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THE QUANTITATIVE ANALYSIS OF COMPONENTS OF FIBRE-REINFORCED CEMENT BOARDS

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A Research Report submitted to the Faculty of Architecture, University of the Witwatersrand, Johannesburg, in fulfilment of the requirements for the degree of Master of Science in Building.

Johannesburg, 1993

DECLARATION

I declare that this Research Report is my own. It is Being submitted for the degree of Master of Science in Building in the University of the Witwatersrand, Johannesburg. It has not been submitted before for any degree or examination in any other University.

A Kuning

(Signature of candidate)

16th day of FEBRUARY 1993

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I would like to thank Prof. J. Morris for his invaluable assistance, encouragement, guidance and information that resulted in the production of this Research Report.

I would also like to thank the staff from Everite for the time spent advising me on this investigation.

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SYNOPSIS

Environmental and health considerations have led to the substitution of cellulosic fibres for asbestos fibres in many cement-based products. Inevitably, the substitution has required modifications to the manufacturing process.

Certain production techniques associated with the switch to cellulosic fibres and other additives needed elucidation. It is possible that to ensure the required concentration of certain additives in the final product, an excess is being used in the process because of uncertainties about the quantitative balance of the process.

My intention was to examine the potential role for Fourier Transform Infrared (FT-IR) Spectroscopy in the investigation of the materials constituting fibre-reinforced cement boards.

I was able to show that qualitative and quantitative determination of certain of the components in the final product are possible with adequate precision and reproducibility to be of value to the manufacturer. I also showed that care taken in the preparation of standard and analytical samples was essential for the success of such analyses.

1 INTRODUCTION

Everite have phased out the production of Asbestos cement boards due to health hazards associated with asbestos fibres. They have developed successful techniques for the production of fibre reinforced cement boards using vegetable rather than asbestos fibres, but depending on certain expensive additives to ensure the durability of the product. The research I undertook involved the identification and quantification of one particular additive, namely Aluminium Tri-hydrate (AH_3) in the fibre-reinforced cement boards which are being produced for the construction industry.

Successful techniques for the production of cement boards reinforced with cellulosic fibres have been developed. However the production needs to be optimised particularly in respect of the role of certain additives. To do this, a quantitative analysis of the final product for comparison with the quantities of materials that go into the production was required.

To carry out this investigation, samples of the boards were examined using Fourier Transform Infrared Spectroscopy (FT-IR), which is an analytical tool of considerable sophistication.

The technique of FT-IR analysis offers an insight into the molecular composition of materials that might be difficult to achieve in other ways. A number of different

analytical methods have become available using the FT-IR instrumentation. The Potassium Bromide Pellet technique for sample preparation and presentation were found to be applicable for the investigation.

It was necessary to run a spectrum of AH_3 to obtain its infrared fingerprint and find at which wavenumbers absorption peaks characteristic of the additive appeared. Evidence of increased absorption with increasing concentration of AH_3 in the fibre-reinforced cement boards was found at 3618cm^{-1}. Thus absorbance at this wavenumber can give qualitative and quantitative information about the presence of the particular additive.

With regard to the quantitative investigation, the recorded spectra were transformed from transmittance to absorbance format. The reason for this is that the absorbance of a molecular species is related to its concentration in accordance with the Beer-Lambert Law.

Boards with different known concentrations of the additives were made up in the laboratory at Everite, and the peak at 3618cm^{-1} was used for calibration of the AH_3 concentrations. Once the calibration curve for AH_3 was calculated using those boards, boards containing 'unknown' (to me) concentrations of AH_3 were made up by Everite, and a quantitative analysis was undertaken. This Research Report shows that the 'unknown' concentrations of AH_3 in the boards were determined with satisfying accuracy using Fourier Transform Infrared (FT-IR) Spectroscopy, but that the consistent curing of the boards (both the standards and the analytical

samples) plays a crucial role in this investigation.

The potential for this technique to be used in forensic studies of boards that have failed also needs investigation, but this was beyond the scope of this Research Report.

2 ASBESTOS SUBSTITUTION IN THE FIBRE CEMENT INDUSTRY[1,2,3]

2.1 Introduction

Asbestos, a mineral fibre with many uses and extraordinary material properties, has been used for centuries. In its various mineralogical forms, asbestos is a unique material combining many desirable properties such as high strength and good chemical and heat resistance.

During the past few decades, much evidence has accrued which shows that asbestos is a hazardous material posing a serious health risk when it is released into the air. Asbestos readily releases fine fibres which can remain suspended in the air for a long time and can also be respirable i.e. be drawn into the extremities of the lungs if the fibres are less than 3μm in diameter. Because these fine asbestos fibres often have a high aspect ratio of length to diameter, the cells which would normally ingest and remove debris from the lungs cannot readily do so and the fibres tend to remain as an irritant; large amounts leading to asbestosis.

In particular, a study by Irving Selikoff, a well known American industrial physician, showed that asbestos can cause asbestosis, and over a longer period of time, the lungs or surrounding tissue can be affected by lung cancer or mesothelioma (a cancer of internal cell linings characteristic of exposure to respirable insoluble fibres and in the main associated with exposure to asbestos) if certain precautionary measures are not used in the handling and application of asbestos.

In the course of his examinations, Selikoff found numerous cases of death caused by asbestos induced illnesses, especially among former workers of the US Naval industry, where asbestos was used as insulation and fire protection material, particularly prior to and during the first world war. As a consequence of the spray technique used, the workers were exposed to high concentrations of fibrous asbestos dust.

Asbestos cement, on the other hand, is produced by means of a wet processing technique. The asbestos fibre is bound in a cement matrix during processing and in the final product, and thus the probability of the fibre being set free in the environment during processing and from the final product is much lower than in the case of sprayed asbestos.

It should be borne in mind that the risk of developing lung cancer for smokers who are exposed to asbestos is greatly increased. As a result of the research done by Selikoff and other scientists, governments and authorities increasingly realised that labour and health legislation had to be reconsidered, and had to take into consideration the average latency for asbestos induced illnesses of between 10 and 40 years.

Today, production and processing of asbestos products are subject to strict safety measures and controls. Some of the problems caused by processing asbestos cement products on construction sites were solved by a high degree of pre-manufacturing. The fibre cement industry has introduced new manufacturing

methods creating lower fine dust concentrations. By consequent and permanent development of dust protection technologies, the production plants belonging to the Swiss Eternit Group have achieved a high standard of occupational hygiene and the danger of asbestos induced occupational illness are thus minimised. However, certain applications of asbestos (insulation for instance) have been banned in many countries.

Due to the long latency of asbestos induced illnesses, however, it is still likely that the number of cases developing lung cancer or mesothelioma will increase in the long term.

2.2 Asbestos Cement and its Production

Asbestos cement was invented by L Hatschek, an Austrian, who in 1900 registered a patent on his procedure for 'the manufacturing process for synthetic stone sheets and hydraulic bonding agents'. Essentially, this invention consisted of manufacturing a sheet material on a rotating sieve machine using a highly diluted suspension of portland cement and asbestos fibres. Because of its excellent properties, this product subsequently dominated the world in the building industry and afterwards, after continual modification of the original procedure, it was used for the manufacture of sheets, pipes, joints and many other building components.

Nowadays asbestos cement is understood to be a composite material with mechanical properties that largely depend on the interaction between the

reinforcing fibres (asbestos) and the matrix (cement).

Apart from reinforcement, asbestos fibres also assume other functions within the composite material such as affecting its porosity as well as its structure. Because of their special morphology and surface structure, asbestos fibres are capable of binding with the cement on their surface, and thus allowing for the production of the asbestos cement.

Asbestos has been widely used in insulation and fire protection, and as a reinforcing agent for both bitumen and cement materials. Asbestos cement may be compressed to varying degrees to form flat or corrugated sheets or moulded into a wide range of components.

Corrugated sheet is the main asbestos cement product in buildings and is applied largely as roofing and wall cladding. The alternative flat sheet is used mostly for panelling and partitions. In addition, highly compressed asbestos cement is used as artificial slate.

2.3 From Asbestos Cement to Fibre Cement

The first approach: 'fibre substitution'

The reinforcement effect of asbestos within the cement is easily understood considering the mixture rule for tensile strength:

$$\sigma_c = \sigma_f . V + \sigma_m (1 - V)$$

where: σ is the tensile strer gth,

V is the fibre volume fraction,

and the subscripts $_{c, m}$ and $_f$ stand for composite, matrix and fibre.

Usually though, the reinforcing fibres within the cement are not continuous and are statistically oriented in such a way that for the real situation correction factors will have to be included in the equation.

Another correction should also be introduced into the ideal equation as the fibre concentration within the composite material is extremely limited in practice: asbestos can be mixed with cement up to 15% by weight whereas with organic fibres, the concentration is limited to about 7-9%. If this value is exceeded, the result is a decline in strength instead of a further increase. This can be explained by the fact that with an increase in fibre volume fraction, the coarse pore volume of the cement matrix in increased as well and can override the reinforcing potential of the fibres.

Also, it has been shown that reinforcement is only possible if the elastic modulus E_f of the fibre is higher than the elastic modulus E_m of the matrix. In this way the reinforcement potential increases with an increasing ratio of E_f/E_m. This means that

the decisive factor for the reinforcement of cement by fibres is the E-modulus of the fibre E_f provided that all other conditions are fulfilled.

In the search for a suitable substitute fibre for asbestos, performance criteria have been established, which, apart from the obvious physical safety aspects, as well as the high fibre E-modulus, define all other technical requirements of the fibre.

In the selection of reinforcing fibres the decisive factor is the combination of properties which are unique to asbestos fibres; these are: mechanical strength, chemical stability, dimensional stability and morphology. The criteria for tensile strength, E-modulus and other properties must also be comparable with those of asbestos fibres.

Research for a suitable asbestos substitute started in 1976 but with limited success. Among the synthetic fibres, polyvinylalcohol produced the best combination of properties. After years of intensive cooperation with Kuraray Co. Ltd, Japan, a fibre-type was developed which met the requirements, and could assume, in many cases, the reinforcing potential which asbestos fibre had within the cement. After successful testing it is now produced in industrial quantities and used for cement reinforcement. Despite this success in fibre research, the original intention that a fibre should be developed which would match the qualities of asbestos fibre, was not achieved.

The fibre evaluation which was conducted with much effort, has led to the

following findings:

- The various functions of asbestos can only be equalled by using combinations of various fibres,
- The behaviour of substitute fibres during processing differs from that of asbestos fibres,
- The substitute fibres produce a porosity and structure of the composite which is different from that of asbestos cement,
- The interaction between the substitute fibre and cement matrix is basically different from that between asbestos and cement.

As a result of these facts, some of the fundamental properties of such fibre cement composites can not be identical with those of asbestos cement (viz. flexural strength, toughness, water absorption etc.).

These findings apply to all present solutions which are basically applied to fibre substitution in asbestos cement products. The most important fibre types and their specific problems related to cement-based composites are listed as follows:

Fibre Type	Related Problems
synthetic mineral fibre	alkali resistance, brittleness
glass fibre	as above
synthetic organic fibres	cement adhesion, chemical stability, thermomechanical properties
cellulose	alkali resistance, swelling properties
synthetic pulp	strength, thermomechanical behaviour
carbon fibres	cement adhesion, fibre brittleness.

With increasing experience and a better understanding of the fibre-matrix interaction, it was realised that the asbestos problem in the industry cannot be solved by simple fibre substitution. This knowledge inevitably led to a new approach.

The New Approach: asbestos-free fibre reinforced cement composite

After exhausting all the possibilities for substitute fibres in the asbestos replacement programme, the next stage was to modify the matrix in order to achieve the desired optimal fibre matrix interaction.

There are a number of possibilities to modify the matrix. These are listed as follows:

For products cured at ambient temperature

- reducing alkalinity
- using inert or active fillers

- influencing structure and porosity by technical methods (eg. fibre alignment, compression, etc.)
- changing the curing conditions
- diverse treatments after curing.

For autoclaved products

- changing the cement and/or sand particle size
- adapting autoclaving conditions to the modified matrix
- using fillers
- changing structure and porosity.

