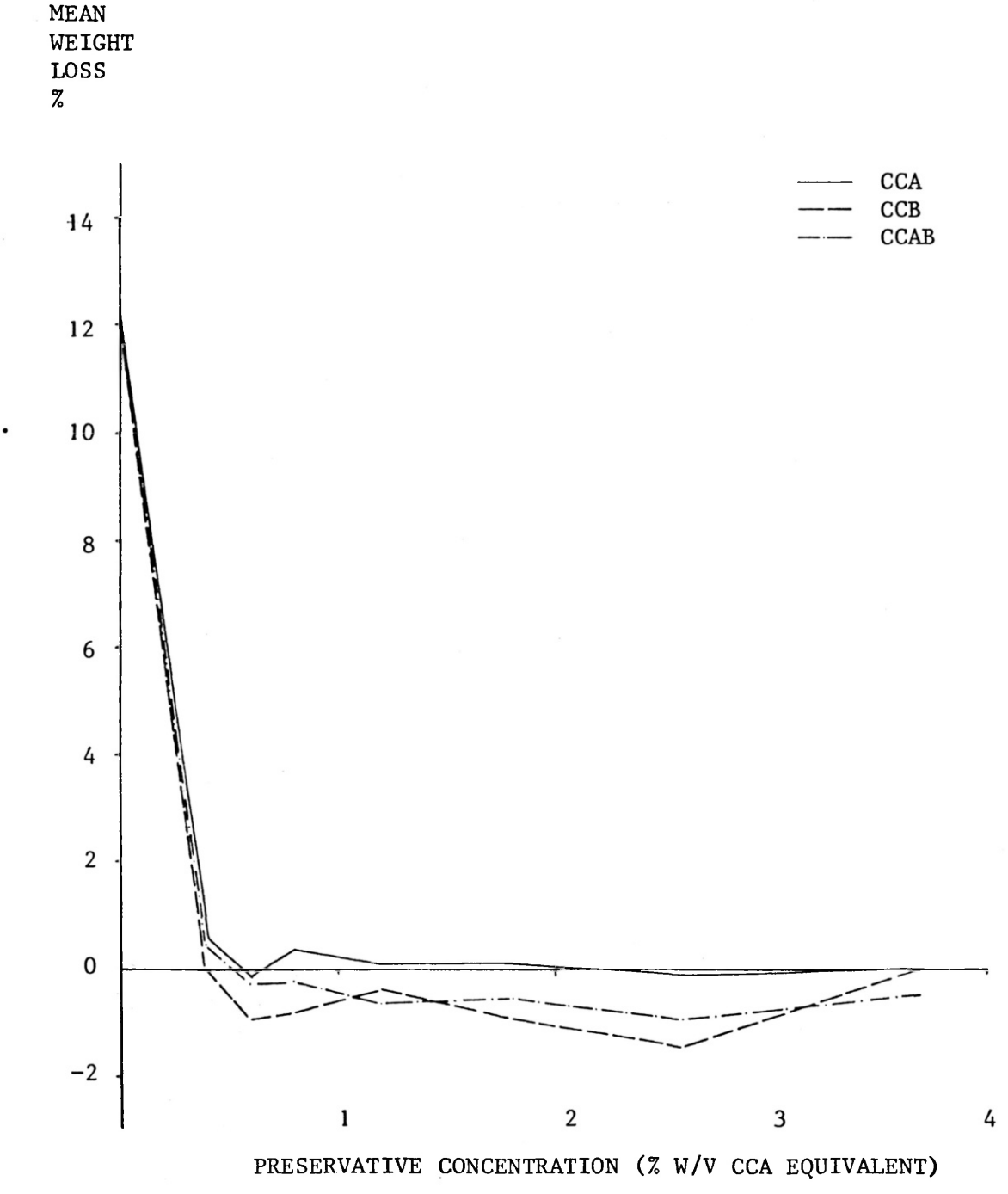


Table 11 -

Mean Copper Retentions and Weight Losses in Birch Tested against Coniophora puteana in Trial 2

Treatment	Mean Copper Retention (kgm^{-3})	Standard Error	Copper Retention (% w/w)	Mean Weight Loss %	Standard Error
CCA 0.4	0.210	0.00	0.033	8.35	1.43
0.8	0.432	0.00	0.069	-2.16	0.04
1.6	0.848	0.01	0.135	0.39	0.52
2.6	1.363	0.01	0.216	-0.05	0.31
3.7	1.980	0.02	0.314	0.33	0.09
CCB 0.4	0.215	0.00	0.034	33.82	0.95
0.8	0.418	0.00	0.066	33.00	1.32
1.6	0.760	0.01	0.121	28.81	2.94
2.6	1.360	0.02	0.216	27.83	1.28
3.7	1.940	0.02	0.308	20.53	2.22
CCB 0.4	0.207	0.00	0.033	37.08	2.94
+ A 0.8	0.417	0.00	0.066	0.48	0.32
1.6	0.763	0.01	0.121	-0.35	0.14
2.6	1.338	0.02	0.212	0.53	0.27
3.7	1.905	0.03	0.302	0.49	0.09
Untreated	-	-	-	34.25	1.44

FIGURE 7 PERFORMANCE OF BIRCH EXPOSED TO CONIOPHORA PUTEANA IN TRIAL 2

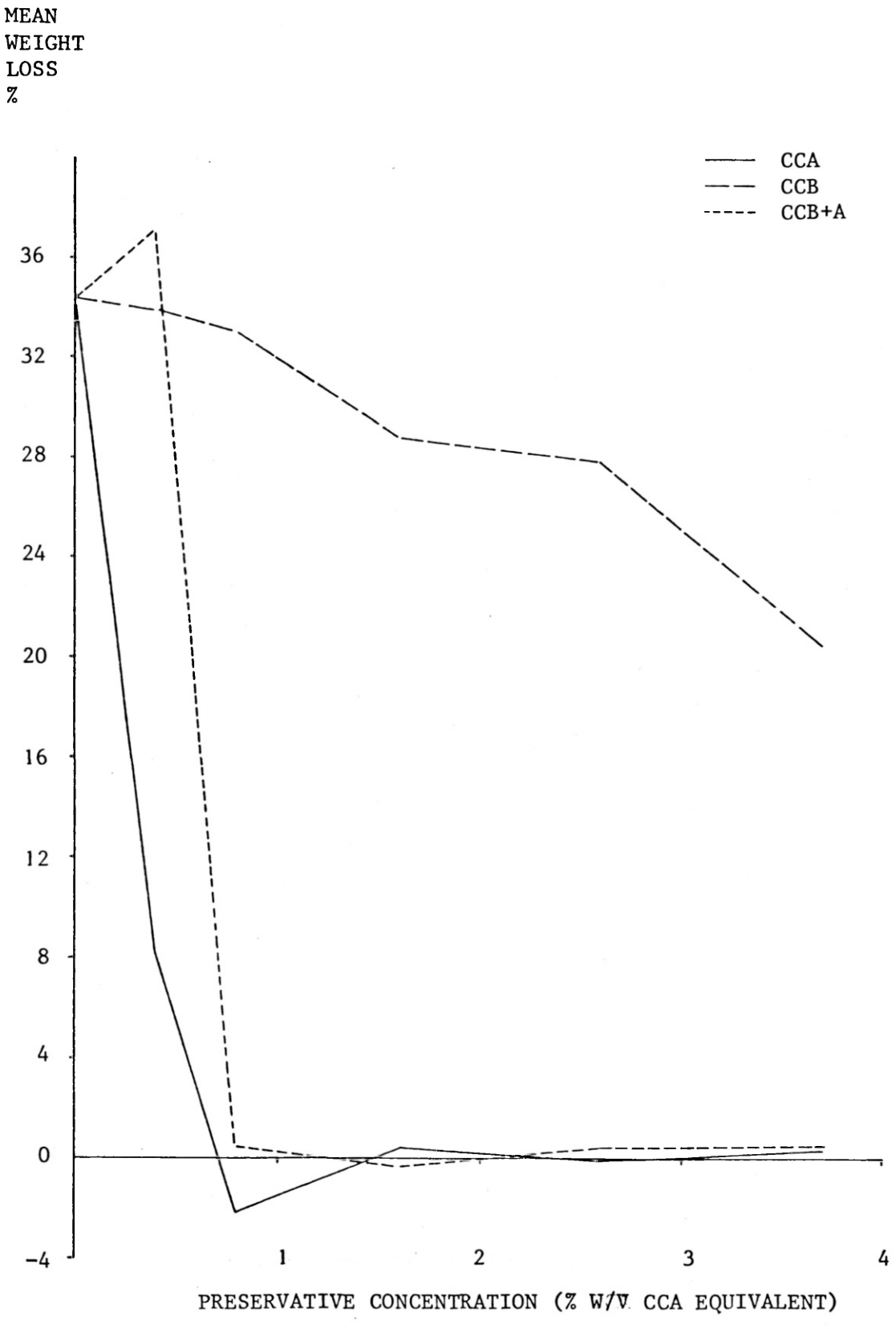


Table 12 -

Mean Copper Retentions and Weight Losses in Birch Tested Against Coriolus versicolor in Trial 2

Treatment		Mean Copper Retention (kgm^{-3})	Standard Error	Copper Retention (% w/w)	Mean Weight Loss %	Standard Error
CCA	0.4	0.207	0.00	0.033	8.35	1.43
	0.8	0.417	0.00	0.066	1.41	0.18
	1.6	0.835	0.01	0.133	-0.42	0.11
	2.6	1.352	0.02	0.215	0.78	0.21
	3.7	2.002	0.07	0.318	-0.04	0.38
CCB	0.4	0.202	0.00	0.032	8.94	1.09
	0.8	0.417	0.00	0.066	0.05	0.20
	1.6	0.770	0.00	0.122	0.46	0.15
	2.6	1.357	0.04	0.215	0.33	0.15
	3.7	1.920	0.04	0.305	0.01	0.17
CCB + A	0.4	0.208	0.00	0.033	4.64	1.91
	0.8	0.422	0.00	0.067	-0.60	0.33
	1.6	0.780	0.01	0.124	-0.23	0.47
	2.6	1.352	0.02	0.215	0.42	0.13
	3.7	1.900	0.02	0.302	0.42	0.40
Untreated		-	-	-	30.83	2.49

FIGURE 8 PERFORMANCE OF BIRCH EXPOSED TO CORIOLUS VERSICOLOR IN TRIAL 2

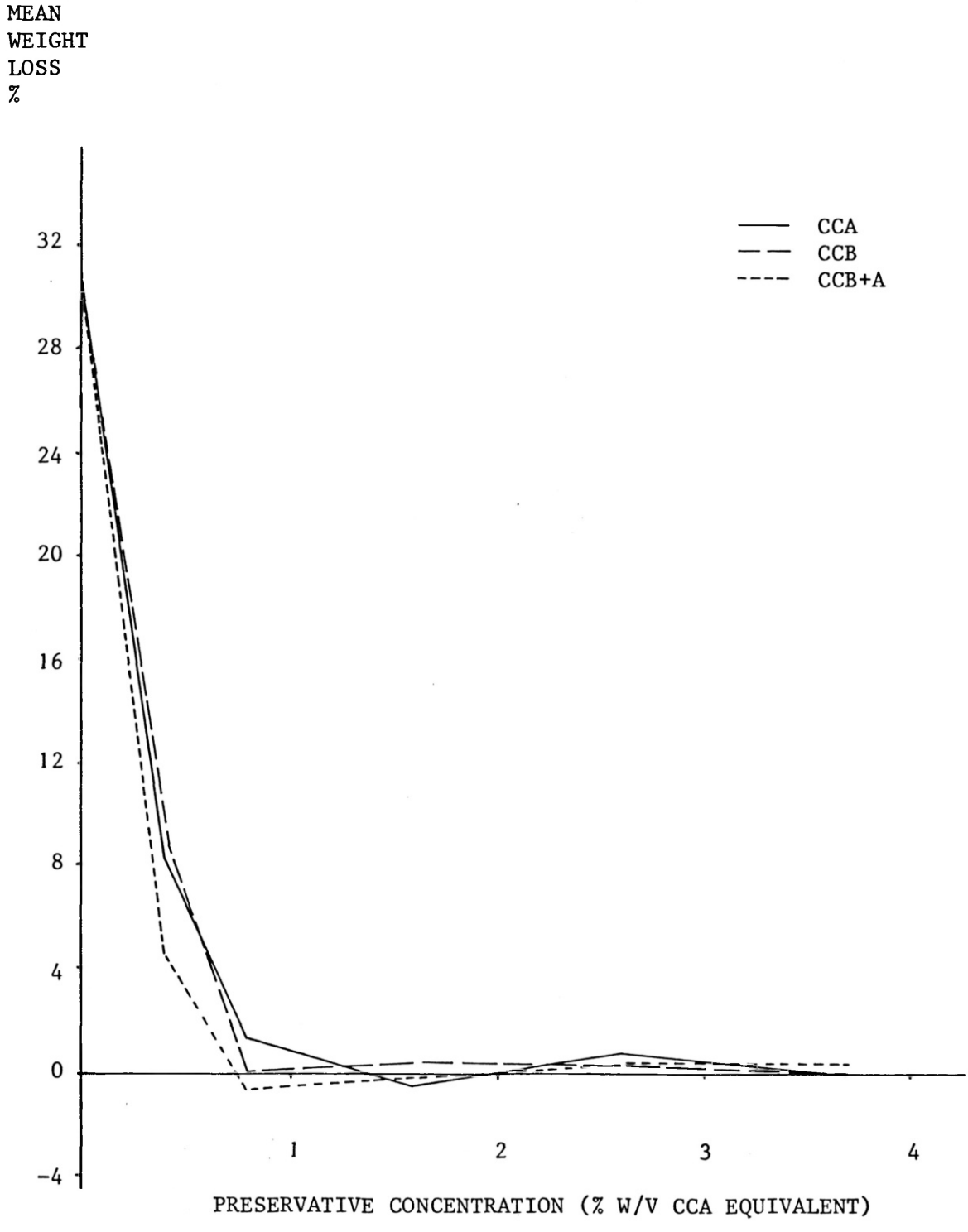


Table 13 -

Mean Copper Retentions and Weight Losses in Scots Pine tested against Coniophora puteana in Trial 2

Treatment		Mean Copper Retention (Kgm^{-3})	Standard Error	Copper Retention (% w/w)	Mean Weight Loss %	Standard Error
CCA	0.4	0.240	0.00	0.057	0.55	0.22
	0.8	0.489	0.00	0.115	0.65	0.22
	1.6	0.832	0.04	0.196	-0.14	0.19
	2.6	1.438	0.02	0.338	0.63	0.16
	3.7	2.048	0.01	0.482	-0.55	0.18
CCB	0.4	0.235	0.00	0.055	29.88	1.21
	0.8	0.477	0.01	0.112	31.46	0.80
	1.6	0.948	0.01	0.223	33.33	0.81
	2.6	1.557	0.02	0.366	34.22	2.13
	3.7	2.213	0.01	0.521	21.02	3.71
CCB + A	0.4	0.235	0.00	0.055	19.42	4.47
	0.8	0.490	0.01	0.115	1.44	0.06
	1.6	0.977	0.01	0.230	-0.51	0.17
	2.6	1.607	0.03	0.378	-0.49	0.16
	3.7	2.265	0.02	0.533	-0.28	0.46
Untreated		-	-	-	32.93	1.93

FIGURE 9 PERFORMANCE OF SCOTS PINE EXPOSED TO CONIOPHORA PUTEANA IN TRIAL 2

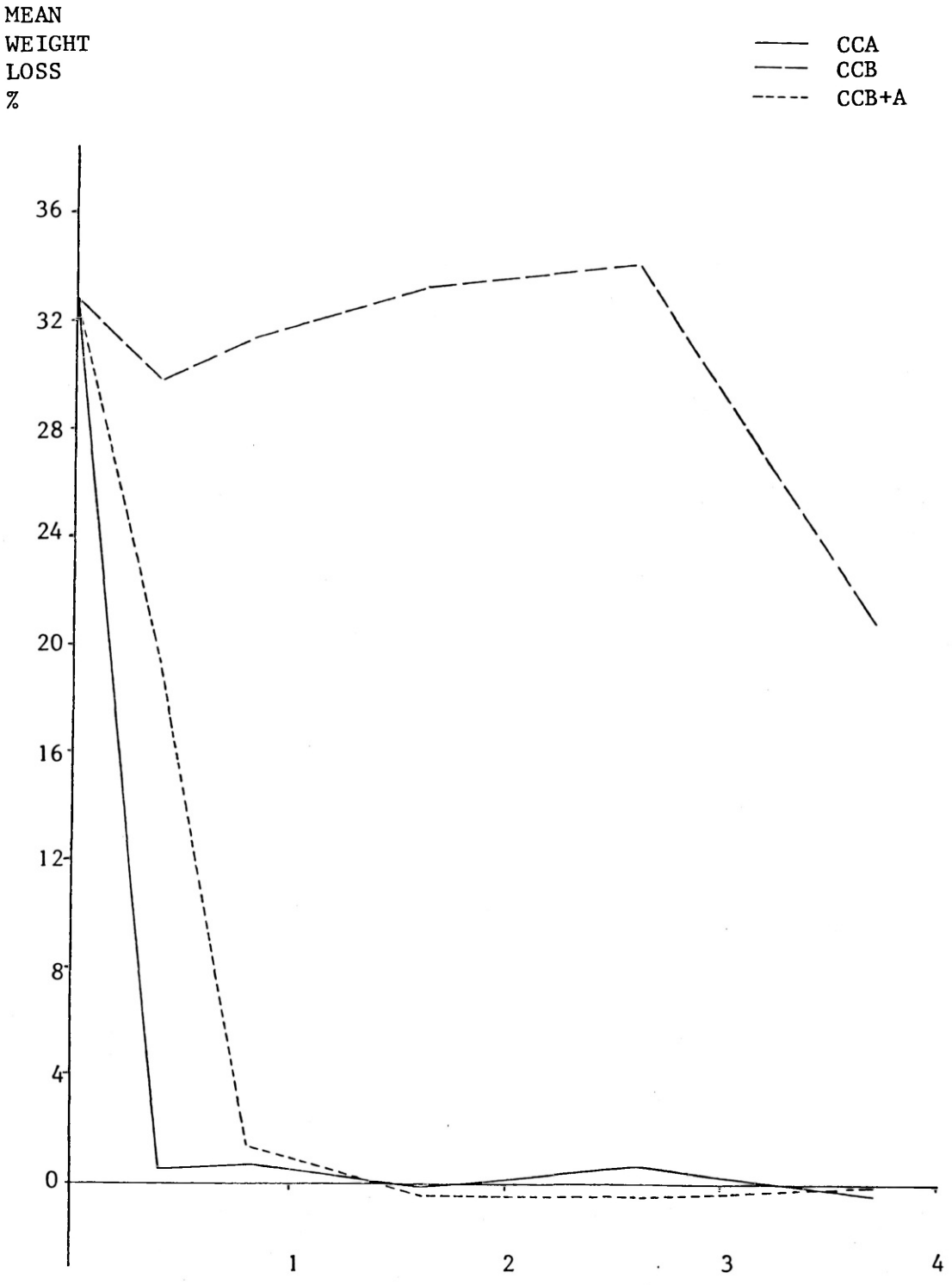


Table 14 -

Mean Copper Retentions and Weight Losses in Scots Pine tested against Coriolus versicolor in Trial 2

Treatment	Mean Copper Retention (Kgm^{-3})	Standard Error	Copper Retention (% w/w)	Mean Weight Loss %	Standard Error
CCA	0.241	0.00	0.057	-0.08	0.11
	0.476	0.01	0.122	-0.18	0.26
	0.857	0.03	0.202	-0.12	0.13
	1.467	0.01	0.345	-0.01	0.15
	2.083	0.02	0.490	0.14	0.25
CCB 0.4	0.227	0.00	0.053	-0.15	0.12
0.8	0.482	0.00	0.113	0.03	0.11
1.6	0.960	0.02	0.226	-0.16	0.27
2.6	1.550	0.02	0.365	-0.42	0.13
3.7	2.228	0.02	0.524	0.14	0.18
CCB 0.4	0.230	0.01	0.054	0.80	0.10
+ A 0.8	0.485	0.00	0.114	1.03	0.16
1.6	0.968	0.01	0.228	0.25	0.17
2.6	1.582	0.02	0.372	1.15	0.21
3.7	2.277	0.01	0.536	-0.38	0.29
Untreated	-	-	-	17.57	1.35

FIGURE 10 PERFORMANCE OF SCOTS PINE EXPOSED TO CORIOLUS VERSICOLOR IN TRIAL 2

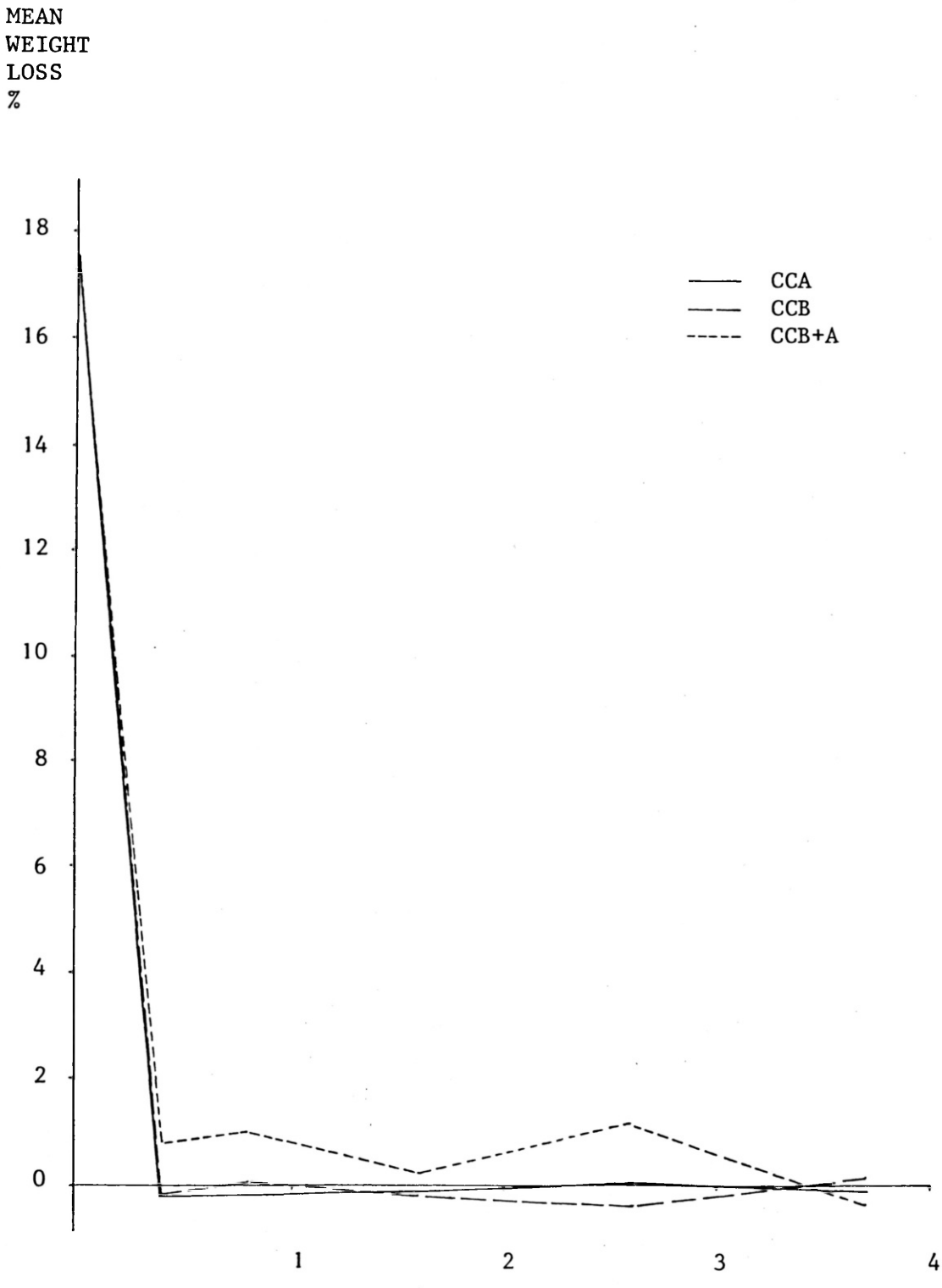


Table 15 -

Mean Copper Retentions and Weight Losses in Birch tested against Poria placenta in Trial 3

Treatment	Mean Copper Retention (Kgm^{-3})	Standard Error	Copper Retention (% w/w)	Mean Weight Loss %	Standard Error
CCA 0.4	.233	0.00	0.045	19.60	1.55
0.8	.465	0.00	0.090	11.78	0.68
1.6	.933	0.01	0.181	7.31	0.65
2.6	1.557	0.01	0.302	4.17	0.32
3.7	2.231	0.02	0.433	3.18	0.55
CCB 0.4	.238	0.00	0.046	22.57	0.65
0.8	.477	0.00	0.093	16.20	0.44
1.6	.926	0.00	0.180	9.06	1.72
2.6	1.553	0.01	0.302	4.39	0.51
3.7	2.203	0.01	0.428	0.29	0.42
CCAB 0.4	.234	0.00	0.045	20.33	1.71
0.8	.470	0.00	0.091	9.01	1.18
1.6	.935	0.00	0.182	5.63	0.77
2.6	1.537	0.01	0.298	3.96	0.68
3.7	2.221	0.02	0.431	3.37	0.24
B + 0.4	.223	0.00	.0452	11.26	2.55
CCA 0.8	.463	0.00	.090	12.43	1.25
1.6	.936	0.00	.182	6.90	1.25
2.6	1.527	0.00	.297	3.24	0.80
3.7	2.221	0.01	.431	1.47	0.31
CCB 0.4	.235	0.01	0.046	17.47	1.18
+ A 0.8	.477	0.00	0.093	10.31	0.72
1.6	.938	0.00	0.182	6.20	0.48
2.6	1.548	0.01	0.301	4.71	0.43
3.7	2.230	0.01	0.433	2.94	0.29
Untreated	-	-	-	26.14	1.58

FIGURE 11 PERFORMANCE OF BIRCH EXPOSED TO PORIA PLACENTA IN TRIAL 3

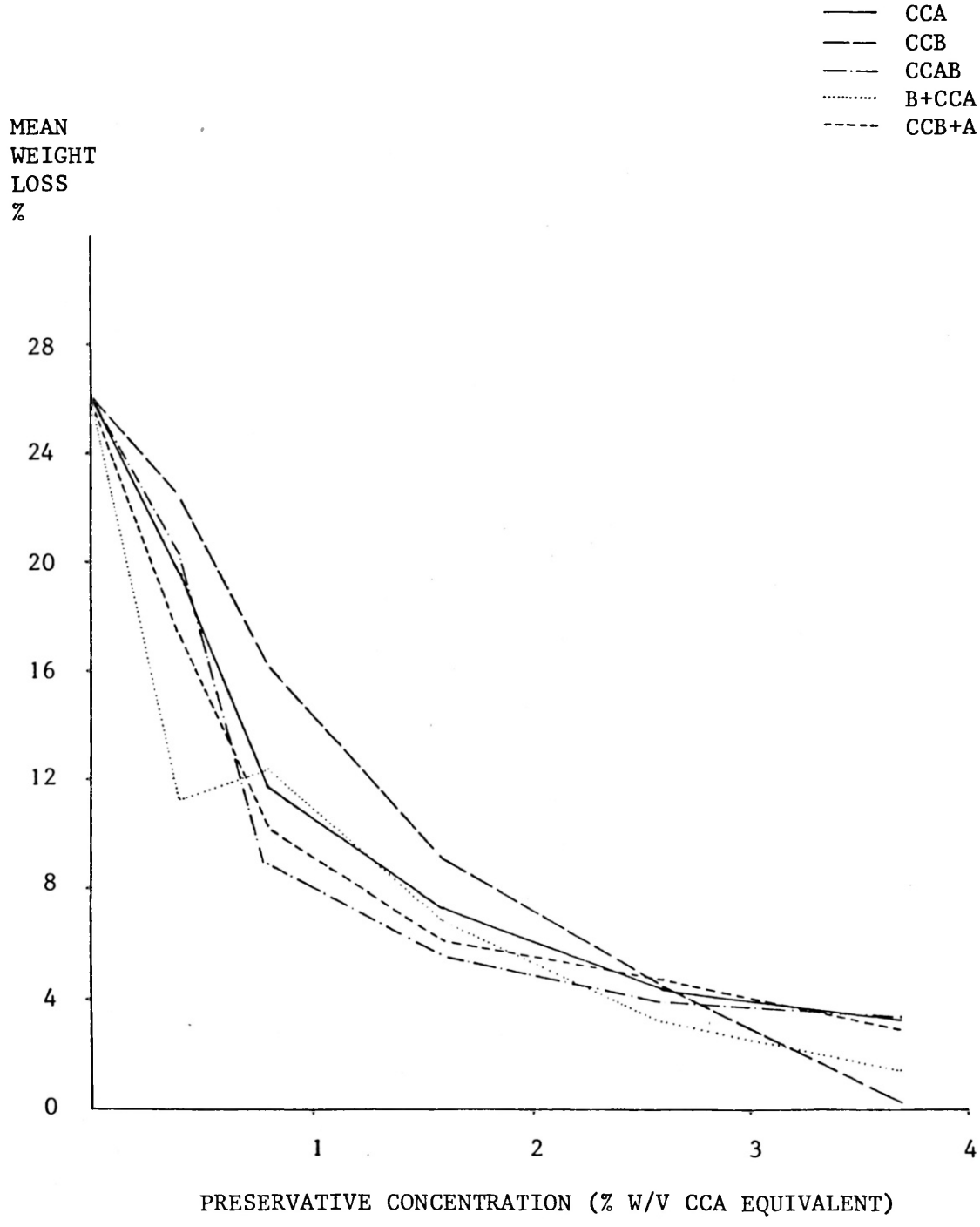


Table 16 -

Mean Copper Retentions and Weight Losses in Birch Tested against Gloeophyllum trabeum in Trial 3

Treatment	Mean Copper Retention (Kgm^{-3})	Standard Error	Copper Retention (% w/w)	Mean Weight Loss %	Standard Error
CCA 0.4	.234	0.00	0.045	-0.08	0.15
0.8	.461	0.00	0.090	0.44	0.17
1.6	.933	0.00	0.181	0.29	0.24
2.6	1.542	0.00	0.299	0.14	0.10
3.7	2.252	0.01	0.437	-0.37	0.11
CCB 0.4	.239	0.00	0.046	0.30	0.09
0.8	.471	0.00	0.092	-0.27	0.08
1.6	.927	0.01	0.180	-0.61	0.18
2.6	1.571	0.01	0.305	-0.62	0.16
3.7	2.225	0.02	0.432	-0.68	0.13
CCAB 0.4	.232	0.00	0.045	0.31	0.12
0.8	.472	0.00	0.092	-0.32	0.11
1.6	.927	0.01	0.180	-0.24	0.12
2.6	1.541	0.01	0.299	0.01	0.14
3.7	2.199	0.02	0.427	-0.19	0.08
B+ 0.4	.234	0.00	.045	0.88	0.63
CCA 0.8	.458	0.01	.089	-0.24	0.08
1.6	.963	0.02	.187	0.39	0.17
2.6	1.535	0.01	.298	-0.19	0.13
3.7	2.234	0.01	.434	-0.59	0.10
CCB 0.4	.232	0.00	0.045	0.37	0.16
+A 0.8	.478	0.00	0.093	-0.30	0.18
1.6	.947	0.01	0.184	0.01	0.22
2.6	1.539	0.01	0.299	-0.15	0.12
3.7	2.200	0.02	0.427	-0.06	0.22
Untreated	-	-	-	23.60	0.70

FIGURE 12 PERFORMANCE OF BIRCH EXPOSED TO GLOEOPHYLLUM TRABEUM IN TRIAL 3

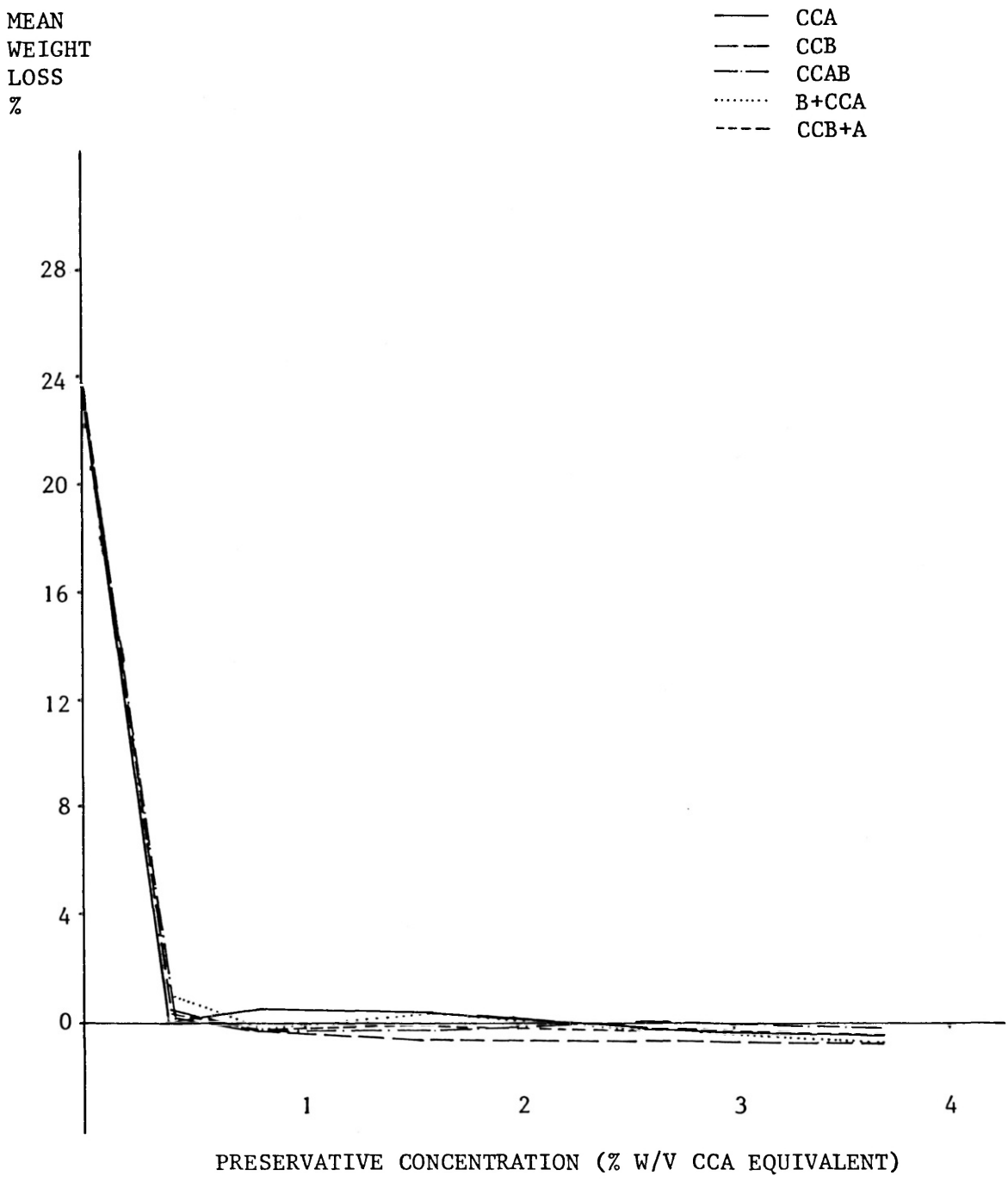


Table 17 -

Mean Copper Retentions and Weight Losses in Scots Pine tested against Poria placenta in Trial 3

Treatment		Mean Copper Retention (Kgm^{-3})	Standard Error	Copper Retention (% w/w)	Mean Weight Loss %	Standard Error
CCA	0.4	0.247	0.00	0.055	30.31	1.31
	0.8	0.515	0.00	.114	15.35	0.98
	1.6	0.019	0.01	.226	7.98	0.80
	2.6	1.675	0.02	.372	6.34	0.67
	3.7	2.382	0.03	.529	3.29	0.98
CCB	0.4	0.257	0.00	.057	32.43	1.13
	0.8	0.501	0.01	.111	25.90	0.85
	1.6	1.031	0.02	.229	15.83	0.82
	2.6	1.707	0.03	.379	7.76	0.81
	3.7	2.318	0.03	.515	3.66	0.38
CCAB	0.4	0.247	0.00	.055	21.61	2.84
	0.8	0.501	0.01	.111	17.06	0.90
	1.6	1.006	0.01	.224	8.30	0.47
	2.6	1.631	0.01	.362	5.90	0.23
	3.7	2.350	0.01	.522	6.44	0.36
B+ CCA	0.4	0.254	0.00	.056	28.86	0.62
	0.8	0.495	0.00	.110	21.74	2.04
	1.6	1.031	0.01	.229	8.76	0.76
	2.6	1.666	0.03	.370	6.80	1.44
	3.7	2.444	0.03	.543	7.43	0.70
CCB + A	0.4	0.257	0.00	.057	26.63	0.70
	0.8	0.523	0.01	.116	17.84	0.71
	1.6	1.038	0.02	.231	9.42	0.45
	2.6	1.669	0.02	.371	7.36	0.86
	3.7	2.418	0.03	.537	4.90	1.38
Untreated		-	-	-	31.25	1.43

FIGURE 13 PERFORMANCE OF SCOTS PINE EXPOSED TO PORIA PLACENTA IN TRIAL 3

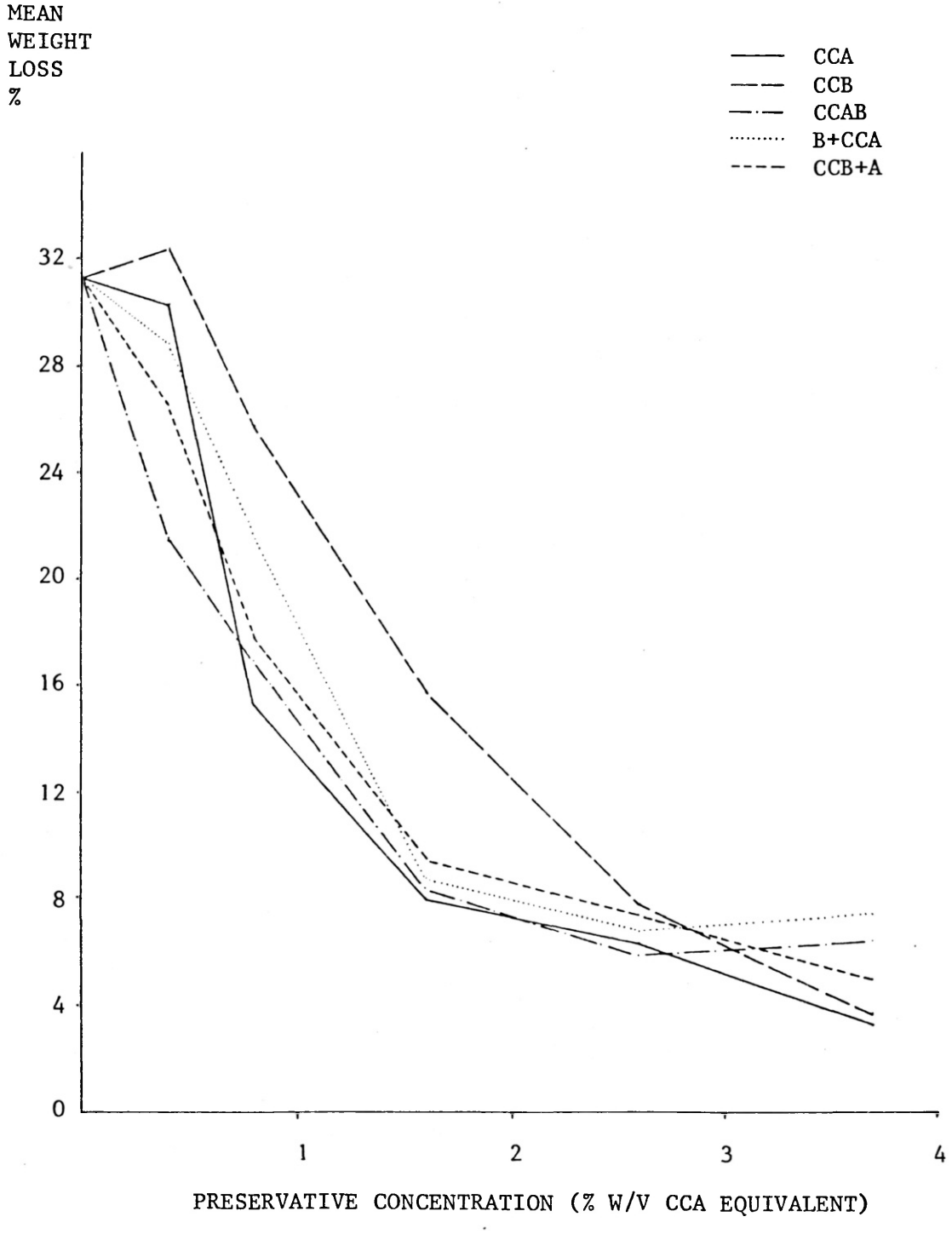


Table 18 -

Mean Copper Retentions and Weight Losses in Scots Pine tested against Gloeophyllum trabeum in Trial 3

Treatment		Mean Copper Retention (Kgm^{-3})	Standard Error	Copper Retention (% w/w)	Mean Weight Loss %	Standard Error
CCA	0.4	0.248	0.00	0.055	1.48	0.60
	0.8	0.500	0.01	0.111	-0.02	0.14
	1.6	1.030	0.02	0.229	0.44	0.36
	2.6	1.624	0.01	0.361	-0.47	0.13
	3.7	2.315	0.02	0.514	0.41	0.30
CCB	0.4	0.257	0.00	0.057	0.32	0.10
	0.8	0.511	0.00	0.1136	-0.82	0.13
	1.6	1.028	0.02	0.228	-0.13	0.17
	2.6	1.677	0.03	0.373	0.06	0.23
	3.7	2.390	0.06	0.531	-0.77	0.50
CCAB	0.4	0.249	0.00	0.055	0.42	0.40
	0.8	0.493	0.00	0.110	0.31	0.25
	1.6	0.997	0.00	0.222	-0.31	0.11
	2.6	1.641	0.00	0.365	0.02	0.09
	3.7	2.427	0.03	0.539	-0.40	0.46
B+	0.4	.255	0.00	.057	1.48	0.42
CCA	0.8	.515	0.00	.114	0.32	0.31
	1.6	1.038	0.02	.231	-0.50	0.17
	2.6	1.664	0.02	.370	0.13	0.36
	3.7	2.410	0.04	.536	0.62	0.36
CCB	0.4	0.254	0.00	0.056	-0.16	0.24
+ A	0.8	0.514	0.01	0.114	-0.70	0.07
	1.6	1.047	0.02	0.233	-0.33	0.19
	2.6	1.677	0.04	0.373	-0.32	0.50
	3.7	2.480	0.03	0.551	-0.37	0.26
Untreated		-	-	-	14.24	0.39

FIGURE 14 PERFORMANCE OF SCOTS PINE EXPOSED TO GLOEOPHYLLUM TRABEUM IN TRIAL 3

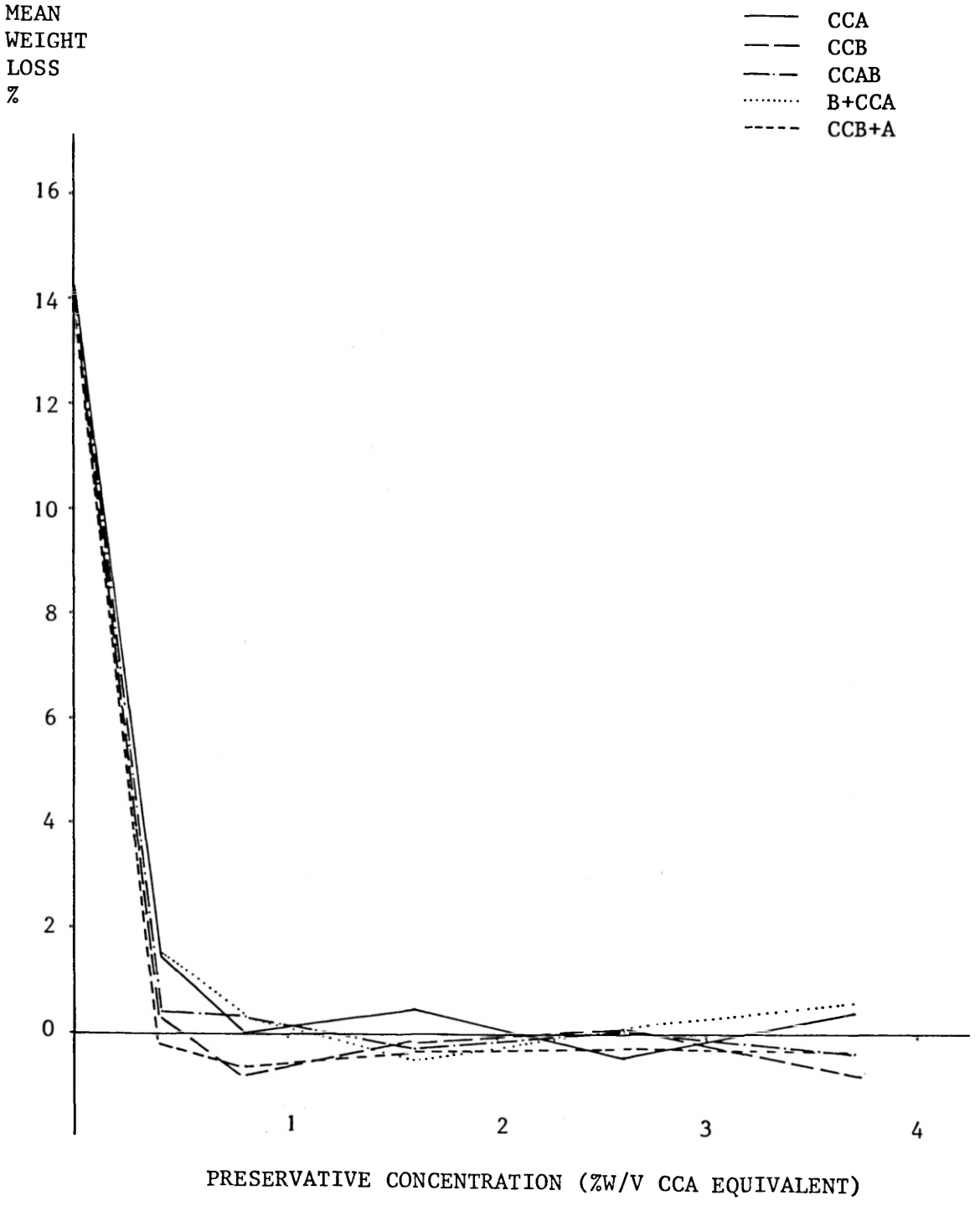


Table 19 -

Analysis of Variance on the Weight Losses due to Poria placenta in Birch

Treatments Compared	Treating Solution % CCA Eq.				
	0.4	0.8	1.6	2.6	3.7
CCA/CCB	-	*	-	-	*
CCA/CCAB	-	*	-	-	-
CCA/B+CCA	*	-	-	-	*
CCA/CCB+A	-	-	-	-	-
CCB/CCAB	-	*	*	-	*
CCB/B+CCA	*	*	-	-	*
CCB/CCB+A	*	*	-	-	*
CCAB/B+CCA	*	*	-	-	*
CCAB/CCB+A	-	-	-	-	-
B+CCA/CCB+A	*	-	-	-	*
F ratio	6.82	8.95	1.46	0.91	12.62
L.S.D.	4.80	2.65	3.16	1.60	1.08

Table 20 -

Analysis of Variance on Weight Losses due to Poria placenta in Scots Pine

Treatments Compared	Treating Solution % CCA Eq.				
	0.4	0.8	1.6	2.6	3.7
CCA/CCB	-	*	*	-	-
CCA/CCAB	*	-	-	-	*
CCA/B+CCA	-	*	-	-	*
CCA/CCB+A	-	-	-	-	-
CCB/CCAB	*	*	*	-	*
CCB/B+CCA	-	*	*	-	*
CCB/CCB+A	*	*	*	-	-
CCAB/B+CCA	*	*	-	-	-
CCAB/CCB+A	*	-	-	-	-
B+CCA/CCB+A	-	*	-	-	*
F ratio	7.17	12.58	23.00	0.71	4.34
L.S.D.	4.50	3.48	1.99	2.60	2.48

— = no significant difference between means
* = significant difference between means (p = 0.05)
significant F ratios underlined.

Table 21 - Toxic Values Established in Basidiomycete Tests
(% CCA Equivalent Treating Solution)

Timber	Birch				Scots Pine			
Treatment	Coniophora puteana	Coriolus versicolor	Poria placenta	Gloeophyllum trabeum	Coniophora puteana	Coriolus versicolor	Poria placenta	Gloeophyllum trabeum
CCA	0.4 - 0.6 0.4 - 0.8	0.4 - 0.6 0.4 - 0.8	>3.7	0 - 0.4	0 - 0.4 0 - 0.4	0 - 0.4 0 - 0.4	>3.7	0 - 0.4
CCB	>3.7 >3.7	0.4 - 0.6 0.4 - 0.8	2.6 - 3.7	0 - 0.4	>3.7 >3.7	0 - 0.4 0 - 0.4	>3.7	0 - 0.4
CCAB	0.4 - 0.6	0.4 - 0.6	>3.7	0 - 0.4	0 - 0.4	0 - 0.4	>3.7	0 - 0.4
B+CCA	-	-	2.6 - 3.7	0 - 0.4	-	-	>3.7	0 - 0.4
CCB+A	0.4 - 0.8	0.4 - 0.8	2.6 - 3.7	0 - 0.4	0.4 - 0.8	0 - 0.4	>3.7	0 - 0.4

3.3 Monoculture Tests with Soft-Rot Organisms

3.3.1 Method

The agar block test derived in section 2.2.3 and described in section 2.2.3.8. was used.

The test organisms were:

Chaetomium globosum (F.P.R.L. S70K)

Phialophora fastigiata (F.P.R.L. S6A)

The requirements of the test organism were that it was a typical, common soft-rot organism which would cause significant weight losses in the test blocks. No one fungus has been found to meet both of these requirements and so two organisms were selected for the present study. Chaetomium globosum was chosen for its ability to cause typical soft-rot cavities, high weight losses in birch and also for its ease of handling. However, this fungus is not common among isolations from timber in the field (e.g. Clubbe, 1980 a; Murphy, 1982). In addition, Phialophora fastigiata was chosen because it has frequently been isolated from decaying treated timber (Nilsson and Henningsson, 1979) and must be considered as one of the main causes of decay of treated wood in the field. It produces typical soft-rot cavities but has proved problematical as a test organism because of the relatively low weight losses it causes in both Scots pine and birch and its tendency to become infested with mites. To overcome the problem of low weight losses the incubation period

for Phialophora fastigiata was doubled to 12 weeks. This must be borne in mind when looking at toxic values but, since only comparative data were required for the formulations, the extended incubation period was justifiable. Scots pine was included for completeness, although it was recognised that the weight losses may be insignificant.

Trial no. 1

Test organisms:	Phialophora fastigiata
Timber species:	Scots pine, birch
Preservatives:	CCA, CCB, CCAB
Treating solutions:	0.4, 0.6, 0.8, 1.2, 1.8, 2.6, 3.7 w/v CCA equivalent.

Trial no. 2

Test organisms:	Phialophora fastigiata, Chaetomium globosum
Timber species:	birch
Preservatives:	CCA, CCB, CCAB, B+CCA, CCB+A
Treating solutions:	0.4, 0.8, 1.6, 2.6, 3.7 % w/v CCA equivalent.

Trial no. 3

Test organisms:	Phialophora fastigiata, Chaetomium globosum
Timber species:	Scots pine, birch
Preservatives:	CCA, CCB, CCB+A
Treating solutions:	0.4, 0.8, 1.6, 2.6, 3.7 % w/v CCA equivalent.

3.3.2 Results

A list of the tables and figures corresponding to each trial will be followed by a description of the main findings for each test organism.

3.3.2.1 Trials

Trial 1.

The mean weight losses and their standard errors are given in tables 22 and 23. The data for birch are plotted against treating solution concentration in figure 15.

Trial 2.

The mean theoretical copper retentions and weight losses with their corresponding standard errors are given in tables 24 and 25. The data are plotted in figures 16 and 17.

Trial 3.

The mean theoretical copper retentions and weight losses with their corresponding standard errors are given in tables 26 - 29. The data for birch are plotted in figures 18 and 19.

A statistical analysis (analysis of variance) was carried out on all of the birch data. The f ratios, least significant differences (L.S.D.) and significant results are given in tables 30 - 34.

Table 35 gives a summary of the toxic values obtained from all three trials.

3.3.2.2 Test organisms

As frequently occurs in laboratory trials (Savory and Bravery, 1970), there was no significant weight loss in untreated Scots pine with either fungus but these were included for completeness. The "toxic values" given for Scots pine in table 35 are therefore meaningless.

Phialophora fastigiata

P. fastigiata caused a significant measurable weight loss in birch in all three trials. However, in trial 2 the P. fastigiata became infested with mites and this part of the trial was terminated after 8 weeks and the results disregarded. In trial 1, CCB was significantly more effective than CCA and CCAB at all concentrations (figure 15). In trial 3, (figure 18), however, CCB appeared to be less effective than either CCA or CCB+A and was significantly worse at one concentration. The toxic values (table 35) for each preservative were slightly different between trials.

Chaetomium globosum

C. globosum caused the predicted (see section 2.2.3.9) maximum weight losses of more than 40% in birch in both trials. In trial 2 (figure 17) CCB+A gave the best performance with less than 3% weight loss at the 1.6% treatment. B+CCA was the least effective of all of the 5 treatments. At each concentration CCB+A was statistically significantly more effective than was B+CCA. CCB+A was also significantly better than all of the other treatments at 2 concentrations. Between the extremes of B+CCA and CCB+A came the remaining treatments; CCA, CCAB and CCB. CCB tended to be more effective than CCA, CCAB being intermediate between the two. Results for the 3 treatments in trial 3 (figure 19) appeared

to support those of trial 2 and, where there were statistically significant differences in effectiveness, CCB+A was indeed superior to CCA, CCB being intermediate. The toxic values (table 35) differed by one concentration between the two trials but, in each case, the toxic values for CCB+A were lower than those of the other preservatives.

Table 22 -

Mean Weight Losses in Scots Pine Tested Against Phialophora fastigiata in Trial 1

Treatment	Concentration % CCA Equivalent	Mean Weight Loss %	Standard Error
U	-	0.46	0.15
CCA	0.4	0.43	0.08
	0.6	0.09	0.07
	0.8	0.10	0.04
	1.2	0.08	0.05
	1.8	-0.12	0.17
	2.6	-0.32	0.12
	3.7	0.01	0.13
CCB	0.4	0.58	0.11
	0.6	0.14	0.05
	0.8	0.16	0.09
	1.2	0.23	0.14
	1.8	-0.23	0.10
	2.6	-0.39	0.14
	3.7	-0.49	0.13
CCAB	0.4	N/S	
	0.6	N/S	
	0.8	N/S	
	1.2	N/S	
	1.8	N/S	
	2.6	N/S	
	3.7	N/S	

N/S = less than 3% weight loss.

Table 23 -

Mean Weight Losses in Birch Tested Against Phialophora fastigiata in Trial 1

Treatment	Concentration % CCA Equivalent	Mean Weight Loss %	Standard Error
U	-	8.70	0.58
CCA	0.4	8.86	0.35
	0.6	8.12	0.78
	0.8	7.83	0.68
	1.2	5.37	0.56
	1.8	4.24	0.66
	2.6	2.71	0.49
	3.7	1.81	0.20
CCB	0.4	4.65	0.34
	0.6	4.15	0.58
	0.8	4.07	0.48
	1.2	3.07	0.42
	1.8	1.50	0.27
	2.6	1.21	0.28
	3.7	0.69	0.23
CCAB	0.4	7.26	0.34
	0.6	7.47	0.93
	0.8	6.75	0.89
	1.2	4.70	0.44
	1.8	3.78	0.39
	2.6	2.10	0.29
	3.7	1.69	0.26

FIGURE 15 PERFORMANCE OF BIRCH EXPOSED TO PHIALOPHORA FASTIGIATA IN TRIAL 1

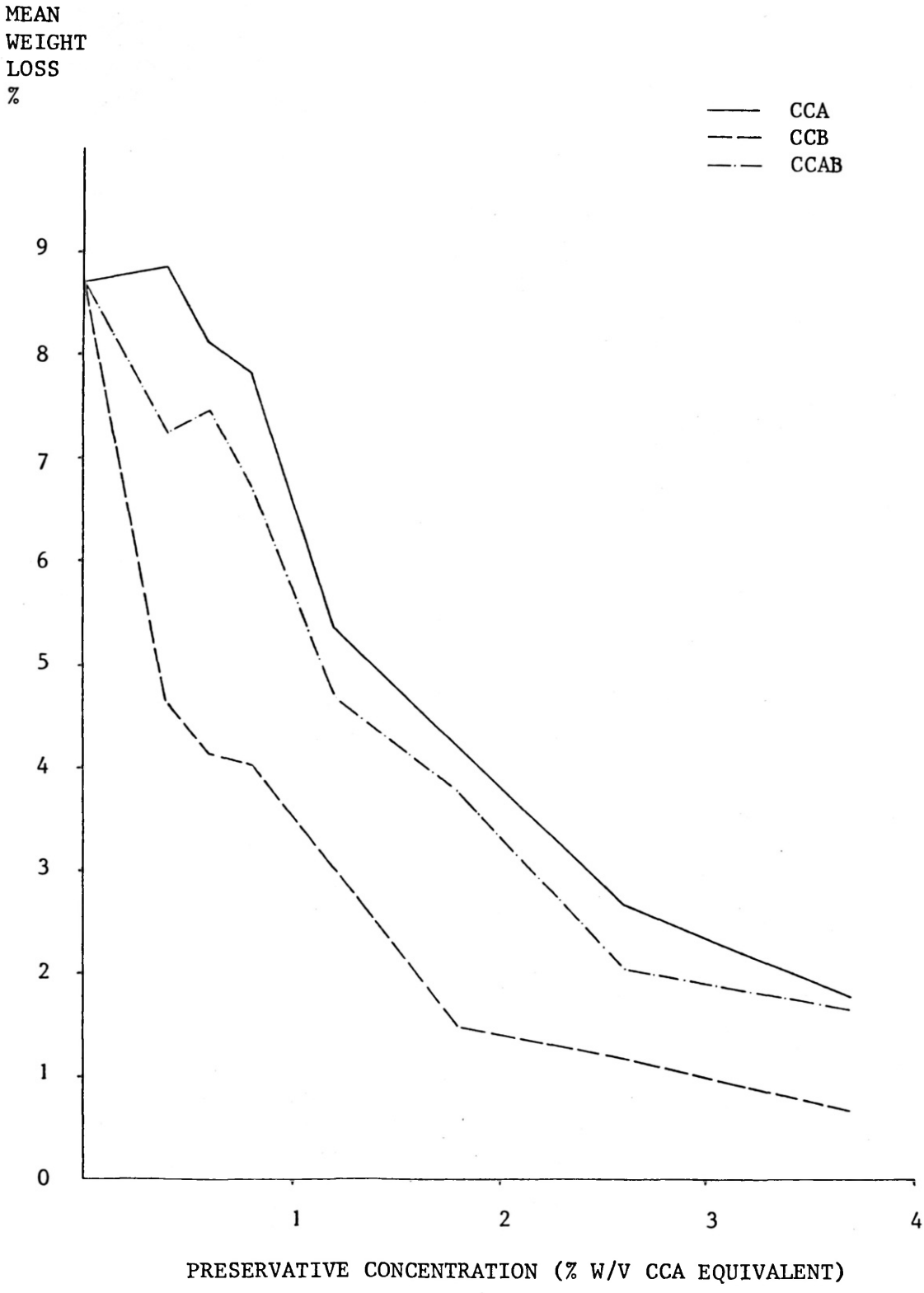


Table 24 -

Mean Copper Retentions and Weight Losses in Birch Tested against Phialophora fastigiata in Trial 2

Treatment		Mean Copper Retention (Kgm^{-3})	Standard Error	Copper Retention (% w/w)	Mean Weight Loss %	Standard Error
CCA	0.4	0.200	0.00	.031	4.24	1.37
	0.8	0.388	0.01	.060	1.73	.44
	1.6	0.872	0.02	.135	0.09	.49
	2.6	1.235	0.02	.192	-0.29	.34
	3.7	1.597	0.04	.248	-1.08	.15
CCB	0.4	0.220	0.00	.034	4.05	.44
	0.8	0.413	0.01	.064	3.09	.51
	1.6	0.817	0.02	.127	1.02	.26
	2.6	1.302	0.03	.202	0.20	.15
	3.7	1.812	0.03	.282	0.21	.33
CCAB	0.4	0.223	0.00	.035	4.44	.79
	0.8	0.432	0.01	.067	2.57	.35
	1.6	0.828	0.01	.129	-0.26	.39
	2.6	1.345	0.03	.209	-0.19	.16
	3.7	1.802	0.08	.280	-0.12	.05
B+ CCA	0.4	0.192	0.00	.030	3.95	0.28
	0.8	0.440	0.00	.068	2.26	0.24
	1.6	0.788	0.02	.122	0.77	0.27
	2.6	1.397	0.02	.217	-0.15	0.18
	3.7	1.815	0.06	.282	0.40	0.21
CCB +A	0.4	0.217	0.00	.034	3.05	0.51
	0.8	0.405	0.01	.063	2.39	0.32
	1.6	0.928	0.02	.144	0.29	0.25
	2.6	1.312	0.03	.204	-0.36	0.16
	3.7	1.782	0.03	.277	-1.08	0.09
Untreated		-	-	-	6.22	0.21

FIGURE 16 PERFORMANCE OF BIRCH EXPOSED TO PHIALOPHORA FASTIGIATA IN TRIAL 2

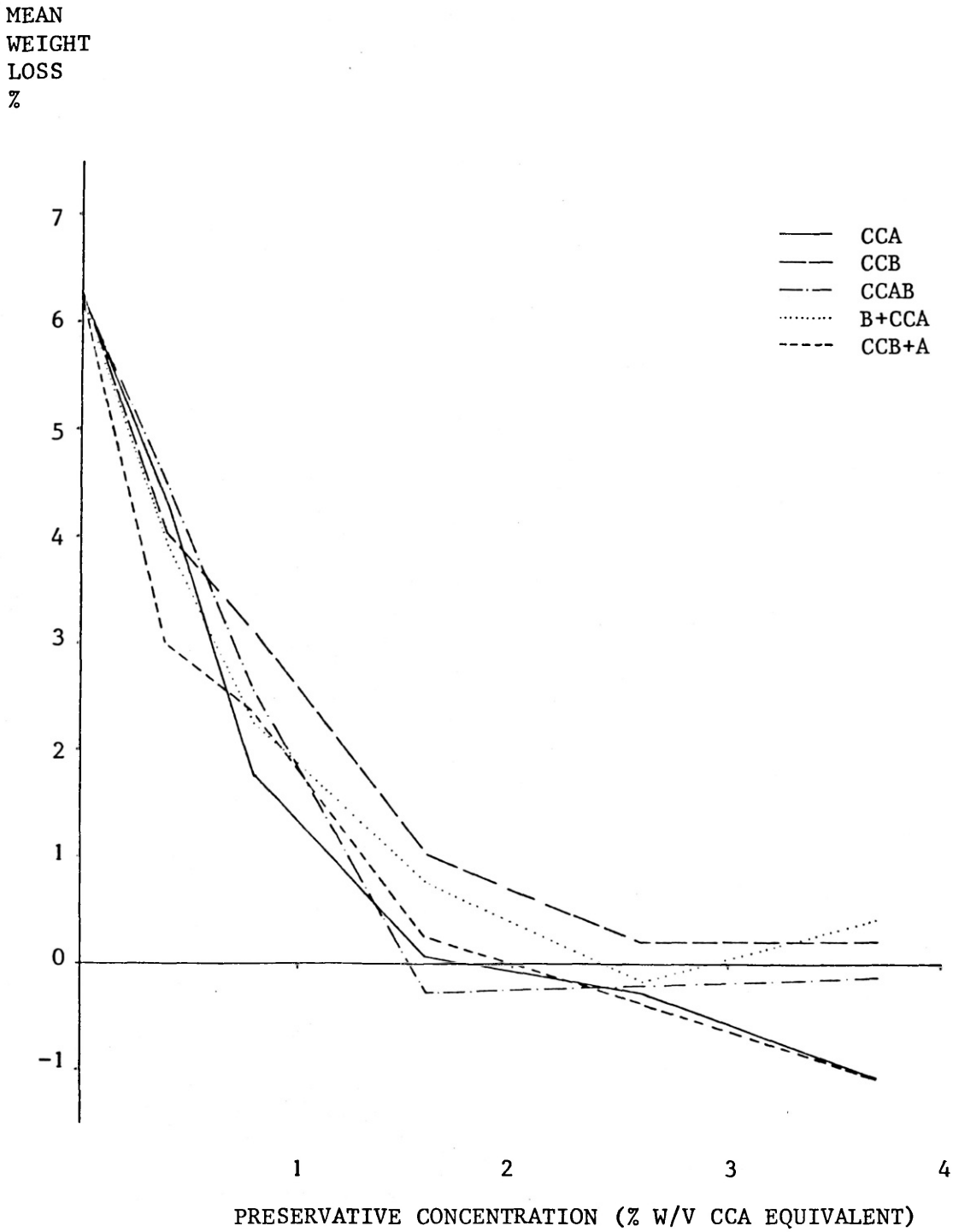


Table 25 -

Mean Copper Retentions and Weight Losses in Birch Tested against Chaetomium globosum in Trial 2

Treatment		Mean Copper Retention (Kgm^{-3})	Standard Error	Copper Retention (% w/w)	Mean Weight Loss %	Standard Error
CCA	0.4	0.208	0.00	0.032	42.30	6.45
	0.8	0.395	0.01	0.061	37.42	2.66
	1.6	0.803	0.02	0.125	20.65	1.21
	2.6	1.294	0.02	0.201	6.41	1.37
	3.7	1.680	0.03	0.261	3.08	.80
CCB	0.4	0.217	0.00	0.034	48.72	2.26
	0.8	0.436	0.00	0.068	33.45	1.32
	1.6	0.808	0.02	0.125	9.21	.99
	2.6	1.250	0.02	0.194	4.32	.73
	3.7	1.844	0.08	0.286	3.06	.82
CCAB	0.4	0.226	0.00	0.035	50.42	2.56
	0.8	0.429	0.01	0.067	34.67	2.90
	1.6	0.825	0.01	0.128	18.25	.71
	2.6	1.328	0.03	0.206	3.95	.74
	3.7	1.831	0.03	0.285	2.57	.59
B+ CCA	0.4	0.188	0.01	0.029	54.21	3.29
	0.8	0.433	0.01	0.067	41.55	2.91
	1.6	0.838	0.01	0.130	20.70	2.34
	2.6	1.384	0.03	0.215	7.18	.52
	3.7	1.829	0.05	0.284	4.19	.70
CCB +A	0.4	0.224	0.00	0.035	35.81	3.37
	0.8	0.413	0.00	0.064	21.29	2.66
	1.6	0.968	0.01	0.150	2.16	.65
	2.6	1.361	0.02	0.211	4.16	.75
	3.7	1.754	0.05	0.272	1.25	.33
Untreated		-	-	-	39.98	3.16

FIGURE 17 PERFORMANCE OF BIRCH EXPOSED TO CHAETOMIUM GLOBOSUM IN TRIAL 2

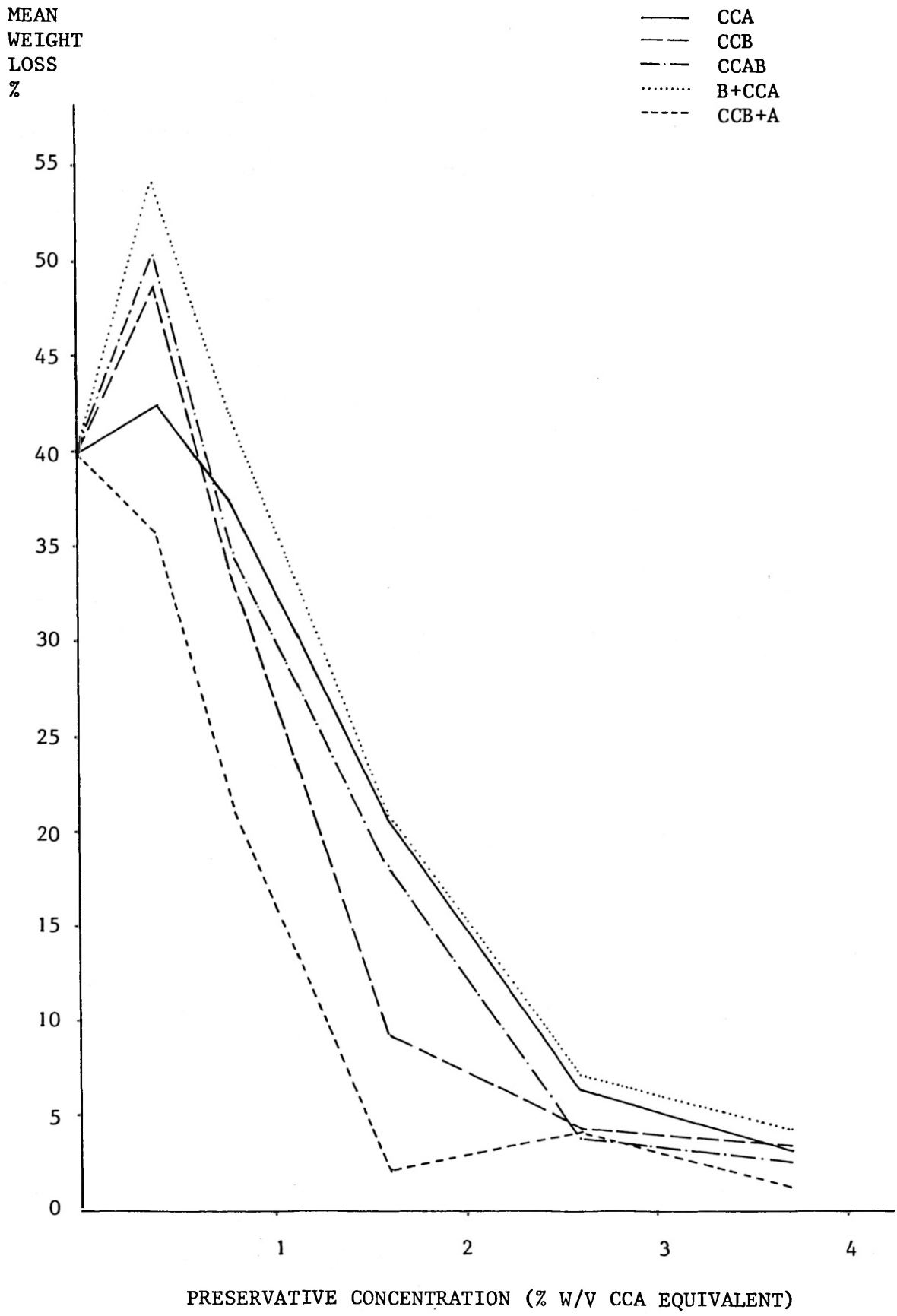


Table 26 -

Mean Copper Retentions and Weight Losses in Scots Pine Tested against Phialophora fastigiata in Trial 3