Systematic evaluation of the modified matrix and substitute fibres and their interaction with each other finally led to the development and establishment of asbestos-free fibre cement products which, after having passed the necessary durability tests, have already been put on the market.

Apart from the usual mechanical, physical and chemical test procedures, different accelerated ageing test methods were developed and used particularly to monitor the long term properties under various climatic conditions.

With fibre cement activities in numerous countries and for very different markets, it is believed that, because of the different requirements of the individual markets, there is no unique solution for the substitution of asbestos fibres. Building products have to satisfy the requirements of various climatic conditions. According to the

type of product (roofing, facade, large, small, etc.) the performance standards may be different for each composite material. For building materials, a wide range of products is available on the market in numerous countries. Many countries have arrived at the final stages of their substitution programmes and have changed their complete production of building materials to asbestos-free material.

Boards in South Africa are now being produced using cellulosic fibres and other additives. The following table indicates the fibre properties of asbestos compared to that of cellulose:

Table 2.1. Fibre Properties of Asbestos and Cellulose

FIBRE	Density g/cm^3	Diameter μm	Elastic Modulus GPa	Tensile Strength MPa	Failure Strain %
Asbestos	2.5	0,1-1	150	3600	0,1-0,3
Cellulose	1.2	15-30	10-15	300-500	20

As with every new development, the industry is subject to a learning curve and therefore economic aspects to date are not yet optimised. The prices of substitute fibres are considerably higher than those of asbestos fibres. Other additional raw material costs as well as rises in production process costs contribute much to the fact that today's production costs are still higher than those of asbestos cement.

3 PORTLAND CEMENT

3.1 Introduction

This section describes the manufacture and hydration of portland cement in detail so that it can be better understood how the curing of cement may effect the apparent concentration of AH_3.

3.2 Manufacture of Portland Cement[4]

Portland cement as manufactured today consists of a mixture of calcium silicates, aluminates and other molecular compounds which have hydraulic properties, that is, when mixed in a finely ground state with water, they take up a proportion of water and hydrate to form further compounds which interlock in a mixture of high physical strength.

3.3 The Hydration of Portland Cement

Mantel[5] describes the hydration process as follows:

When water is added to cement, the first compound to start reacting is tri-calcium aluminate (C_3A). The reaction is virtually instantaneous and if nothing were added

to the cement, the whole mix would turn into an unworkable solid mass. This is the so called Flash-Set. When gypsum ($CaSO_4.2H_2O$) is present, some of this gypsum dissolves in the water and reacts with the hydration products of the C_3A forming an insoluble calcium sulphoaluminate hydrate called ettringite ($C_3A.3CaSO_4.32H_2O$). As an explanation of this set control, it could be visualised that the ettringite forms a skin around the individual C_3A crystals, but as it is formed, it tends to trap a little water between itself and the C_3A.

This water reacts with the C_3A giving an increase in volume. This results in the bursting of the skin which is then again sealed off by a new skin but again trapping some water. In this manner, the hydration of the C_3A is controlled, giving the user a chance to work with the cement before it sets.

The calcium sulphoaluminate hydrate (ettringite) is thought to form the framework in which the formation of the subsequent calcium silicate hydrate structures take place.

Calcium alumina ferrite (C_3AF), simultaneously with C_3A, starts to hydrate reacting with calcium hydroxide to produce mainly hydrogarnet. It is generally considered that the C_3AF hydration products do not contribute materially to strength development.

The next product to hydrate after the C_3A and C_3AF is tricalcium silicate (C_3S), and subsequently dicalcium silicate (C_2S) starts to react with the water. The slow

hardening and strength development of the cement is ascribed to new crystal formation and re-crystallisation of the hydrated silicates from supersaturated solutions and the gradual filling of the spaces in the skeleton framework by these new products, thus increasing the solidity of the material.

Whilst the C_3A tends to contribute to very early strengths, it is the C_3S that is the main contributor to early strengths up to about seven days. During this time, the C_2S also starts to react, which results in the continued increase in strength.

It must be noted that these reactions are extremely complex. Different types of hydrates have been identified at points even around one calcium silicate particle. To summarise, the following figure schematically shows the reactions and approximate reaction products in the hydration process of portland cement:

$C_3A + 6H$	$\rightarrow C_3AH_6$	Tri-Calcium Aluminate Hydrate
$2C_3S + 6H$	$\rightarrow C_3S_2H_3 + 3CH$	Tri-Calcium Silicate Hydrate and Calcium Hydroxide
$2C_2S + 4H$	$\rightarrow C_3S_2H_3 + CH$	Tri-Calcium Silicate Hydrate and Calcium Hydroxide
$C_3A + CH + 18H$	$\rightarrow C_4AH_{19}$	Tetra Calcium Aluminate Hydrate
$C_3A + 3C\check{S}H + 29H$	$\rightarrow C_3A3(C\check{S})H_{32}$	Ettringite
$C_4AF + 2CH + 10H$	$\rightarrow C_6AFH_{12}$	Hydrogarnet

where:

C	=	Calcium Oxide
S	=	Silica
A	=	Alumina
H	=	Water
Š	=	Sulphurtrioxide
C_3S	=	Tri-Calcium Silicate
C_2S	=	Di-Calcium Silicate
CH	=	Calcium Hydroxide
C_3A	=	Tri-Calcium Aluminate
C_4AF	=	Tetra-Calcium Alumina Ferrite

4 PROBLEM IDENTIFICATION

4.1 Board Manufacture

The process by which the fibre-reinforced cement board is made is very complicated. A simplified explanation of the process is presented with the aid of Figure 4.1.

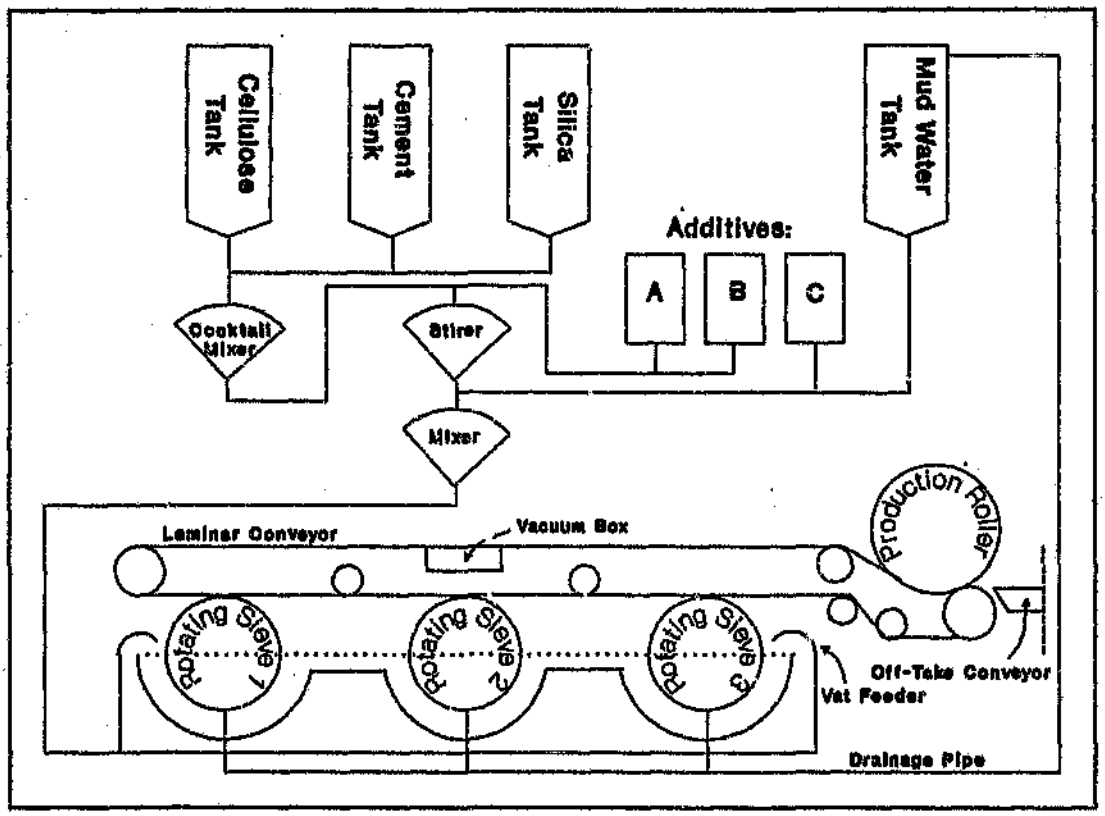


Figure 4.1 Manufacturing process

Two proprietary additives, Aluminium Tri-hydrate (AH_3) and bentonite, as well as

a flocculant are added to the mix. These three additives help control the properties of fibre-reinforced cement boards. Other ingredients are Ordinary Portland Cement, Ground Silica, and a Cellulose Fibre.

The cellulose fibre, cement and silica are stored in three separate holding tanks. These three materials are conveyed to the Cocktail Mixer in their respective quantities. Water is mixed with these three materials in the Cocktail Mixer. The mixture is then pumped into the Stirrer. At this stage, AH_3 and bentonite (which are also separately stored in holding tanks) are pumped into the Stirrer with the mixture. Once uniformity of the mixture is achieved, it is pumped into the Mixer, together with the flocculant and 'mud water'.

The 'mud water' contains all the additives contained within the mix, as is explained hereunder.

Once all the components are uniformly mixed in the Mixer, and the desired consistency has been reached, the mixture is pumped into the Vat via the Vat Feeders at both ends of the Vat. The centre Vat is filled via the overflow of the two outer Vats.

There are three Rotating Sieves. They are hollow cylinders, which are half submerged in the mixture. The liquid mixture tries to penetrate through the Rotating Sieve and fill the inside. The Sieve openings are however smaller than the cellulose fibres in the liquid mixture. As a result, the Sieve openings are blocked

off by the cellulose fibres, thus restricting the flow of the liquid mixture through the Sieve openings. Some of the liquid mixture does pass through the openings of the Rotating Sieve. This liquid mixture is pumped into the Mud Water Tank. The 'mud water' contains some proportion of all the additives, OPC and silica, thus it would be uneconomical to waste it. It is therefore added back into the mix.

The Rotating Sieve is in a continual, anti-clockwise motion and is in contact with the Laminar Conveyor. The mixture that adheres to the Rotating Sieve's outer surface, then adheres to the Laminar Conveyor. About a 1mm thick laminar layer is produced by the addition of each laminar layer from all three Rotating Sieves.

When the laminar layer reaches the Vacuum Box (which is under the top Laminar Conveyor), the excess water is sucked off from the laminar layer. This excess water is also pumped back into the Mud Water Tank.

The 1mm thick laminar layer is transferred onto the Production Roller, which rotates as many times as is needed until the required thickness is attained. Each rotation of the Production Roller increases the thickness of the cement fibre board by 1mm. The bigger the Production Roller, the longer the sheet will be.

A taut wire, which is recessed into the outer metal skin of the Production Roller, projects away from the roller very quickly, cutting the soft cement fibre board. The board is then conveyed onto the Off-Take Conveyor. It is cut by a guillotine to the size required and stockpiled before being transferred to the Autoclave for curing.

The process is continuous.

Once curing in the Autoclave is completed, the cement fibre boards are ready for distribution to retailers.

4.2 Additives

Fibre-reinforced cement board manufactured by Everite contains the following additives:

- **Ground Silica** which makes up 52.2% by mass of the mix,
- **OPC** which makes up 34.8% by mass of the mix,
- **Cellulose Fibre** which makes up 8.0% by mass of the mix,
- **AH_3** which makes up 4.0% by mass of the mix,
- **Bentonite** which makes up 1.0% by mass of the mix,
- **Flocculant** which makes up 50 parts per million of the mix,

Silica and cement make up the bulk of the mix.

The cement is used to give the fibre sheet strength. AH_3 prevents the sheet from cracking. The type of cracking that is prevented occurs when the product is

exposed to the weather for long periods. It was found that this additive prevents water from being retained within the mix. Thus, bentonite was introduced which holds the water within the mix, improving the interlaminar bonds. Strong interlaminar bonds are needed for the manufacturing process to be efficient. The flocculant helps the fibre to form a filter-mat on the rotating sieves. The cellulose fibre known as Pinus-patula or Sappi-pine is added to the mixture in a paper pulp form.

4.3 Tracing Additives in Product to Elucidate Process

Everite has phased out the production of asbestos cement boards due to the potential health hazards to the workers manufacturing the boards as well as to the consumer. (Asbestos fibres cause a disease called Asbestosis which is deadly).

The company has paid chemists large amounts of money to formulate a new mix that has similar properties to the cement/asbestos mix that had been used. This new mix requires five extra additives to those used in asbestos cement boards.

To ensure that the concentration of the additives designed for is retained throughout the whole process, it is necessary to trace the additives from the time they are added to the mix right through to the final product.

As discussed in Chapter 4.1, there are certain processes that can change the

concentration of the components of the mix, such as when liquid is drained through the vacuum box from the sheet. This liquid is transferred back into the mix. It is known that a very small percentage of the additives are drained out at these vacuum boxes, but the liquid is transferred back into the mix so that the required design concentrations are thought to be retained. But confirmation was necessary hence the decision to investigate the composition of the product.

Carrying out a quantitative analysis on the autoclaved boards from the manufacturing process was beyond the scope of this Research Report.

My objectives are two-fold:

1) To determine whether FT-IR techniques are applicable to identify the additives contained within the matrix of fibre-reinforced cement boards, and

2) if this could be successfully carried out, then a quantitative analysis of AH_3 contained within fibre-reinforced cement boards made up in the laboratory at Everite would be undertaken.

4.4 Proposal to use Infrared Spectroscopy as an Investigative Tool

As previously mentioned, the research undertaken involved the identification and quantification of an additive, namely *Aluminium Tri-hydrate* (AH_3), in the fibre-reinforced cement board as currently produced by Everite for the construction

industry. Everite have developed successful techniques for the production of cement boards reinforced with cellulosic fibres, but wish to optimise the production particularly in respect of certain additives. To do this, they need quantitative analysis of the final product for comparison with the quantities of the materials that go into the production.

was decided to investigate the use of Fourier Transform Infrared Spectroscopy (FT-IR), which is an analytical tool of considerable sophistication, for the analysis. Fourier Transform Infrared Spectroscopy (FT-IR) is one of the most versatile techniques available for characterizing molecular species and providing quantitative information. The reason for this is that each chemical compound has a unique infrared spectrum, and the intensity of the spectral details reflect the quantity of the compound present.

The Building Science Laboratory at WITS University has a Fourier Transform Infrared spectrometer with an extensive range of accessories in its laboratory coupled with considerable expertise among the staff members in this specific field.

To carry out this investigation, it was necessary to examine samples of AH_3 as well as of samples of the final product i.e. fibre-reinforced cement board, and identify the additive contained within the fibre-reinforced cement board qualitatively as well as quantitatively.

5 INFRARED SPECTROPHOTOMETRY[6]

5.1. Introduction

The goal of infrared spectroscopy is to determine the chemical functional groups contained in a particular material. Each functional group absorbs characteristic frequencies of infrared radiation uniquely. Thus a plot of radiation intensity versus frequency (the infrared spectrum' fingerprints the identifiable chemical groups of the unknown material.

In infrared spectroscopy, a beam of infrared radiation, whose wavelength, λ, varies from 2μm to 50μm (known as the range of medium infrared which is expressed in terms of wavenumber from 5000cm^{-1} to 200cm^{-1}, where wavenumber is equal to the reciprocal of wavelength multiplied by the speed of light) is passed through a sample of the compound being investigated.

Infrared waves, like X-rays, light and radio waves, are classified as electromagnetic radiation. The frequency of the vibration of the atoms within the molecules is of the same order as that of radiation in the infrared region of the electromagnetic spectrum.

When the material is irradiated with light of the same frequency as a particular intramolecular vibration, some of the radiant energy is absorbed and the vibration of the molecule is stimulated, and the intensity of the transmitted radiation is

reduced. Absorbed radiation is identified by its wavelength, its frequency or its wave number. Radiation absorption is detected electronically and recorded in some suitable form as a graphic trace. A strong absorption throughout a narrow range of frequencies causes a sharp "peak" in the recorded spectrum.

Infrared spectroscopy reached its greatest popularity as an investigative tool, mainly in the field of organic chemistry, during the decades from 1955 to 1975.

No known infrared detector can accurately monitor both frequency and intensity of infrared radiation with any practical resolution. It is necessary to distinguish between frequency and intensity to be able to record absorption spectra. There are two practical approaches to circumvent this problem, namely, the dispersive technique and the Fourier transform technique. The dispersive technique is briefly described and compared to the FT-IR spectroscopy technique in order to point out the inherent advantages available in FT-IR spectroscopy.

5.2 Dispersive Spectrometers

In the traditional dispersive infrared spectrometer, radiation from the source passes through the sample and is dispersed into its co. ituent range of frequencies by some optical element, usually a diffraction grating. The beam then passes to a slit mechanism. The slit width determines the degree to which the radiation reaching the detector at any given moment is monochromatic. In theory, the narrower the slit the better the instrument is able to distinguish more closely spaced frequencies of light, i.e. the higher the resolution. A simplified diagram of a dispersive instrument is shown in Figure 5.1.

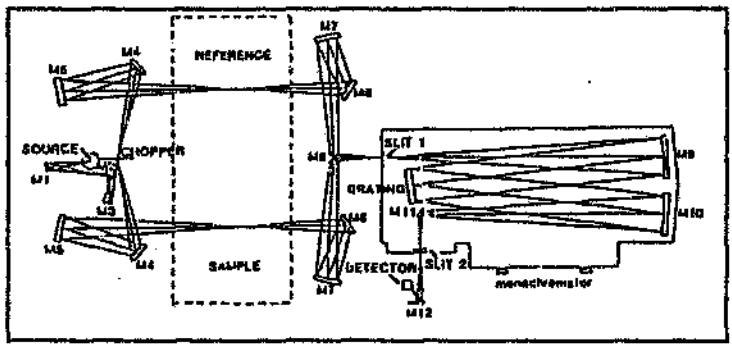


Figure 5.1 Typical Dispersive Spectrometer Design

An integrating infrared detector can be used in a dispersive spectrometer because the final radiation corresponds to only a narrow frequency band. Varying the frequency passed by the slit produces a plot of intensity versus frequency.

Dispersive systems work reasonably well, however as current applications

constantly push for greater speed, sensitivity and accuracy, a number of problems still persist. These include:

1) Large number of moving parts which are subject to mechanical wear and slippage. If any part is broken, the entire spectrometer is inoperable.
2) Slow scanning speed.
3) Decreased system sensitivity with slit effects.
4) No internal reference for frequency accuracy.
5) Allows stray light to reach the detector.
6) Sample heat-up due to the sample being positioned close to the infrared source which increases the potential for decompo..tion or other changes, particularly for solid samples.
7) Sample emission.

5.3 The Fourier Transform Infrared Spectrometer

5.3.1 Introduction

The ear formulates a transform by converting sound, i.e. the waves of pressure travelling through time and the atmosphere, into a spectrum, which is a description of the sound as a series of intensities at distinct pitches. The brain turns this information into perceived sound.

The mathematician, Baron Jean-Baptiste-Joseph Fourier developed a mathematical technique in 1807 which decomposed functions representing fluctuations such as sound waves and light waves into a set of sinusoidal components. The Fourier transform is a function that describes the amplitude and phase of each sinusoid, which corresponds to a specific frequency. Amplitude describes the height of the sinusoid and phase specifies the starting point in the sinusoid's cycle.

Fourier applied his mathematical technique to explain many instances of heat conduction. The Fourier transform has become a powerful tool in diverse fields of science. In some cases, the Fourier transform can provide a means of solving unwieldy equations that describe dynamic responses to electricity, heat or light. In other cases, it can identify the regular contributions to a fluctuating signal, thereby helping to make sense of observations in astronomy, medicine and chemistry. This led to the development of **Fourier Transform Infrared (FT-IR) spectrophotometry** (or FT-IR spectroscopy).[7] FT-IR spectroscopy is an analytical tool of considerable sophistication. It is one of the most versatile techniques available for analysing materials.

Towards the end of the 1960s the first FT-IR instruments became available. The basis of FT-IR spectroscopy is that the information from infrared frequencies are converted to audio frequencies, where detectors and electronics are able to track both frequency and intensity. Based on this, a more sensitive, accurate and reliable spectrometer can be constructed.

FT-IR depends on the combination of a Michelson's interferometer, the heart of any FT-IR spectrometer, and the so-called Fast Fourier Transform of the interferogram. The early instruments were hampered by the cost and slowness of the computers available to perform the Fast Fourier Transform. Advances in computer technology have overcome this problem and many of the latest FT-IR spectrometers are now driven by PC-AT or PS-2 type commercially available computers.

A Fourier Transform Infrared Spectrometer, namely a Bomem MB-102 driven by a PC-386 SX-AT computer, was used for the research. This non-dispersive interferometer - based FT-IR equipment allows very rapid scanning of the entire spectral range.

The FT-IR spectrometer has three basic components:

- A source
- A Michelson interferometer
- A detector

The Michelson interferometer, which consists of a beam splitter, a fixed mirror and a moving mirror, preserves both frequency and intensity information and replaces the conventional monochromator. Figure 5.2 shows a simplified diagram of the FT-IR spectrometer.

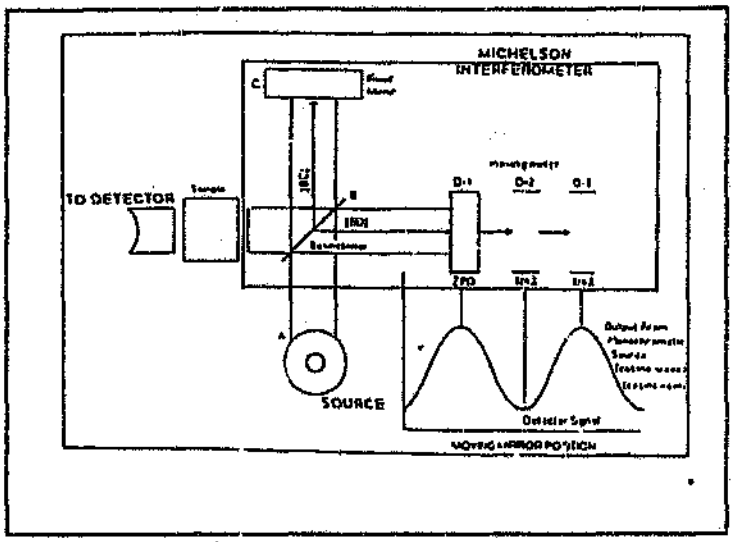


Figure 5.2 FT-IR System Concept

The following summarises how the spectrometer works:

1) Collimated radiation from the broad band infrared source, A, is directed into the interferometer and impinges on the beam splitter B (eg. a very thin film of germanium). The beamsplitter splits the incoming beam into two "arms" of about equal energy.

2) Approximately 50% of the light is transmitted through the film and is directed onto the fixed mirror, C. The light reflected off the beamsplitter is directed onto the moving mirror, D.

3) The beams reflect off the surfaces of the two mirrors (C+D) and recombine at the beamsplitter. Here constructive and destructive interference occurs, depending on the position of the moving mirror relative to the fixed mirror.

4) The resulting beam passes through the sample where selective absorption takes place, and then continues on to the detector.

5.3.2 FT-IR Data Collection

The "scan" in FT-IR spectroscopy is the mechanical displacement of the moving mirror assembly; not a scan of individual frequencies as with a monochromator type system.

Consider the detector response for a single frequency component from the infrared source. This simulates a monochromatic source, for example, a laser. The single frequency beam passes through the beamsplitter. The resulting two beams move through a sequence of constructive and destructive interference, depending on the position of the moving mirror relative to the fixed mirror.