Treatment		Mean Copper Retention (Kgm^{-3})	Standard Error	Copper Retention (% w/w)	Mean Weight Loss %	Standard Error
CCA	0.4	0.237	0.00	0.056	-0.22	0.12
	0.8	0.481	0.00	0.113	-0.84	0.15
	1.6	0.833	0.03	0.196	-0.13	0.16
	2.6	1.435	0.02	0.338	-0.42	0.13
	3.7	2.040	0.02	0.480	0.25	0.13
CCB	0.4	0.225	0.01	0.053	1.89	0.16
	0.8	0.488	0.00	0.115	1.39	0.13
	1.6	0.967	0.01	0.228	1.15	0.07
	2.6	1.557	0.02	.366	1.05	0.09
	3.7	2.225	0.02	.524	1.45	0.30
CCB +A	0.4	0.213	0.01	0.050	0.80	0.20
	0.8	0.483	0.01	.114	0.54	0.09
	1.6	0.977	0.02	.230	0.03	0.25
	2.6	1.610	0.01	.379	-0.13	0.39
	3.7	2.212	0.02	.521	0.81	0.09
Untreated		-	-	-	0.80	0.21

Table 27 -

Mean Copper Retentions and Weight Losses in Scots Pine Tested Against Chaetomium globosum in Trial 3

Treatment		Mean Copper Retention (Kgm^{-3})	Standard Error	Copper Retention (% w/w)	Mean Weight Loss %	Standard Error
CCA	0.4	0.238	0.00	0.056	0.58	0.23
	0.8	0.470	0.00	0.111	0.00	0.26
	1.6	0.875	0.01	0.205	0.47	0.16
	2.6	1.490	0.05	0.351	0.44	0.09
	3.7	2.065	0.01	0.486	0.67	0.15
CCB	0.4	0.227	0.01	0.053	0.21	0.23
	0.8	0.482	0.00	0.113	0.72	0.22
	1.6	0.965	0.01	0.227	0.36	0.20
	2.6	1.530	0.02	0.360	0.48	0.22
	3.7	2.237	0.02	0.526	0.81	0.16
CCB +A	0.4	0.223	0.01	0.053	0.93	0.16
	0.8	0.497	0.00	0.117	0.41	0.11
	1.6	0.977	0.01	0.230	0.61	0.18
	2.6	1.590	0.01	0.374	-0.08	0.11
	3.7	2.265	0.01	0.533	0.50	0.21
Untreated		-	-	-	1.11	0.17

Table 28 -

Mean Copper Retentions and Weight Losses in Birch Tested against Phialophora fastigiata in Trial 3

Treatment		Mean Copper Retention (Kgm^{-3})	Standard Error	Copper Retention (% w/w)	Mean Weight Loss %	Standard Error
CCA	0.4	0.208	0.00	0.033	8.39	1.49
	0.8	0.425	0.00	0.068	6.31	1.31
	1.6	0.838	0.02	0.133	2.56	0.31
	2.6	1.382	0.02	0.219	1.07	0.80
	3.7	1.950	0.02	0.310	-0.83	0.35
CCB	0.4	0.210	0.00	0.033	10.34	.83
	0.8	0.418	0.00	0.066	7.68	.82
	1.6	0.788	0.01	0.125	6.05	1.78
	2.6	1.373	0.01	0.218	1.11	.90
	3.7	1.900	0.04	0.302	1.54	.18
CCB +A	0.4	0.205	0.00	0.033	10.87	1.14
	0.8	0.408	0.01	0.065	5.34	.74
	1.6	0.793	0.01	0.126	2.11	.45
	2.6	1.323	0.05	0.210	1.11	1.11
	3.7	1.983	0.05	0.315	-0.27	.13
Untreated		-	-	-	15.39	1.40

FIGURE 18 PERFORMANCE OF BIRCH EXPOSED TO PHIALOPHORA FASTIGIATA IN TRIAL 3

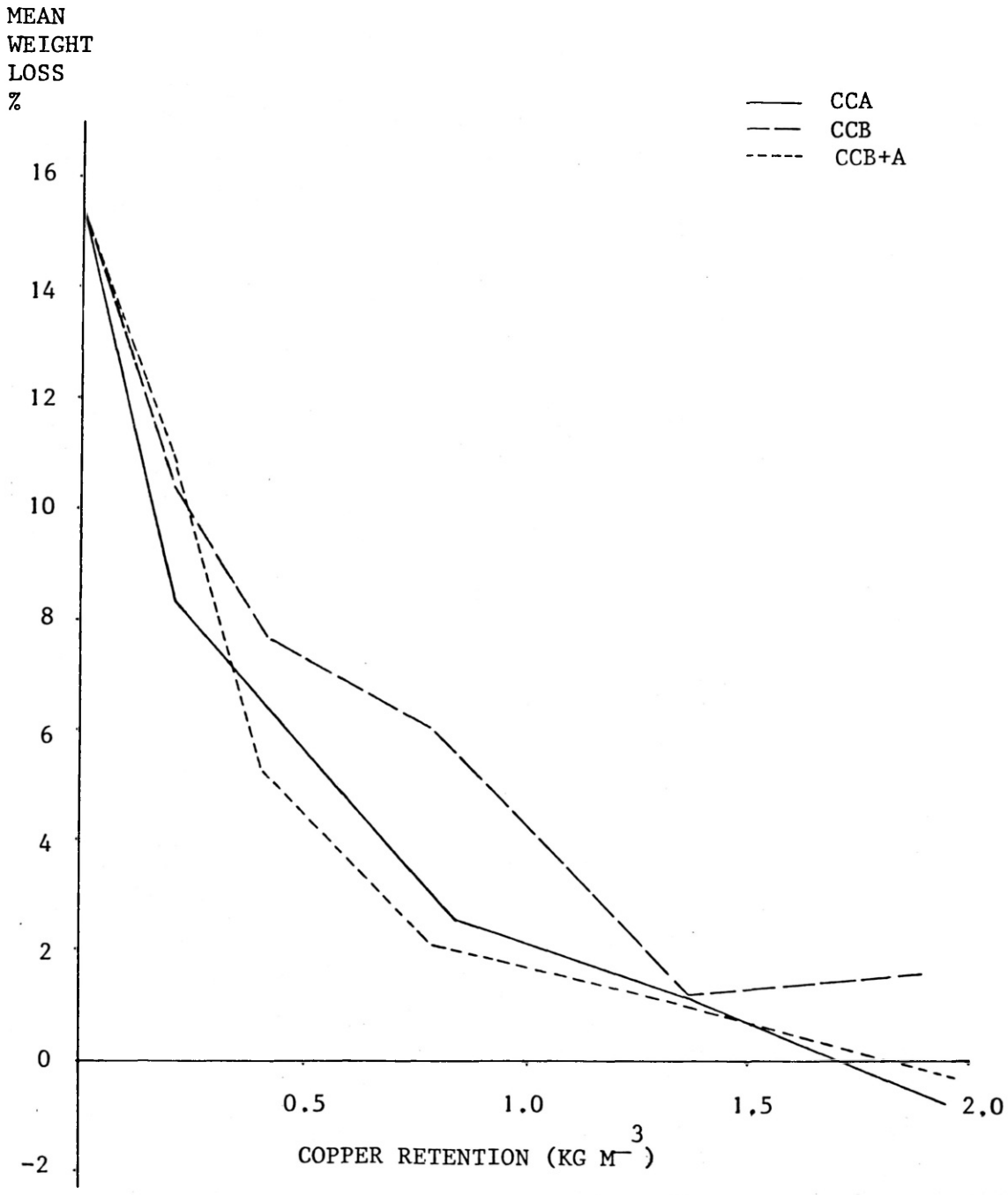


Table 29 -

Mean Copper Retentions and Weight Losses in Birch Tested against Chaetomium globosum in Trial 3

Treatment		Mean Copper Retention (Kgm^{-3})	Standard Error	Copper Retention (% w/w)	Mean Weight Loss %	Standard Error
CCA	0.4	0.203	0.00	0.032	30.48	2.24
	0.8	0.412	0.00	0.065	23.06	1.47
	1.6	0.848	0.01	0.135	17.51	.45
	2.6	1.347	0.02	0.214	7.60	1.36
	3.7	1.933	0.02	0.307	1.30	.53
CCB	0.4	0.207	0.00	0.033	34.81	1.83
	0.8	0.410	0.01	0.065	22.39	.65
	1.6	0.793	0.01	0.126	10.27	.37
	2.6	1.390	0.02	0.221	5.12	.37
	3.7	1.900	0.02	0.302	2.05	.54
CCB +A	0.4	0.205	0.00	0.033	33.78	1.28
	0.8	0.417	0.01	0.066	22.33	1.64
	1.6	0.772	0.01	0.123	13.04	1.32
	2.6	1.370	0.02	0.218	1.99	.57
	3.7	1.917	0.02	0.304	2.62	.38
Untreated		-	-	-	41.30	2.25

FIGURE 19 PERFORMANCE OF BIRCH EXPOSED TO CHAETOMIUM GLOBOSUM IN TRIAL 3

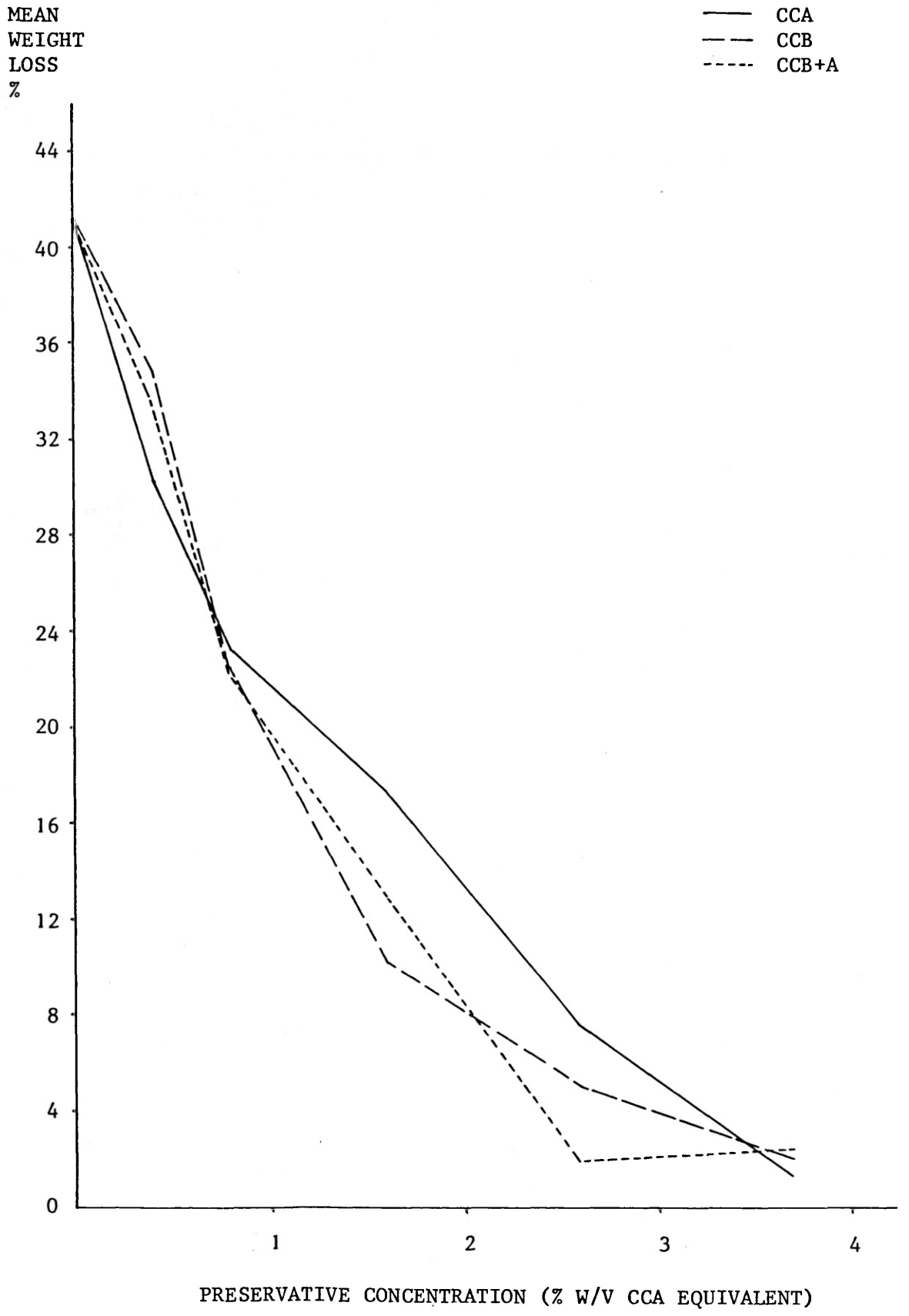


Table 30 -

Analysis of Variance on the Weight Losses Due to Phialophora fastigiata in Birch in Trial 1

Treatments Compared	Treating Solution						
	0.4	0.6	0.8	1.2	1.8	2.6	3.7
CCA/CCB	*	*	*	*	*	*	*
CCA/CCAB	*	-	-	-	-	-	-
CCB/CCAB	*	*	*	*	*	-	*
F Ratio	38.41	7.51	7.62	6.28	9.72	4.30	7.10
L.D.	1.03	2.34	2.12	1.42	1.42	1.10	0.696

Table 31 -

Analysis of Variance on the Weight Losses due to Phialophora fastigiata in Birch in Trial 2

Treatments Compared	Treating Solution				
	0.4	0.8	1.6	2.6	3.7
CCA/CCB	-	*	-	-	*
CCA/CCAB	-	-	-	-	*
CCA/B+CCA	-	-	-	-	*
CCA/CCB+A	-	-	-	-	-
CCB/CCAB	-	-	*	-	-
CCB/B+CCA	-	-	-	-	-
CCB/CCB+A	-	-	-	-	*
CCAB/B+CCA	-	-	-	-	-
CCAB/CCB+A	-	-	-	-	*
B+CCA/CCB+A	-	-	-	-	*
F Ratio	0.47	1.60	2.23	1.04	13.29
L.S.D.	2.26	1.21	1.01	0.612	0.563

\- = no significant difference between means
* = significant difference between means (p = 0.05)
significant ratios underlined

Table 32 -

Analysis of Variance on the Weight Losses
Due to Chaetomium globosum in Birch in Trial 2

Treatments Compared	Treating Solution				
	0.4	0.8	1.6	2.6	3.7
CCA/CCB	-	-	*	-	-
CCA/CCAB	-	-	-	-	-
CCA/B+CCA	*	-	-	-	-
CCA/CCB+A	-	*	*	-	-
CCB/CCAB	-	-	*	-	-
CCB/B+CCA	-	*	*	*	-
CCB/CCB+A	*	*	*	-	-
CCAB/B+CCA	-	-	-	*	-
CCAB/CCB+A	*	*	*	-	-
B+CCA/CCB+A	*	*	*	*	*
F Ratio	4.40	6.69	50.89	2.91	2.23
L.S.D.	9.52	7.19	3.14	2.53	1.92

Table 33 -

Analysis of Variance on the Weight Losses
Due to Phialophora fastigiata in Birch in Trial 3

Treatments Compared	Treating Solution				
	0.4	0.8	1.6	2.6	3.7
CCA/CCB	-	-	*	-	*
CCA/CCB+A	-	-	-	-	-
CCB/CCB+A	-	-	*	-	*
F Ratio	1.07	1.15	3.33	0.00	22.54
L.S.D.	3.64	3.06	3.46	2.64	0.789

Table 34 -

Analysis of Variance on the Weight Losses
Due to Chaetomium globosum in Birch in Trial 3

Treatments Compared	Treating Solution				
	0.4	0.8	1.6	2.6	3.7
CCA/CCB	-	-	*	-	-
CCA/CCB+A	-	-	*	*	-
CCB/CCB+A	-	-	-	*	-
F Ratio	1.54	0.09	19.24	10.26	2.31
L.S.D.	5.50	4.01	2.51	2.65	1.41

Significant F ratios underlined.

- = No significant difference between means.

* = Significant difference between means (P = 0.05).

Table 35 -

Toxic Values Established in
Soft-Rot Organism Monoculture Tests
(% CCA Equivalent Treating Solution)

Timber	Birch		Scots Pine	
Treatment	Phialophora fastigiata	Chaetomium globosum	Phialophora fastigiata	Chaetomium globosum
CCA	1.8-2.6(1) 0.4-0.8(2) 0.8-1.6(3)	2.6-3.7(3) >3.7(2)	0-0.4(1) 0-0.4(3)	0-0.4(3)
CCB	1.2-1.8(1) 0.8-1.6(2) 1.6-2.6(3)	2.6-3.7(3) >3.7(2)	0-0.4(1) 0-0.4(3)	0-0.4(3)
CCAB	1.8-2.6(1) 0.8-1.6(2)	>3.7(2)	Not Tested	Not Tested
B+CCA	0.4-0.8(2)	>3.7(2)	Not Tested	Not Tested
CCB+A	0.8-1.6(3) 0.4-0.8(2)	1.8-2.6(3) 2.6-3.7(2)	0-0.4(3)	0-0.4(3)

Trial no. in parenthesis.

3.4 Soil Burial

3.4.1 Method

The miniblock soil burial test described in section 2.2.4.3 was used. The incubation period was extended to 20 weeks as there was no significant weight loss in sample blocks after 12 weeks. The preservatives tested were CCA, CCB and CCAB in both birch and Scots pine.

3.4.2 Results

A list of the tables and figures will be followed by a description of the main finds.

The mean weight losses and their standard errors for Scots pine are given in table 36. The mean copper retentions and weight losses with their standard errors for birch are given in table 37 and plotted in figure 20. A statistical analysis (analysis of variance) was carried out. The F ratios, L.S.D.s and significant results are given in table 38.

The weight losses in both treated and untreated Scots pine were insignificant except in the case of the lowest level of CCB (table 36). In birch, all of the treatments performed equally except at one concentration where CCA was markedly poorer than CCB and CCAB (table 37). The toxic values established for all three preservatives were 1.8 - 2.6% CCA equivalent.

Table 36 -

Mean Weight Losses in
Scots Pine Exposed to Soil Burial

Treatment	Concentration (% CCA Equivalent)	Mean Weight Loss %	Standard Error
U	-	2.26	.18
CCA	0.4	.90	.09
	0.6	.22	.10
	0.8	.75	.08
	1.2	.19	.11
	1.8	.03	.07
	2.6	.01	.08
	3.7	-.32	.08
CCB	0.4	20.17	.11
	0.6	.49	.10
	0.8	.87	.14
	1.2	.46	.12
	1.8	.64	.10
	2.6	-.06	.08
	3.7	.27	.09
CCAB	0.4	N/S	-
	0.6	N/S	-
	0.8	N/S	-
	1.2	N/S	-
	1.8	N/S	-
	2.6	N/S	-
	3.7	N/S	-

N/S = Less than 3% weight loss.

Table 37 -

Mean Copper Retentions and Weight Losses in Birch Exposed to Soil Burial

Treatment	Copper Retention (Kgm^{-3})	Standard Error	Weight Loss %	Standard Error
U	-	-	13.24	1.12
CCA 0.4	.233	.04	13.04	1.85
0.6	.355	.04	11.59	2.22
0.8	.471	.07	6.68	1.26
1.2	.709	.11	2.97	.78
1.8	1.029	.23	6.97	.56
2.6	1.443	.32	1.02	.21
3.7	1.949	.41	-0.01	.16
CCB 0.4	.230	.02	12.63	1.07
0.6	.349	.06	9.87	2.15
0.8	.446	.08	6.71	1.48
1.2	.697	.13	3.67	1.32
1.8	1.022	.16	1.51	.96
2.6	1.428	.41	-.59	.15
3.7	1.970	.51	-.66	.08
CCAB 0.4	.239	.03	14.22	.94
0.6	.353	.06	12.61	1.28
0.8	.464	.08	8.02	1.45
1.2	.716	.12	4.08	1.01
1.8	1.022	.16	1.92	.68
2.6	1.482	.47	-1.28	.14
3.7	1.986	1.47	.90	1.14

FIGURE 20 PERFORMANCE OF BIRCH EXPOSED TO SOIL BURIAL

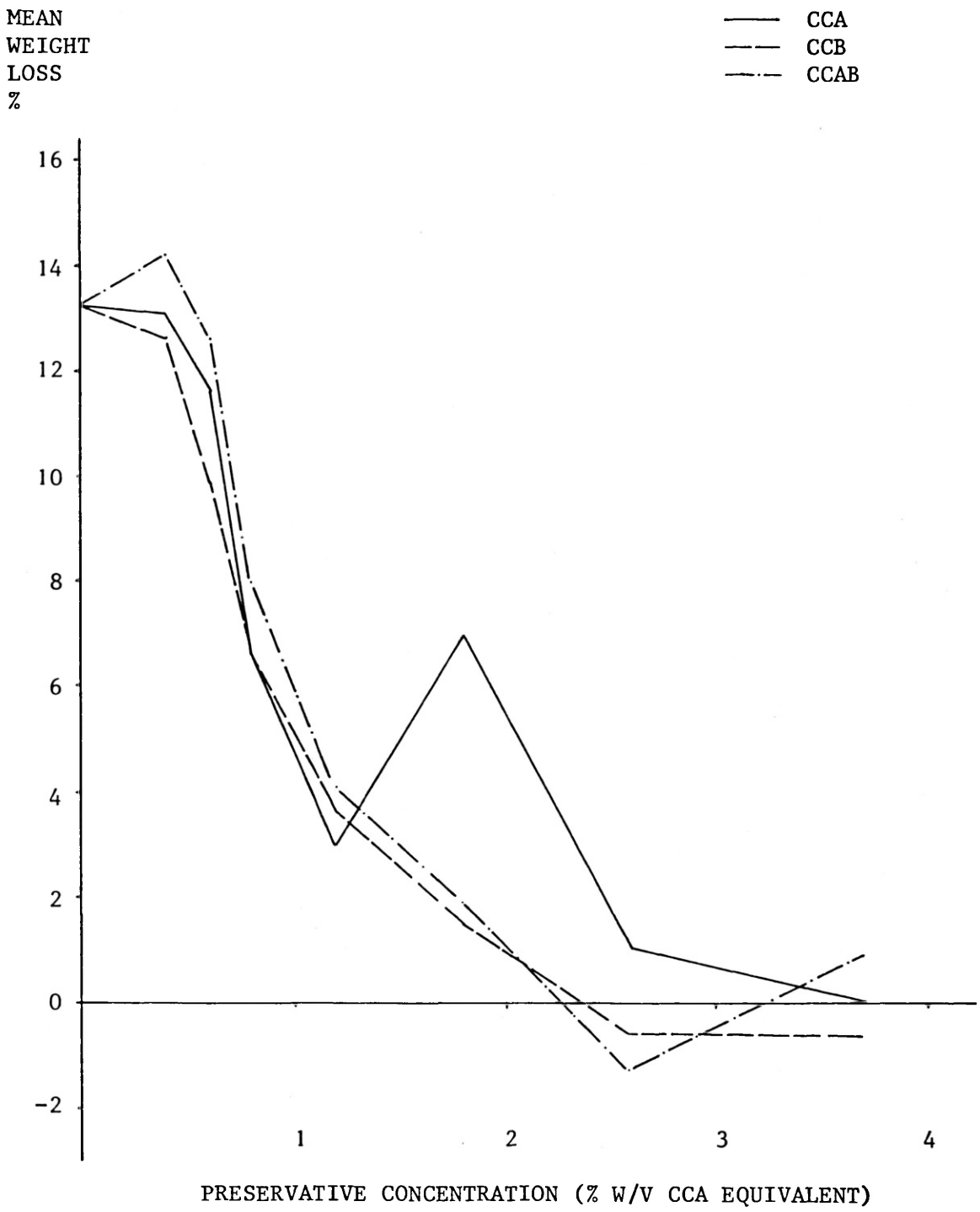


Table 38 -

Analysis of Variance on Weight Losses in Birch After Soil Burial

Treatments Compared	Treating Solution				
	0.4	0.6	0.8	1.2	1.8
CCA/CCB	-	-	-	-	*
CCA/CCBA	-	-	-	-	*
CCB/CCBA	-	-	-	-	-
F Ratio	0.38	0.52	0.30	0.28	14.87
L.S.D.	3.88	5.57	3.78	3.07	2.17

Significant F ratios underlined.

- = no significant difference between means.

* = significant difference between means (p = 0.05).

3.5 Soil-Bed

3.5.1 Method

The method involving partial burial of small stakes in soil, described in section 2.2.6, was used in conjunction with the static bending method of assessment described in section 2.3.4. In addition, weight loss determinations (section 2.3.3) were made at the time of failure or at the end of the test for stakes which had not failed.

3.5.1.1 Test Specimens

Birch and Scots pine stakes treated with a range of concentrations (0.4, 0.8, 1.6, 2.6, 3.7% w/v CCA equivalent) of CCA, CCB and CCB+A were assayed. The soil bins had a limited capacity accommodating 10 replicates of birch and 7 of Scots pine for each treatment concentration, preference being given to the hardwood. The 3.7% treatment of birch with CCB+A had to be eliminated from the test due to an error in the treatment. The timing of the test meant that this could not be corrected.

Deflection readings for each stake were taken (section 2.3.4.2) at various time intervals over a period of 400 days. From the deflection data the % residual strengths of the stakes were calculated (section 2.3.4.4). Stakes which failed under load were said to have a residual strength of 0%. Weight loss determinations were made at the time of failure or at the end of the test. The soil moisture was monitored and maintained during the exposure period.

3.5.2 Results

A list of the tables and figures will be followed by a description of the results.

The mean values of % residual strength and their standard errors for the treatments at the different time intervals are given in tables 39 for birch and 44 for Scots pine. The values for birch are plotted against time in figure 21 for CCA, 22 for CCB and 23 for CCB+A. The lines on these figures are the result of regression analyses for all of the individual data (not mean values) and details of these are given in table 40. Individual values which constituted means of less than 20% residual strength were not included in the analyses as such values are thought to represent the "senescent" phase of decay where the rate of decay decreases (Vinden et al, 1982). Table 41 gives the result of a statistical analysis (analysis of variance, t tests) comparing the strength data for the three treatments. The mean % residual strengths are plotted against time for the lowest concentration of the three treatments in Scots pine in figure 25, and the results of a statistical test are given in tables 46 and 47.

In birch, a comparison of the three treatments was made by plotting the logarithms of the slopes of the graph in figures 21 - 23, (i.e. the logarithm rate of loss in strength) against the mean copper retentions (given in table 42). Regression analyses were carried out and were plotted in figure 27, details being given in table 49.

The mean weight losses of stakes which did not fail or failed at the last assessment, and their standard errors for each treatment, are given with the mean copper retentions for birch in table 42 and for Scots pine in table 45. Where there were no remaining stakes at the end of the test (i.e. all had failed prior to the final assessment) no result is given. The mean weight losses are plotted against copper retention in figure 24 for birch and figure 26 for Scots pine, and the results of a statistical test are given in table 43 and table 48 respectively. The moisture contents of the soil expressed as % of the moisture content at the water holding capacity are given in table 50. Finally, details of a linear regression analysis of weight loss and the corresponding % residual strength in birch are given in figure 28. Again, values of less than 20% residual strength were omitted.

The soil moisture content (table 50) varied between 18.9 and 33.6% during the course of the test, that is, between 64 and 114% of the moisture content at the water holding capacity.

In birch (table 39), despite the variation between the replicates, there were significant differences between the treatments with regard to their % residual strengths. At the 0.4% concentration CCB performed poorly, giving significantly lower residual strengths than CCA and CCB+A at many time intervals. At the 0.8% concentration, however, both CCB and CCB+A were significantly better than CCA, CCB+A giving the best performance. This trend was more marked at the 1.6% concentration where the

residual strength in the CCB+A treated stakes was consistently significantly higher than in those treated with CCA and CCB. Similarly, CCB+A gave the best performance at the 2.6% concentration. At the 3.7% treatment there was no significant difference between the residual strength of the CCA and CCB treated stakes. The correlation coefficients (table 40) of the regression lines plotted for each treatment concentration were all highly significant and the lines tended to go through the origin.

When the logarithms of the rates of loss in strength (slopes from figures 21 - 23) were plotted (figure 27) against the mean copper retentions of the 3 treatments, a regression analysis again yielded highly significant correlation coefficients despite the small numbers of data points. From these graphs and table 49 it can be seen that for a rate of loss in strength of 0.1% per day (i.e. a life of 1,000 days in the soil-bed) a birch stake requires 1.68 times as much copper in the form of CCA as it does in the form of CCB+A and 1.45 times as much in the form of CCB. For a longer theoretical life (not taking senescence into account) of 10000 days before failure the differences between the treatments are more marked, although this type of extrapolation is inadvisable when dealing with a biological system.

In the case of Scots pine (table 44), the rate of loss in strength was much lower with all treatments than in birch, and in many cases did not reach a significant level. When a significant level was attained the ranking of the preservatives in order of performance (tables 46; 47) was similar to that in birch. Once again CCB performed poorly at its lowest concentration.

A comparison of the loss in weight of the birch stakes was difficult to make at the lower concentrations since many of the replicates had failed earlier in the test and it is meaningless to compare weight losses after different incubation periods. However, there were substantial weight losses at all concentrations, and from figure 24 and the statistical analysis (table 43) it can be seen that the CCB+A treatment resulted in the lowest weight losses, CCA and CCB being indistinguishable.

In Scots pine (table 45), weight losses were only significant in size at the two lowest concentrations. A statistical comparison (table 48) at the lowest concentration ranked the preservatives in the order CCB+A, CCA, CCB, with CCB+A being the most protective treatment.

When the weight losses in the birch stakes were plotted against the residual strengths (figure 28) there was a good correlation. A linear regression analysis indicated that an 80% residual strength (the assumed level of significance in section 2.3.4.5) corresponded to a loss in weight of 7.5%.

Table 39 -

Mean % Residual Strengths in Treated Birch Exposed in the Soil-Bed

(i) 0.4% CCA Equivalent Treating Solution

Time (days)	Treating Solution: 0.4%					
	CCA		CCB		CCB+A	
	Mean	Standard Error	Mean	Standard Error	Mean	Standard Error
7	91.0	2.69	92.5	3.71	93.6	1.89
32	-	-	84.3	3.02	90.4	3.73
105	70.6	3.67	52.1	3.64	59.6	3.45
134	60.3	4.62	32.1	6.67	51.2	3.57
175	43.4	6.29	17.3	4.21	34.4	4.46
200	34.5	6.96	14.0	3.98	28.8	4.02
248	23.5	5.53	9.4	2.81	16.9	3.86
284	15.6	4.04	4.4	1.92	11.1	3.08
324	7.4	2.68	0.9	0.60	6.6	2.26
365	2.4	1.31	0.0	0.00	2.0	1.45
400	0.0	0.00	0.0	0.00	0.0	0.00

Table 39 continued -

(ii) 0.8% CCA Equivalent Treating Solution

Time (days)	Treating Solution: 0.8%					
	CCA		CCB		CCB+A	
	Mean	Standard Error	Mean	Standard Error	Mean	Standard Error
7	95.7	1.86	89.9	3.25	98.7	1.29
32	-	-	86.5	2.94	96.6	2.43
105	68.0	1.59	72.1	2.72	80.5	2.39
134	61.6	0.95	69.1	2.69	77.5	3.89
175	51.7	2.66	61.3	3.79	64.1	3.29
248	29.3	2.31	39.5	3.83	45.6	3.83
284	20.4	2.49	31.7	3.34	37.4	2.89
324	13.2	3.07	24.2	3.07	24.0	4.24
365	4.2	2.55	13.9	2.35	12.5	2.40
400	1.5	1.45	8.0	1.79	5.5	1.99

Table 39 continued -

(iii) 1.6% CCA Equivalent Treating Solution

Time (days)	Treating Solution 1.6%					
	CCA		CCB		CCB+A	
	Mean	Standard Error	Mean	Standard Error	Mean	Standard Error
7	103.8	3.94	99.7	1.27	89.7	3.49
32	-	-	91.4	2.76	87.5	3.48
105	76.0	3.97	78.1	2.63	78,9	2.81
134	74.6	2.50	76.4	2.91	85.7	3.31
175	72.7	3.18	68.2	2.58	76.7	3.02
248	48.4	2.30	50.5	4.05	61.1	3.32
284	40.3	2.47	40.1	3.42	53.6	4.84
324	29.3	3.00	34.2	3.42	49.0	5.15
365	20.2	2.70	23.1	3.07	34.4	4.46
400	12.8	2.56	13.7	1.92	23.4	3.55

Table 39 continued -

(iv) 2.6% CCA Equivalent Treating Solution

Time (days)	Treating Solution 2.6%					
	CCA		CCB		CCB+A	
	Mean	Standard Error	Mean	Standard Error	Mean	Standard Error
7	101.0	0.88	99.3	1.63	99.7	1.43
32	-	-	89.3	2.32	92.3	2.52
105	86.7	2.25	78.4	3.86	86.7	2.43
134	87.1	2.56	82.4	3.51	86.1	3.42
175	85.2	3.57	86.5	2.43	86.8	4.17
248	66.5	4.02	69.9	3.86	86.1	2.02
284	63.9	5.53	65.4	5.63	76.6	1.83
324	63.5	6.42	61.1	6.36	81.2	3.29
365	53.2	6.36	47.3	6.99	63.8	4.08
400	42.1	6.10	33.6	6.13	51.4	3.48

Table 39 continued -

(v) 3.7% CCA Equivalent Treating Solution

Time (days)	Treating Solution 3.7%			
	CCA		CCB	
	Mean	Standard Error	Mean	Standard Error
7	106.1	2.49	98.7	1.94
32	-	-	91.9	3.24
105	86.4	3.19	88.7	2.65
134	91.3	3.02	92.2	2.37
175	93.0	4.08	95.5	1.92
248	81.2	2.85	85.0	3.67
284	81.8	3.32	77.2	2.80
324	82.0	4.14	79.0	3.89
365	63.3	5.38	64.1	3.98
400	51.0	6.01	52.5	3.35