Constructive Interference

$2(BD) = 2(BC)$

When the position of the moving mirror, D, is such that the distance between the beamsplitter and the mirror, BD, is exactly the same as the distance between the beamsplitter and the fixed mirror, BC, the two reflected beams pass through exactly the same path length and consequently are totally in phase with each other. As a result, the two beams interfere constructively and the detector observes a

maximum signal intensity. This position of the moving mirror is called the point of 'Zero Path Difference', or ZPD.

Destructive Interference

$2(BD)-2(BC) = \frac{1}{2}\lambda$

As the mirror moves away from the ZPD, the distance BD increases relative to the fixed distance BC. When the distance between the beamsplitter and moving mirror, BD, is ¼ of the wavelength of light being observed, longer than BC, the total optical path (beamsplitter-mirror-beamsplitter) difference between the two beams is ½ wavelength. The two beams are now 180° out of phase with each other and, at this point in the scan, interfere with each other destructively, causing a minimum in the detector response.

Constructive Interference

$2(BD)-2(BC) = 2 * \frac{1}{2}\lambda$

Continuing the scan, the mirror reaches a position where the distance BD is ½ wavelength longer than BC. At this point the total path difference between the two beams is one full wavelength. The two beams are back in phase and constructive interference occurs again.

Destructive/Constructive/Destructive

$2(BD)-2(BC) = n * \frac{1}{2}\lambda$

With each ¼ wavelength displacement, this pattern of constructive and destructive interference repeats itself. Since data sampling occurs continuously, a cosine wave results, like the one shown in Figure 5.3.

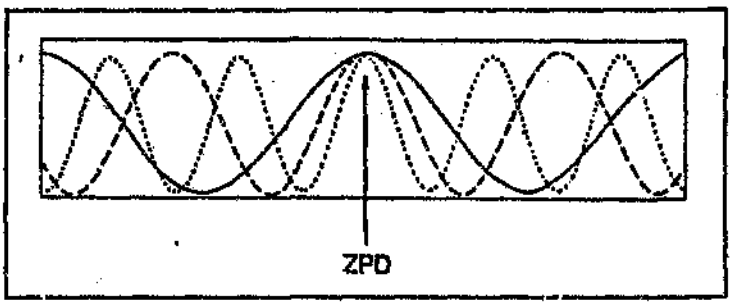


Figure 5.3 Three Modulated Cosine Waves as Produced by Three Monochromatic Light Beams Entering the Interferometer

It has now been established that after subjection to interferometry, the radiation of a single frequency results in an interference pattern in which the radiant intensity is a cosine wave. However, this is a modulated or modified cosine wave whose frequency is determined by the velocity of the moving mirror. The higher the velocity, the higher the frequency of the modulated cosine function. Mathematically, the Fourier transformation of a single frequency, is a cosine wave. Therefore, the interferometer is actually taking the Fourier transform of the incoming signal.

The same process occurs for every frequency emitted from the broad band infrared source. Figure 5.3 shows the cosine waves of three component frequencies. When three frequencies are sampled at once, the resulting signal observed by the detector is the signed summation of the individual modulated cosine waves. This type of signal, shown in Figure 5.4, is called an interferogram or time domain spectrum (intensity versus time within the mirror scan).

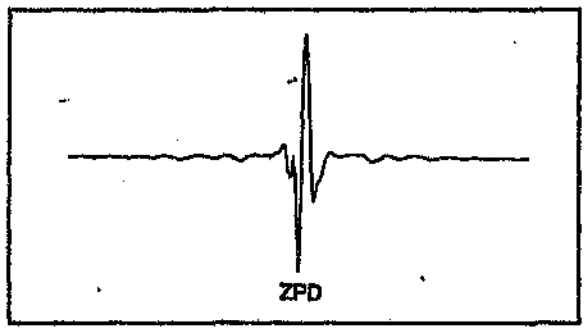


Figure 5.4 Typical Interferogram

One should take note from Figure 5.3 that all of the cosine waves have a maximum at the ZPD. This is the only position within the moving mirror scan where the optical paths are identical, so all of the frequencies are in phase simultaneously. This produces a large signal at the ZPD point in the interferogram with rapid cancellation on either side.

Resolution in an FT-IR system is defined by the length of mirror travel beyond the ZPD point. The further the mirror travels, the higher the resolving power of the instrument.

This phenomenon occurs because the Fourier transformation can only distinguish between two different frequencies if there is a difference in their modulated cosine wave. If two frequencies are very similar, the resulting cosine waves will also be similar. Only a longer mirror travel can pick out the subtle differences.

To summarise, the interferometer encodes the initial frequencies (by optically taking the Fourier transformation of the incoming signal) into a special form that the detector can observe in time. The inverse Fourier transformation is a mathematical means of resorting the individual frequencies for the final presentation of the infrared spectrum. So, a Fourier transformation simply converts from one domain into another; in this case, from the time domain (measured) to the frequency domain (desired). It is this final spectrum that is of interest.

Any data point of the interferogram represents the summation of components from each modulated frequency. Each data point contains information over the entire infrared region to which the detector is sensitive. In reality, the detector observes all frequencies simultaneously.

5.3.3 Advantages of the FT-IR Spectrometer

FT-IR spectrometers have distinct advantages over the earlier dispersive instruments. These can be outlined as follows:

1) Mechanical simplicity (one moving part). The only continuously moving

component in the FT-IR system is the moving mirror. Thus there is little system wear and high system reliability.

2) Increased speed and sensitivity (Felgett Advantage). The interferogram signal is termed "multiplexed" because the detector observes all frequencies simultaneously. As a result, even at the slowest mirror velocities a standard resolution scan of the moving mirror takes only about one second. This single scan collected on a FT-IR spectrometer yields a measurement of equal sensitivity (as defined by the signal to noise ratio, S/N) to that of a dispersive spectrometer. However, the FT-IR scan takes about one second, compared to 10 to 15 minutes for the dispersive unit. Normal throughput experiments can be accomplished very rapidly and with good sensitivity. This is beneficial in two ways:

- More samples can be measured per unit time,
- A kinetic process can be monitored, i.e. chemical reactions or curing processes can be measured in real time.

When a kinetic process is monitored on an FT-IR instrument, a complete infrared spectrum of the product is produced, whereas, dispersive instruments can only monitor a single band.

The Felgett Advantage is also a sensitivity advantage. Since the time required to collect each scan is short, measurements can be repeated and coadded to take advantage of a signal-averaging process. The sensitivity of a measurement is determined by the signal to noise ratio. To define S/N for a measurement, take the ratio of the sample signal size to the magnitude of the noise. Sensitivity, therefore, is the ability to distinguish the smallest peak from the measurement noise.

For a given amount of material analyzed, the signal (S) is a constant size. The noise (N) of the measurement, however, is random. By coadding several scans, the random noise averages out (the noise decreases while the signal remains constant and the ratio of signal to noise increases). In this way, tiny signals may be "pulled out" by decreasing the noise to a satisfactory level.

The S/N ratio is proportional to the square root of the total number of scans. Thus, 4 scan measurements are twice ($\sqrt{4}$) as sensitive (S/N) as a single scan measurement; 16 scans give twice the sensitivity as 4 scans. This means an FT-IR instrument can obtain far greater sensitivity than a dispersive instrument, if the FT-IR spectrometer is allowed to signal-average for the same length of time that the dispersive spectrometer requires for a single measurement, usually 10 to 15 minutes. This sensitivity advantage allow FT-IR instruments to measure nanogram quantities, while dispersive instruments are usually limited to microgram quantities.

3) Greater optical throughput (Jaquinot Advantage). There are no slits in the interferometer (as in the dispersive unit) to define resolution or to limit the amount of energy reaching the detector. An FT-IR spectrophotometer does not require slits. It uses an optical aperture; the proper aperture diameter must be used to achieve the desired resolution.

The beam area of an FT-IR system is 75 to 100 times larger than the slit width of a typical dispersive system. Thus, more energy is allowed to flow through the FT-IR system, resulting in greater sensitivity.

4) Internal laser reference (Connes Advantage). All FT-IR spectrometers use an internal HeNe laser to monitor the position of the moving mirror within the scan. Since the wavelength of this laser is accurately known, it provides an internal wavelength calibration standard.

Any measured data point is automatically calibrated by the system to be both precise and accurate to within 0.01 cm^{-1}. This accuracy level can be extremely important, for example, in digitally comparing two spectra for spectral subtraction or library searching. The accuracy of the FT-IR system guarantees than any differences found between two spectra are real differences, and not due to a calibration problem.

5) Eliminates stray light. In an FT-IR system, the interferometer modulates each infrared frequency uniquely, thus there is no equivalent to stray light. As a

result, the quantitative linear relationship between the measured absorbance values and the sample concentration is accurate even for strongly absorbing bands (beyond three absorbance units or 0.1 %T). This advantage eliminates a significant amount of sample preparation or repreparation for quantitative analysis.

6) Less sample heat-up. The sample is well removed from the source, making sample heat-up less of a proclem. In addition, the interferometer is only approximately 50% efficient (part of the beam returns to the source).

7) No sample emission contributions. The detector responds to audio frequencies (the interferogram), which result from infrared frequencies that are modulated as they pass through the interferometer. The sample is typically placed after the interferometer and before the detector. Thus, radiation of infrared frequencies that might be emitted by the sample is not modulated and, consequently, is not detected. As a result, no emission bands appear in the spectrum to complicate spectral interpretation.

5.4 Considerations in FT-IR Spectroscopy

5.4.1 Interferogram Sampling

The position of each data point in the interferogram must be accurately known. In addition, in order for the signal averaging process to work precisely, a specific data point must occur at exactly the same mirror position for every coadded scan.

Data sampling is timed using a separate interferogram from the internal HeNe reference laser. The resulting interferogram is a cosine wave since the reference laser is monochromatic. Each zero crossing of the interferogram signals the computer to collect data points. This system allows the spectrometer to monitor the exact position of the mirror.

If the velocity of the mirror varies during a scan, the laser cosine wave elongates and the data system "waits" until the mirror gets to the correct position for the next data point. This process also activates a servo mechanism that corrects for the velocity change. Thus, the data points line up from scan to scan and the signal averaging process operates correctly. The laser also guarantees that each data point is accurate and precise to within $0.01 cm^{-1}$.

The band width (wavelength range) sample depends on the number of laser crossings skipped between each collected data point. For most measurements, the system collects a data point at every other laser crossing, which gives a sampling

range of 0 to 7899cm^{-1}. In many systems, the measured wavelength range can be increased or de- ed by altering the sample spacing.

5.4.2 Resolution

In FT-IR spectroscopy the measurement is made in the time domain with the final spectral presentation in the frequency domain. To determine resolution, one must consider the parameters for the time domain measurement and those for the transformation into the frequency domain.

Time Domain

Resolution is determined by the length of the mirror scan away from the ZPD i.e. the number of data points collected. Longer mirror travel is required to distinguish small differences between the modulated cosine waves of two very similar frequencies. It is the "interference" of these two signals that distinguish them through the Fourier transformation.

Under most conditions, the resolution is equal to the inverse of the maximum optical path difference (twice the physical mirror travel away from the ZPD). Thus, if the path difference is 0.25cm, the resolution for the measurement will be 4.0cm^{-1}.

This path difference, or retardation, is adequate to achieve a resolution in the spectrum as measured by the FWHM (Full Width, Half Maximum) of a peak that is

4.0cm^{-1} wide. The exact final resolution is determined by the apodization function, discussed later.

Frequency Domain

For resolution in the frequency domain (after the Fourier transformation), consider the sampling theorem. This theorem states that to accurately reproduce a given frequency ; discreet sampling, a data point must be collected at least twice every wavelength. In other words, there must be at least two data points per resolution element. In the example above, the FWHM cannot be met if only one data point occurs every 4.0cm^{-1}.

In the mathematical Fourier transformation, half of the points are real and half become imaginary and are thrown away. Therefore the total number of transform points must be twice the number of data points required to end up with in the final frequency spectrum. For most measurements, the spectral range sample is between 0 and 7899 cm^{-1} (half the laser frequency). For simplicity, if a 4.0 cm^{-1} resolution is required in the final frequency spectrum, one must collect 4000 data points (one every 2.0 cm^{-1}) on the longest "side" of the interferogram away from the ZPD.

Thus, one can collect 4000 data points in the time domain, but the system requires a transformation of 8000 points in order to end up with the 4000 points in the frequency domain for 4.0cm^{-1} resolution. There are two techniques in spectrometers one of which solves this mismatch.

1) **"Double-sided"** data collections are used. Here, an equal number of data points are collected on each side of the ZPD. In the example above, 4000 data points are collected on each side of the ZPD for a total of 8000 data points. All 8000 points are transformed for a final resolution of 4.0 cm^{-1}.

2) **"Single-sided"** data collections are used where 4000 data points are actually collected. Subsequently, a equal number of zeros are added onto the interferogram before it is transformed. Thus, 8000 points are still transformed.

Both techniques result in a transformation yielding two data points per resolution element, which is adequate to represent the FWHM resolution of the instruments. In reality, the number of transformation points must be a power of 2. Therefore, a 8000 point transform actually requires 8192 data points and the number of data points collected in the examples above are 4096 and 8192 respectively. Collecting more data points results in longer mirror travel and higher resolution.

5.4.3 Apodization

The mathematics of the Fourier transformation involve integrals that go to infinity, thereby assuming an infinitely long interferogram. Practical measurements, however, deal with finite or "truncated" interferograms. If the measured interferogram is left as is (truncated), it is equivalent to multiplying the true

interferogram by a box function called a "boxcar". This convolutes the Fourier transformation of the interferogram (the true spectrum) with the Fourier transformation of a box, which results in the function (sinx)/x shown in Figure 5.5.

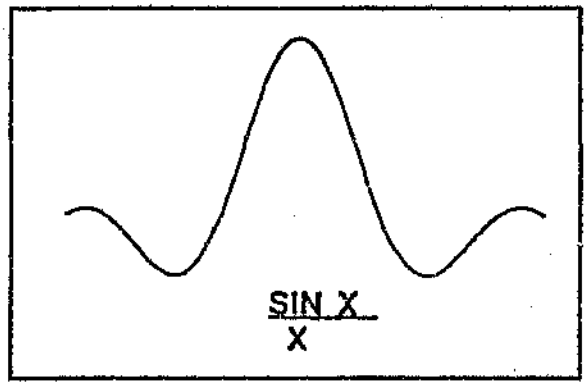


Figure 5.5 Fourier Transformation of a Boxcar Function (sin x)/x

As a result, spectral features that are narrower than the instrument resolution, take on the appearance of the (sin x)/x function, causing a "ringing" effect in the baseline on either side of each band. These sidebands can be a problem, especially if they interfere with adjacent bands.

Apodization minimizes the sidebands at the expense of slightly lowering the final spectral resolution. The apodization technique multiplies the interferogram by a function designed to reduce the truncated effects. Although triangular, trapezoidal, cosine, and boxcar functions are occasionally used, the most practical apodization function is called the Happ-Genzel. A Happ-Genzel apodization multiplies each data point by:

$$0.54+0.46\ \cos\left(\frac{\pi}{2}\left|\frac{ni-Z}{NDP-Z}\right|\right)$$

where: ***ni*** is the displacement of point i from the start of scan,
Z is the location of the ZPD point, and
NDP is the number of data points collected.

For most applications, the Happ-Genzel apodization function results in excellent attenuation of the sidebands with minimal reduction of instrument resolution. This is the standard apodization function of all spectrometers. By changing a software parameter, the apodization function can be changed.

5.4.4 Phase Correction

To minimise detector noise, components of noise outside the spectral region of interest are electronically filtered out. However, the filters introduce some signal phase shift that is not constant with frequency.

Only a few data points (approximately 256) around the ZPD are used to calculate a transformation. Due to the high signal intensity in this region, the S/N ratio is also high. Using the 256 data points around the ZPD, the system calculates a phase array, θ, where:

$$\theta = \arctan\left(\frac{Im_i}{Re_i}\right)$$

and, *i* denotes the point in the array,
Im is an imaginary number, and
Re is a real number resulting from the transformation.

The calculated phase array is essentially noise free and assumed to be the true phase array for the spectrum.

Now the system calculates a magnitude spectrum using the full data array. At this point, all the noise is positive. To make the noise randomly positive or negative, the magnitude spectrum is multiplied by:

$$\cos(\phi - \theta)$$

Where: ϕ is the phase array calculated from the full transformation, and
θ is the phase array calculated from the 256 point transformation.

If, for a given point, $\phi = \theta$ (no phase noise), then $\cos(\phi - \theta) = 1$ and there is no diminution of the point.

The phase multiplication introduces random noise of random sign where there was only positive noise in the magnitude calculation. In practice, the magnitude calculation, instrumental phase correction and mathematical correction for the ZPD point shift are combined into one quick calculation.

5.4.5 Data Processing

After the phase correction, the data are in a form of a single-beam spectrum. To get a transmittance spectrum, the ratio of the single beam spectrum against a background spectrum (known as a reference spectrum) must be taken.

The transmittance is defined as:

$$T=\left(\frac{I_s}{I_o}\right)_v$$

where:

I_s is the instrument response function (single-beam spectrum) with the sample, and
I_o is the instrument response function without the sample.
v is frequency.

If the instrument response is identical with and without the sample, the transmittance value will be one. If the sample absorbs light, less energy reaches

the detector and the transmittance value is less than one. If the sample is totally absorbing, no energy passes to the detector and the transmittance value is zero. The system being used for the research has multiplied the transmittance value by 100, defining percent transmittance.

In taking the ratio of 2 spectra, it is important that the velocity, filter settings, aperture and apodization functions be the same for both. The gain values and number of scans collected may be different. The system uses the following formula to convert a percent transmittance spectrum to absorbance:

$$A = -\log_{10}\left(\frac{T}{100}\right)$$

where: T is percent transmittance,
and
A is absorbance.

The absorbance scale is useful for quantitative analysis where Beer's law states that a linear relationship exists between the measured absorbance and the concentration of a sample. (This will be dealt with in more detail.)

Additional data processing capabilities of the software -SPECTRACALC- used for this Research Report include interactive spectral subtraction, interactive baseline correction, integration, peak picking and smoothing.

6 QUALITATIVE AND QUANTITATIVE INFRARED SPECTROPHOTOMETRY

6.1 Qualitative Infrared Spectrophotometry[8,9]

6.1.1 Introduction

Qualitative infrared spectroscopy is a very valuable analytical tool which allows the examination of the materials contained within one final product. An infrared spectrum indicates the overall composition of any unknown material in terms of its functional groups. Substantial information can be gained from an infrared spectrum by simple functional group identification.

6.1.2 Preliminary Studies

There must be considerable knowledge of the materials that are used to make up the final product. This knowledge is then utilised to guide the interpretation. This type of information is essential for rapid, intelligent identification.

When the infrared spectrum is examined, three important characteristics of the bands in a spectrum need to be considered.

They are:

1) **Position** - In most cases, band positions are indicative of the functional groups present. The research undertaken deals with the spectral region

between 5000 cm^{-1} and 200 cm^{-1}. Caution needs to be exercised when assigning a band at a particular frequency to a specific functionality, since different types of functional groups may absorb at approximately the same wavenumber.

2) **Shape** - The shape of the bands also gives information concerning the functionality of a molecule. As an example, broad bands such as those caused by hydrogen bonding or ionic functional groups are very useful in characterising a specific functionality.

3) **Intensity** - The relative intensity of a band in comparison to the intensity of other bands provides information pertaining to the amount and identity of a specific functional group present in a molecule. Adjacent atoms, such as halogens, increase the intensity of weakly absorbing vibrations such as CH wagging, twisting, or bending, and these increased intensities provide an indication for the presence of these atoms.

6.1.3 Techniques of Interpretation

Probably, the simplest method of interpretation is to consider the entire spectrum as though it were a picture and compare this picture to those of known materials which have been physically catalogued. If the spectra are the same, or very similar, it is a reasonable assumption that the materials are nearly identical. As experience is gained, many materials can be recognised by inspection. For purposes of the

research, this technique of interpretation was used for identifying the additive under investigation contained within the final product.

6.1.4 Additional Considerations

1) **Sample Purity** - The spectrum of a mixture will normally be more complex than the spectrum of each individual component. When the spectrum of a multi-component mixture is analyzed, a mass of unrelated information may be obtained which could lead to erroneous data and nonspecific conclusions. Therefore, pure fractions are desirable and may be necessary when a detailed analysis is required. Even the presence of some contamination in a supposedly pure sample can lead to incorrect conclusions. Great care was taken in keeping the samples free from contamination.

2) **Limits of Detectability** - In most cases, the limit of detectability of one material in another by infrared spectroscopy is 5%. However, depending on the type of material, it may be less than 1% or as high as 30%. The limit of detection will depend on the phase, the absorptivity of the particular absorption being used, and the proximity of this band to other strong absorptions.

3) **Indistinguishable Spectra** - Occasionally, spectra of different materials appear virtually indistinguishable. This is especially true with the spectra of large molecules with minor differences, such as paraffin and polyethylene

waxes and bisphenol-a epoxies above 1000 number average molecular weight. This can also be the case with mixtures where only the minor components vary in quantity or type.

6.2 Quantitative Infrared Spectrophotometry[8,10,11]

There are a number of different methods that can be used for Quantitative Analysis. Two methods were used in this Research Report. The first one is commonly known as the **Standard Addition Method**. The second method involved the manufacture of fibre-reinforced cement boards in the laboratory at Everite, each of which contained different known concentrations of the additive under investigation.

In the **Standard Addition Method**, the absorbance of the analytical band for the component to be quantitated is measured. Known amounts of this component are then added to the sample, with absorbance measurements being made after each addition.

The absorbance of a species is related to its concentration through the Beer-Lambert Law:

$$A(\nu)=a(\nu)bc$$

where: $A(v)$ = absorbance at wavenumber v

$a(v)$ = molar absorbency at wavenumber v

b = cell path

c = concentration of the species

A mixture in which the species of interest are in known concentrations is called a **Standard.** The standard is used for calibration so that when a few mixtures with different known concentration percentages are made up, concentrations of unknown components of the same species can be determined.

A plot can therefore be made of absorbance, or concentration found through analytical results with the aid of the computer used for the research (which is discussed hereunder), versus the amount of the component added. This curve is extrapolated to zero absorbance (or concentration), and the intersection of this curve with the x-axis (known concentration added to pure board) gives a measure of the original quantity of the component present in the sample.

The standard addition method may be employed in multi-component analysis by repeating this procedure for each component to be quantitated. There must be no interference with the analytical bands and no sample interaction.

This method is subject to error if the absorption law is not obeyed across the extrapolated concentration range, or if the analytical absorption band is not due

solely to the component being determined, as was the case in this investigation. It was realised that the curing of the boards plays an important role in determining the concentration of the additive under investigation since the absorption band due to the hydration of cement falls within the same band as that of the additive under investigation.

It was found that the **Standard Addition Method** was unsuccessful in determining the concentration of the additive under investigation. It was decided to employ the second method described above for the analysis. This method also requires the measurement of the absorbance of the analytical band for the component to be quantitated. However, fibre-reinforced cement boards with known concentrations of all the components were manufactured in the laboratory at Everite. Their respective spectra were recorded and used to establish a calibration curve. Unknown concentrations of the component within fibre-reinforced cement boards of the same species were determined using the software provided for the analysis.

KBr discs were used as a method for preparing the samples for quantitative analysis. The process of making KBr discs is discussed in Chapter 7.

When using the quantitative analysis method provided by the software which was used for the research, the known concentrations added to a species were entered in the computer once the absorbance spectra were recorded, using discs.

The next step was to set up the Region which defines the particular area of the

peak under investigation. Each time the concentration of additive was increased, the peak identifying the specific additive increased in intensity. A baseline, which refers to the peak height related to the spectrum, was automatically calculated. Because of differences in concentrations and other impurities within a disc, the whole spectrum may increase or decrease with respect to the y-axis, i.e. absorbance changes.

The matrix was then calculated using Partial Least Squares (PLS) provided by the software. This calculates the calibration matrix that corresponds to the standards that have been entered. A standard deviation value or error appears which should be as close to zero as possible.