FIGURE 21 PERFORMANCE OF CCA TREATED BIRCH EXPOSED IN A SOIL-BED

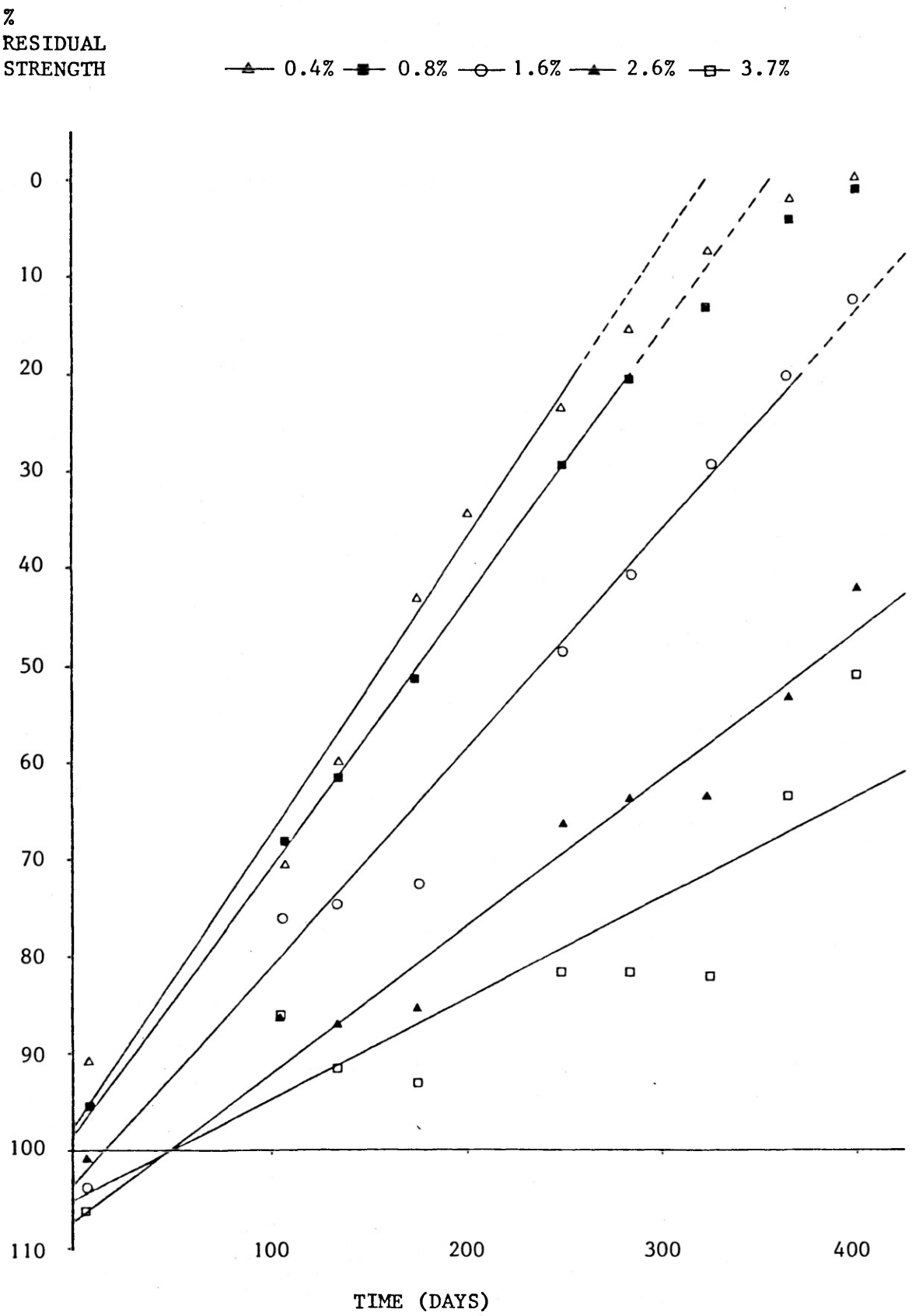


FIGURE 22 PERFORMANCE OF CCB TREATED BIRCH EXPOSED IN A SOIL-BED

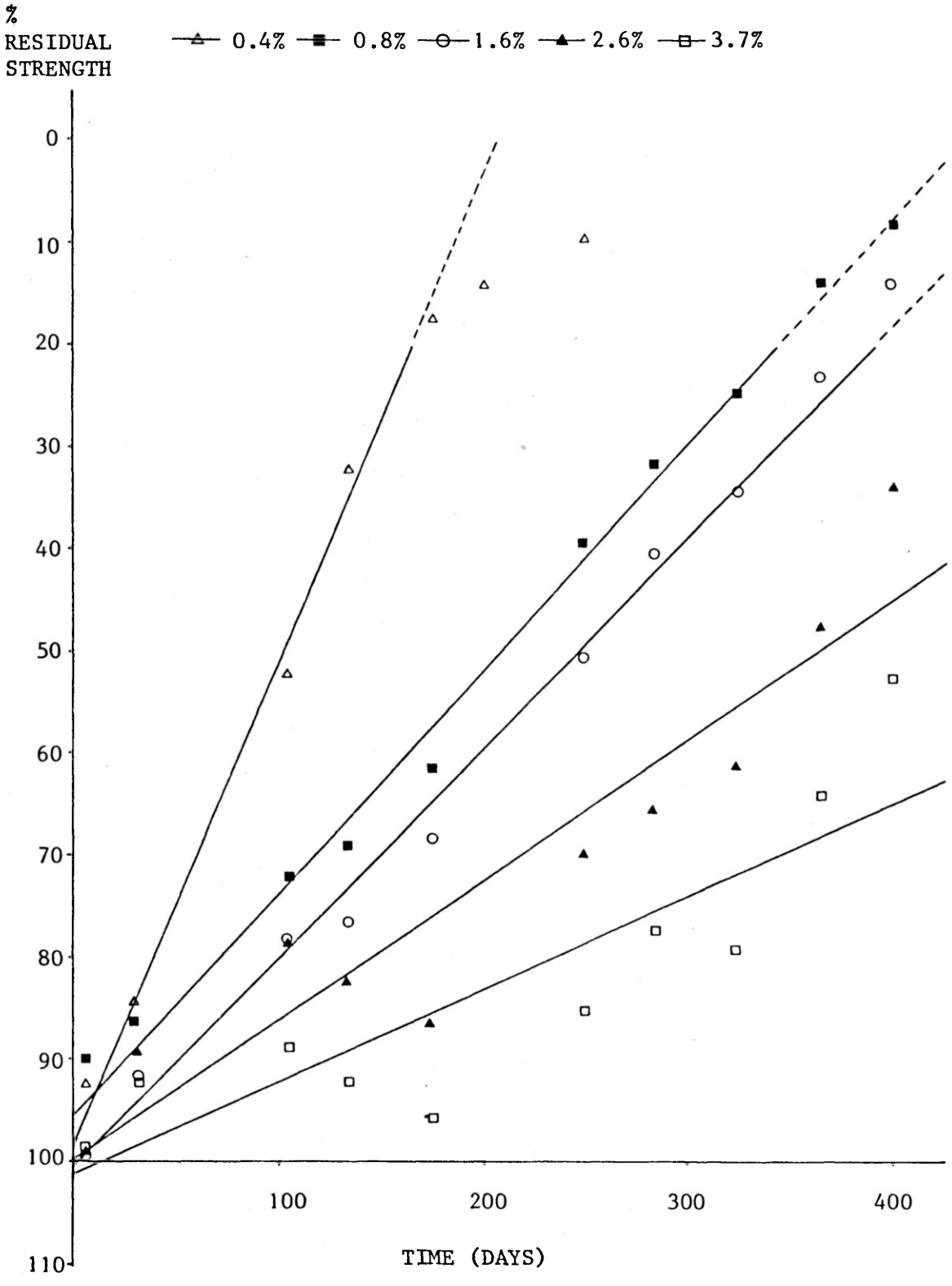


FIGURE 23 PERFORMANCE OF CCB+A TREATED BIRCH EXPOSED IN A SOIL-BED

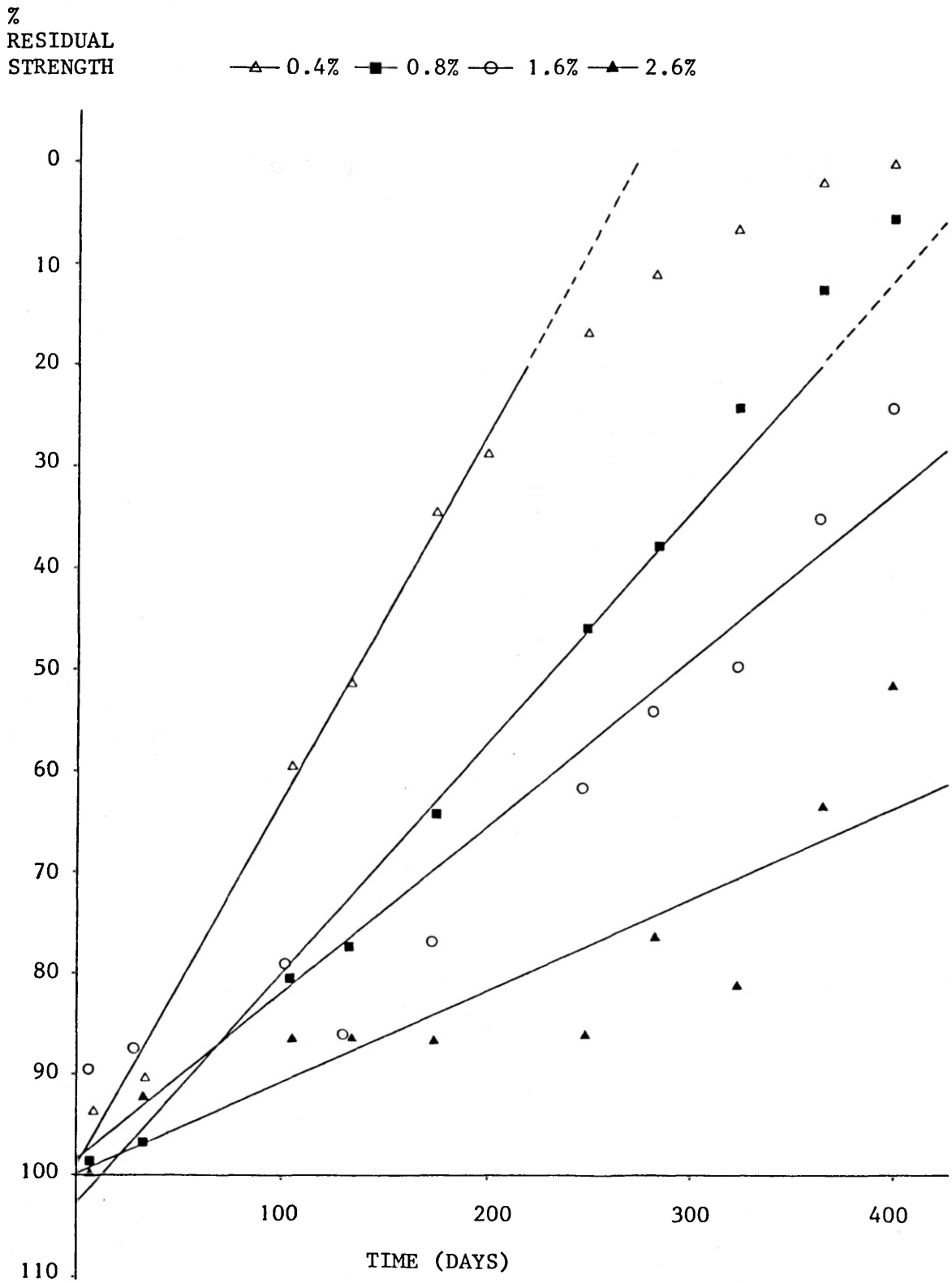


Table 40 -

Regression Analysis on % Residual Strength
Data of Birch Exposed in the Soil-Bed

Treatment	Concentration (% CCA Eq.)	Residual Strength on Day Zero	Time to Zero Residual Strength	Slope	Correlation Coefficient	Probability
CCA	0.4	97.97	324	-.302	-.873	<.001
	0.8	98.61	357	-.276	-.979	<.001
	1.6	103.59	463	-.224	-.952	<.001
	2.6	107.26	703	-.153	-.824	<.001
	3.2	105.01	1007	-.104	-.728	<.001
CCB	0.4	98.73	207	-.477	-.902	<.001
	0.8	95.95	434	-.221	-.935	<.001
	1.6	100.87	486	-.207	-.949	<.001
	2.6	99.90	725	-.138	-.794	<.001
	3.7	101.45	1101	-.092	-.763	<.001
CCB+A	0.4	98.91	274	-.359	-.935	<.001
	0.8	102.84	451	-.228	-.945	<.001
	1.6	98.43	593	-.166	-.882	<.001
	2.6	99.79	1107	-.090	-.764	<.001

Table 41 -

Analysis of Variance on Residual Strength Data of Birch Exposed in the Soil-Bed

	Treatments Compared	TIME (DAYS) 105	134	175	248	284	324	365	400
0.4	CCA/CCB	*	*	*	*	*	*	-	-
	CCA/CCB+A	*	-	-	-	-	-	-	-
	CCB/CCB+A	-	*	*	-	-	*	-	-
	F Ratio	6.72	7.91	6.83	2.83	3.23	3.00	1.34	
	L.S.D.	10.38	14.85	14.74	12.24	9.11	5.96	3.27	
0.8	CCA/CCB	-	-	*	*	*	*	*	*
	CCA/CCB+A	*	*	*	*	*	*	*	-
	CCB/CCB+A	*	*	-	-	-	-	-	-
	F Ratio	7.82	8.11	3.88	5.86	8.69	3.24	4.63	3.60
	L.S.D.	6.63	8.08	9.54	9.88	8.50	10.14	7.06	5.10
1.6	CCA/CCB	-	-	-	-	-	-	-	-
	CCA/CCB+A	-	*	-	*	*	*	*	*
	CCB/CCB+A	-	*	-	*	*	*	*	*
	F Ratio	0.22	4.07	2.10	4.14	4.22	6.48	4.44	4.50
	L.S.D.	8.97	8.44	8.5I	9.64	10.84	11.52	10.16	7.95
2.6	CCA/CCB	-	-	-	-	-	-	-	-
	CCA/CCB+A	-	-	-	*	-	*	-	-
	CCB/CCB+A	-	-	-	*	-	*	-	*
	F Ratio	2.63	0.61	0.06	9.38	2.18	3.93	1.99	2.73
	L.S.D.	8.52	9.27	10.09	9.93	13.58	16.11	17.24	15.65
3.7	CCA/CCB	-	-	-	-	-	-	-	-
	t		-.232		-.829	1.072			

Significant F ratios underlined

- = no significant difference between means

* = significant difference between means (p = 0.05)

Table 42 -

Mean Copper Retentions and Weight Losses in the Birch Stakes Remaining After 400 Days Exposure in the Soil-Bed

Treatment	Copper Retention	Standard Error	Weight Loss	Standard Error	No. of Stakes
CCA 0.4	0.220	0.00	52.63	3.70	3
0.8	0.435	0.00	44.48	2.33	3
1.6	0.846	0.01	37.39	2.93	9
2.6	1.376	0.02	22.30	2.17	10
3.7	1.995	0.03	14.86	1.65	10
CCB 0.4	0.218	0.00	-		0
0.8	0.425	0.00	44.09	1.37	9
1.6	0.792	0.01	35.94	1.33	10
2.6	1.428	0.02	24.20	1.77	10
3.7	1.949	0.02	15.71	0.91	10
CCB 0.4 +A	0.194	0.00	52.12	1.21	2
0.8	0.398	0.01	40.43	0.80	8
1.6	0.802	0.01	31.21	1.70	10
2.6	1.345	0.02	18.03	0.94	10

FIGURE 24 PERFORMANCE OF BIRCH EXPOSED FOR 400 DAYS IN A SOIL-BED

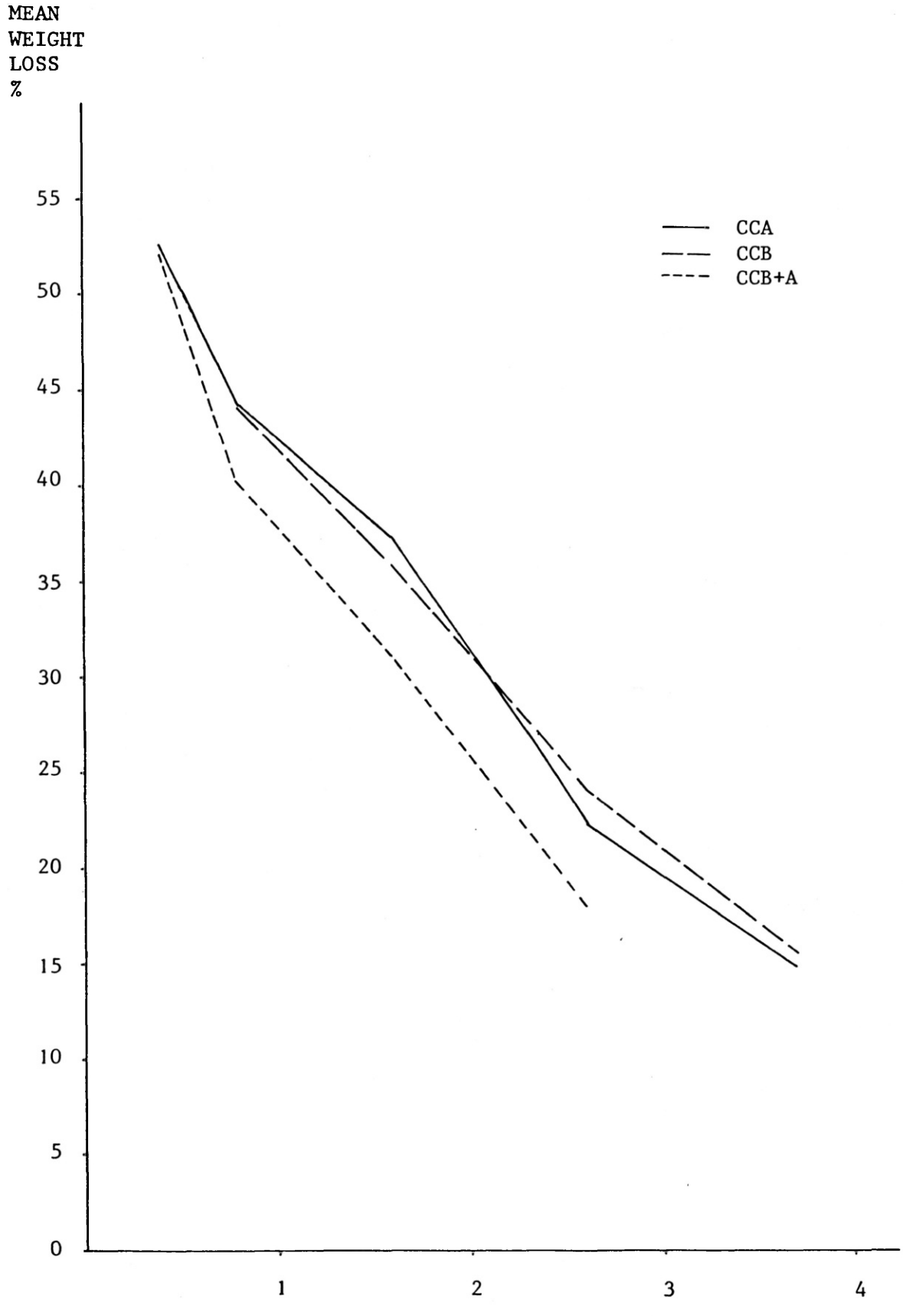


Table 43 -

Analysis of Variance on Weight Losses
in Birch Exposed in the Soil-Bed for 400 Days

Treatments Compared	Treating Solution (% CCA Equivalent)				
	0.4	0.8	1.6	2.6	3.7
CCA/CCB	-	-	-	-	-
CCA/CCB+A	-	*	*	-	
CCB/CCB+A	-	*	-	*	
F Ratio		2.85	2.53	<u>3.44</u>	
L.S.D.		3.64	5.81	4.95	

- = no significant difference between means

* = significant difference between means (p = 0.05)

significant F ratios underlined

Table 44 -

Mean % Residual Strengths in Treated Scots Pine Exposed in the Soil-Bed

(i) 0.4% CCA Equivalent Treating Solution

(ii) 0.8% CCA Equivalent Treating Solution

(i) Time (days)	Treating Solution 0.4%					
	CCA		CCB		CCB+A	
	Mean	Standard Error	Mean	Standard Error	Mean	Standard Error
7	91.5	2.65	95.9	5.26	92.9	0.97
16	99.0	6.65	88.1	4.05	100.2	3.29
175	93.3	4.23	71.9	3.05	96.5	2.48
284	74.8	4.04	48.5	5.14	93.7	2.00
365	62.8	3.33	37.3	5.93	90.4	2.83
400	53.7	3.33	30.2	5.40	85.9	4.35
(ii)	Treating Solution 0.8%					
7	98.5	0.97	99.6	5.56	102.6	1.43
16	93.7	2.95	96.2	4.90	104.4	2.83
175	92.0	1.68	93.4	3.93	99.8	1.96
284	87.3	3.53	98.8	3.30	98.1	3.41
365	99.1	3.02	107.0	5.37	103.1	1.88
400	89.5	3.12	98.8	3.19	106.3	3.32

Table 44 continued -

(iii) 1.6% CCA Equivalent Treating Solution
(iv) 2.6% CCA Equivalent Treating Solution
(v) 3.7% CCA Equivalent Treating Solution

(iii) Time (days)	Treating Solution 1.6%					
	CCA		CCB		CCB+A	
	Mean	Standard Error	Mean	Standard Error	Mean	Standard Error
7	96.5	2.56	95.0	4.20	102.7	2.32
16	101.1	7.14	99.5	3.12	109.5	7.48
175	97.8	2.38	93.9	3.85	100.8	2.33
284	98.6	2.93	102.9	3.30	102.0	2.31
365	104.4	3.19	109.6	4.78	106.3	2.43
400	109.4	1.77	105.1	2.31	105.2	1.63
(iv)	Treating Solution 2.6%					
7	95.8	3.14	104.9	7.75	100.6	2.75
16	94.1	3.92	102.8	4.87	108.7	4.42
175	89.8	4.43	92.8	2.12	99.9	3.53
284	92.7	2.45	95.0	1.89	98.0	3.38
365	98.2	3.12	105.8	2.91	96.4	2.83
400	102.2	3.19	106.3	2.15	108.7	1.73
(v)	Treating Solution 3.7%					
7	102.8	3.87	101.5	4.12	99.0	2.55
16	102.3	6.04	96.8	3.11	100.8	3.66
175	100.6	5.59	98.8	2.10	99.5	3.39
284	102.9	5.40	96.2	4.39	98.9	2.09
365	103.5	4.18	107.5	4.26	107.6	4.70
400	107.6	4.59	108.5	2.53	108.0	1.50

FIGURE 25 PERFORMANCE OF 0.4% CCA EQUIVALENT TREATED SCOTS PINE EXPOSED IN A SOIL-BED

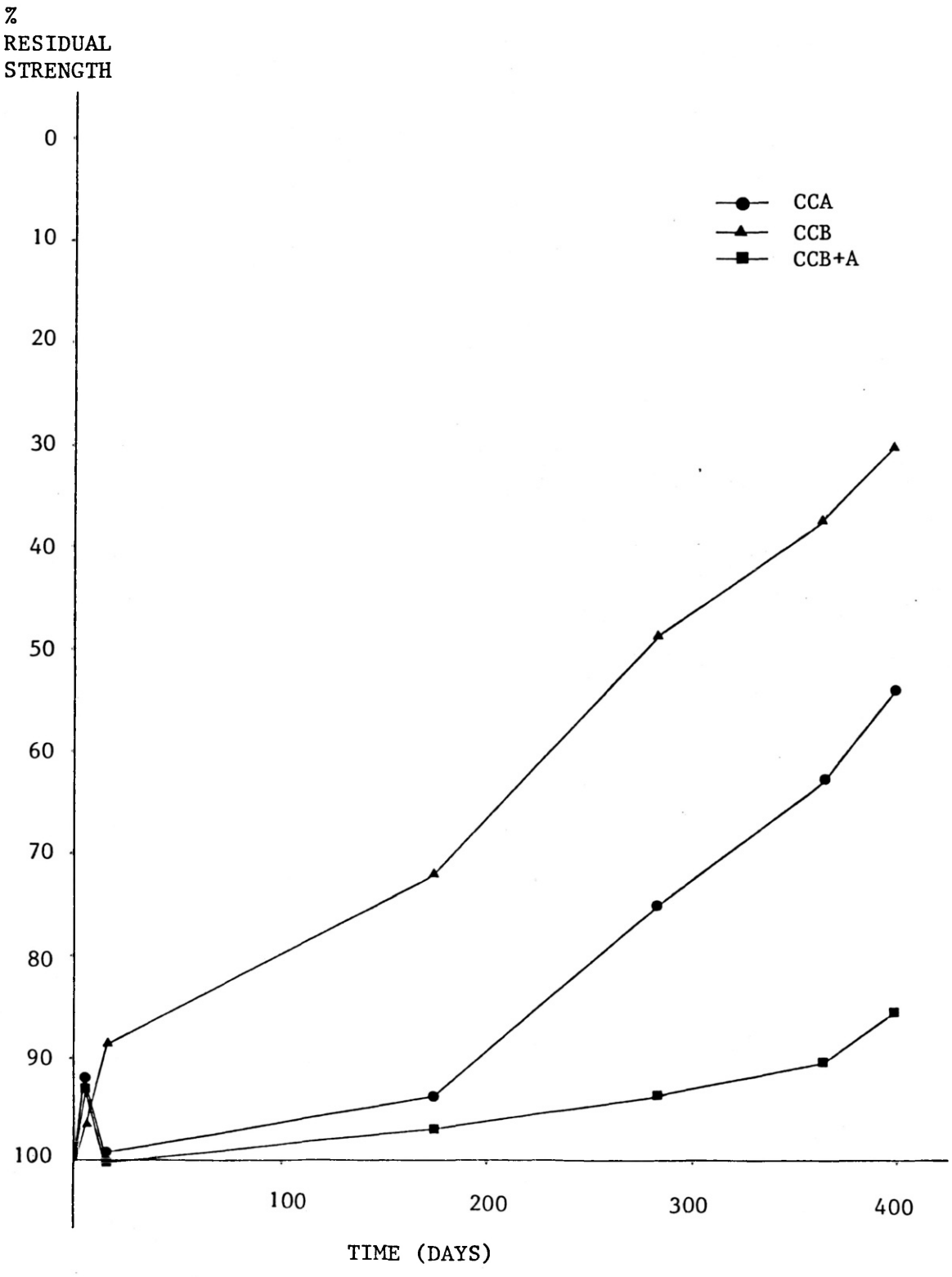


Table 45 -

Mean Copper Retentions and Weight Losses in Scots Pine After 400 Days Exposure in the Soil-Bed

Treatment		Copper Retention (Kgm^{-3})	Standard Error	Weight Loss	Standard Error
CCA	0.4	0.245	0.00	15.02	1.30
	0.8	0.506	0.01	4.06	0.54
	1.6	0.920	0.00	0.23	0.16
	2.6	1.483	0.02	-1.21	0.05
	3.7	2.169	0.02	-2.41	0.12
CCB	0.4	0.236	0.00	24.14	2.11
	0.8	0.500	0.01	3.62	0.29
	1.6	0.990	0.01	0.66	0.07
	2.6	1.606	0.02	0.04	0.23
	3.7	2.367	0.02	-0.19	0.18
CCB+A	0.4	0.241	0.00	7.66	1.21
	0.8	0.494	0.00	3.31	0.63
	1.6	0.999	0.01	0.67	0.15
	2.6	1.669	0.02	-0.50	0.41
	3.7	2.343	0.04	-2.57	0.20

FIGURE 26 PERFORMANCE OF SCOTS PINE EXPOSED IN A SOIL-BED FOR 400 DAYS

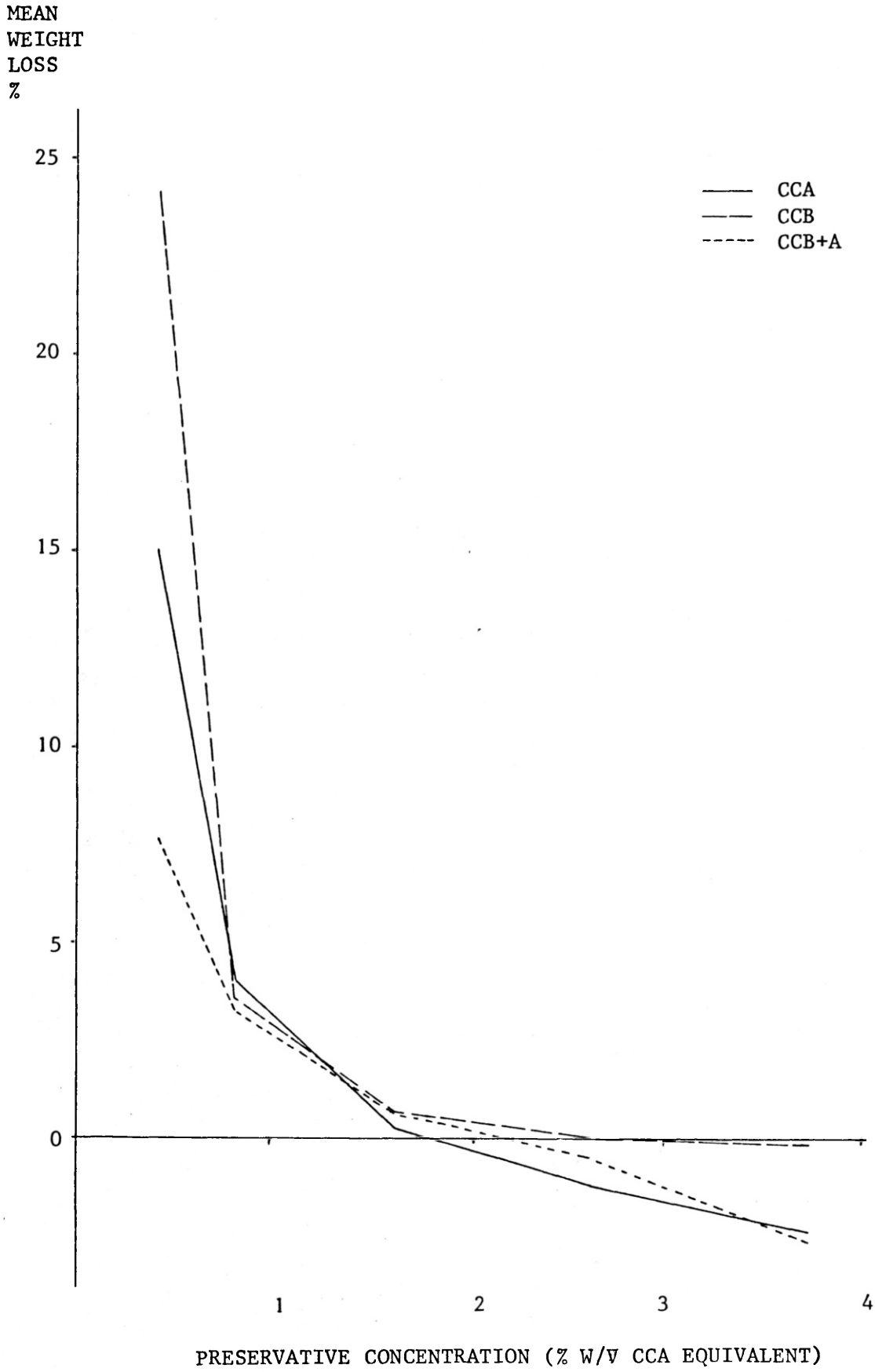


Table 46 -

Analysis of Variance on Residual Strength Data of Scots Pine Exposed in the Soil-Bed

Treatments Compared	Days				
	32	175	284	365	400
0.4%					
CCA/CCB	-	*	*	*	*
CCA/CCB+A	-	-	*	*	*
CCB/CCB+A	-	*	*	*	*
F Ratio	1.00	16.06	32.94	39.04	39.54
L.S.D.	15.11	9.90	11.72	12.61	13.24

Table 47 -

Analysis of Variance on Residual Strengths in Scots Pine After 400 Days' Exposure in the Soil-Bed

Treatments Compared	0.4%	0.8%	1.6%
CCA/CCB	*	-	-
CCA/CCB+A	*	*	-
CCB/CCB+A	*	-	-
F Ratio	39.54	6.83	1.66
L.S.D.	13.24	9.56	5.74

Table 48 -

Analysis of Variance on Weight Losses in Scots Pine Exposed in the Soil-Bed for 400 Days

Treatments Compared	0.4%	0.8%
CCA/CCB	*	-
CCA/CCB+A	*	-
CCB/CCB+A	*	-
F Ratio	26.92	0.54
L.S.D.	4.72	1.51

Significant F Ratios underlined
- = no significant difference between means
* = significant difference between means (p = 0.05)

FIGURE 27 RATE OF LOSS IN RESIDUAL STRENGTH AGAINST COPPER RETENTION IN TREATED BIRCH EXPOSED IN A SOIL-BED

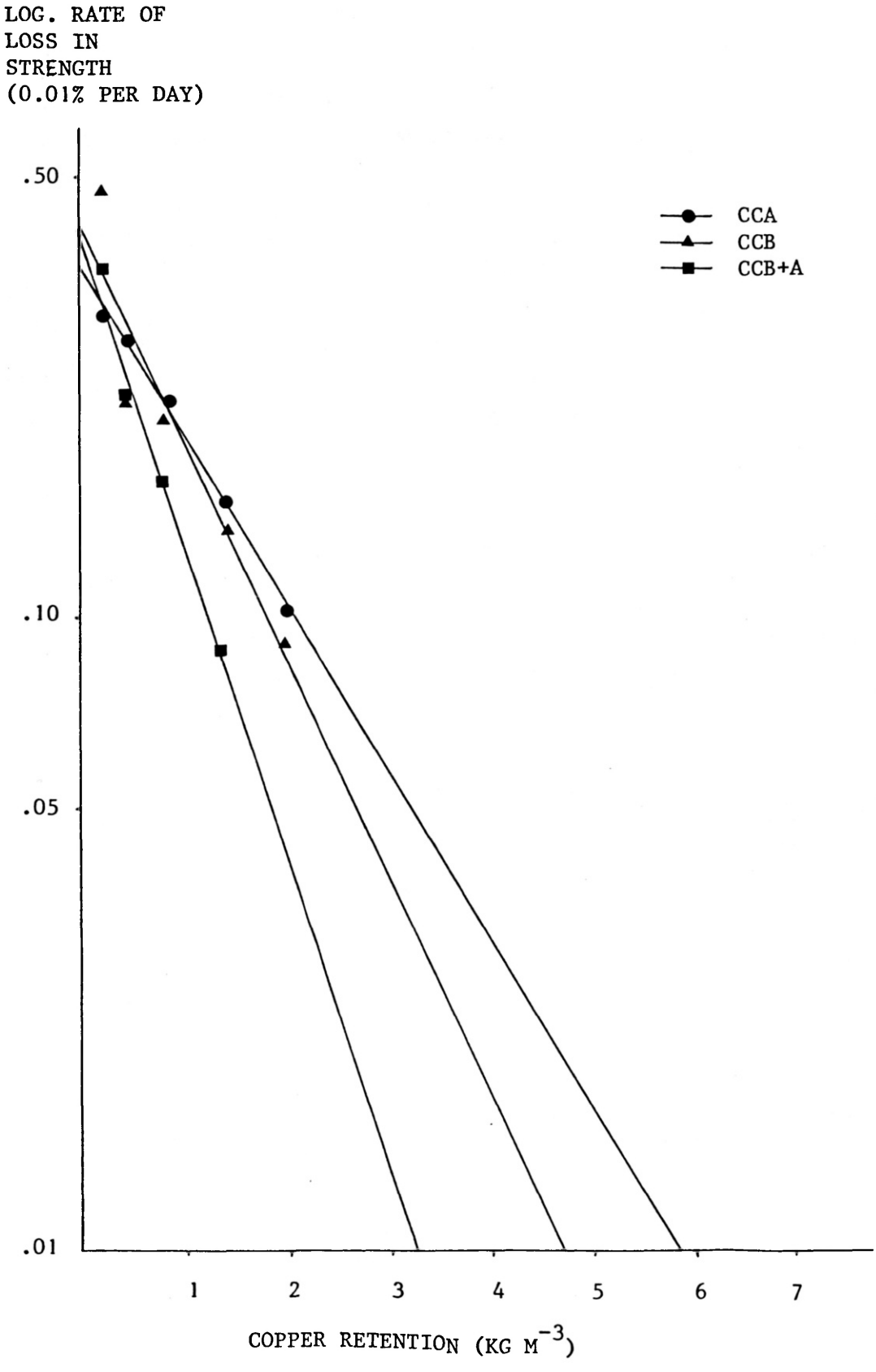


Table 49 -

Regression Analysis on log. Rate of Loss in Strength
Against Copper Retention in Birch Exposed in the Soil-Bed

Treatment	Rate (not log.) at Zero Retention	Slope	Rate = 0.01 Retention =	Rate = 0.1 Retention =	Correlation Coefficient	n	Probability
CCA	.358	-.266	5.840	2.082	-.998	5	$<.005$
CCB	.419	-.346	4.681	1.795	-.934	5	$<.02$
CCB+A	.406	-.491	3.274	1.238	-.987	4	$<.02$

Rate = 0.01% day^{-1}, stake life of 10,000 days

$\frac{CCA}{CCB+A} = 1.784$

$\frac{CCA}{CCB} = 1.248$

$\frac{CCB}{CCB+A} = 1.430$

Rate = 0.1% day^{-1}, stake life of 1,000 days

$\frac{CCA}{CCB+A} = 1.682$

$\frac{CCA}{CCB} = 1.160$

$\frac{CCB}{CCB+A} = 1.450$

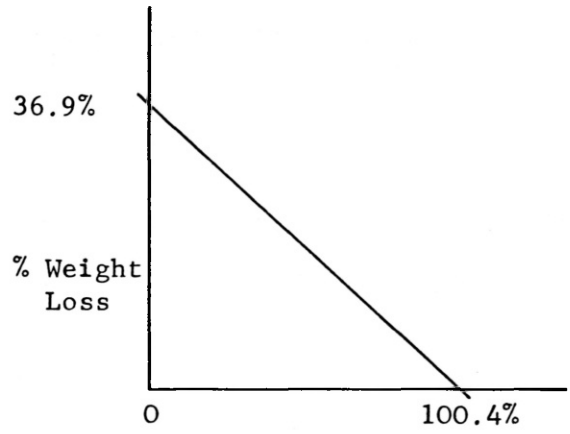
Table 50 -

Soil Moisture Content Expressed as Percentage of that at the Water Holding Capacity

DAY	BIN 1		BIN 2	
	% M.C.	% W.H.C.	% M.C.	% W.H.C.
0	25.60	87	-	-
16	30.00	102	28.30	96
32	30.95	105	31.80	108
49	29.88	102	29.68	101
66	33.60	114	29.95	102
73	26.74	91	26.43	90
77	24.30	83	24.34	83
80	24.96	85	25.30	86
86	22.06	75	24.15	82
105	20.11	68	18.89	64
122	21.11	72	20.00	68
134	23.75	81	22.56	77
156	24.20	82	23.20	79
175	24.26	83	22.26	76
200	25.89	88	22.55	77
248	24.50	83	23.83	81
284	27.31	93	26.67	91
324	22.35	76	23.51	80
365	24.70	84	24.90	85
400	25.29	86	24.48	83

Figure 28 -

Regression Analysis on Residual Strengths and Weight Losses in Birch Exposed for 400 Days in the Soil-Bed



Slope = -.367

3% weight loss ≡ 92.3% residual strength

80% residual strength ≡ 7.5% loss in weight

20% residual strength ≡ 29.5% loss in weight

n = 57

correlation coefficient = -.7726

probability = <.001

TREATMENT CONCENTRATION

(% W/V CCA EQ.)

UNTREATED 0.8 1.6 3.7

PRESERVATIVE

CCA

CCB

CCB+A

PLATE 7

TREATED BIRCH BLOCKS AFTER 16 WEEKS' EXPOSURE IN A WATER COOLING TOWER

3.6 Water Cooling Tower

3.6.1 Method

The treated samples (section 2.4) were exposed to the severe leaching and soft-rot hazards of a water cooling tower. The method of test was described in section 2.2.5. CCA, CCB and CCB+A were assayed in both birch and Scots pine wood blocks at concentrations of 0.8, 1.6 and 3.7% CCA equivalent. There were 3 replicates of each block size. The exposure period was increased from 12 to 16 weeks as the cooling tower was only in use part-time during the test period.

3.6.2 Results

A list of the tables and figures will be followed by a description of the results.

The mean copper retentions and weight losses with their standard errors are given for each block size in tables 51 for birch and 52 for Scots pine. The results of an analysis of variance on the birch data are given in table 53a for the small blocks and 53b for the larger blocks.

In Scots pine (table 52) the weight losses in the untreated wood blocks were significant but the treated blocks did not lose a significant amount of weight and had a tendency to gain weight.

In birch (table 51) the weight losses in the untreated blocks were again significant. The smaller blocks showed a greater percentage weight loss than did the larger blocks. In the case of the small blocks, the CCB treated wood suffered the smallest weight losses (table 51a) and these were statistically significantly lower than those of the CCA and CCB+A treated samples (table 53a). In the large blocks (table 51b) the weight losses at the 0.8% concentration were the only ones which were significant (i.e. greater than 3%). At this concentration (table 53b), the CCB+A treated samples were significantly less decayed than were the CCA treated samples, as measured by weight loss. (see Plate 7)

Table 51 -

Mean Copper Retentions and Weight Losses in Birch Exposed in a Water Cooling Tower

(a) 50 x 25 x 5 mm Blocks

Treatment		Mean Copper Retention (Kgm^{-3})	Standard Error	Mean Weight Loss	Standard Error
CCA	0.8	0.45	0.00	5.77	.35
	1.6	0.89	0.00	3.43	.30
	3.7	2.09	0.01	2.53	.09
CCB	0.8	0.42	0.00	4.49	.24
	1.6	0.79	0.00	1.90	.36
	3.7	1.93	0.03	1.67	.07
CCB +A	0.8	0.43	0.01	5.06	.25
	1.6	0.77	0.01	3.69	.28
	3.7	2.07	0.00	2.67	.13
U		-	-	11.70	-

(b) 50 x 25 x 15 mm Blocks

CCA	0.8	0.44	0.00	3.44	.41
	1.6	0.88	0.00	.60	.20
	3.7	2.04	0.02	-1.01	.34
CCB	0.8	0.44	0.00	2.91	.19
	1.6	0.78	0.01	.30	.05
	3.7	2.06	0.03	-1.41	.04
CCB +A	0.8	0.44	0.05	2.17	.14
	1.6	0.80	0.02	1.16	.06
	3.7	2.02	0.01	-.82	.03
U		-	-	8.02	.31

Table 52 -

Copper Retentions and Weight Losses
in Scots Pine Exposed in a Water Cooling Tower

(a) 50 x 25 x 5 mm Blocks

Treatment		Mean Copper Retention (Kgm^{-3})	Standard Error	Mean Weight Loss	Standard Error
CCA	0.8	0.51	0.00	2.46	0.22
	1.6	0.93	0.00	-	-
	3.7	2.20	0.00	4.52	1.34
CCB	0.8	0.50	0.00	1.31	0.23
	1.6	1.01	0.00	1.24	0.18
	3.7	2.37	0.01	2.30	0.14
CCB +A	0.8	0.50	0.00	1.47	0.09
	1.6	1.01	0.00	2.51	0.08
	3.7	2.39	0.00	4.09	0.08
U		-	-	7.55	0.14

(b) 50 x 25 x 15 mm Blocks

CCA	0.8	0.51	0.00	-0.03	0.09
	1.6	0.94	0.00	-	-
	3.7	2.18	0.00	1.03	0.06
CCB	0.8	0.51	0.00	-0.41	0.08
	1.6	1.02	0.01	-0.78	0.06
	3.7	2.37	0.02	-0.97	0.04
CCB +A	0.8	0.51	0.00	-0.24	0.07
	1.6	1.03	0.00	-0.62	0.08
	3.7	2.40	0.01	-1.22	0.10
U		-	-	5.80	0.15

Table 53 -

Analysis of Variance on Weight Loss Data in Birch Exposed in a Water Cooling Tower

(a) 50 x 25 x 5 mm Blocks

Treatments Compared	Treating Solution		
	0.8	1.6	3.7
CCA/CCB	*	*	*
CCA/CCB+A	-	-	-
CCB/CCB+A	-	*	*
F Ratio	5.10	9.41	28.68
L.S.D.	0.98	1.09	0.35

(b) 50 x 25 x 15 mm Blocks

Treatments Compared	Treating Solution		
	0.8	1.6	3.7
CCA/CCB	-	-	-
CCA/CCB+A	*	*	-
CCB/CCB+A	-	*	-
F Ratio	5.42	12.28	2.29
L.S.D.	0.95	0.43	0.69

Significant F ratios underlined

- = no significant difference between means

* = significant difference between means (p = 0.05)

3.7 Table 54 - Summary of Biological Test Results

Test	Coniophora puteana		Coriolus versicolor		Gloeophyllum trabeum		Poria placenta		Phialophora fastigiata		Chaetomium globosum		Soil Burial		Soil Bed		Cooling Tower	
Treatment	B	SP	B	SP	B	SP	B	SP	B	SP	B	SP	B	SP	B	SP	B	SP
CCA	4	4	4	4	4	4	-	-	3	0	1	0	2	0	1	4	3	0
CCB	-	-	4	4	4	4	1	-	4	0	3	0	4	0	2	3	4	0
CCAB	4	4	4	4	4	4	-	-	3	0	2	0	3	0	0	0	0	0
B+CCA	0	0	0	0	4	4		-	4	0	-	0	0	0	0	0	0	0
CCB+A	4	4	4	4	4	4	1	-	4	0	4	0	0	0	3	4	3	0

KEY 0 not tested, no significant decay

\- significant weight loss at all concentrations

1, 2, 3, 4 effectiveness (1 being the least effective)

B = birch
SP = Scots pine

3.8 Discussion

When accelerated tests are carried out in the laboratory it is not possible to simulate all the complex interactions which occur in nature. Since the conditions of the test may be quite different from those in the field, care must be taken in the interpretation of laboratory test data. With experience, the minimum capacity of the preservatives to give the desired protection can be estimated. This estimate can only be confirmed by use of the preservatives under natural conditions in the form of long term service trials. With this in mind, a short appraisal of the methods of test used in this work will be followed by a comparison of the results with those of other workers and, where available, with results obtained in the field.

3.8.1 Methods of Test

There were few problems associated with the actual method used for the basidiomycete monoculture tests but, without initial tests, it was often difficult to find a range of concentrations over which to test the preservatives. Examples of this difficulty are evident in the case of Gloeophyllum trabeum where all of the concentrations tested were toxic, and Poria placenta where often protection was not achieved by any of the concentrations. On the other hand, the problem with the soft-rot monoculture tests, particularly in the case of Phialophora fastigiata, was the need for an extended test period and the risk of contamination of the plates by mites.

In the soil burial test there was little decay of the wood blocks despite the extended incubation period. This has also been found by other workers (Bravery, 1972) using soil from a similar source. The apparent inactivity of the soil could be due to its nutrient status or pH but the problem may arise from waterlogging of the samples. Soil with a moisture content of 19% at the water holding capacity is greatly affected by slight errors in watering which can result in severe waterlogging or drying of the samples (cf. New Zealand soil of 65% moisture content at the water holding capacity (Murphy, Schasching and Dalley, 1982) which is less sensitive to over or under-watering). Once again, in the initial stages in the soil-bed, waterlogging of the samples was a problem. To begin with, all of the samples were planted saturated with water according to Vinden (1982). The soil at this time was of a suitable moisture content for decay being 87% of the moisture content at the water holding capacity (Duncan, 1965; Carey and Grant, 1975). However, this environment was upset by the introduction of water with the samples and the moisture content rose steeply to a level above that at water holding capacity, which is unsuitable for decay (Carey and Grant, 1975). This period of wetness seemed only to affect the progress of decay in untreated samples which, in cross-section, showed that soft-rot attack was restricted to the outer layers. Subsequently the soil moisture content was maintained at about 80% of that at the water holding capacity. Observations on the moisture content with depth showed that deeper down in the soil the moisture content was slightly higher. With this moisture profile the range of untreated and

treated samples' moisture requirements were met at some point in their length. Clear differences in moisture uptake by treated and untreated samples have been shown by Murphy (1982). Further investigations of this nature are currently being undertaken at Imperial College.

Once equilibrated the soil-bed provided a good test system and its use overcame many of the problems associated with the other test methods. The biological hazard comprises a range of micro organisms, including, presumably, those responsible for detoxification and initial colonisation as well as insect and other pests. The fungi present in the soil-bed used in this work are currently being investigated by Clubbe (1983).

The water cooling tower trial was unique in being a field test carried out under accelerated conditions. The running hours and the conditions in this particular cooling tower gave rise to relatively little decay in the wood samples as measured by loss in weight. In the light of the discussion in section 2.3.1 strength loss may have been a more appropriate method of assessment, or the microscopical method (S.R.D.) of Hoffmeyer (1976) although decay is said to be confined to the surface layers which are subsequently washed away. This was evident in the samples as erosion of the stamped identification marks.

Each of the test methods showed a degree of suitability for assessing the performance of the preservatives in birch (the object of the study), comparative data being obtained in all cases. However, in several of the tests, untreated Scots pine did not

reach a satisfactory level of decay for measurement and comparison of the treated samples to be possible. This is a problem in tests where the samples are only assessed at one time, such as weight loss or strength testing to failure. On the other hand, the methods of test and assessment in the soil bed investigation were suitable for extended exposure periods and continuous assessment. Indeed, comparative data were obtained for treated Scots pine and more data would have been available if the test had been continued. The main point is that the assessment was not made after an arbitrary time period which risked being unsuitable for the material under test (c f. soft-rot organism monoculture tests and soil burial tests). What the soil bed gained in flexibility it lost in reproducibility and sensitivity. The wide variation in the strength data for the replicates, be it due to the test apparatus or test specimens or conditions, meant that a level of 80% residual strength was taken as being significant (Vinden, 1982; Bravery and Lavers, 1971). It is interesting to note that it was at about 80% residual strength that significant differences were first detected in many of the statistical tests but, in a correlation with loss in weight, this level of residual strength was equivalent to a weight loss of 7.5% in birch, greater than the 3% level of significance assumed in many standard tests (e.g. EN 113, 1982). This lack in sensitivity was overcome by plotting linear regression lines calculated from all of the data between 100 and 20% residual strength. The high levels of significance associated with these analyses indicated that the method was valid. It seems that even in the decayed stakes of less than 20% residual strength there was a linear relationship between the load applied and the resulting deflection. If this stage were beyond the limit of proportionality then, rather than measuring a deflection which resulted in an unexpectedly high % residual strength, the measured deflection

would be relatively larger and the % residual strength unexpectedly low. Since the opposite was apparent at residual strengths of less than 20%, Vinden et al's (1982) "senescence" seems to be in evidence. The term "senescence" refers to the final stages of decay where the rate of attack is decreased. A further problem with the Scots pine specimens was the apparent increase in residual strength. This has also been noted by Baines (1982a) and Vinden (1982).

A similar problem was encountered in the water cooling tower trial where some of the samples showed an apparent gain in weight. This has also been reported by Irvine, Eaton and Jones (1972) who found that samples frequently showed the greatest weight losses after 12 weeks of a 40 week exposure. Since the purpose of the timber in the water cooling tower is to provide a large surface area for evaporation, it follows that any impurities in the water will be left on the timber surface and may result in a weight gain regardless of decay. This may well have occurred on the test blocks. In the case of the water cooling towers at Little Barford, many of the existing timbers were coated with a scale similar to that found in a kettle.

The performance and interpretation of the long-established basidiomycete tests presented little difficulty. However, problems are encountered in all types of soft-rot testing but, by using several different approaches which gave similar results, it is felt that a valid picture of performance has been built up,

particularly with regard to the treated hardwood.

3.8.2. Results

An attempt to summarise the results of the biological tests has been made in table 54. The level of performance referred to is a measure of the concentration of preservative required to give protection and also the comparative performance of the formulation within the group under test.

3.8.2.1 Basidiomycetes

All of the treatments tested performed well in both birch and Scots pine when exposed to Coriolus versicolor and Gloeophyllum trabeum. The total salt retentions at the toxic values in pine and birch were similar to those referred to by Tillott and Coggins (1981) for CCA in pine and beech with Gloeophyllum trabeum and Coriolus versicolor respectively. However, the salt retention at the toxic value in CCB treated Scots pine was approximately an order of magnitude lower than that referred to by Tillott and Coggins (1981). In the case of Coniophora puteana in birch all of the treatments performed well with the exception of CCB where weight losses were great at the highest treatment concentration. Coniophora was apparently tolerant to copper, chromium and boron at the levels present in the leached wood blocks. The results for Coniophora in Scots pine were similar for CCA, CCB and CCAB but CCB+A was slightly less protective in this case. The retention of arsenic or its state in the wood may have been responsible for this discrepancy. The toxic retentions in the Scots pine agree with those referred to by Tillott and Coggins (1981) for CCA but a higher level must be required than that established for CCB.

When tested against Poria placenta all of the preservatives performed badly at the concentrations used in both birch and Scots pine. The toxic values established were misleading in indicating that CCB performed better than CCA and CCAB in birch. From the graphs it can be seen that CCB gave the poorest performance in both timber species, the formulations containing all 4 constituents giving a better level of protection at most concentrations. In Scots pine CCA performed relatively well. The retention of CCA required for protection of Scots pine against Poria must be significantly higher than the 3.5 - 5.8 kgm^{-3} referred to by Tillott and Coggins (1981), since the highest concentration used in this study corresponded to a retention of about 22 kgm^{-3}. Considering the performance of the CCB relative to the other preservatives, it appears as though Poria placenta (F.P.R.L. 280) is not only copper tolerant but shows a substantial degree of tolerance to arsenic as well. Assuming that boron is highly leached, when the results obtained for CCB against Poria and Coniophora are compared, it would appear that Coniophora exhibits a greater tolerance to copper in this form than does Poria. It can be seen that organisms tolerant to copper are not controlled by CCB after leaching, probably because of loss of boron, and are only controlled where arsenic is present in the initial or subsequent treating solution, indicating the need for both arsenic and copper to give a wide spectrum of protection against basidiomycetes. Poria remains a problem.

3.8.2.2. Soft-rot organisms

In all of the tests where soft-rot attack was a hazard, that is: soil burial; soil bed; water cooling tower, and Phialophora and Chaetomium monoculture tests, CCB performed more effectively in birch than did CCA. In general, the results do not agree with the majority of those obtained in the International Research Group on Wood Preservation collaborative soil burial trial (Carey and Savory, 1975) nor those obtained by Kerner-Gang (1975) in beech, where CCA was usually more effective than CCB or equally effective. Bearing in mind the remaining test data, the unusually rapid decay of the Scots pine and birch treated with the lowest concentration of CCB in the soil bed was probably due, not entirely to soft-rot organisms, but to basidiomycete attack, or, more likely, to insect and animal invasion which is normally associated with active brown rot. This has been noted in the field (Tamblyn and Levy, 1981; Tillott and Coggins, 1981).

With the exception of the cooling tower material where decay was slight, when CCB+A was tested, it performed even better than did CCB. The superiority of CCB+A over both CCA and CCB was clearly evident in the Chaetomium globosum monoculture and soil bed tests. Considering the data available from the soil-bed test CCB+A showed a marked improvement over CCA in Scots pine. From the results of the test of all 5 formulations against Chaetomium globosum in birch a pattern of preservative performance in relation to soft-rot can be derived: the formulations in which copper and boron were applied together in solution (CCB, CCB+A) performed better than those in which copper and arsenic

were applied together (B+CCA, CCA) with those in which copper, arsenic and boron were applied together (CCAB) being intermediate in performance. The performance of CCB was enhanced by an additional treatment of arsenic but a prior treatment of boron, if anything, was detrimental to the performance of CCA. This clearly suggests that the key to performance against soft-rot organisms in hardwoods lies in the copper-boron rather than copper-arsenic relationship.

In general, there is a remarkable consistency in the results obtained from the various tests, the soil-bed results providing a summary of the main finds. According to Hedley (1980) performance in the soil-bed cannot clearly be related to performance in the field when different types of preservative are considered. However, in this case all of the treatments were similar, being waterborne, fixed copper chromates, and as such their relative performance in the soil bed may be indicative of their likely performance in the field. The combined results of the tests seem to explain observations made in the field: Tamblyn and C.R. Levy (1981) noted the failure of CCB treated pine to brown rot organisms and, in a field trial of CCA and CCB treated pine and beech, Tillott and Coggins (1981) observed the failure of low concentrations of CCB in pine and the superior performance of CCB treated beech over CCA treated beech in the U.K. and India. Failures in India were effected by termites in the case of CCB and in the case of CCA by fungal decay alone or fungal and termite attack. From results of tests already carried out on CCB+A treated Scots pine and birch, it would appear that failures due to copper tolerant brown rot organisms and termites would be avoided by the arsenic present and that the overall performance of specimens in the field would be enhanced. This is currently being investigated.

SECTION IV: CHEMICAL ASSESSMENTS

4. Section IV - Chemical Assessments

4.1 Introduction

This section deals with several investigations into the chemical differences in the treated wood with regard to leaching, fixation and preservative availability as a result of the various preservative treatments. The most important differences in the results of the biological assessments were the relative activities of CCA and CCB+A in birch when tested against soft-rot organisms. Therefore the chemical investigations were restricted to birch, although, where possible, an assessment was made of the whole range of formulations tested in section III. A single sub-toxic treating concentration of 2% w/v CCA equivalent was selected for study in many cases since, frequently at this level, there were major differences between the performances of the formulations in the soft-rot tests.

4.2 Chemical Analysis of Test Blocks

4.2.1 Introduction

Calculated preservative retentions based on uptake data may only be relied upon in situations where the relationship between calculated retentions and those established by analysis and also the timber and preservative system, are well known. However, there are several reasons why such retentions could not be relied upon as a measure of the components present in the test blocks in this case, namely:

(i) some of the formulations were different from those of preservatives previously studied, and it could not be assumed that the preservative components were taken up into the wood blocks in the same ratios as they were present in the treating solution;

(ii) in cases where there were two treatments, chemicals present in the wood following the first treatment may have been leached during the second treatment or could have affected the uptake of elements from the second treating solution;

(iii) the blocks were subjected to a laboratory leaching procedure prior to testing and, therefore, retentions calculated from uptake data could not be relied upon as true indications of the amounts of residual chemical in the wood, particularly in the case of boron.

There are many methods in use for the quantitative analysis of wood treated with CCA and these have been reviewed by Ofori (1977). They can be divided into two groups, the first involving analysis of the preservative components in situ in the wood and the second involving the extraction of the preservative elements from the wood prior to their accurate determination in solution. An in situ method commonly employed in industry makes use of X-ray fluorescence spectrometry. The samples are ground to a fine flour of which 0.25g (oven dry weight) is subjected to 15 tons weight in a die to form a pellet. The pellets are bombarded with X-rays and the spectroscopic properties of the secondary radiations are compared with those of standard samples. Boron, however, cannot be determined by this method. In the second group of methods there are many variations in both

the extraction technique and the method of analysis. Extraction techniques usually involve acid digestion (wet ashing) or leaching. Analytical techniques often employ titration, colorimetry, atomic absorption spectrometry or argon plasma emission spectrometry. A leaching method developed by Williams (1970) was selected for the British Standard (B.S. 5666, Part 3, 1979) in which one sample is leached to give a solution for the analysis of copper, chromium and arsenic. Ofori (1977) compared argon plasma emission spectrometry and atomic absorption spectrometry as the most desirable analytical techniques and found no significant difference between the results. He concluded that argon plasma emission spectrometry was the best method since it is rapid, sensitive and many elemental determinations can be made simultaneously. The problem with the present investigation was the need for the determination of copper, chromium, arsenic and boron. Many of the above methods are unsuitable for the determination or extraction of boron since it is partly lost on oven-drying and volatilised in hot acidic solutions. However, boron can be efficiently extracted from wood using a leaching method described by Williams (1968) and a dry ashing procedure using barium hydroxide and nitric acid (Reid, 1982). Using this leaching method it is not possible to extract fixed copper, chromium and arsenic and arsenic is lost during the dry ashing.

Since it was desirable to determine all of the elements using only one sample of each replicate if possible, a preliminary test was carried out to establish whether boron could be extracted from wood using the leaching method described by Williams (1970) and whether copper, chromium, arsenic and boron could be analysed simultaneously without interference using an argon plasma emission spectrometer.

4.2.2 Preliminary Test

4.2.2.1 Introduction

The objective of the preliminary test was twofold:

(1) to establish whether boron could be extracted from wood using Williams' (1970) method;

(2) to check that copper, chromium, arsenic and boron could be detected simultaneously using an argon plasma emission spectrometer.

As the two objectives of the test were interrelated, the tests were carried out simultaneously. Woodflour (see section 4.2.2.2.2) was treated with preservative to give samples of known retention. These were leached by Williams' (1970) method and the resulting solutions analysed by argon plasma emission spectrometry. The results of the analysis were compared with the theoretical retentions. At the same time standard solutions with and without boron were compared with each other and with the leachates of known theoretical composition to establish whether or not copper, chromium, arsenic and boron could be detected simultaneously.

4.2.2.2 Preparation of Materials

4.2.2.2.1 Calibration Solutions

A standard solution containing 500 ppm copper, 1,000 ppm chromium and 1,000 ppm arsenic was made up as described in BS 5666 Pt. 3, para. 3.2.5. A CCAB solution was made up in the same way but in the final stages 0.57144 g boric acid (H_3BO_3) was added to give a solution containing 500 ppm copper, 1,000 ppm chromium, 1,000 ppm arsenic and 200 ppm boron. For each standard solution a range of calibration solutions was prepared as described in paragraph 3.4.3 of BS 5666 Pt. 3. The concentrations of the various elements in the calibration solutions are given in table 53.

Table 53 -

Elemental Concentrations in the Calibration Solutions Prepared for Argon Plasma Emission Spectrometry

Solution	Elemental Concentration (ppm) --------CCA Standard----- --------CCAB Standard---------- Copper	Chromium	Arsenic	Boron
1	0	0	0	0
2	2.5	5	5	1
3	5	10	10	2
4	10	20	20	4
5	15	30	30	6
6	20	40	40	8
7	25	50	50	10
8	30	60	60	12
9	35	70	70	14
10	40	80	80	16
11	45	90	90	18
12	50	100	100	20
13	60	120	120	24

4.2.2.2.2 Treatment of Woodflour Samples

5% w/v CCA equivalent solutions of CCA, CCB and CCAB were made up as described in section 2.4.1.2. Serial dilutions were made to give the following range of solution concentrations: 2.5, 1.75, 1.0, 0.5, 0.25 % w/v CCA equivalent for each formulation. Birch woodflour was prepared by grinding untreated test blocks in a Wiley mill. Woodflour was used in preference to wood blocks for the preparation of standard samples since accurate uniform retentions could be achieved in woodflour but not in wood blocks. It was assumed that the interaction of the preservative with woodflour was similar to that with wood blocks. The woodflour was oven-dried to constant weight, cooled and divided into 2 g portions in small clean beakers. To each beaker 4 ml of a different treating solution was added, water being used to prepare untreated controls. In this way 2 samples of each of 5.0, 3.5, 2.0, 1.0 and 0.5 % w/w CCA equivalent were prepared for CCA, CCB and CCAB. The woodflour was thoroughly stirred and one set of samples was allowed to air dry immediately, the other set being sealed for 2 weeks and then slowly air dried to allow fixation to take place. After air drying the woodflour was thoroughly stirred and conditioned in a constant temperature room for 2 days before moisture content determinations were carried out on each sample.

4.2.2.2.3 Extraction of Treated Woodflour

Taking the moisture content into account, a sample of woodflour representing 1.000 g oven dry weight was weighed into a 50 ml volumetric flask for each of the 0.5, 1.0 and 2.0 concentrations and into a 100 ml volumetric flask for each of the 3.5 and 5.0 concentrations. The samples were then leached as described

in BS 5666 Part 3, paragraph 3.4.5, but on a smaller scale since the wood samples were small. In the case of the 50 ml volumetric flasks, 10 ml 2.5M sulphuric acid and 2 ml 100 volumes hydrogen peroxide were added to the woodflour. The flasks were heated in a water bath at 75°C for 30 minutes with occasional swirling to mix the contents. After cooling 20 ml water and 5 ml of a mixture of 0.5M sulphuric acid and 3 g l^{-1} sodium sulphate solution were added to the flasks which were topped up with water and left to stand overnight to equilibrate (Cox, 1982). Equilibration of the woodflour with the solution meant that the correction factor for wood volume used in BS 5666 was no longer required. Each mixture was then filtered under vacuum through a clean sintered glass filter to give the final solution for analysis. A sintered glass filter was used in preference to a cellulose filter paper (as used in BS 5666) since copper is thought to adsorb to cellulose particularly under acid conditions. Blank solutions were prepared as above with the woodflour omitted.

4.2.2.3 Details of the Solutions Analysed

The solutions resulting from section 4.2.2.2.3 were:

(i) a series of CCA calibration solutions;

(ii) a series of CCAB calibration solutions;

(iii) a series of leachates from woodflour untreated and treated with a range of partly fixed CCA, CCB and CCABs;

(iv) a series of leachates from woodflour untreated and treated with a range of fixed CCA, CCB and CCABs;

(v) several blank tests, where the woodflour was omitted.

An argon plasma emission spectrometer (model ARL 34000) was calibrated using the CCAB calibration solutions and the solutions in (i) - (v) were analysed for copper, chromium, arsenic and boron.

Theoretical values in ppm in the final solutions were calculated from the elemental % w/w retentions in the woodflour where appropriate.

4.2.2.4 Results

The analysed elemental concentrations of copper, chromium, arsenic and boron in the final solutions are given with the calculated values in table 54 for the CCA calibration solutions (i), table 55 for the partly fixed preservatives in the woodflour (iii) and table 56 for the fixed preservatives in the woodflour (iv). The blank values (v) are given with the results for the woodflour.

The values for the CCA calibration solutions closely resembled the theoretical values and indicate that the boron in the CCAB solution used to calibrate the spectrometer did not interfere with the detection of copper, chromium and arsenic. The results for the partly fixed preservatives compared well with the calculated values particularly for boron and indicate that all four elements can be analysed simultaneously using the argon plasma emission spectrometer. They also showed that boron was not lost during the extraction process. The values for the fixed preservatives in woodflour were in agreement with the calculated values particularly at the lower concentrations. The boron detection was slightly on the low side especially in the case of CCAB. This could be explained by the fixation of boron in the wood and the inability of the extraction process to recover it. However, considering the results for the other elements and the fact that the theoretical values were based on 100% pure reagents and total accuracy in the prepration of the solutions, this explanation was rejected.

4.2.2.5 Conclusions of the Preliminary Test

Copper, chromium, arsenic and boron can be extracted from woodflour using the method described in section 4.2.2.2.3 and detected simultaneously in the resulting solution by argon plasma emission spectrometry with accuracy particularly at levels below mid-range of the calibration series. This procedure was therefore adopted for the detailed chemical analysis of the treated wood used in the biological tests.

Table 54 -

Analysed Elemental Concentrations of Copper, Chromium, Arsenic and Boron in the CCA Calibration Solutions. Theoretical Values are shown in Parentheses

Sample	Elemental Concentration (ppm)			
	Copper	Chromium	Arsenic	Boron
1	- (-)	0.05 (-)	- (-)	- (-)
2	3 (2.5)	5 (5)	5 (5)	- (-)
3	5 (5)	10 (10)	11 (10)	- (-)
4	10 (10)	21 (20)	20 (20)	- (-)
5	15 (15)	31 (30)	31 (30)	- (-)
6	20 (20)	41 (40)	41 (40)	- (-)
7	25 (25)	51 (50)	51 (50)	- (-)
8	31 (30)	62 (60)	63 (60)	- (-)
9	36 (35)	72 (70)	72 (70)	- (-)
10	40 (40)	81 (80)	83 (80)	- (-)
11	45 (45)	91 (90)	91 (90)	- (-)
12	50 (50)	99 (100)	100 (100)	- (-)
13	60 (60)	119 (120)	119 (120)	- (-)

Table 55 -

Analysed Elemental Concentrations of Copper, Chromium, Arsenic and Boron in Extractions from Partly Fixed Woodflour Samples. Theoretical Values are shown in Parentheses

Sample	Elemental Concentration (ppm)			
	Copper	Chromium	Arsenic	Boron
Blank	- (-)	0.05 (-)	- (-)	- (-)
Blank	0.1 (-)	0.2 (-)	- (-)	- (-)
Untreated	0.2 (-)	0.2 (-)	- (-)	- (-)
CCA 0.5	9 (9)	16 (16)	12 (11)	- (-)
1.0	19 (18)	32 (32)	23 (22)	- (-)
2.0	37(35.5)	64(63.5)	46(44.5)	0.2 (-)
3.5	31 (31)	55(55.5)	39 (39)	- (-)
5.0	43(44.5)	77(79.5)	54 (55)	- (-)
CCB 0.5	10 (9)	16 (16)	0.4 (-)	3 (3.5)
1.0	19 (18)	33 (32)	1 (-)	7 (7)
2.0	36(35.5)	63(63.5)	1 (-)	14 (14)
3.5	32 (31)	57(55.5)	1 (-)	12 (12)
5.0	43(44.5)	76(79.5)	0.9 (-)	17 (17.5)
CCAB				
0.5	10 (9)	18 (16)	11 (11)	3 (3.5)
1.0	18 (18)	33 (32)	23 (22)	7 (7)
2.0	37(35.5)	64(63.5)	44(44.5)	14 (14)
3.5	31 (31)	54(55.5)	37 (39)	12 (12)
5.0	45(44.5)	79(79.5)	53 (55)	17 (17.5)

Table 56 -

Analysed Elemental Concentrations of Copper, Chromium, Arsenic and Boron in Extractions from Fixed Woodflour Samples. Theoretical Values are shown in Parentheses

Sample	Elemental Concentration (ppm)			
	Copper	Chromium	Arsenic	Boron
Blank	- (-)	0.05 (-)	- (-)	(-)
Blank	0.1 (-)	0.2 (-)	- (-)	- (-)
Untreated	0.2 (-)	0.2 (-)	- (-)	- (-)
CCA 0.5	10 (9)	17 (16)	12 (11)	0.1 (-)
1.0	18 (18)	31 (32)	22 (22)	0.6 (-)
2.0	36 (35.5)	62 (63.5)	42 (44.5)	- (-)
3.5	30 (31)	53 (55.5)	37 (39)	- (-)
5.0	43 (44.5)	76 (79.5)	50 (55)	- (-)
CCB 0.5	9 (9)	15 (16)	- (-)	4 (3.5)
1.0	18 (18)	31 (32)	0.3 (-)	8 (7)
2.0	35 (35.5)	61 (63.5)	1 (-)	12 (14)
3.5	31 (31)	53 (55.5)	- (-)	12 (12)
5.0	42 (44.5)	74 (79.5)	- (-)	16 (17.5)
CCAB 0.5	8 (9)	16 (16)	11 (11)	2 (3.5)
1.0	19 (18)	32 (32)	22 (22)	6 (7)
2.0	36 (35.5)	62 (63.5)	42 (44.5)	12 (14)
3.5	30 (31)	53 (55.5)	35 (39)	11 (12)
5.0	43 (44.5)	76 (79.5)	50 (55)	15 (17.5)

4.2.3 Chemical Analysis of the Variously Treated Test Blocks

Using the procedure established in the preliminary test two main investigations were carried out: the first involving the analysis of leached test blocks from the soft-rot monoculture trial 2 and the second involving the analysis of the 50x25x5 mm exposed water cooling tower test blocks and their unexposed counterparts taken from the same treated blocks (section 2.2.6.3). The first test included, in addition, birch blocks treated only with the boric acid solutions used in the B+CCA treatments, and then conditioned and leached in the same way as the test blocks. The objective of analysing these blocks was to find out how much of the boron was leached in comparison with the other boron-containing treatments. The water cooling tower blocks were analysed to establish the extent of additional leaching which may have occurred during exposure.

4.2.4 Method

Three replicate test blocks from each of the following treatments were taken for analysis:

Birch (30x15x5 mm miniblocks)

Treatments	Concentrations
Boric acid (B) CCA CCB CCAB B+CCA CCB+A	0.4, 0.8, 1.6, 2.6, 3.7 + untreated % w/v CCA equivalent

Birch cooling tower blocks (50x25x5 mm)

both exposed and unexposed

Treatments	Concentrations
CCA CCB CCB+A	0.8, 1.6, 3.7 % w/v CCA equivalent + untreated

A chisel was used to convert the blocks into matchsticks which were then ground to a coarse dust in a "Moulinex" coffee grinder. The dust was converted into a fine woodflour in a Wiley mill. To reduce contamination the blocks were dealt with in order of increasing concentration and the mills were cleaned with a modified vacuum cleaner between samples. The woodflour was conditioned in a constant temperature room at 22°C for two days before moisture content determinations were carried out. The moisture content was used as a corrective factor in the preparation of 1.000 g equivalent oven dry weight of flour which was extracted in a 50 ml volumetric flask in each case by the modified method described in section 4.2.2.2.3. The final solutions were analysed for copper, chromium, arsenic and boron by argon plasma emission spectrometry using the CCAB calibration solutions described in section 4.2.2.2.1.