The analytical package was used to calculate the concentrations of the compound in the samples. A graph was plotted to illustrate the relationship between known concentration and calculated values.

7 ANALYTICAL TECHNIQUES

7.1 KBr DISC[12]

7.1.1 Introduction

Preparation of pressed disc samples takes a lot of effort and time, but the spectra that were investigated using KBr pressed disc samples were of a high quality. This was especially evident when undertaking quantitative analysis.

Typical evacuable pellet dies consist of (Refer to Figure 7.1):

i)	Base
ii)	Cylinder
iii)	Two pellets
iv)	Plunger
v)	Plunger Seal
vi)	Evacuation Tube
vii)	Base seal
viii)	Extraction ring

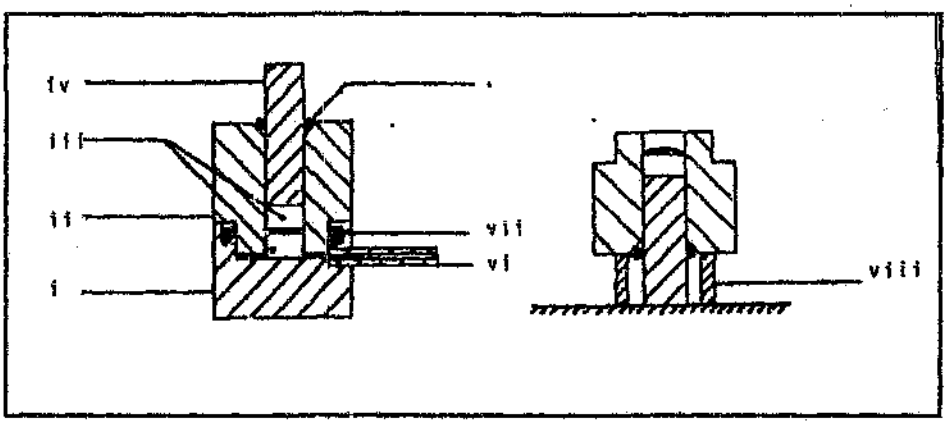


Figure 7.1 Typical Evacuable Pellet Die

7.1.2 Preparing the Die for Use (See Figure 7.1)

1) The optically polished pellets must be thoroughly cleaned with an organic solvent to remove any oil or other contamination before use. Abrasive cleaning cloth should not be used to wipe the polished faces.

2) The base was placed on the bench top. The seal was correctly positioned in its groove. The cylinder was assembled onto the base, as shown in Figure 7.1 above.

3) One of the pellets, with its polished face up, was placed into the bore of the cylinder and the evacuation tube was connected to a vacuum pump capable of obtaining a pressure of less than 2cm Hg.

7.1.3 Preparing the Sample

The Potassium Bromide (KBr) in powder form together with the desired concentration of sample material is dried out in the oven at 100°C for 24 hours, and is then mixed together using the vibratory-mill as shown below:

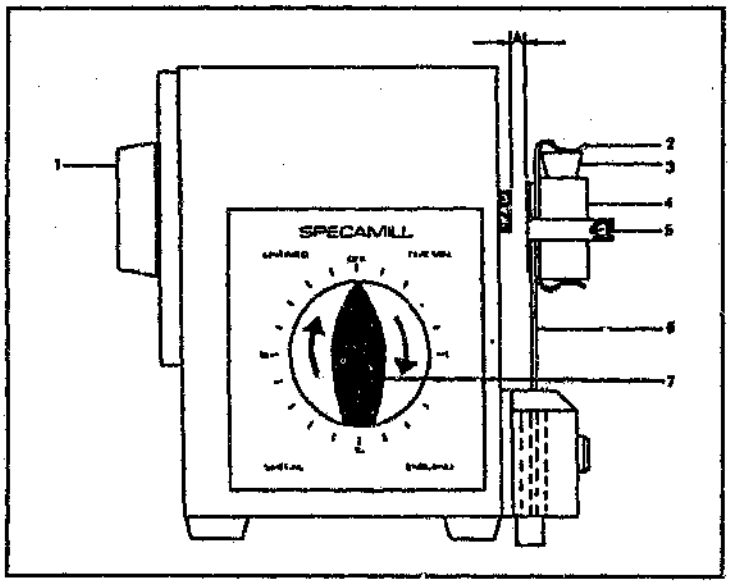


Figure 7.2 Specamill

1 = Rotating wheel to change amplitude,
2 = Vial retaining clip,
3 = Vial cap,
4 = Vial,
5 = Head screw,
6 = Blade,
7 = Timer switch,
8 = Clamp Block,
9 = Securing screw,

Pressed discs generally show bands due to water absorbed on the KBr particles, but this interference can be reduced to relatively low levels if the grinding time is not too long.[13]

It was found that grinding the mixture for one minute was sufficient to ensure dispersion of the additive within KBr, and to prevent the absorption of water on the KBr particles.

7.1.4 Charging the Die with Sample

1) The material to be compacted was poured into the bore of the cylinder. The side of the die was lightly tapped so that the powder was evenly distributed across the face of the polished pellet. It was found that when the vacuum pump was connected during this process, discs of a higher quality were obtained.

2) The material was then hand pressed with the plunger to level it before putting in the second pellet.

3) The second pellet was then inserted with the polished face down, taking care not to jam the pellet into the bore. When it was entered squarely, it fell down onto the powder. Note that the vacuum pump was still in operation.

4) The plunger was then inserted into the cylinder. The seal was placed around the plunger and seated in the cylinder chamfer as shown in the Figure above.

7.1.5 Making the Disc

1) The die assembly was placed under a hydraulic press. (The hydraulic press is illustrated in the figure below).

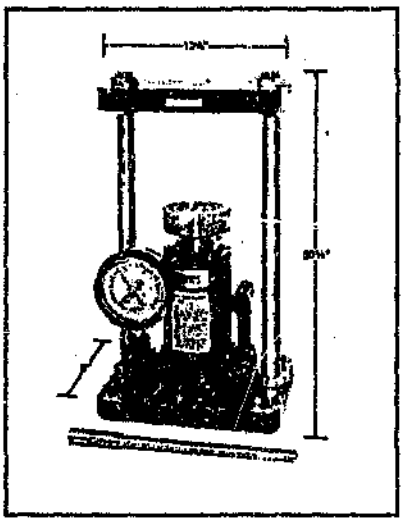


Figure 7.3 Hydraulic Press

2) The die assembly was evacuated for about two to five minutes, depending on the dryness of the sample. Sufficient pressure to produce the desired quality of the disc was applied. A load of 9 tonnes was found to produce good quality 0.5mm thick by 13mm diameter KBr discs.

Evacuation proceeded during the application of the load and was maintained for a further two to three minutes.

3) The load on the die was then released, and then the vacuum.

7.1.6 Removing Disc from Die

1) The die base was removed from the cylinder, leaving the plunger in position.

2) The die was inverted and the extractor ring was placed onto the cylinder round the cavity as shown in Figure 7.4.

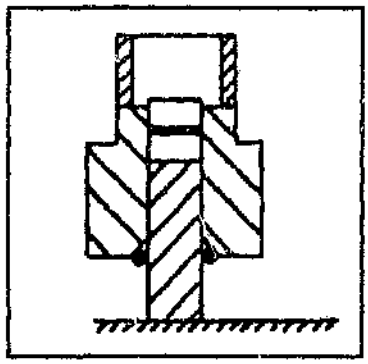


Figure 7.4 Removing Disc from Die

3) The inverted assembly was placed under the hydraulic press and a light load applied across the plunger and extractor ring until first the lower pellet emerged from the cylinder, then the compacted disc, followed by the upper pellet. The disc was removed from the press, taking care not to damage it

in the process.

4) The pressed disc was then mounted in a disc holder to facilitate spectrophotometric study.

7.1.7 Disc Quality

Generally, it is easy to produce a good quality disc, if the die is used correctly, but certain faults may occur due to a variety of reasons. Some of these and their remedies are listed below in Table 7.1. The faults described are for pure KBr or other halides which do not contain sample. When the sample is added to the halide, the clarity of the disc will depend on the quantity and type of sample. The quality of a disc will depend largely on the quality of the KBr or KCl powder used which should always be of a spectroscopic purity.

Table 7.1 Faults and Remedies for Good Quality Discs

	FAULT	REMEDY
1.	Disc not clear, lacks clarity or is opaque.	Cause, powder damp or contaminated or insufficient pressure when compacting. Dry powder and increase compacting force.
2.	Disc clear but appears to distort when being ejected.	Powder not ground fine enough, grind for longer period to produce fine powder.
3.	Disc clear but shows opaque spots.	Powder not uniformly ground fine, leaving large particles which do not sinter when pressed. Sieve powder to extract coarse grains, then regrind.
4.	Disc cloudy.	Insufficient evacuation time or leaky seals. Check seals and lengthen evacuation period.
5.	Disc clear at first but quickly becoming cloudy.	Damp powder, remedy as in 1 and 4.

To ensure that a disc is produced which will enable accurate spectra of sample to be obtained, it is essential that the sample is thoroughly blended with the halide powder. Blending was achieved using a mill, namely a 'Specamill' (shown in Figure 7.2 on page 59) which crushes and blends the sample in a vial. A pestle and mortar was also used to crush the KBr before mixing it with the desired additive.

The following illustration shows an Evacuated Pellet Die Accessory in an assembled condit'.n. The flat shaped object on the right is a pressed disc holder. The pressed disc is clamped into the centre of the holder which is placed into the slide mount inside the spectrometer.

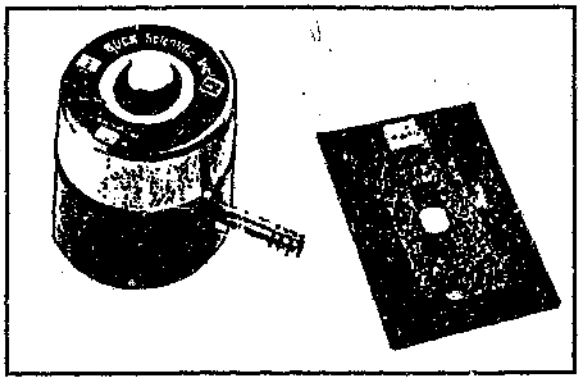


Figure 7.5 Pellet Die Accessory

7.1.8 Recording the Spectra

The following procedure was carried out in recording the spectra of the samples:

1) A pressed disc of pure KBr was placed into the disc holder which was subsequently placed into the spectrometer, and was used to record a background spectrum. This spectrum was filed as a reference spectrum. Graph 7 1 on page 67 is a printout of this spectrum. Note the spectral characteristics due to carbon dioxide in the atmosphere.

2) One percent of the desired additive was then mixed up with KBr and ground to a fine powder using a mill (Specamill) shown in Figure 7.2 on page 59. The sample was then pressed to form a disc and loaded into the spectrometer. The spectrum was then run and recorded as either transmittance or absorbance. (This is explained in more detail in Chapter 8.)

Graph 7.2 on page 68 shows the transmittance spectrum which is the result of the raw spectrum (in this case the board material, KBr and air) minus the reference spectrum (which is KBr and air), i.e. showing the board spectrum on its own.