4.2.5 Results

The mean elemental retentions of the miniblocks, expressed as % w/w in wood, and their standard errors are given in table 57 for copper, table 58 for chromium and table 59 for arsenic and plotted for copper in figure 29 and chromium in figure 29. The calculated retentions, based on uptake, are given in table 60. The corresponding results for the water cooling tower samples are given in table 61 together with values for boron and the mean chromium to copper ratios for each treatment. The values for copper are plotted in

figure 31 and chromium in figure 32. The mean chromium to copper ratios are presented separately for exposed and unexposed cooling tower blocks. An analysis of variance was carried out on the retention data and the results are given for copper in table 64, chromium in table 65, arsenic in table 66 and the chromium to copper ratio in table 67, in the case of the miniblocks. The corresponding results for the cooling tower material are given in table 68 together with the results of T tests performed on the chromium to copper ratios in exposed and unexposed blocks.

In general, the copper retentions of the miniblocks (table 57) were lower than those calculated from uptake data (table 60) although in the case of the CCB treatment the analyses yielded retentions which were slightly higher than the calculated values. Copper retentions of the CCB+A treatments were usually the lowest of all of the treatments (table 64) except at the 1.6% level where the value for CCB+A was high (figure 29). Comparison of the theoretical and analysed chromium retentions (tables 60 and 58) reveals that the values for CCB were similar, in CCB+A the analysed retentions were slightly lower than the theoretical ones and in CCA, CCAB and B+CCA the retentions from the analysis were dramatically higher than theoretical values. Again, the retention for the 1.6% level of CCB+A was high. In the case of arsenic, the analysis yielded higher than calculated values (tables 59, 60) for CCA and CCAB, approximately equal values for B+CCA and slightly lower than calculated values for CCB+A. Boron levels in the blocks did not exceed those of the blank solutions. The chromium to copper ratios in CCA, CCAB and B+CCA treated blocks (tables 62, 67) were

significantly greater than those in CCB and CCB+A treated blocks. The lowest ratios were found in the CCB treated samples. The ratios in the case of CCB and CCB+A rose with increasing treating solution concentration.

In the cooling tower material (tables 61 and 63, and figures 31 and 32) the results followed the same trends but the differences were less marked. In addition, a very low level of boron was detected in the highest treatment of CCB+A (table 61), more being found in the unexposed than exposed samples. Considering the effect of exposure on the levels of the other elements, there was no difference between the retentions in unexposed and exposed samples although the chromium to copper ratio tended to increase following exposure in the water cooling tower (table 67).

Table 57 -

Mean Copper Retentions (% w/w)
of Miniblocks Determined by Analysis

Treatment	Treating Solution (% w/v CCA Equivalent)				
	0.4	0.8	1.6	2.6	3.7
CCA	0.042 (0.002)	0.065 (0.003)	0.120 (0.005)	0.168 (0.004)	0.235 (0.005)
CCB	0.037 (0.002)	0.068 (0.002)	0.140 (0.006)	0.188 (0.011)	0.270 (0.005)
CCAB	0.032 (0.002)	0.067 (0.002)	0.117 (0.002)	0.177 (0.004)	0.225 (0.012)
B+CCA	0.032 (0.002)	0.062 (0.002)	0.107 (0.004)	0.172 (0.007)	0.227 (0.004)
CCB+A	0.037 (0.002)	0.058 (0.002)	0.163 (0.009)	0.158 (0.002)	0.200 (0.008)
B	-	-	-	-	-

Standard errors in parentheses.

Table 58 -

Mean Chromium Retentions (% w/w)
of Miniblocks Determined by Analysis

Treatment	Treating Solution (% w/v CCA Equivalent)				
	0.4	0.8	1.6	2.6	3.7
CCA	0.102 (0.007)	0.163 (0.002)	0.288 (0.009)	0.402 (0.006)	0.592 (0.009)
CCB	0.053 (0.002)	0.110 (0.003)	0.235 (0.013)	0.333 (0.023)	0.472 (0.007)
CCAB	0.080 (0.003)	0.170 (0.006)	0.292 (0.002)	0.433 (0.013)	0.560 (0.023)
B+CCA	0.075 (0.003)	0.152 (0.006)	0.278 (0.010)	0.423 (0.009)	0.545 (0.003)
CCB+A	0.065 (0.005)	0.103 (0.002)	0.328 (0.014)	0.325 (0.009)	0.423 (0.015)
B	-	-	-	-	-

Standard errors in parentheses.

Table 59 -

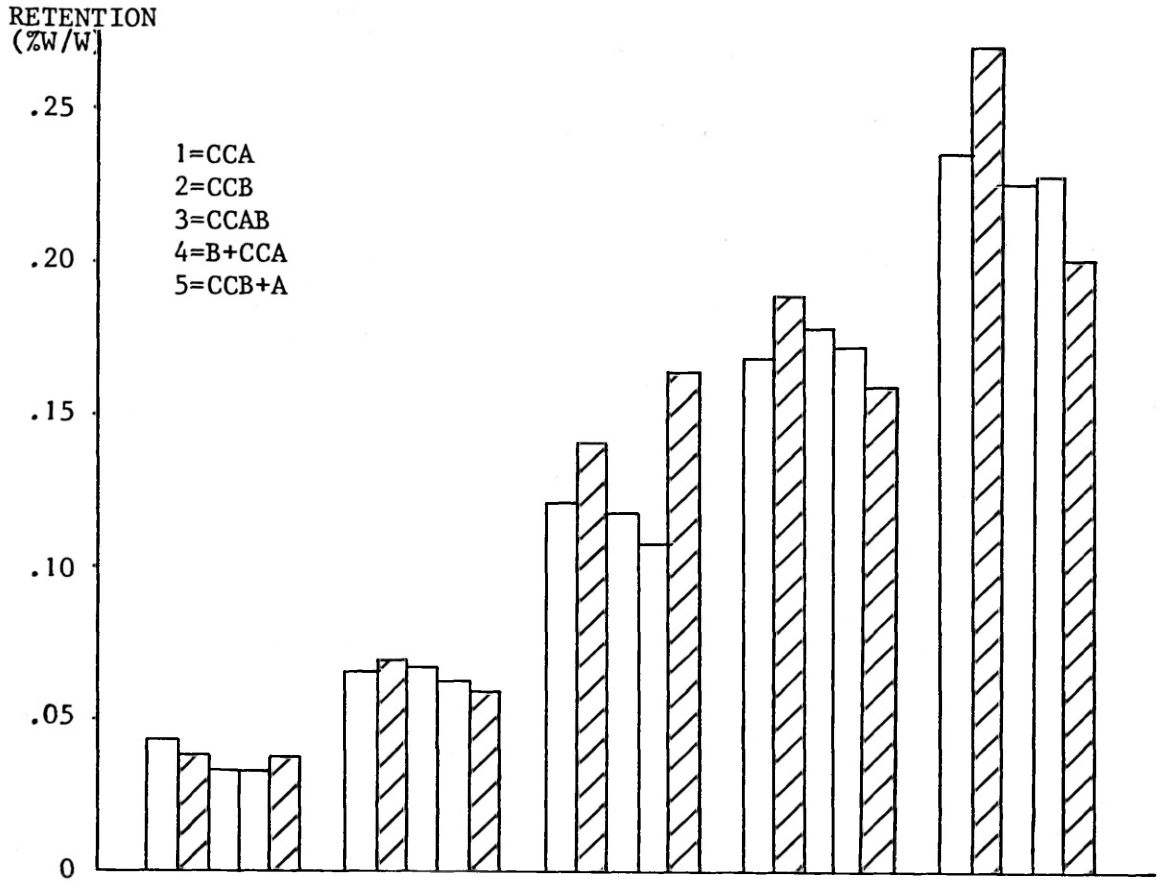
Mean Arsenic Retentions (% w/w)
of Miniblocks Determined by Analysis

Treatment	Treating Solution (% w/v CCA Equivalent)				
	0.4	0.8	1.6	2.6	3.7
CCA	0.045 (0.003)	0.085 (0.003)	0.167 (0.007)	0.242 (0.003)	0.363 (0.006)
CCB	-	-	-	-	-
CCAB	0.035 (0.003)	0.090 (0.003)	0.170 (0.003)	0.262 (0.010)	0.340 (0.015)
B+CCA	0.032 (0.002)	0.080 (0.003)	0.155 (0.006	0.253 (0.006)	0.328 (0.003)
CCB+A	0.023 (0.003)	0.042 (0.002)	0.160 (0.003)	0.227 (0.011)	0.323 (0.012)
B	-	-	-	-	-

Standard errors in parentheses.

FIGURE 29 MEAN RETENTIONS OF MINIBLOCKS DETERMINED BY ANALYSIS

a COPPER



b ARSENIC

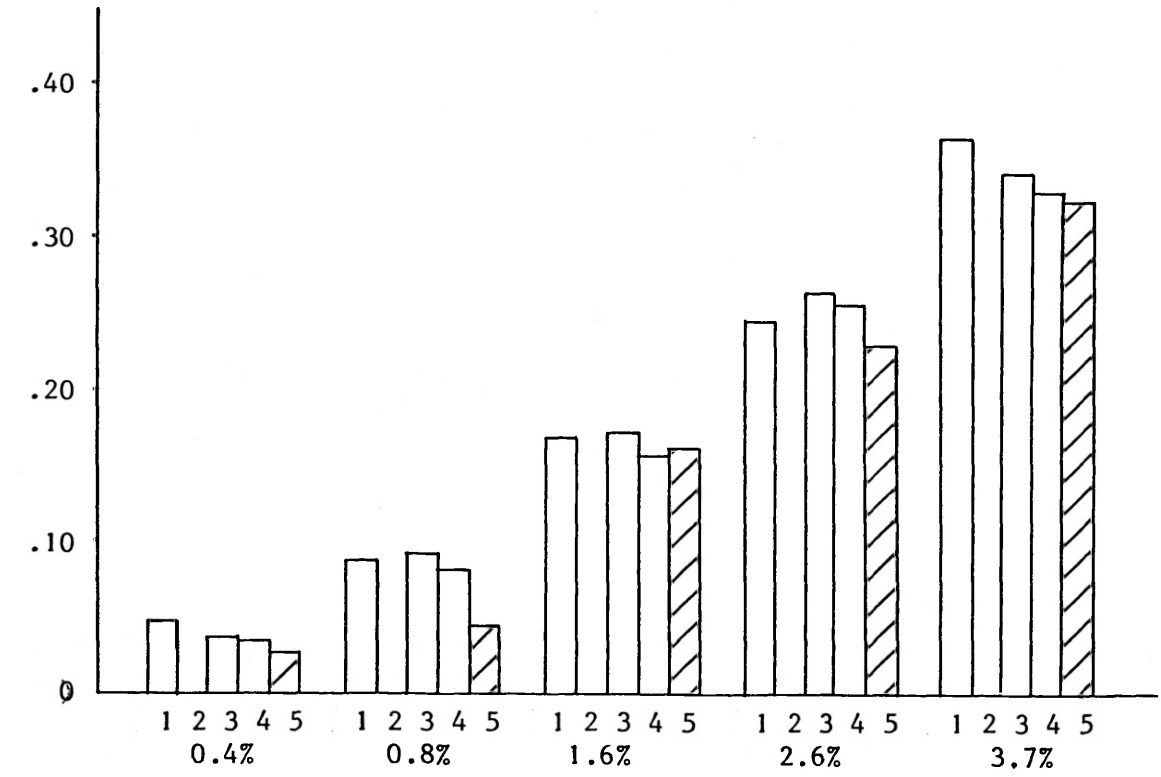


FIGURE 29c MEAN CHROMIUM RETENTIONS OF MINIBLOCKS DETERMINED BY ANALYSIS

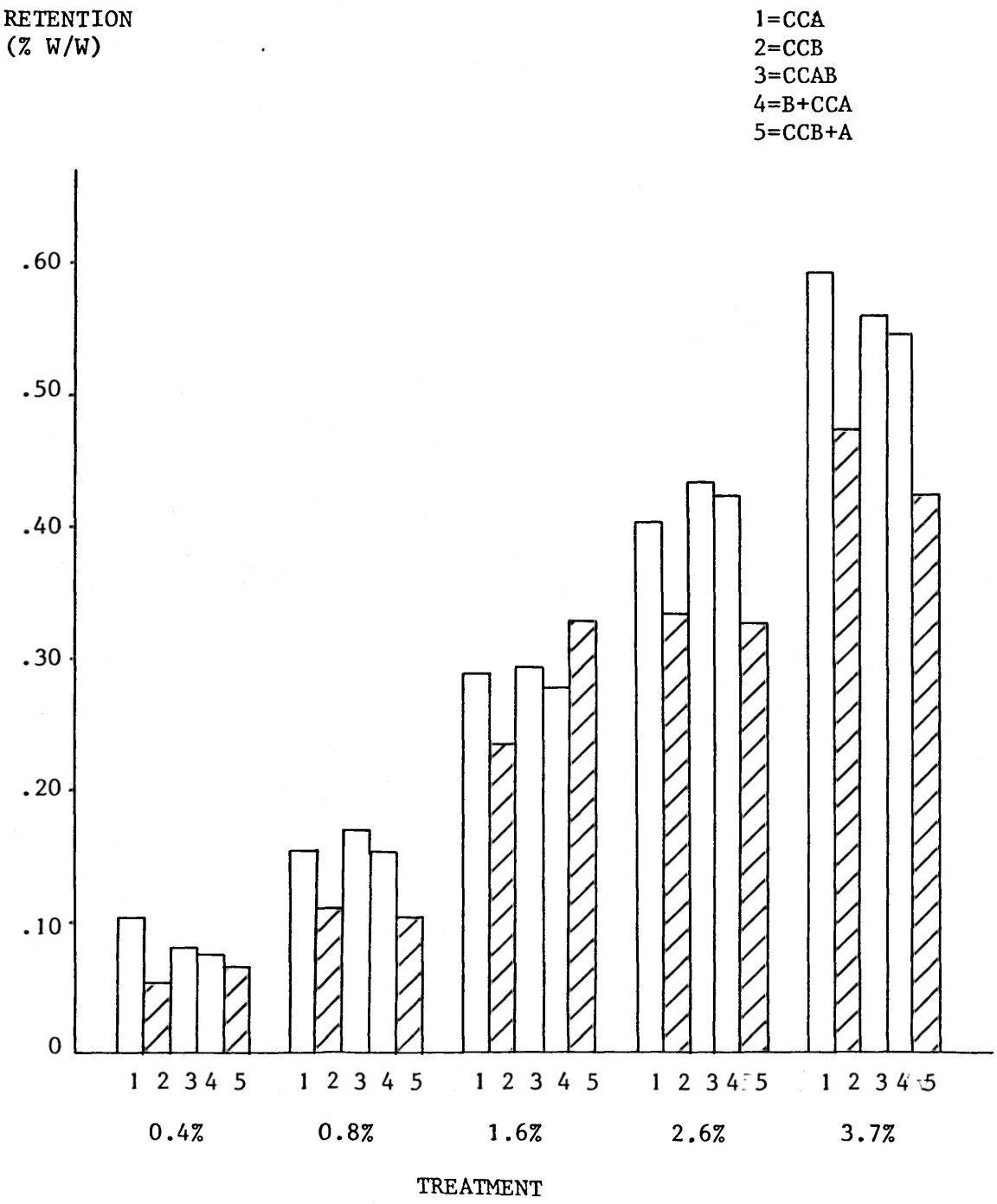


FIGURE 30 PERFORMANCE OF TREATED BIRCH EXPOSED TO CHAETOMIUM GLOBOSUM IN TRIAL 2

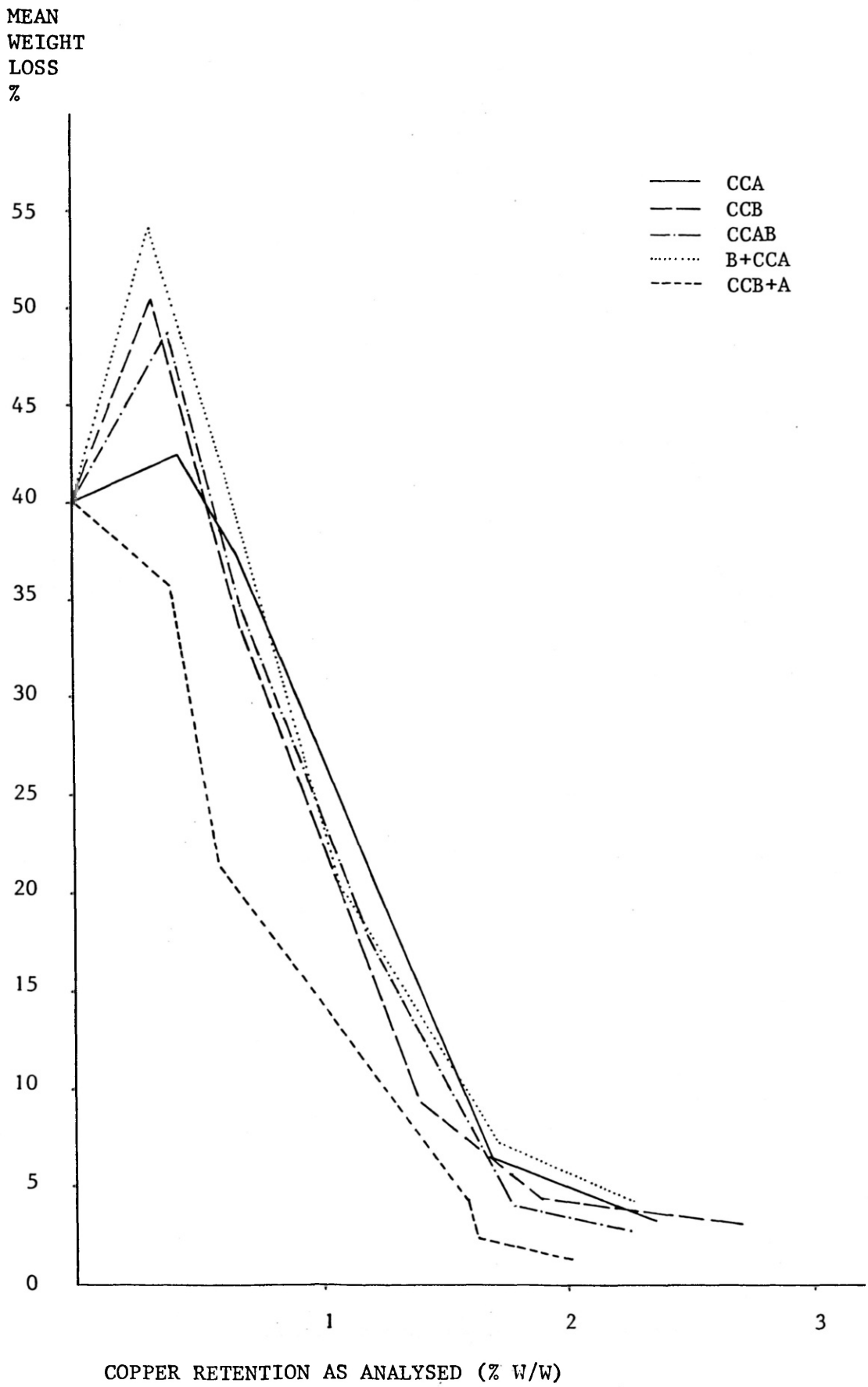


Table 60 -

Mean Retentions (% w/w)
of Miniblocks Calculated from
Preservative Uptake Data

Treatment	Treating Solution (% w/v CCA Equivalent)				
	0.4	0.8	1.6	2.6	3.7
Copper					
CCA	0.031	0.061	0.122	0.186	0.254
CCB	0.032	0.063	0.123	0.174	0.266
CCAB	0.031	0.053	0.122	0.190	0.259
B+CCA	0.029	0.064	0.116	0.203	0.270
CCB+A	0.031	0.061	0.131	0.190	0.252
Chromium					
CCA	0.055	0.109	0.217	0.332	0.453
CCB	0.056	0.113	0.220	0.310	0.475
CCAB	0.055	0.113	0.219	0.339	0.463
B+CCA	0.052	0.115	0.207	0.362	0.484
CCB+A	0.055	0.109	0.234	0.339	0.450
Arsenic					
CCA	0.038	0.076	0.151	0.231	0.315
CCB	-	-	-	-	-
CCAB	0.038	0.078	0.152	0.236	0.322
B+CCA	0.036	0.080	0.144	0.253	0.337
CCB+A	0.039	0.061	0.156	0.247	0.356
Boron					
CCA	-	-	-	-	-
CCB	0.012	0.025	0.048	0.068	0.104
CCAB	0.012	0.025	0.048	0.075	0.102
B+CCA	0.012	0.021	0.043	0.078	0.112
CCB+A	0.012	0.024	0.052	0.074	0.099

Table 61 -

Mean Retentions (% w/w) in Cooling Tower Blocks Determined by Analysis (a) Copper, (b) Chromium, (c) Arsenic, (d) Boron, (e) Chromium : Copper Ratios

Treatment	Treating Solution (% w/v CCA Eq.)					
	0.8		1.6		3.7	
	Mean	S.E.	Mean	S.E.	Mean	S.E.
(a)						
CCA	0.081	0.002	0.154	0.003	0.373	0.006
CCB	0.073	0.003	0.137	0.003	0.375	0.010
CCB+A	0.078	0.001	0.127	0.002	0.355	0.002
(b)						
CCA	0.152	0.005	0.299	0.009	0.727	0.011
CCB	0.119	0.004	0.239	0.005	0.674	0.017
CCB+A	0.133	0.001	0.238	0.005	0.698	0.005
(c)						
CCA	0.093	0.002	0.198	0.005	0.483	0.006
CCB	-	-	-	-	-	-
CCB+A	0.053	0.002	0.115	0.003	0.399	0.002
(d)						
CCA	0.001	0.001	0.002	0.001	0.001	0.000
CCB	0.003	0.000	0.004	0.001	0.018	0.003
CCB+A	0.001	0.001	0.000	0.000	0.002	0.001
(e)						
CCA	1.875	0.044	1.940	0.030	1.952	0.021
CCB	1.660	0.079	1.750	0.032	1.798	0.018
CCB+A	1.725	0.035	1.885	0.054	1.963	0.009

FIGURE 31 MEAN COPPER RETENTIONS IN COOLING TOWER SAMPLES DETERMINED BY ANALYSIS

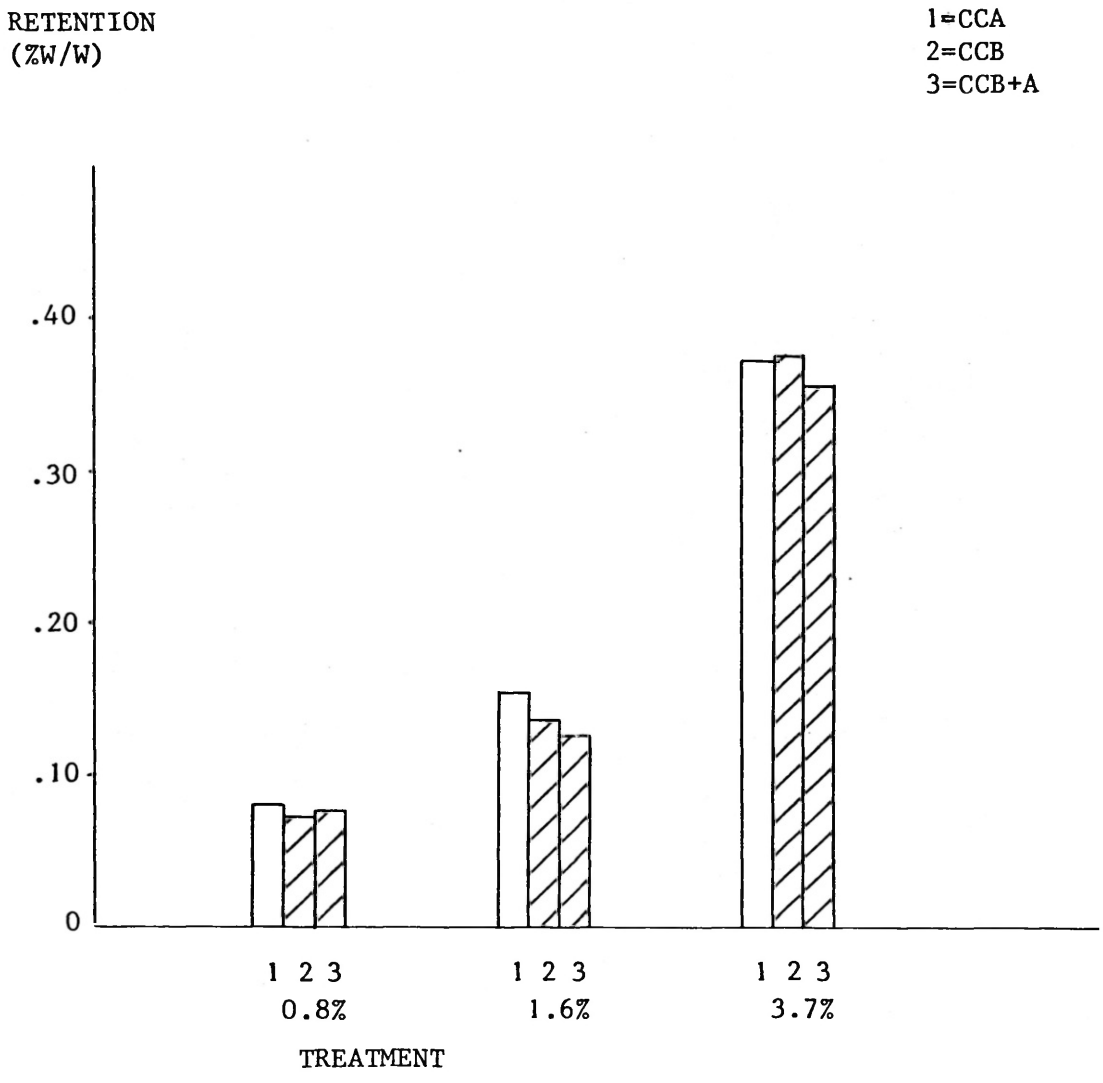


FIGURE 32 MEAN CHROMIUM RETENTIONS IN COOLING TOWER SAMPLES DETERMINED BY ANALYSIS

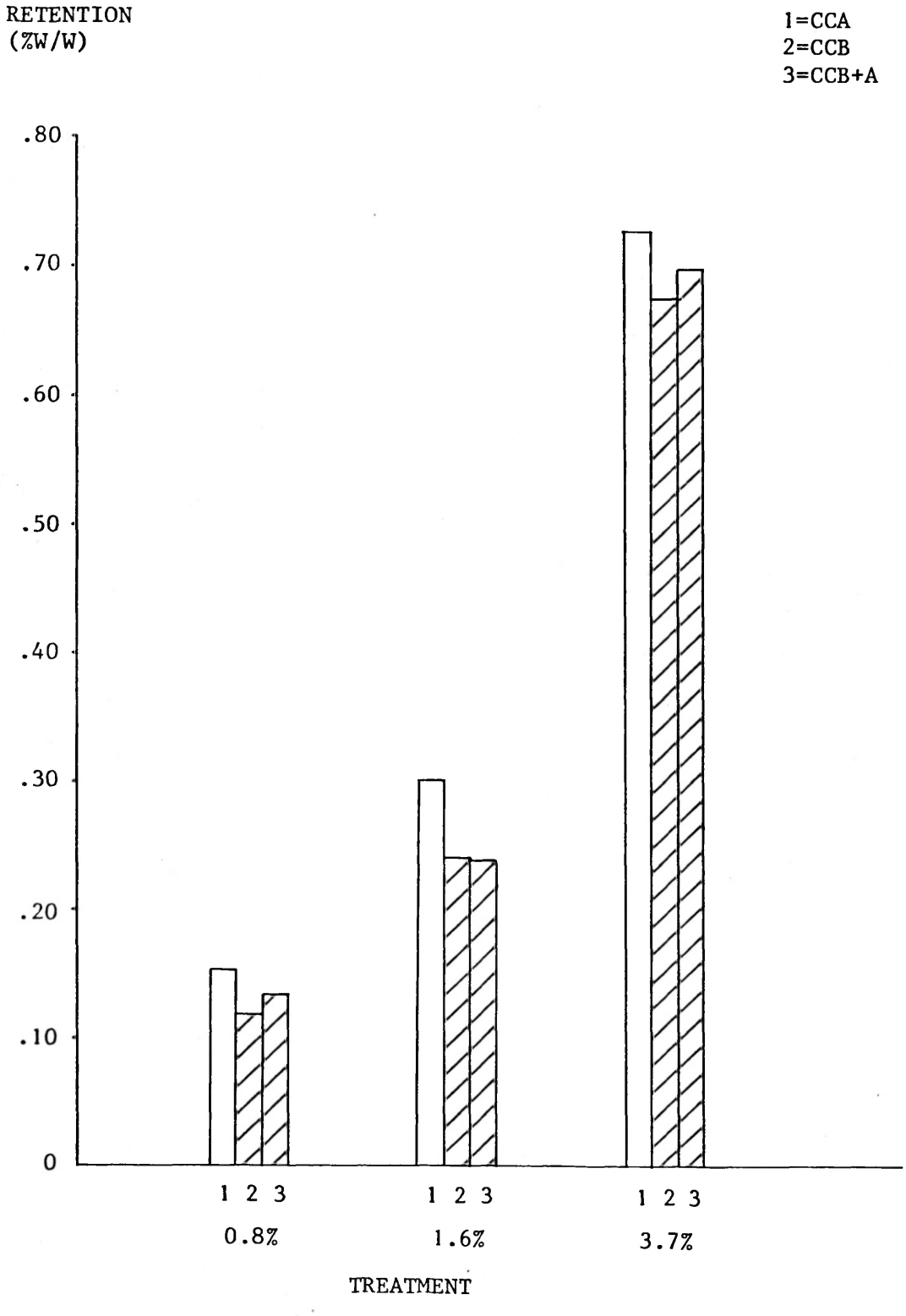


Table 62 -

Mean Chromium to Copper Ratios in Treated Miniblocks Determined by Analysis

Treatment	Treating Solution (% w/v CCA Equivalent)				
	0.4	0.8	1.6	2.6	3.7
CCA	2.440 (0.060)	2.523 (0.090)	2.407 (0.038)	2.387 (0.029)	2.520 (0.042)
CCB	1.460 (0.057)	1.610 (0.057)	1.673 (0.028)	1.767 (0.026)	1.747 (0.012)
CCAB	2.533 (0.071)	2.550 (0.047)	2.500 (0.020)	2.453 (0.023)	2.493 (0.055)
B+CCA	2.373 (0.065)	2.460 (0.106)	2.613 (0.030)	2.470 (0.049)	2.403 (0.033)
CCB+A	1.767 (0.057)	1.773 (0.023)	2.013 (0.030)	2.053 (0.039)	2.120 (0.036)

Table 63 -

Mean Chromium to Copper Ratios in
Cooling Tower Samples Determined by Analysis

Treatment		Blocks			
		Unexposed		Exposed	
		Mean	S.E.	Mean	S.E.
CCA	0.8	1.790	0.03	1.960	0.04
	1.6	1.490	0.01	1.830	0.05
	3.7	1.650	0.02	1.800	0.00
CCB	0.8	1.903	0.04	1.977	0.04
	1.6	1.700	0.01	1.800	0.05
	3.7	1.827	0.03	1.943	0.10
CCB+A	0.8	1.910	0.01	1.987	0.03
	1.6	1.760	0.01	1.837	0.01
	3.7	1.947	0.01	1.980	0.01

Table 64 -

Analysis of Variance on Copper Retention Data in Treated Miniblocks

Treatments Compared	Treating Solution (% w/v CCA Equivalent				
	0.4	0.8	1.6	2.6	3.7
CCA/CCB	*	-	*	-	*
CCA/CCAB	-	-	-	-	-
CCA/B+CCA	-	-	-	-	-
CCA/CCB+A	*	*	*	-	*
CCB/CCAB	-	-	*	-	*
CCB/B+CCA	-	*	*	-	*
CCB/CCB+A	-	*	*	*	*
CCAB/B+CCA	-	-	-	-	-
CCAB/CCB+A	-	*	*	-	*
B+CCA/CCB+A	-	-	*	-	*
F Ratio	6.30	4.14	16.04	2.96	12.22
L.S.D.	0.005	0.006	0.018	0.020	0.023

Table 65 -

Analysis of Variance on Chromium Retention Data in Treated Miniblocks

CCA/CCB	*	*	*	*	*
CCA/CCAB	*	-	-	-	-
CCA/B+CCA	*	-	-	-	*
CCA/CCB+A	*	*	*	*	*
CCB/CCAB	*	*	*	*	*
CCB/B+CCA	*	*	*	*	*
CCB/CCB+A	-	-	*	-	*
CCAB/B+CCA	-	*	-	-	-
CCAB/CCB+A	*	*	*	*	*
B+CCA/CCB+A	-	*	*	*	*
F Ratio	18.36	57.37	10.28	14.32	27.18
L.S.D.	0.013	0.013	0.033	0.042	0.042

* = significant difference between mean values.

\- = no significant difference between mean values.

significant F ratios underlined (p = 0.05)

Table 66 -

Analysis of Variance on Arsenic Retention Data in Treated Miniblocks

Treatments Compared	Treating Solution % w/v CCA Equivalent				
	0.4	0.8	1.6	2.6	3.7
CCA/CCB					
CCA/CCAB	*	-	-	-	-
CCA/B+CCA	*	-	-	-	*
CCA/CCB+A	*	*	-	-	*
CCB/CCAB					
CCB/B+CCA					
CCB/CCB+A					
CCAB/B+CCA	-	*	-	-	-
CCAB/CCB+A	*	*	-	*	-
B+CCA/CCB+A	-	*	-	-	-
F Ratio	10.52	70.00	1.91	3.42	3.05
L.S.D.	0.009	0.009	0.016	0.027	0.033

Table 67 -

Analysis of Variance on Chromium to Copper Ratios in Treated Miniblocks

CCA/CCB	*	*	*	*	*
CCA/CCAB	-	-	-	-	-
CCA/B+CCA	-	-	*	-	-
CCA/CCB+A	*	*	*	*	*
CCB/CCAB	*	*	*	*	*
CCB/B+CCA	*	*	*	*	*
CCB/CCB+A	*	-	*	*	*
CCAB/B+CCA	-	-	*	-	-
CCAB/CCB+A	*	*	*	*	*
B+CCA/CCB+A	*	*	*	*	*
F Ratio	58.24	40.65	170.79	78.14	72.55
L.S.D.	0.196	0.224	0.094	0.110	0.121

* = significant difference between mean values

\- = no significant difference between mean values

significant F ratios underlined (p = 0.05)

Table 68 -

Analysis of Variance on Retention Data in Cooling Tower Samples

(a) Copper, (b) Chromium, (c) Arsenic,
(d) Chromium : Copper Ratio in all Blocks
(e) Chromium : Copper Ratio in Exposed vs. Unexposed Blocks

Treatments Compared	Treating Solution (% w/v CCA Eq.)		
	0.8	1.6	3.7
(a)			
CCA/CCB	*	*	-
CCA/CCB+A	-	*	-
CCB/CCB+A	-	*	-
F Ratio	3.55	20.82	2.25
L.S.D.	0.007	0.009	0.021
(b)			
CCA/CCB	*	*	*
CCA/CCB+A	*	*	-
CCB/CCB+A	*	-	-
F Ratio	23.03	26.23	4.98
L.S.D.	0.010	0.021	0.035
(c)			
CCA/CCB+A	*	*	*
T	13.42	14.94	12.30
(d)			
CCA/CCB	*	*	*
CCA/CCB+A	-	-	-
CCB/CCB+A	-	*	*
F Ratio	3.89	5.92	30.65
L.S.D.	0.168	0.121	0.050
(e)			
CCA	*	-	-
CCB	*	-	*
CCB+A	*	-	-

* = significant difference between mean values ($p = 0.05$)
- = no significant difference between mean values ($p = 0.05$)
significant F ratios underlined

4.3 Fixation Studies in Sawdust - Preservative Retention With Time

4.3.1 Introduction

There have been many reports on the leaching of preservatives such as CCA from treated woodblocks after the standard period of fixation (inter alia: Irvine, Eaton and Jones, 1972; D.N.R. Smith and Williams, 1973 a; Morgan, 1975). Most of these investigations have indicated that there is a high degree of fixation of the preservative components. However, this reveals nothing of the processes leading up to maximum fixation of the preservative and so for this reason an experiment was carried out to compare the various formulations in this respect.

The objective was to compare the percentage of each of the preservative components which had become resistant to leaching after various time intervals, in an attempt to distinguish between the treatments. The most straightforward method of achieving this was to analyse the leachates.

4.3.2 Method

2% w/v CCA equivalent solutions of copper sulphate, copper chrome (CC), CCA, CCB and CCAB were made up as described in section 2.4.1.2. The main investigation was of CCA and CCB and the other formulations were included for completeness. 10 g quantities of air dry birch sawdust of particle size 0.2 mm or less were weighed into glass jars and wetted with 70 ml of one of the solutions or distilled water. Sawdust was used in preference to woodblocks because of its relative homogeneity and ease of handling. The mixtures were thoroughly stirred and the jars were

sealed and stored in a constant temperature room at 22 $\pm$ 2°C. Three replicates of each treatment were removed after 1, 2, 8, 24, 48, 96, 192 and 384 hours. The jars destined for 96, 192 and 384 hours' incubation were sterilised by ionizing radiation to prevent the growth of microorganisms capable of detoxifying the solutions (Murphy, 1982). The copper chrome treatment was only represented at the 384 hour (16 day) time interval. After the storage time had elapsed the mixtures were emptied into Buchner funnels over 2 layers of glass fibre filter paper and a vacuum was drawn while the sawdust was washed with distilled water. Glass fibre was used in preference to cellulose filter paper since copper is thought to adsorb to cellulose. The washing was stopped when the leachate had amounted to one litre. The leachate was mixed thoroughly and a sample taken for analysis. In preliminary trials, further leaching did not result in the removal of significant quantities of preservative.

A standard solution containing 50 ppm copper, 900 ppm chromium, 600 ppm arsenic and 200 ppm boron was made up in the leachate from the distilled water treatment stored for 16 days and diluted with this leachate to give a range of calibration solutions, details of which are given in table 69. The leachate was used in preference to water since it was thought to contain extractives (Gray, 1979), as were the other leachates, which may have interfered with the preservatives components. The ratio of the components in the calibration solution resembled that of the CCAB treating solution. The samples were analysed by argon plasma emission spectrometry except those from the copper sulphate treatment which, for economy, were analysed using a copper electrode

(Orion Research Model 94 - 29) fitted to an Orion Research Microprocessor pH/millivolt meter model 811 (MSC Scientific Instruments). 70 ml of the original treating solutions made up to 1 litre were included in the analyses to give 100% leached values.

Table 69 -

Elemental Concentrations in the Calibration Solutions Prepared for Argon Plasma Emission Spectrometry

Solution	Elemental Concentration (ppm)			
	Cu	Cr	As	B
1	0	0	0	0
2	1	1.8	1.2	0.4
3	2	3.6	2.4	0.8
4	5	9	6	2
5	10	18	12	4
6	20	36	24	8
7	40	72	48	16
8	60	108	72	24
9	80	144	96	32
10	100	180	120	40
11	120	216	144	48
12	150	270	180	60

4.3.3 Results

The mean percentage of unleached material is given for each time interval in table 70 for copper, table 71 for chromium, table 72 for arsenic, table 73 for boron, table 74 for copper in the copper sulphate treatment and table 75 for copper and chromium in the copper chrome treatment. The data are plotted in figure 33 for copper, figure 34 for chromium, figure 35 for arsenic and figure

36 for boron. Table 76 gives the results of a statistical analysis (analysis of variance and t tests) of the mean values for each treatment.

In the case of copper, the amount of unleached material was greater in CCB than in either CCA or CCAB in the initial stages (figure 33), all three rising to about 100% by 16 days, the normal fixation period for CCA. The picture was reversed in the case of chromium (figure 34) where the amount of unleached material was lower in CCB than in CCA and CCAB, once again all reaching a maximum by 16 days. CCA and CCAB were indistinguishable regarding arsenic fixation (figure 35), both showing a gradual increase in unleached material rising to a maximum at 4 days. In CCB treated sawdust there appeared to be a gradual decrease in the amount of leachable boron (figure 36), reaching a level of 7 5% at 16 days. In CCAB treated sawdust this trend was less marked. In the copper chrome treatment some of the copper and chromium remained unfixed after 16 days. When sawdust was treated with copper sulphate, the amount of unleachable copper varied slightly but showed no real trend with time. The mean percentage of unleachable copper corresponded to a copper content of 0.37% w/w air dry sawdust ($\triangleq$ 0.34% w/w ovendry sawdust). In CCA, CCB and CCAB there was a sharp increase in the amounts of fixed copper and chromium between 48 and 96 hours. This was also apparent, to a limited extent, with copper in the copper sulphate treatment.

Table 70 -

Mean Percentage Unleachable Copper with Time in CCA, CCB and CCAB Treated Sawdust

Time (hours)	CCA		CCB		CCAB	
	Mean	S.E.	Mean	S.E.	Mean	S.E.
1	19.10	1.75	27.80	1.20	18.57	4.20
2	18.85	1.18	27.30	1.20	18.10	0.00
8	26.33	1.48	35.27	1.07	25.60	0.50
24	37.20	0.50	41.80	0.64	34.10	0.00
48	44.43	0.47	46.40	1.27	44.47	0.87
96	94.70	0.50	90.33	1.33	90.83	0.23
192	93.77	0.96	94.20	1.91	95.63	0.73
384	98.60	0.00	99.37	0.03	97.60	0.64

Table 71 -

Mean Percentage Unleachable Chromium with Time in CCA, CCB and CCAB Treated Sawdust

1	16.03	1.79	10.47	1.64	16.73	4.27
2	15.30	1.70	9.37	1.07	15.87	0.17
8	24.57	1.02	20.87	1.24	25.23	0.27
24	32.77	0.43	25.83	0.78	31.63	0.13
48	39.00	0.81	32.33	0.72	39.00	0.38
96	89.80	1.71	82.57	2.34	84.43	0.87
192	89.07	1.44	87.10	2.64	93.07	2.20
384	99.60	0.00	99.43	0.17	99.27	0.17

Table 72 -

Mean Percentage Unleachable Arsenic with Time in CCA and CCAB Treated Sawdust

1	19.50	1.90			18.97	4.28
2	19.90	1.10			20.47	0.32
8	38.80	1.00			38.60	0.00
24	57.40	0.35			54.93	0.70
48	71.23	0.37			70.47	0.32
96	99.90	0.07			99.70	0.03
192	99.90	0.07			99.90	0.10
384	100.00	0.00			99.90	0.07

Table 73 -

Mean Percentage Unleachable Boron with Time in CCB and CCAB Treated Sawdust

Time (hours)	CCA		CCB		CCAB	
	Mean	S.E.	Mean	S.E.	Mean	S.E.
1			12.50	1.80	13.67	4.88
2			8.30	1.20	10.70	0.00
8			10.70	1.80	10.70	0.00
24			13.70	0.60	10.70	0.00
48			14.90	0.60	11.90	0.60
96			18.47	0.57	15.50	0.60
192			17.30	0.60	16.70	0.60
384			25.00	2.08	18.47	1.56

Table 74 -

Mean Percentage Unleachable Copper with Time in Copper Sulphate Treated Sawdust

Time (hours)	$CuSO_4$	
	Mean	S.E.
1	32.23	1.13
2	30.80	3.11
8	30.43	0.79
24	26.37	1.57
48	28.07	1.88
96	37.03	1.74
192	31.67	1.99
384	41.75	5.67

Mean % Cu "fixed" = 31.94
i.e. 0.37% w/w air dry wood

Table 75 -

Mean Percentage Unleachable Copper and Chromium in CC Treated Sawdust

Treatment	Copper		Chromium	
	Mean	S.E.	Mean	S.E.
CC 384 hours	93.50	0.50	86.60	1.20

FIGURE 33 FIXATION OF COPPER IN SAWDUST

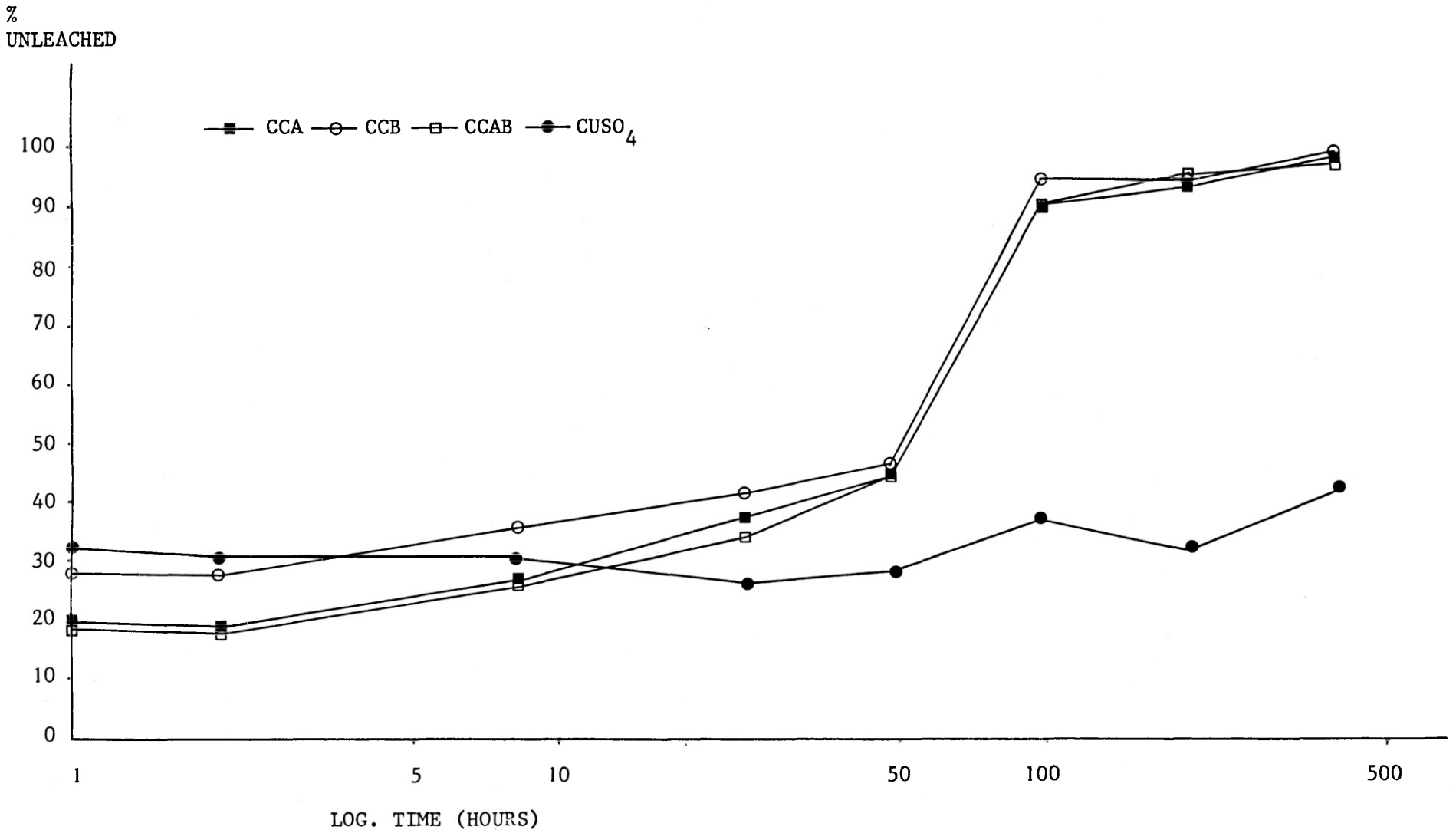


FIGURE 34 FIXATION OF CHROMIUM IN SAWDUST

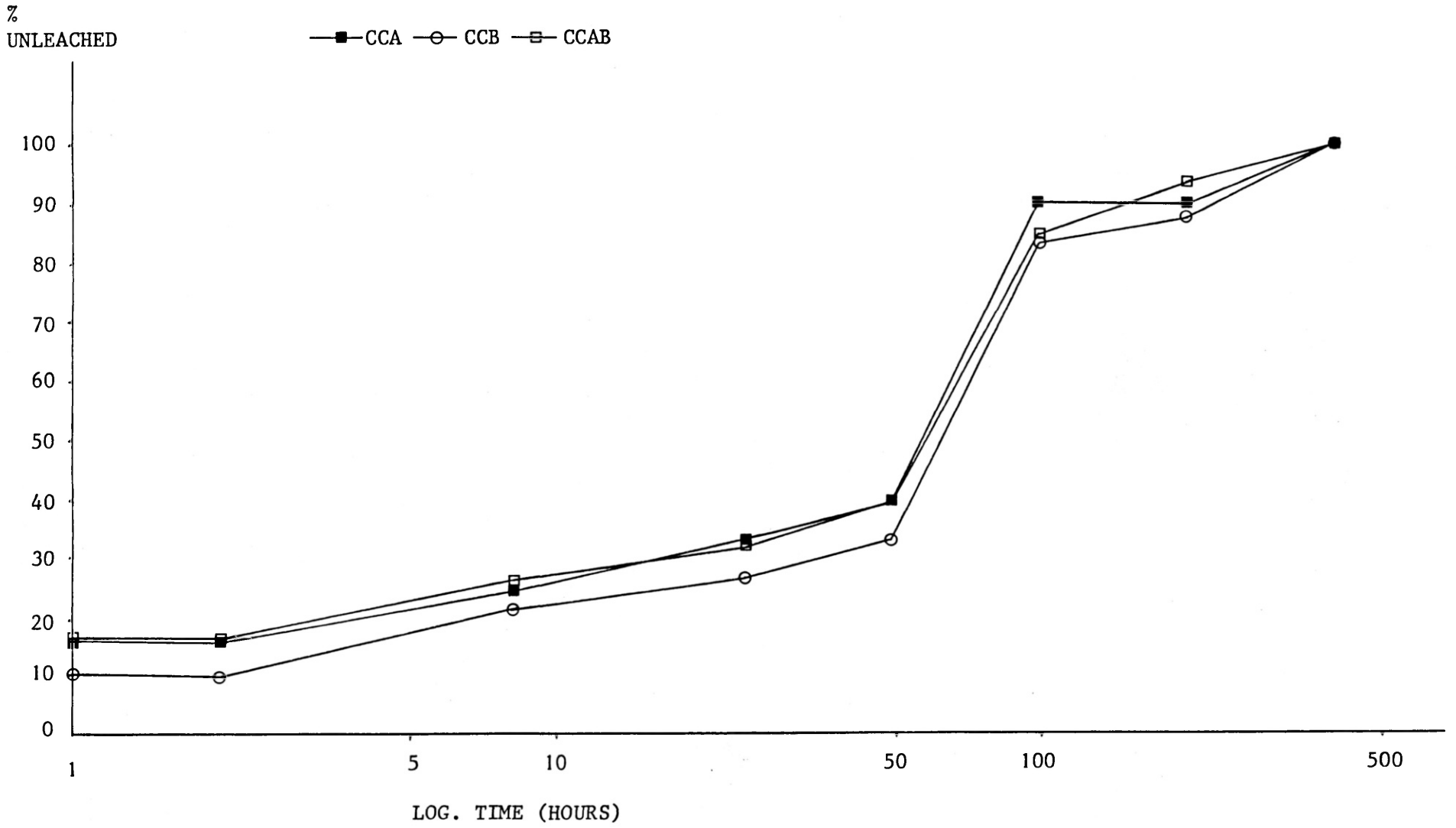


FIGURE 35 FIXATION OF ARSENIC IN SAWDUST

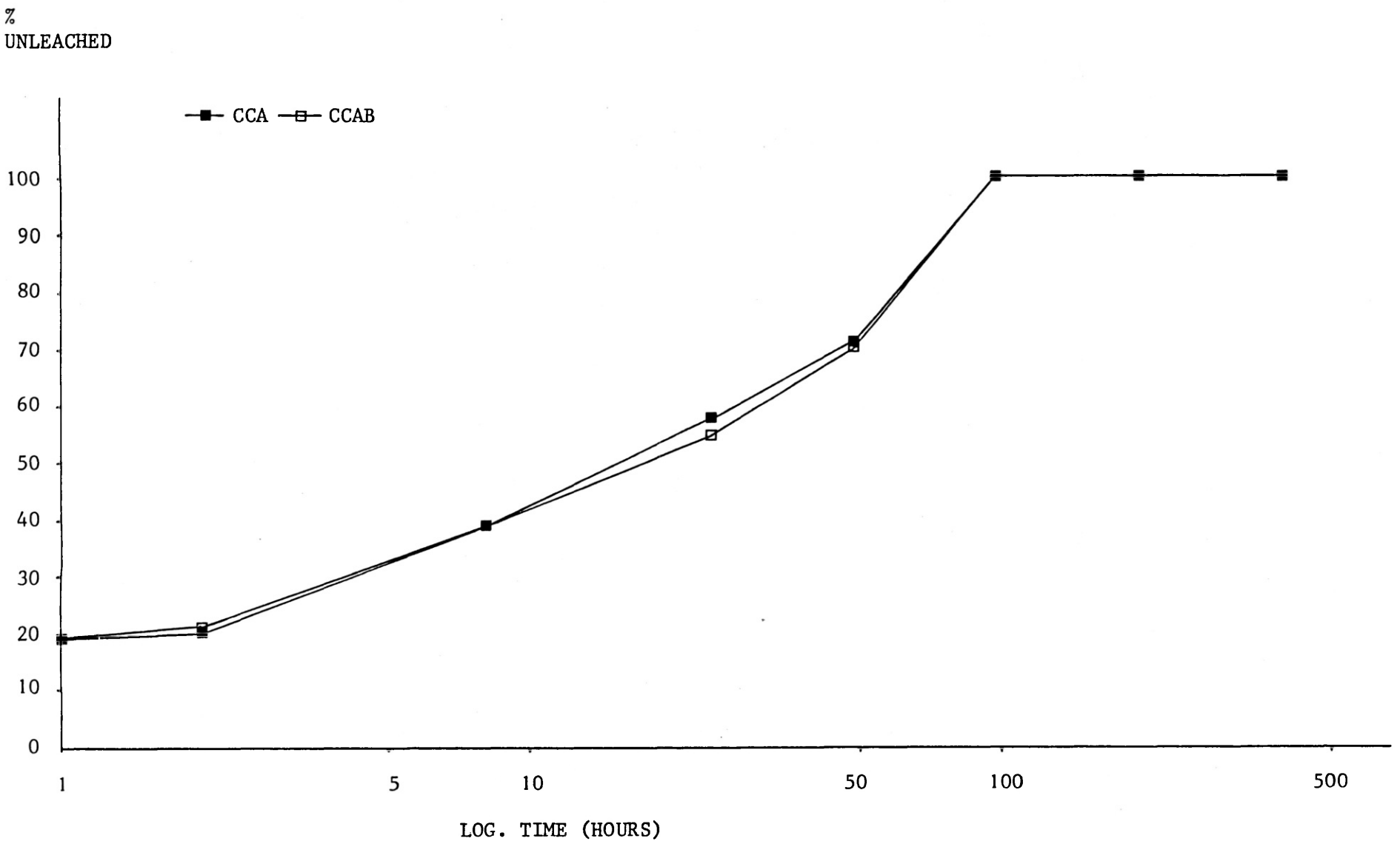


FIGURE 36 FIXATION OF BORON IN SAWDUST

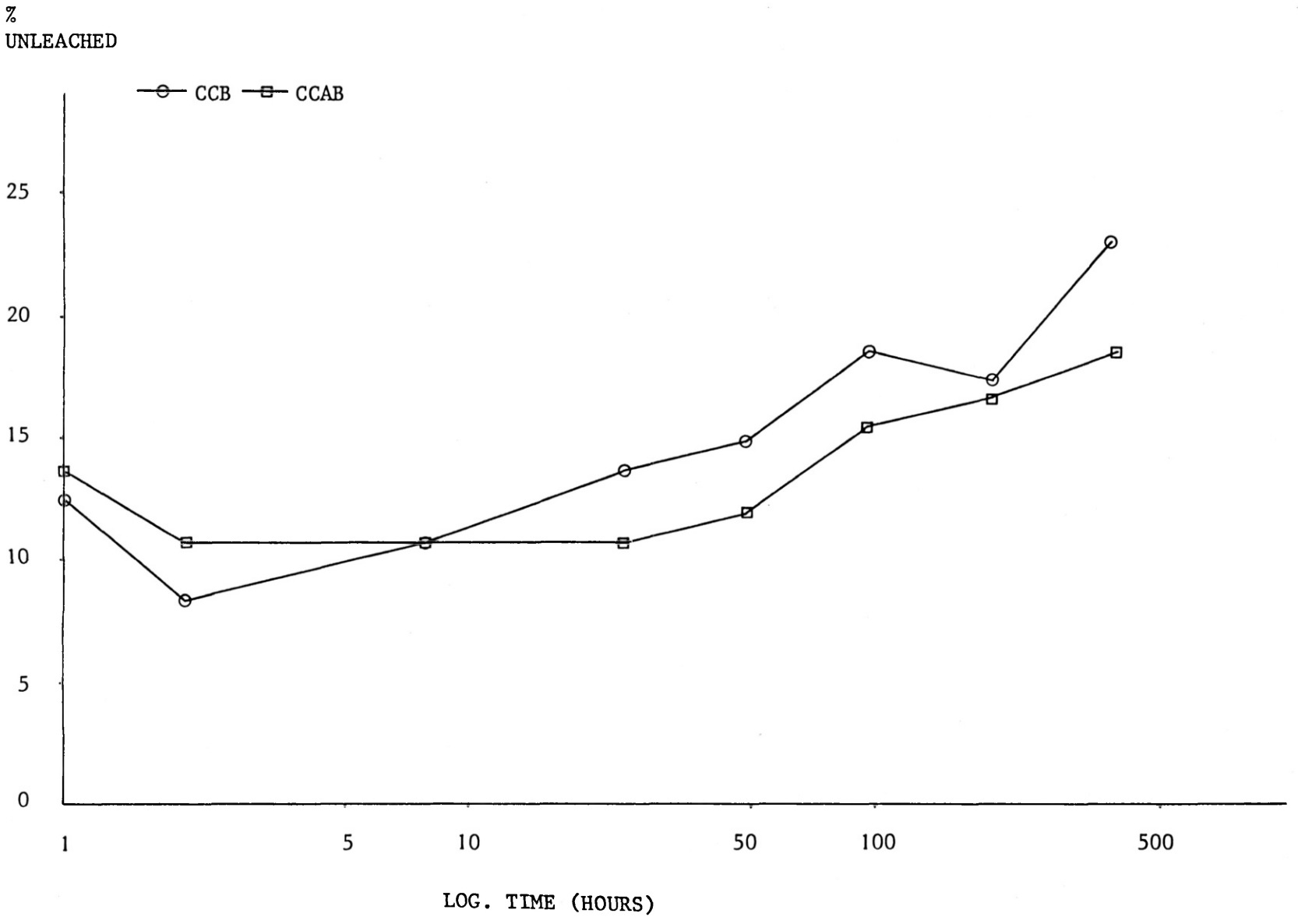


Table 76 -

Analysis of Variance
on Percentage "Fixation" Data

a) Copper

Treatments Compared	Time (Hours)							
	1	2	8	24	48	96	192	384
CCA/CCB	-	*	*	*	-	*	-	-
CCA/CCAB	-	-	-	*	-	*	-	-
CCB/CCAB	-	*	*	*	-	-	-	*
F Ratio	3.64	29.04	24.23	67.88	1.47	8.24	0.56	41.11
L.S.D.	9.39	3.20	3.79	1.63	3.21	2.88	4.52	1.33

N.B. 384 hour F ratio includes CC. (all > CC)

b) Chromium

CCA/CCB	-	*	*	*	*	*	-	-
CCA/CCAB	-	-	-	-	-	-	-	-
CCB/CCAB	-	*	*	*	*	-	-	-
F Ratio	1.47	14.43	6.27	51.44	33.73	4.62	1.99	110.17
L.S.D.	9.81	3.37	3.25	1.79	2.30	6.05	7.45	1.99

N.B. 384 hour F ratio includes CC. (all > CC)

c) Arsenic

CCA/CCAB	-	-	-	-	-	-	-	-
T	0.114	-0.495	0.200	3.164	1.580			

d) Boron

CCB/CCAB	-	-	-	*	*	*	-	-
T	-0.224	-2.000	0.000	5.000	3.536	3.595	0.707	2.516

* = significant difference between mean values

\- = no significant difference between mean values
(p = 0.05)

significant F ratios underlined

4.4 Fixation Studies in Sawdust - pH Changes with Time

4.4.1 Introduction

The objective of this investigation was to look for differences in the fixation products of the various formulations which, according to Dahlgren (1972), can be predicted by following changes in pH.

The chemical reactions occurring during the fixation of CCA preservatives to wood have been studied in detail by numerous workers (inter alia Dahlgren and Hartford, 1972 a, b, c; Dahlgren 1972, 1974, 1975 a, b; Eadie and Wallace, 1962; Pizzi, 1981, 1982 a, b, c; Kubel and Pizzi, 1982; Pizzi and Kubel, 1982), and the fixation of CCB has recently been studied by Kubel and Pizzi (1982) and Pizzi and Kubel (1982). No attempt was made to extend this approach to the fixation of the 5 formulations used in the present study, although one of Dahlgren's (1972) techniques was used to follow the pH changes during the course of fixation.

4.4.2 Method

The requirements of the method were that the pH of sawdust treated with a preservative solution should be recorded over a time period without drying of the sawdust. Several approaches to this problem were made before the final technique was established. The final procedure was as follows: the sawdust to be treated was weighed into a polythene bag and then wetted with a precise quantity of preservative solution. The bag was shaken vigorously to ensure an even distribution of the preservative. Then the

moistened sawdust was collected in the corner of the bag, the electrode was pushed into the centre of the sawdust and the bag was sealed tightly around the electrode with waterproof tape so that there was no sawdust/air interface. The whole assembly was then lowered into a waterbath maintained at 25°C to give a constant temperature environment since the rate of fixation is temperature-dependent (Wilson, 1971). The electrode was a flat, combination, temperature compensating pH electrode (Orion Research model 91-35) and was connected to an Orion Research model 811 (MSE Scientific Instruments) digital pH meter. The temperature probe was placed in the waterbath.

In early pilot trials, coarse birch sawdust of particle size less than 1mm and more than 0.2mm was used but this did not ensure a good contact with the surface of the electrode, and in the reported trials sawdust with a particle size of less than 0.2mm was used. The particle size had no effect on the results but the fine sawdust required more preservative solution; instead of 8 ml per 6 g sawdust (Dahlgren, 1972), 10 ml was required. Before treatment, the preservative was warmed to 25°C so that accurate readings could be taken straight away as the temperature probe could not be put into the sawdust. pH readings were taken at intervals during a minimum of 14 days as this is the usual period allowed for fixation prior to slow drying (EN 113, 1982). To allow replication four electrodes were used simultaneously. Since only one electrode could be used to calibrate the pH meter, readings for the other three were taken in five different buffer solutions and the final pH values were then calculated from a linear regression analysis

between the meter reading and pH value.

At first oven dry sawdust was used but, because of the pH changes observed with distilled water, it was later found to be simpler to use air dry sawdust (about 8% moisture content) than to correct all of the preservative readings to give figures for pH changes over and above those obtained with distilled water. Replicates of the following trials were carried out:-

distilled water
copper sulphate
copper chrome (CC)
CCA
CCB
CCAB

} 2% w/v CCA equivalent

In addition, the following second treatments were carried out:- arsenic pentoxide on sawdust previously treated with CCB conditioned and dried, and CCA on sawdust previously treated with boric acid conditioned and dried, all solutions being 2% w/v CCA equivalent.

4.4.3 Results

The pH values of the 2% w/v CCA equivalent treating solutions at 25°C are given in table 77. The values of pH against time are plotted for distilled water, copper sulphate, CC, CCA, CCB and CCAB in figure 37 and for the CCA treatment of B+CCA and the arsenic treatment of CCB+A in figure 38, using a logarithmic scale for time.

The CCA and CCAB solutions were more acidic than the CC and CCB solutions (table 77). Boric acid and copper sulphate were only

slightly more acidic than water (table 77). When treated with the distilled water and copper sulphate the pH of the sawdust equilibrated very quickly (figure 37). The pH of the sawdust in the case of CC, CCA, CCB and CCAB rose steadily to a maximum at about 300 hours and then began to fall (figure 37). The curve for CCAB closely resembled that of CCA (figure 37). The curves for CCB and CC (figure 37) were similar up to 300 hours but subsequently the pH of the CC treated sawdust fell as in the case of CCA, but the curve for CCB fell more slowly, if at all. The difference in pH between CCA and CCB treated sawdust (figure 37) was quite marked at first but decreased as the maximum pH for CCA was approached. The curve for CCA added to boric acid treated sawdust as the second treatment of B+CCA (figure 38) was almost identical to that of CCA (figure 38) after the first 30 minutes. The pH changes during the arsenic treatment of the CCB treated sawdust (figure 38) that is, the second treatment of CCB+A, did not resemble those of any of the other treatments. There was an initial small fall in pH and then a rise which steadied after about 100 hours and then fell slightly. The highest pH value during the arsenic treatment was lower than that during the CC, CCB, CCA and CCAB treatments (figures 37 and 38).

Table 77 -
pH Values of Treating Solutions

Treating Solution (2% w/v CCA Equivalent	pH
Distilled Water	5.34
Copper Sulphate	4.92
Copper Chrome	4.01
Copper Chrome Arsenic	2.10
Copper Chrome Boron	3.86
Copper Chrome Arsenic Boron	2.11
Arsenic Pentoxide	2.39
Boric Acid	5.25

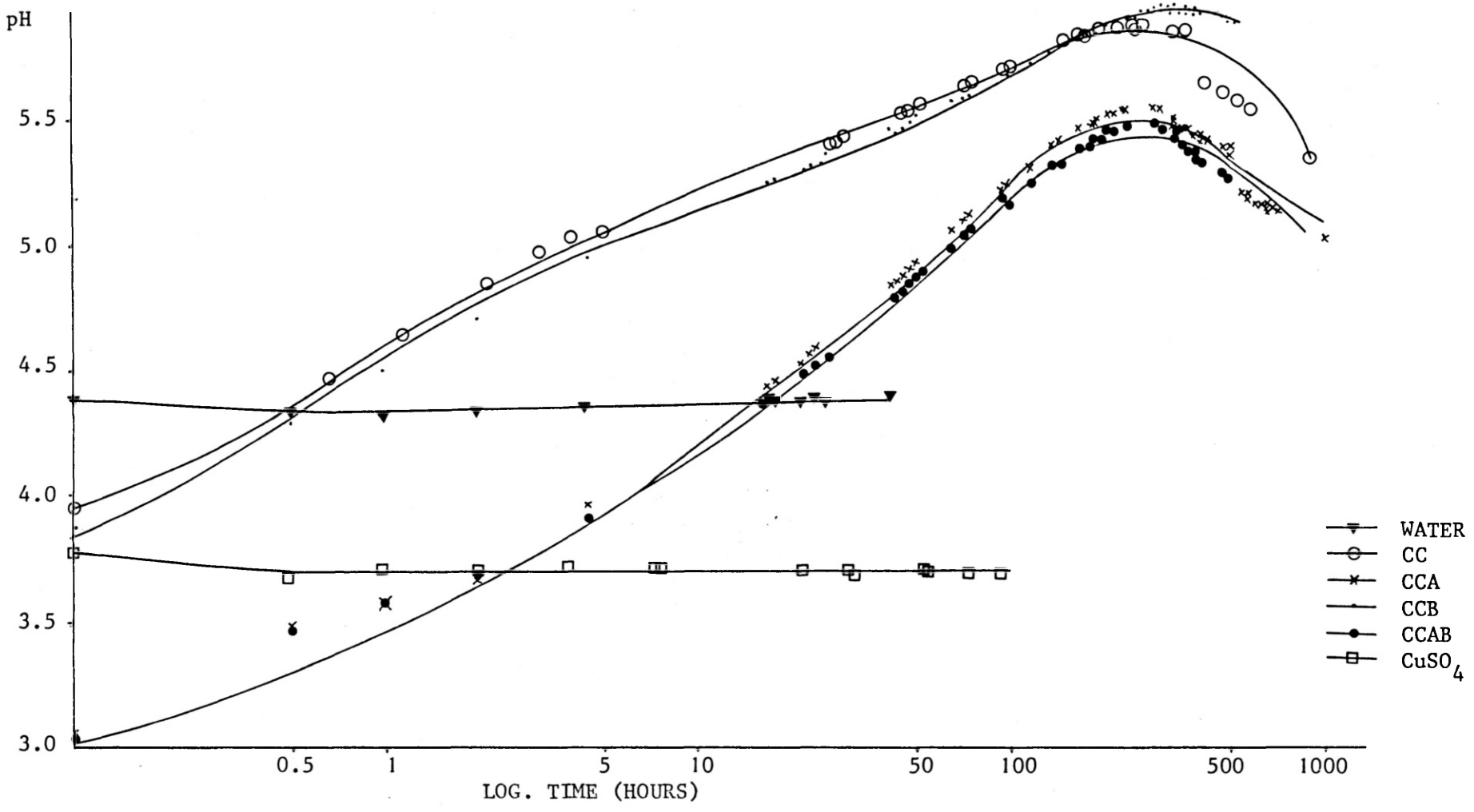


FIGURE 37 PH CHANGES DURING FIXATION IN SAWDUST - SINGLE TREATMENTS

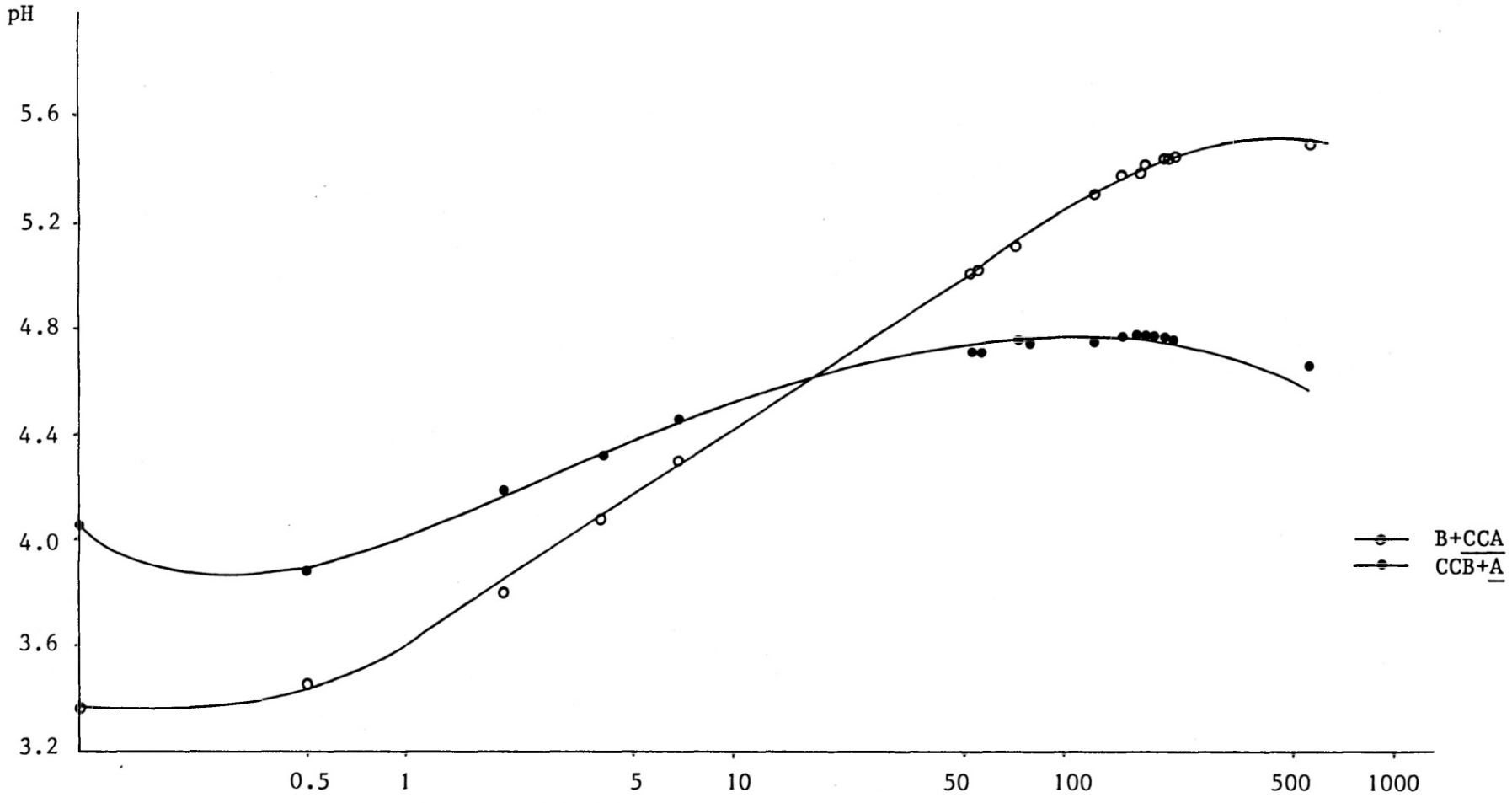


FIGURE 38 PH CHANGES DURING FIXATION IN SAWDUST - 2ND TREATMENTS

4.5 Discussion

4.5.1 Chemical Analysis of Treated Woodblocks

The theoretical copper retentions of the miniblocks were calculated from the amount of treating solution taken up and compared with the actual retentions as determined by chemical analysis after leaching. The comparison revealed that there was more copper than expected at the lower concentrations and less than expected at the higher concentrations. The exception was the CCB treated blocks where there was more copper than calculated at most of the treatment levels. The higher levels of copper could be a result of over-absorption which has been noted by several authors for both copper and chromium in small CCA treated samples. (Drysdale, 1979; D.N.R. Smith and Williams, 1973 a,b). The lower levels of copper are, presumably, the result of loss of the preservative during the laboratory leaching procedure. It is possible that the higher levels of copper in the CCB treated blocks are a result of the greater fixation of copper from this preservative. The results for the 16 days' fixation in section 4.3 indicate that copper was less well fixed in CCA and CCAB than in CCB. The lower levels of copper in the CCB+A treated blocks suggest that copper was leached during the acidic second treatment with arsenic (pH 2.4 at 2% w/v CCA equivalent). Analysis of the arsenic solution after the second treatment showed that this was the case. Only a comparison of leached and unleached blocks would indicate how well fixed each of the formulations was.