Graph 7.3 on page 69 shows the absorbance spectrum where absorbance equals the $\log_{10}$ of the reciprocal of the transmittance, i.e.:

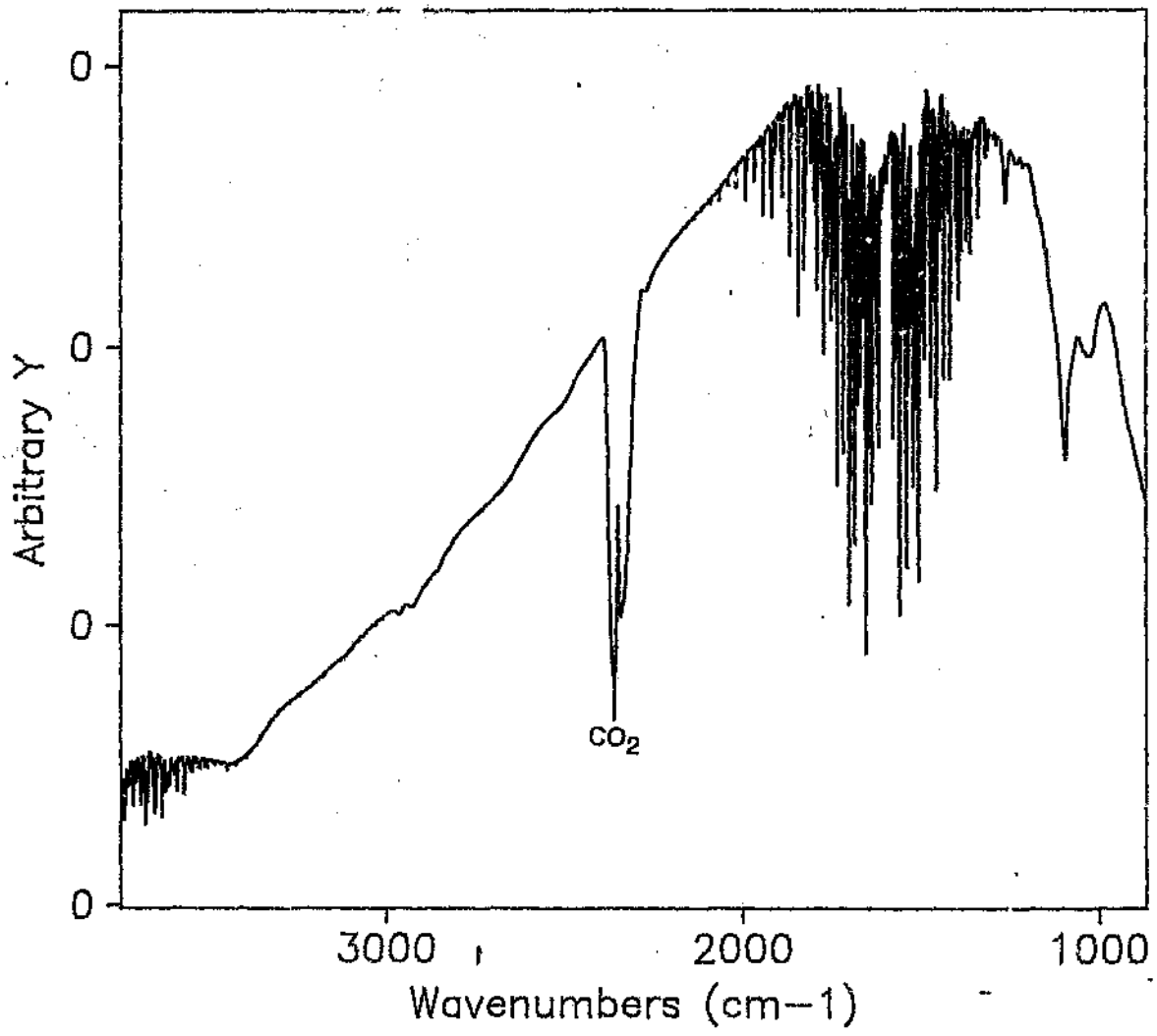
$$A=\log_{10}(\frac{1}{T})$$

This form of the spectrum is desirable when quantitative work is undertaken.

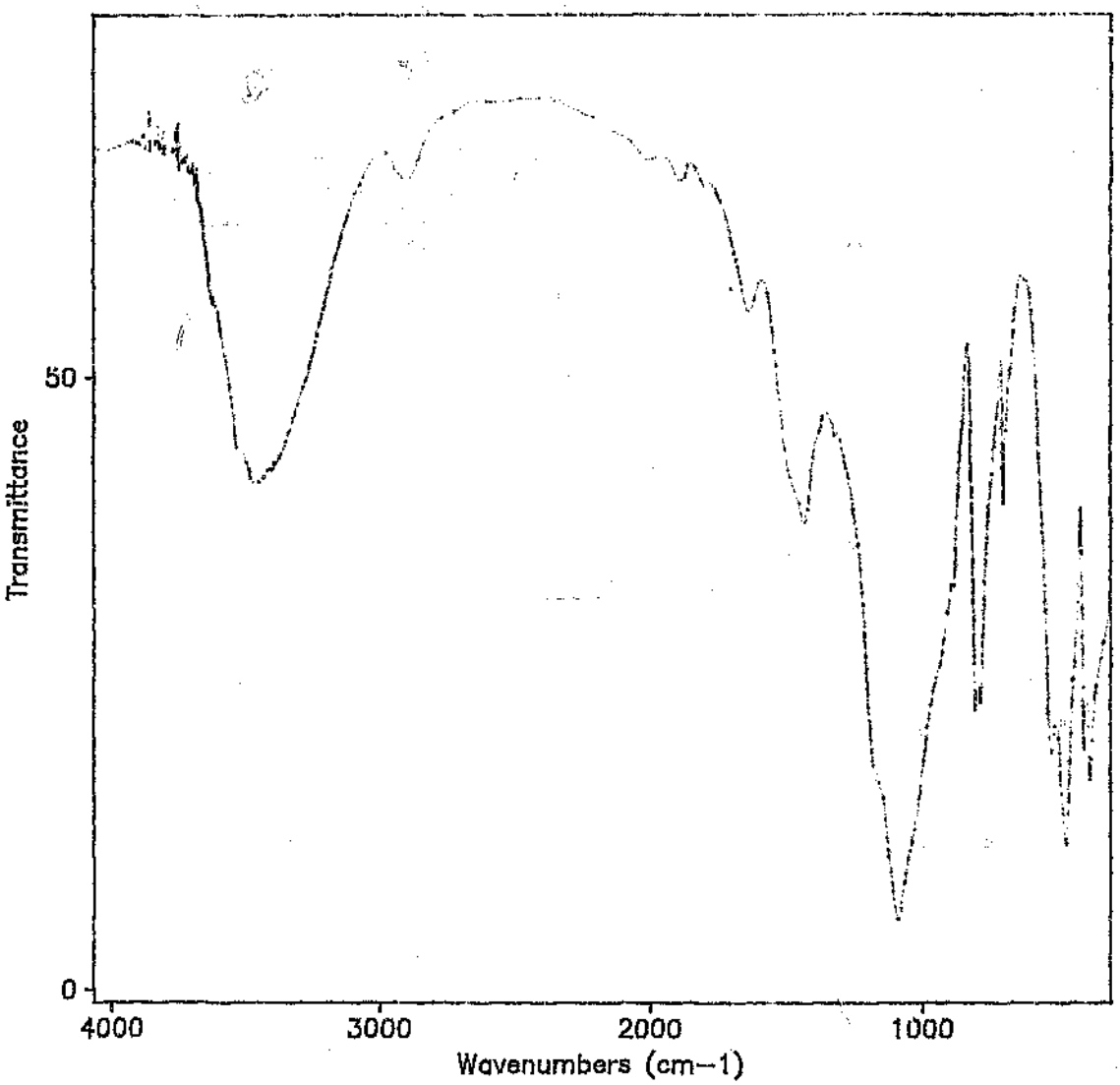
Many days were spent in becoming familiar with the hardware, software of and testing procedures for the FT-IR spectrometer. Many experiments, which will be discussed hereunder, were carried out before any relevant information was found. Of the range of FT-IR sampling procedures that are available, the KBr pellet technique appeared most appropriate and was used throughout the research. Horizontal Attenuated Total Reflectance (HATR), Diffuse Reflectance Infrared Fourier Transform (Drift) and Photoacoustic detection (PAS) were not investigated as they are unlikely to have provided better quantitative results.

All the boards made up, experiments carried out and findings are described in Chapter 8.

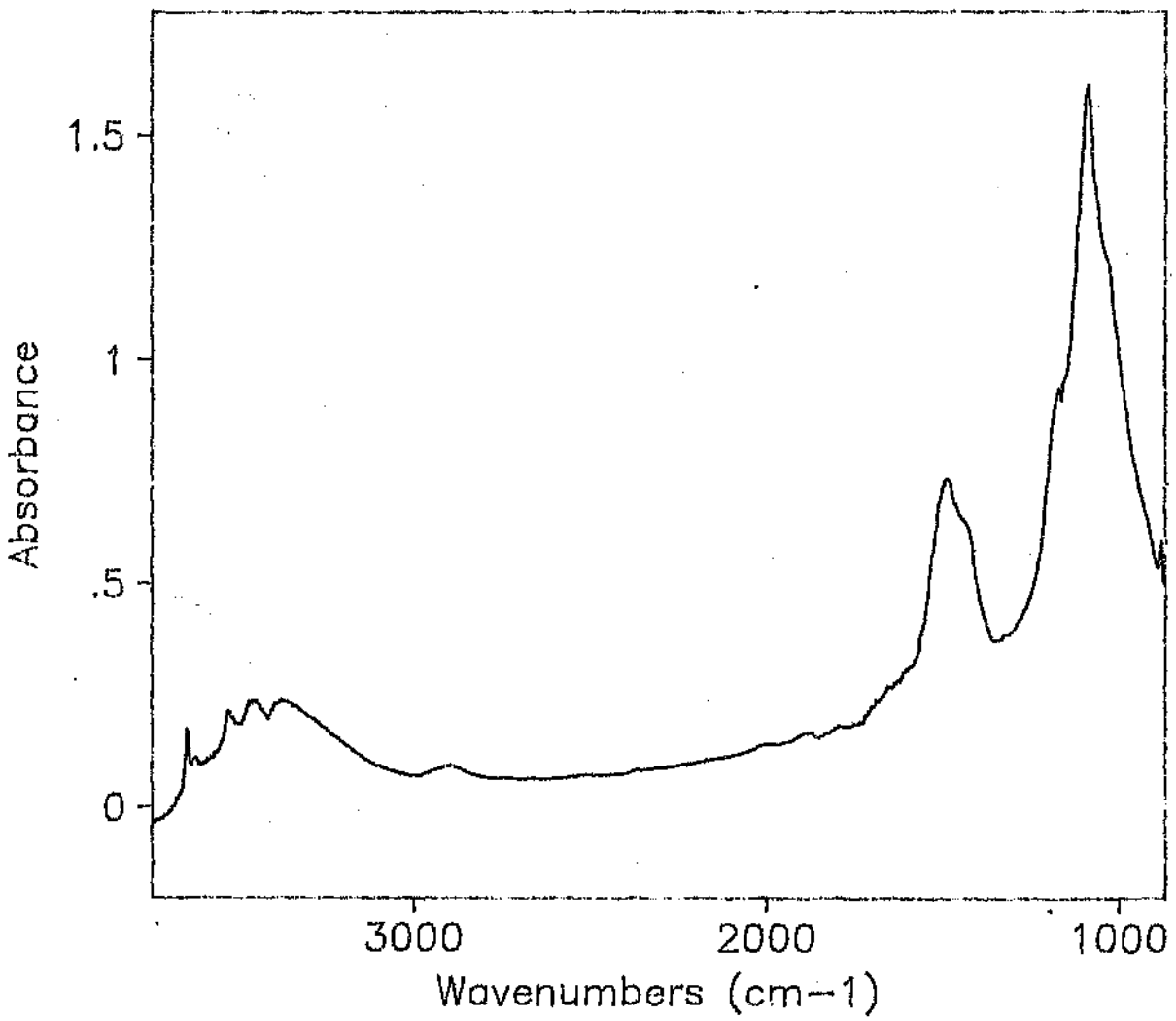
Graph 7.1. Reference Spectrum



Graph 7.2. Transmittance Spectrum



Graph 7.3. Absorbance Spectrum



8 WORK DONE

8.1 Site Visit

Several visits were made to the factory where the fibre-reinforced cement boards are made. The first three days of my research were spent in the factory where I was introduced to the Hatschek manufacturing method. I examined the manufacturing process for the boards. I met the Engineers and the labourers on site, and the potential problems of the board manufacturing process were discussed.

This proved to be very interesting and worthwhile, since it was imperative that I should understand the manufacturing process to recognise the problems encountered by Everite.

Thereafter, I spent another two days manufacturing model fibre-reinforced cement boards in the laboratory. This will be explained in detail in section 8.2. Many other visits were made to Everite during the course of my research in order to manufacture fibre-reinforced cement boards in the laboratory for analytical investigation.