In the case of chromium there was commonly an over-absorption of 20 - 50% in CCA and CCAB, this effect being less marked in B+CCA treated blocks. In contrast, the chromium retentions in the CCB

and CCB+A treated blocks were approximately as calculated. A possible explanation for this is that less chromium was used in fixation where arsenic was not present in the treating solution. The arsenic retentions in the CCA and CCAB treated blocks were frequently 10% higher than the calculated values, although there was no increase in the case of the B+CCA treatment. In all but the 1.6% concentration of CCB+A, the arsenic content was between 60 and 90% of the calculated value. It is possible that there was insufficient chromium available for the fixation of arsenic in these blocks (Eadie and Wallace, 1962). Where the chromium to copper ratio was high, there was more arsenic fixed and where the chromium to copper ratio was low there was less arsenic fixed. It appears that in this double treatment chromium fixed copper in preference to arsenic. This is the opposite of the deductions of D.N.R. Smith and Williams (1973 a,b) from their work with a single treatment of CCA.

It is interesting to compare the analysed retention data for CCA and CCB+A at the 2.6% treating solution concentration. In the CCB+A treated blocks the copper and arsenic retentions were both 94% of the corresponding values for CCA. However, the chromium retention was only 81% of that in CCA. Since arsenic is said to be fixed only in combination with chromium (Eadie and Wallace, 1962, Pizzi, 1982c), it appears that some of the copper in CCB+A must be fixed independently of chromium, such as by adsorption.

In the case of boron, it appears that all of this was lost in the leaching procedure. Pizzi and Kubel (1982) suggest that no insoluble boron compounds are formed during the fixation of CCB but Tillott and Coggins (1981) have quoted a figure of 10% fixation. It is possible that a small amount of boron may have been overlooked due to experimental error in the extraction process (table 56).

The values for the Cr : Cu ratios in the CCA, CCAB and B+CCA treated samples were higher than those for CCB and CCB+A but were independent of solution strength. On the other hand, the values for CCB and CCB+A were lower and tended to rise with increasing retention. A possible explanation for this last observation is that some of the copper was fixed independently of chromium and, if this amount were constant, the proportion of copper requiring chromium for fixation would increase as the total amount of copper increased, thus there would be a rise in the Cr : Cu ratio. Wilson (1971) showed that the amount of copper that reacted instantly with the cell wall was independent of treating solution concentration.

The results of the analysis of the water cooling tower blocks followed a similar trend although the Cr : Cu ratios in the CCA treated samples were smaller. This may indicate that the massive over-absorption of chromium is an outer layer phenomenon since the miniblocks were much smaller than the water cooling tower blocks (when treated) as were those of Drysdale (1979) and D.N.R. Smith and Williams, (1973 a,b) who also noted this effect. The additional leaching undergone in the cooling tower had no significant effect on the preservative retentions except in the case of the 3.7% CCB treatment where unexposed blocks contained small amounts of boron and exposed blocks contained none. Another effect was the slight increase in the Cr : Cu ratios particularly at the 0.8% concentration. This could indicate that there was a slight leaching of copper during the exposure period. Eadie and Wallace (1962) have shown that there is a marked reduction in the proportion of copper fixed at treating solution strengths below 0.5% w/v CCA.

Comparison of the actual gross retentions of copper, chromium, arsenic and boron between the five treatments would indicate that CCB+A treated wood ought to give the worst performance of all. However, this is the

opposite of what actually happened, particularly in the case of soft-rot. If the gross copper retention were solely responsible for soft-rot performance the results suggest that CCB should have provided the best protection at the higher concentrations. Using the results of the copper analyses the weight losses due to Chaetomium globosum (figure 17) were replotted (figure 30). Despite the fact that there was no data corresponding to a retention of 0.12% w/w (where the graph dipped in the other cases), the performance of CCB+A was clearly superior to that of the other treatments, which in this second figure (figure 30) had become more closely grouped than they were before (figure 17). Similar weight losses were obtained at several concentrations in CCB+A treated blocks with less than two-thirds the copper retention of the equivalent CCA treated blocks. This was also noted in the soil-bed when theoretical retentions (which may be misleadingly high in the case of CCB+A) were taken into account (figure 27, table 49). This suggests that in the case of CCB+A, the copper was acting more efficiently in protecting the wood against soft-rot than in all of the other treatments.

These results lead to speculation on the causes of the difference between CCB+A and all of the other treatments. Suppose that in CCB some of the copper is adsorbed as copper sulphate and the rest is fixed by reaction with chromium (Pizzi and Kubel, 1982). During the second treatment with arsenic pentoxide some of the arsenic is fixed. Arsenic is said not to be fixed independently of chromium (Pizzi, 1982c; Eadie and Wallace, 1962) and must therefore displace some of the copper fixed by chromium, since there is less copper in CCB+A treated blocks than in those treated with CCB alone. This would agree with D.N.R. Smith and Williams' (1973 a,b) suggestion that chromium fixes arsenic in

preference to copper in CCA. The copper remaining after the arsenic treatment is equally as effective against soft-rot as all of the copper in the other treatments. This would explain the difference in performance of CCB and CCB+A when compared on a gross copper retention basis - both sets of treated blocks have the same amount of "effective" copper, but in addition the CCB treated blocks have a percentage of relatively "ineffective" copper as far as soft-rot is concerned. From Nilsson's hypothesis (1982) it would follow that the "effective" copper masks the T-branch induction sites.

4.5.2 Fixation in Sawdust - Preservative Retention with Time

The results for CCA broadly resemble those obtained by Wilson (1971) using a similar method, although there are some points of diasagreement. When comparing the data it must be borne in mind that Wilson took the maximum amount fixed as 100% for each element rather than expressing the amount of unleachable material as a percentage of the total applied in the treating solution. In addition, the concentrations, temperatures and timber species, shown to affect the rate of fixation (Wilson, 1971), were also different. Another process which may have affected the results of the present study was the sterilisation by ionizing radiation. Wilson makes no mention of any precautions taken to avoid fungal contamination of the solutions during fixation which could well have interfered with the results (Murphy, 1982). Taking all of this into account, the only main difference between the results is that Wilson claimed that in the initial stages the fixation of copper proceeded at a greater rate than that of arsenic and chromium, whereas

in the present study, arsenic was fixed more rapidly than copper and chromium.

The proportion of unleachable copper, chromium and arsenic was almost identical at each time period for CCA and CCAB. This suggests that boron did not interfere with the fixation processes of CCA. However, there were marked differences between the CCA and CCB; particularly during the early stages of fixation. In the case of chromium the amount fixed in the CCB treatment was consistently lower than that in CCA until the last period was reached. This was probably a result of the fixation of arsenic by chromium during the entire period. The situation was reversed in the case of copper, where the amount which was unleachable was higher in the CCB treatment than the CCA treatment for the first 48 hours. When the results for copper sulphate alone are plotted on the graph it becomes apparent that the amounts of copper "fixed" in CCB and copper sulphate were very similar initially. This, together with the fact that smaller quantitites of chromium were involved than in CCA suggests that at least in the early stages, the copper fixation in CCB resembles that in copper sulphate solution and is largely independent of chromium. This "adsorption" of copper to form complexes with the wall components has been referred to many times in the literature (Dahlgren, 1972; Levi, 1969; Wilson, 1971; Eadie and Wallace, 1962) and seems to be more extensive in CCB than in CCA. Kubel and Pizzi (1982) suggest that 5 - 20% of the copper is adsorbed as copper sulphate in CCA whereas there may be 30% adsorbed in CCB. These figures are almost identical to those in the present study. It appears that the adsorption of copper is partly, at least, prevented in the presence of arsenic (as in CCA). This phenomenon has recently

been simply illustrated by Vinden (1983) in a copper adsorption study where the amount of copper adsorbed to sawdust was decreased by two-thirds in a mixture of copper and arsenic, compared to copper alone. In his study Wilson (1971) extrapolated the graphs to zero time and estimated that the amounts of copper sulphate taking part in an instantaneous reaction with the cell wall were about 0.24% w/w in both redwood and spruce. In the present study, after one hour 0.37% w/w copper had fixed in the copper sulphate treatment. However, when the equivalent value for CCA was calculated the figure was 0.24% w/w in birch. Bearing in mind that this value is for one hour and the timber species was different the two results compare very well. Wilson (1971) notes that this value seems to be independent of temperature and solution concentration.

As far as the boron was concerned, 25% was unleachable after 16 days in the case of CCB, slightly less in the case of CCAB. These results suggest that at least some of the boron is retained in the wood. This small amount was undetected in the miniblocks but could have been concealed in the small errors which occurred in the "fixed" woodflour extraction (table 56). However, the assumption that the reactions that take place in sawdust mirror those in solid wood may be in error. In the copper chrome treatment the proportion fixed at the end of the 16 days was lower for both copper and chromium than in the other treatments. An explanation for this has not been given in the literature when it was been observed previously. The sharp increase in the rate of fixation of copper and chromium in all of the treatments between 48 and 96 hours could have been due to the slight breakdown of cellulose which may occur during irradiation although there was no effect on arsenic.

4.5.3 Fixation in Sawdust - pH Changes

The pH changes observed for the 2% CCA solution were virtually identical to those obtained by Dahlgren (1972) using a 2.5% Tanalith C CCA solution with Scots pine sapwood sawdust. From this information and other results from kinetics studies Dahlgren and Hartford (1972 a,b,c) and Dahlgren (1972, 1974, 1975 a,b) have identified 3 periods of fixation: a period of momentary initial reactions, a period of primary fixation and a period of final conversion reactions. In addition a generalised scheme of chemical reactions for CCA fixation was proposed and intermediate and final reaction products suggested (Dahlgren, 1972). However, Pizzi (1982 c) has reported that when sodium or potassium dichromate is present, the sodium or potassium tends to buffer and mask the pH changes and give a false curve below pH 5. Therefore he replaced dichromate with chromic acid to obtain a different picture. Pizzi (1981, 1982 a,b,c), Kubel and Pizzi (1982) and Pizzi and Kubel (1982) have recently studied the fixation of the components of CCA and CCB to the components of wood and have made predictions of preservative activity (Pizzi and Kubel, 1982) and proposals for CCA improvement (Pizzi, 1983) which will be dealt with in Section V. Nevertheless, the intention at the outset of this experiment was to compare the treatments and not to try and follow the progress of the various reactions.

The CCA, CCAB and CCA second treatment, and the CC and CCB treatments gave such similar results that it appears that boron had no effect on the fixation except possibly in the CCB treatment after the peak where the pH did not fall sharply as in the CC treatment. The adsorption of copper sulphate, which is said to occur through ion exchange reactions,

was not accompanied by any significant changes in pH, in fact the changes that did occur resembled those of the reaction of sawdust and water. However, the equilibrium pH of the copper sulphate treated wood was approximately 1·2 pH units below that of 2% w/v CCA equivalent copper sulphate solution whereas in water it was about 0.9 pH units below.

The difference in pH between CCA and CCB was approximately 1.6 in the solutions to begin with but during fixation the difference became progressively smaller and was about 0.4 at the peak value. The peak was less well defined for CCB and occurred about 100 hours after that in CCA. The oddest results were for the second treatment in the CCB+A. At first the pH fell as expected on addition of the acidic (pH 2.4) arsenic pentoxide solution to the wood. Then the pH gradually rose to a peak earlier than that of CCA. The peak was at about pH 4.8, lower than that in CCA (5.5) and CCB (6.9). Obviously some complex reactions other than adsorption (c f. copper sulphate) occurred during the second treatment (A) of CCB+A.

It was necessary in these experiments to use well defined wood (sawdust), solutions and conditions but it must be borne in mind that these would not necessarily exist in practice and there may be additional problems of solution disproportionation, temperature fluctuations, variation in treating solution composition and preservative redistribution on drying in the treatment of solid wood. It is difficult to draw conclusions from the results but the main features were:

(1) boron had little or no effect on the pH changes;

(2) the pH changes in CCB, CC, CCA and CCAB treated sawdust followed the same general pattern;

(3) distilled water and copper sulphate treatment of sawdust was accompanied by little change in pH;

(4) the second treatment of CCB+A (i.e. arsenic) resulted in pH changes of the same general pattern as those of CCA although the changes were not so great.

SECTION V: GENERAL DISCUSSION

5. SECTION V - General Discussion

In the past there have been two main approaches to research into waterborne multisalt preservatives. One of these has been concentrated on finding the optimum conditions for 100% fixation (i.e. no leaching by water following treatment) (inter alia Jain and Lagus, 1960; Dunbar, 1962; Falstrom et al, 1967; Henry and Jeroski, 1967; Arsenault, 1973; Hartford, 1973; D.N.R. Smith and Williams, 1973 b; Evans, 1978). The motives for this research include economy, reduction in pollution, safety and perhaps the most important, permanence of the preservative. The CCAs currently in use have been formulated for maximum fixation. The factors affecting leaching of preservatives in practice have been reviewed by Wallace (1964) and more recently by Cockcroft and Laídlaw (1978). The main points can be summarised as follows:

(i) CCA components are leached in different amounts and at different rates from treated wood. Arsenic is generally more leachable than copper which is more leachable than chromium.

(ii) the factors affecting leaching include:

  (a) the timber species (Tamblyn et al), pH, extractives, density, permeability, moisture content, dimensions (Puroshotham and Tewari, 1960) etc.

  (b) the preservative solution (constitution, concentration, temperature, pH, etc.)

  (c) the processing conditions (treatment method, conditions of drying and storage)

  (d) the service environment (moisture, temperature, pH, ionic strength (Irvine, Eaton and Jones, 1972))

However, in a comprehensive review of the factors affecting the permanence of wood preservatives, Wallace (1964) pointed out that although permanence is an essential quality of a preservative, in some cases there is possibly an advantage in adding a less permanent component which could supply a temporary initial added toxicity. This can be achieved in CCA by varying the proportions of the copper, chromium and arsenic (Henry and Jeroski, 1967; D.N.R. Smith and Williams, 1973 a,b; Wallace, 1964). An example of its potential is in poles, particularly eucalypt which tend to split after treatment thus exposing untreated heartwood, where a small quantity of a diffusible (and therefore leachable) component could provide protection in the short term. A similar phenomenon was observed by D.N.R. Smith and Williams (1973 a,b) in experiments to determine the influence of composition on the effectiveness and fixation of CC and CCA preservatives. They found that Cr : As and Cr : Cu salt ratios for maximum fixation were 1.9 and 1.7 respectively. However, the formulation for maximum effectiveness was not coincident with that for maximum fixation but slightly displaced towards a higher level of copper where there was still maximum fixation of arsenic but some loss of copper. A possible explanation for this was brought up in the discussion following the presentation of Wallace's (1964) paper. It was suggested that for wood to be effectively protected by a preservative, the attacking organism must be able to render the toxic material sufficiently soluble for it to be toxic. If the toxic compounds were made too insoluble (such as fluorides in the presence of calcium) then they would become less toxic and less effective.

The other approach to looking at CCAs has been that of Dahlgren and Hartford (1972 a,b,c), Dahlgren (1972, 1974, 1975 a,b), Pizzi (1981, 1982 a,b,c) and Kubel and Pizzi (1982) whose work has already been referred to. In particular Pizzi (1981, 1982 a,b,c) and Kubel and Pizzi (1982) have studied the reactions of the components of CCA and CCB with wood components and have built up a picture of the fixation sites of the various elements. For instance, they suggest that the positions and forms in which copper is likely to be fixed in CCA and CCB treated wood are as follows:

CCA (type C)	CCB
1. 10 - 15% bound as $CuCrO_4$ to lignin guaiacyl units.	1. 18 - 20% bound as $CuCrO_4$ to lignin guaiacyl units.
2. 10 - 22% bound directly as Cu^{2+} to carbohydrates and lignin guaiacyl units.	2. $\pm$ 50% bound to carbohydrates.
3. 40 - 70% as Cu^{2+} bound to lignin functional groups other than guaiacyl units.	3. $\pm$ 30% uncertain position; possibly just physically adsorbed by wood constituents as $CuSO_4$ (see point 4, CCA).
4. 5 - 20% merely physically adsorbed as $CuSO_4$ by wood constituents (particularly carbohydrates?)	

From this type of information Pizzi and Kubel (1982) have deduced the properties of the two preservatives and their summary of the differences between CCA and CCB is as follows:

1. CCB treated wood is slightly more water-repellant than CCA (type C) treated wood.
2. CCA (type C) treated wood has much better long-term but slightly worse short-term resistance to termites than CCB treated wood.

3. CCB treated wood has better long-term resistance but less intense short-term activity against fungi and mould attack than CCA (type C) treated wood.

4. CCB treated wood should leach less Cr than CCA (type C) treated wood at parity of Cr retention after preservative treatment of the wood.

Unfortunately Pizzi and Kubel (1982) have only accounted for the general features of the groups of wood-attacking organisms, that is, they have assumed that wood-rotting fungi are controlled by copper and that arsenic is only effective against insects. It has been shown in this present work (Section 3) that copper tolerant basidiomycetes are important in the decay of wood and there is evidence that they are often responsible for the failure of CCB treated timber in practice (Tillott and Coggins, 1981; Tamblyn and C.R. Levy, 1981). It can be seen that it is erroneous to predict preservative performance purely as a result of observations on the chemical reactions taking place in the wood. To obtain a realistic picture of preservative performance the study of fixation reactions in wood must not be made in isolation but must go hand in hand with biological assessments. In the present study this approach was taken one step further in that the preservative formulations were screened for biological activity before a chemical explanation for their activity was sought. Because of the numerous exceptions to the rule in artificial biological groups, an attempt was made to assess all of the different types of organisms which could attack the treated timber in practice (N.B. animals were beyond the scope of this project) including organisms reported to be arsenic or copper tolerant.

In the case of soft-rot organisms, the most important part of the work and where the test parameters are still being evolved, a multi-faceted approach was made to its assessment (sections 2.2.3., 2.2.4., 2.2.5., 2.2.6.).

In all of the biological tests CCB+A performed equally as well as or better than all of the other formulations, particularly in birch. The chemical assessments revealed that boron was absent from the treated wood after leaching and that the quantities of copper, chromium and arsenic in the CCB+A treated blocks were smaller than those in the equivalent CCA treatments. There were no striking differences in the pH changes during fixation of the various treatments and the presence of boron had little or no effect in any of the formulations. However, in sawdust, about 50% more copper was fixed in the first hour in CCB than in CCA, this being equivalent to the quantity fixed from the copper sulphate solution alone. At the same time the amount of chromium retained by the sawdust was smaller in the CCB treatment than in the CCA treatment. Once again CCAB behaved in a similar way to CCA.

5.1. Mode of Action of CCB/CCB+A

The striking feature of the results is that in CCB+A treated wood about two-thirds of the quantity of the copper in CCA treated wood gave the same levelof protection in the soft-rot tests, that is the soil-bed and the Chaetomium globosum monoculture. Additionally, the main apparent difference between the two preservatives (CCA and CCB) is that two-thirds the quantity of copper was rapidly fixed in CCA compared with CCB. These results could explain each other if two assumptions are made:

1. all of the copper retained initially is fixed by adsorption
2. this copper is probably located in the S_2 layer and at normal retentions controls soft-rot (c f. Butcher and Drysdale, 1978)

Pizzi (1982 c) and Pizzi and Kubel (1982) have shown that in the initial instant reactions copper is fixed solely by ion exchange, and so is the chromium which is fixed. The proportions of copper which could potentially be fixed by adsorption (Kubel and Pizzi, 1982) are in the ratio of 2:3 for CCA and CCB respectively (and are actually about 20 and 30% as found in the experiment in section 4.3.). However, if only adsorbed copper were effective against soft-rot organisms then copper sulphate would be just as effective a preservative against soft-rot as CCB, and CCB+A would be no more effective than CCB. (N.B. see discussion to analyses, section 4.6.1.). Obviously, the explanation for the observations is more complicated than this, but the hypothesis may be true to some extent.

5.2 Other Hypotheses

5.2.1. Lignin Hypothesis

After consideration of a great deal of data, Butcher and Nilsson (1982) have put forward a hypothesis which links soft-rot susceptibility and the copper loading required for soft-rot control with lignin content. The hypothesis suggests:

1. Wood species with low lignin content are very prone to soft-rot attack because cellulose is readily available for enzymatic degradation.
2. Wood species with high lignin content have a high natural resistance to soft-rot because cellulose microfibrils are protected from enzymatic breakdown by lignin encrustation.

3. Wood species containing guaiacyl lignin are more resistant to soft-rot than those containing syringyl-guaiacyl lignin.

4. Lignin provides the major fixation sites for copper in CCA treated wood.

5. In wood of low lignin content, copper can be fixed only to a retention level which is below the toxic threshold for soft-rot fungi. Above this level, copper in S_2 layers is subject to leaching which will impart only temporary protection, and control is eventually achieved by lumen (and possibly middle lamella) deposits of copper.

6. In wood of high lignin content, fixation of copper is enhanced, and retention levels in S_2 layers are well in excess of toxic thresholds.

An actual mechanism of action of the lignin has been put forward by Nilsson (1982). The hypothesis suggests:

1. Soft-rot attack in low susceptibility wood species is prevented at CCA levels which are too low for preventing growth of soft-rot fungi.

2. High susceptibility hardwoods are only temporarily protected by high retentions of CCA. The concentrations of CCA are so high that they will be expected to considerably affect the growth of soft-rot fungi.

3. Formation of T-branches is induced by a chemical factor, most probably of carbohydrate nature, in wood cell walls.

4. The number of sites where this chemical factor occurs is dependent on the carbohydrate/lignin ratio. Few sites occur in high lignin timbers whereas a high number of sites can be expected in low lignin timbers.

5. CCA treatment masks or modifies the sites so that the penetrating hyphae are unable to detect them. The masking is complete in timbers with a high lignin content whereby soft-rot is prevented. Only partial masking occurs in hardwoods with a low content of lignin which will allow soft-rot attack to occur. But the soft-rot decay rate in such hardwoods treated to high retentions of CCA will be reduced because of the toxic effects of the preservative.

There is a lot of supporting evidence for these hypotheses but some of the data cited (Butcher and Nilsson, 1982) is of particular interest. It gives the amounts of copper fixed in several timber species after treatment with copper sulphate solutions of different concentrations. The results indicated that more copper was fixed in species with higher lignin contents. The copper fixed in this experiment was equivalent to the copper adsorbed from copper sulphate solution in the present study in section 4.3. The results here indicate that the same quantity of copper was also adsorbed in the case of CCB (Kubel and Pizzi, 1982) but only two-thirds of this quantity was adsorbed in the CCA treatment (Kubel and Pizzi, 1982). It would appear that the maximum possible adsorption of copper did not occur in the case of CCA due to interference by arsenic. Since birch is a susceptible hardwood and has a low lignin content it is probably not possible to fix sufficient copper in the S_2 layer to exceed the toxic threshold. However, raising the quantity of fixed copper in this layer by 50% should substantially increase the durability of this hardwood. Information for this explanation may be gained by microanalysis of the S_2 layer of the fibre cell wall and by using the thin section technique of Nilsson (1981) on CCB and CCB+A treated birch blocks.

If the hypothesis of Butcher and Nilsson (1982) is correct, there is little hope of protecting some susceptible hardwood species against soft-rot attack in the long term. But if treatment with CCB/CCB+A allows more copper to be fixed in the S_2 layer of the fibre cell wall then the susceptible species will show a markedly improved long term performance against soft-rot. There are indications (figure 25) that this may also hold true for softwood species. In the past it has been assumed that well treated softwoods are resistant to decay by soft-rot organisms but recently there have been several

reports of serious soft-rot decay in the field (Henningsson and Nilsson, 1971, 1976 b; Murphy, 1983). If it were proven that adsorbed copper protects wood from soft-rot cavity formation, a simple comparison of the quantities of copper adsorbed in a CCA treatment and a copper sulphate treatment would indicate whether or not a species had potential for improvement by treatment with CCB/CCB+A.

In the short term susceptible hardwoods can be protected by increased loadings of CCA (Butcher and Drysdale, 1978) but Drysdale et al (1980) have shown that the quantity of copper fixed in the S_2 layer of the cell wall does not increase above a certain threshold with increased gross retention, and found that the excess copper was located elsewhere e.g. lumen, middle lamella. Copper deposits in these sites can obstruct the spread of soft-rot organisms but not prevent cavity formation in the fibre cell wall. The difference in mode of action of the copper in these two sites must be made clear: copper, possibly fixed to lignin in the S_2 layer, is thought to block cavity formation whereas copper deposits in the lumen are thought to act as toxicants to soft-rot fungi and other decay fungi.

5.2.2. Microdistribution Theory

Many authors have examined the microdistribution of CCA components within the cell wall layers in search of an explanation for the poor performance of CCA treated hardwoods (Dickinson, Sorkhoh and J.F. Levy, 1976; Drysdale et al, 1980; Dickinson, 1974 a;) as compared with that of softwoods. They have found that the distribution of preservative elements within the cell wall layers of hardwoods, notably in the S_2 layer, is poorer than in softwoods. It is within the S_2 layer of fibre cell walls that soft-rot cavity formation occurs. In addition, Drysdale (1979) frequently found that there was

a marked disproportionation of the preservative elements in the S_2 layer, copper often being found in the absence of chromium and arsenic.

These observations could be symptoms of the effects reported in the previous hypotheses and that of the present work, in that a susceptible timber species with a low lignin content would possess few sites for the fixation of copper in the S_2 layer (although there would be many T-branch induction (TI) sites (Nilsson, 1982)). Additionally, it would follow that if copper were fixed to lignin in the S_2 layer by adsorption, then it could frequently be found in the absence of chromium and arsenic. Thus both of these observations fit in with the deductions from the present work.

5.2.3. Pizzi's Theory

In a discussion of the practical significance of his recent work (referred to earlier), Pizzi (1983) has suggested that treatment temperature and treating solution concentration and pH, have a marked effect on the relative distribution of chromium (and copper and arsenic reacted with it) between lignin and holocelluloses. Of particular relevance to the present study is that raising the pH of the CCA results in an increase in the amount of chromium (and copper and arsenic reacted with it) fixed to the lignin. As has been noted previously (section 4.4.0 the pH of CCB is higher than that of CCA, and presumably more chromium (and copper and arsenic reacted with it) is fixed to lignin than in the case of CCA. However, this does not fit in with the hypothesis put forward in the present work since it has been proposed that adsorbed copper (without chromium) is important in controlling soft-rot cavity formation.

Accepting Butcher and Nilsson's (1982) hypothesis and assuming that CCA fixed to lignin is effective against soft-rot, and CCA fixed to holocellulose is effective against other organisms, Pizzi (1983) has concluded that different treatment conditions are necessary to optimise the durability of treated softwoods and hardwoods. In particular he points out that softwoods require more CCA fixed to holocellulose than lignin (for protection against basidiomycetes) and hardwoods need more CCA fixed to lignin than holocellulose (for protection against aoft-rot organisms). He emphasises that it may be possible to improve the resistance to soft-rot of wood species of lower lignin content, i.e. hardwoods, by decreasing the amount of arsenic in CCA or eliminating it altogether. The effect of eliminating arsenic (from the first treatment) has already been demonstrated in the work presented in this thesis and in addition there is some evidence for a better performance in softwoods. Vinden (1983) has shown that arsenic interference with copper adsorption is independent of arsenic concentration, therefore, if adsorbed copper is responsible for blocking Nilsson's TI sites, reducing the concentration of arsenic in CCA will not necessarily improve its performance against soft-rot attack. The reason put forward by Pizzi for the increased protection is that more copper would react with chromium and would be fixed through chromium to lignin as a copper chromate complex. This is not part of the explanation given in the present hypothesis.

5.3. Hypothesis

1. Adsorbed copper is responsible for blocking Nilsson's TI sites in the S_2 layer of the fibre cell wall.
2. Arsenic interferes with copper adsorption, therefore CCA treatment (i.e. copper in the presence of arsenic) of the timber results in only a proportion of these TI sites being masked by copper, whereas a treatment of copper in the absence of arsenic (CCB) leaves more of the sites obscured by copper.
3. Treatment of some hardwoods and softwoods with fixed copper followed by arsenic would increase their resistance to soft-rot decay whilst affording protection against fungi and insects.

5.4. Future Work

In addition to the suggestions already made it would be interesting to examine the relative activities of CCA and CCB+A in a range of hardwoods. Perhaps the exceptions which required more CCA than predicted in Butcher and Nilsson's (1982, figure 1) data e.g. Dysoxylum huntii, Alnus glutinosa, Betula alba and Fagus sylvatica would benefit most from the CCB+A treatment, but there are many species not tested by Butcher (1979) e.g. softwoods. As pointed out previously, if the hypothesis is true, then the potential for adsorbed copper could be found by treatment with copper sulphate solution. A comparison of the amount of copper adsorbed here with that of CCA treated wood should indicate whether or not there is potential for improvement with a CCB/CCB+A treatment.

It would be interesting to microscopically examine CCA, CCB and CCB+A treated samples exposed to monocultures of soft-rot organisms to note the mode of attack and compare the frequency of cavity formation, which should be lower in the CCB/CCB+A treated

samples.

Other future work could examine the significance of boron in the treatment since most of the data indicated that boron had no role to play. It seems likely that only a double treatment where copper and arsenic are applied separately would give the enhanced performance. However, experimentation with other fixation agents such as ammonia may prove rewarding and other treatment methods such as diffusion of one or other or both of the treatments may make the double process commercially viable.

APPENDIX A : Soft-Rot Pilot Tests

Test 1. Selection of Nutrient Medium

Media

(a) Based on Abrams (1948)

6.0 g	NH_4NO_3	ammonium nitrate
2.0 g	K_2HPO_4	di-potassium hydrogen phosphate
2.5 g	KH_2PO_4	potassium dihydrogen phosphate
2.0 g	$MgSO_4.7H_2O$	magnesium sulphate
1 ml	trace element solution	
20 g	agar	

per litre distilled water

(b) Based on Gersonde and Kerner-Gang (1976)

6.00 g	NH_4NO_3	ammonium nitrate
2.56 g	K_2HPO_4	di-potassium hydrogen phosphate
1.02 g	$MgSO_4$	magnesium sulphate
0.25 g	KCl	potassium chloride
0.005 g	NaCl	sodium chloride
0.001 g	$FeSO_4$	ferrous sulphate
0.001 g	$MnSO_4$	manganese sulphate
1 ml	trace element solution	
20 g	agar	

per litre distilled water

Results

Test	Medium	Mean % Weight Loss	S.E.	t	Significance
beech veneers 16 days	(a)	5.07	0.20	-1.007	-
	(b)	5.52	0.40		
beech veneers 28 days	(a)	9.79	0.33	1.290	-
	(b)	8.83	0.68		
birch mini-blocks 28 days	(a)	4.71	0.20	3.770	*
		6.12	0.31		

* = significant difference between mean values

\- = no significant difference between mean values ($p = 0.05$)

Test 2. Alternative Carbon Source

Media

(1) 4% malt agar
(2) basic medium (b) (as above)
(3) " " " " + 0.05% glucose
(4) " " " " + 0.10% "
(5) " " " " + 0.25% "
(6) " " " " + 1.00% "
(7) " " " " + 2.50% "

Results

Beech Veneers

Incubation Period	Medium	Mean % Weight Loss	S.E.
14 days	1	-2.70	0.32
	2	0.96	0.49
	3	0.79	0.34
	4	3.20	0.13
	5	0.58	0.18
	6	0.62	0.25
	7	0.82	0.27
28 days	1	3.53	0.17
	2	3.78	0.57
	3	4.52	0.47
	4	3.27	0.65
	5	0.90	0.34
	6	1.50	0.70
	7	4.48	0.56

Analysis of Variance

Media Compared	14 days	28 days
1/2	*	-
1/3	*	-
1/4	*	-
1/5	*	*
1/6	*	*
1/7	*	-
2/3	-	-
2/4	*	-
2/5	-	*
2/6	-	*
2/7	-	-
3/4	*	-
3/5	-	*
3/6	-	*
3/7	-	-
4/5	*	*
4/6	*	*
4/7	*	-
5/6	-	-
5/7	-	-
6/7	-	-
F ratio	32.26	7.30
L.S.D.	0.76	1.30

* = significant difference between mean values

- = no significant difference between mean values (p = 0.05)

Test 3. Selection of Test Organism and Use of Filter Paper Feeder

Beech Veneers, 8 replicates.

Treatment = 0.75% w/v CCA.

+ = filter paper

- = no filter paper

T = treated

U = untreated

Results

Organism	Test	Mean % Weight Loss	S.E.
C.globosum	untreated -	53.76	3.78
	untreated +	40.14	2.30
	treated -	45.30	3.71
	treated +	31.74	2.05
P.hoffmannii	untreated -	5.66	0.44
	untreated +	2.74	0.41
	treated -	2.63	0.36
	treated +	1.25	0.62

t tests

Tests compared	t	Significance
C.globosum		
U +/-	2.935	*
T +/-	3.206	*
+ U/T	2.725	*
- U/T	1.546	-
P.hoffmannii		
U +/-	4.849	*
T +/-	1.927	-
+ U/T	2.016	-
- U/T	5.297	*

* = significant difference between mean values
- = no significant difference between mean values

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