8.2 Manufacture of Boards in the Laboratory

Fibre-reinforced cement boards were made up in the laboratory at Everite to ensure that the dried boards contained precisely known quantities of the additives. This is of great importance since the quantitative investigation relies on standards of known composition. The exact concentrations for each of a range of samples is entered into the computer for calibration, so that when the unknown concentration of an additive is calculated, the precise concentration can be calculated.

The procedure for manufacturing the standard boards in the laboratory was as follows:

300ml of cellulosic pulp was placed in a funnel. A stirrer motor attached to the apparatus was started. The solids mixture of known concentrations of AH_3, bentonite, silica and cement were then poured in. (The solids mixture varied for each experiment, which will be discussed in detail in Chapter 8.5 on page 74). The slurry was stirred for 60 seconds to become thick and fully mixed.

The stopper under the funnel was then pulled and the mix was allowed to run down a chute into a mould. The stirrer was simultaneously slowed down to the maximum splash free speed. The mix was then levelled out with a plastic comb until a further 30 seconds had elapsed.

A vacuum pump attached to the mould was then switched on. The pressure was maintained at 400mm Hg for 5 minutes. The water drawn from the board was caught in a flask. As soon as the sample was reasonably dry, it was patted with a float and a weight was placed on top of the sample.

After 5 minutes, the vacuum was released, the weight removed and the sample was extracted by gentle tapping. The sample was then pressed between pallets as shown below:

Top	: Thick steel plate
	: Rubber pad
	: Sample
	: Wire gauze
	: Filter paper
	: Perforated plate (Fine)
	: Filter paper
	: Perforated plate (Coarse)
	: Two sheets filter paper
	: Thick steel plate
Bottom	: Tray

This stack was then placed into the press and brought up to the top plate and pressed until the dial gauge just moved. The pressure was then brought up in 6 steps of 10 seconds by proportional amounts until a total load of 3.7 tonnes was attained. This was held for 60

seconds. Once pressure was released, the sample, measuring 8 X 20 X 0.6cm, was left to cure.

The samples I made up during the course of my research were not autoclaved.

8.3 Sample Collection

All the components were obtained from the factory where the boards are manufactured. AH_3, Bentonite, the cement and the silica were received in powder form. The spectra of the different samples were recorded and are illustrated and discussed in Chapter 8.5.

8.4 Technique Used

As mentioned in Chapter 4.4 on page 23, Fourier Transform Infrared (FT-IR) spectroscopy was used to investigate the composition of fibre-reinforced cement boards made in the laboratory. Everite wish to optimise the production of their boards particularly in respect of certain additives. To do this, they needed an analysis of the final product for comparison with the materials that go into the production. Arising from previous studies, it was decided to investigate the suitability of Fourier Transform Infrared (FT-IR) Spectroscopy as an analytical

technique for establishing the balance between the components of the raw material and the finished board.

8.5 Experiments carried out

Because of the sensitivity of the balance being used, which measures to 1/10 of a milligram, the mass of the additive and that of the sample taken from the board could be measured accurately and made up with 200mg of KBr to make a disc.

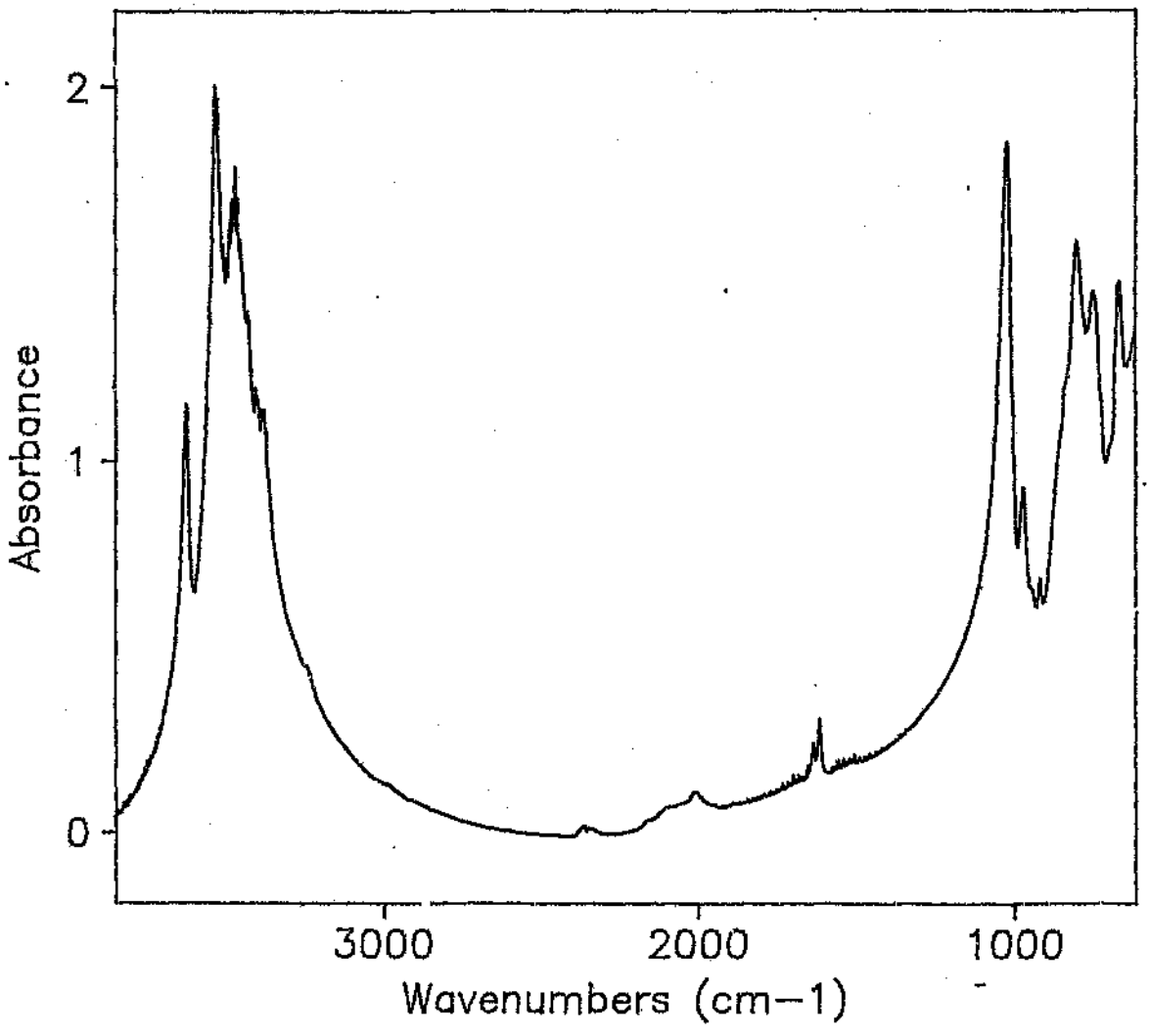
The preparation of the samples using discs has been discussed in Chapter 7. For qualitative analysis to be accurate, the pure spectra of the individual additives were recorded using KBr discs. The concentrations of the components in KBr were varied to determine the concentration / absorbance relationship which would be crucial to any quantitative work, and to determine at what concentration of the board material in KBr the best spectra for identification of peaks would be attained. It was found that a concentration of 1% of the sample material in KBr yielded acceptable spectra. The samples made up are as follows:

Table 8.1. Calculation for Individual Additives using KBr Discs

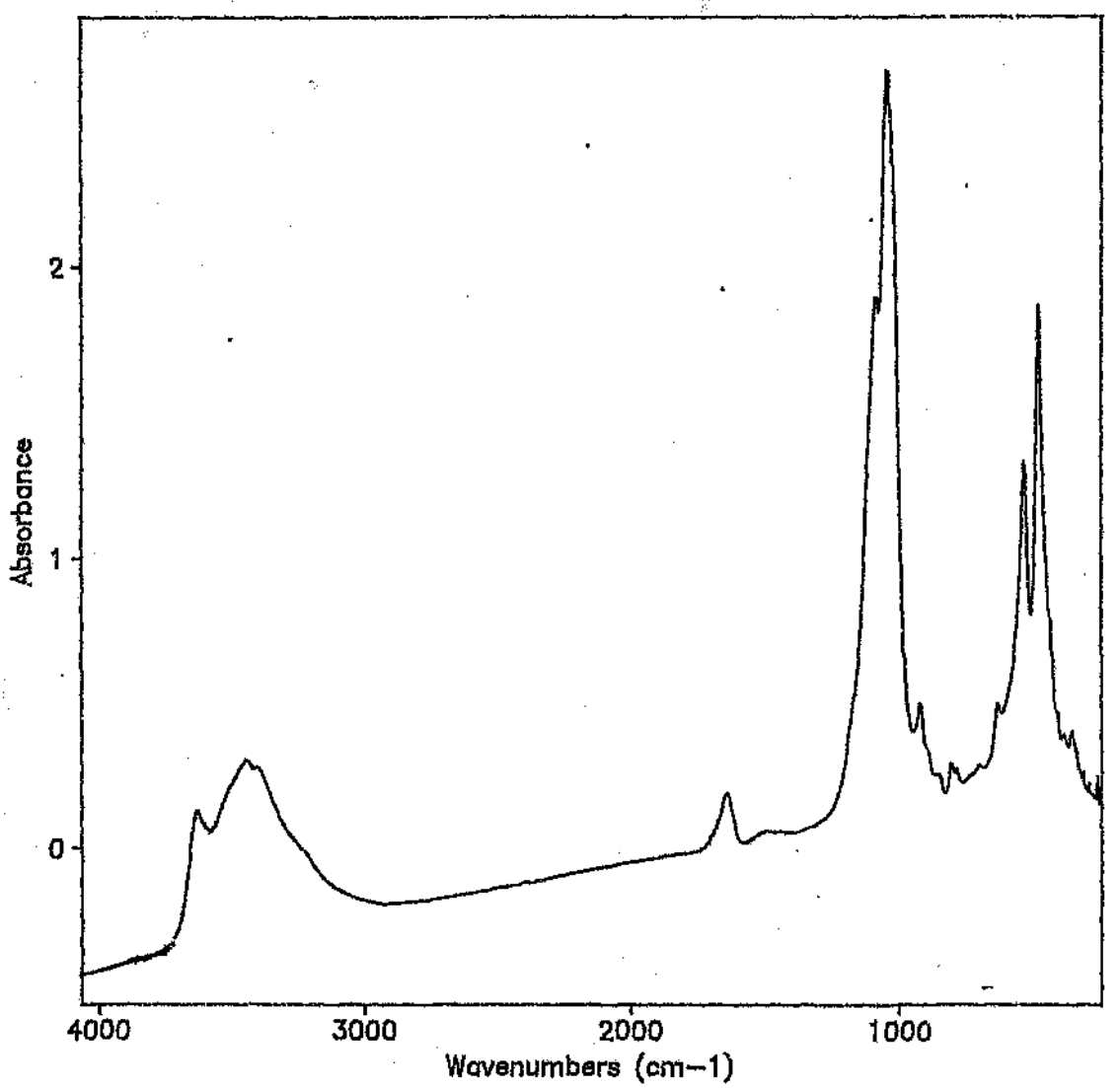
Exp. No.	Description	Mass of Additive (mg)	Mass of Kbr (mg)	Total Mass (mg)	% Additive in Kbr
1.1.1-1.1.5	AH_3	2	198	200	1
1.2.1-1.2.5	Bentonite	2	198	200	1
1.3.1-1.3.5	Cement	2	198	200	1
1.4.1-1.4.5	Silica	2	198	200	1

Each individual component's spectrum was recorded because it was necessary to find the relevant peak/peaks on the transmittance or the absorbance spectrum, which could be linked unequivocally to the specific product which was being investigated. Thus, when investigating the spectrum of the fibre-reinforced cement board, which theoretically should contain all the peaks of the individual components added to make it up, one hoped to identify the relevant peaks of the individual components under investigation. The absorbance spectra of AH_3, bentonite, cement and silica are shown in Graphs 8.1. to 8.4.

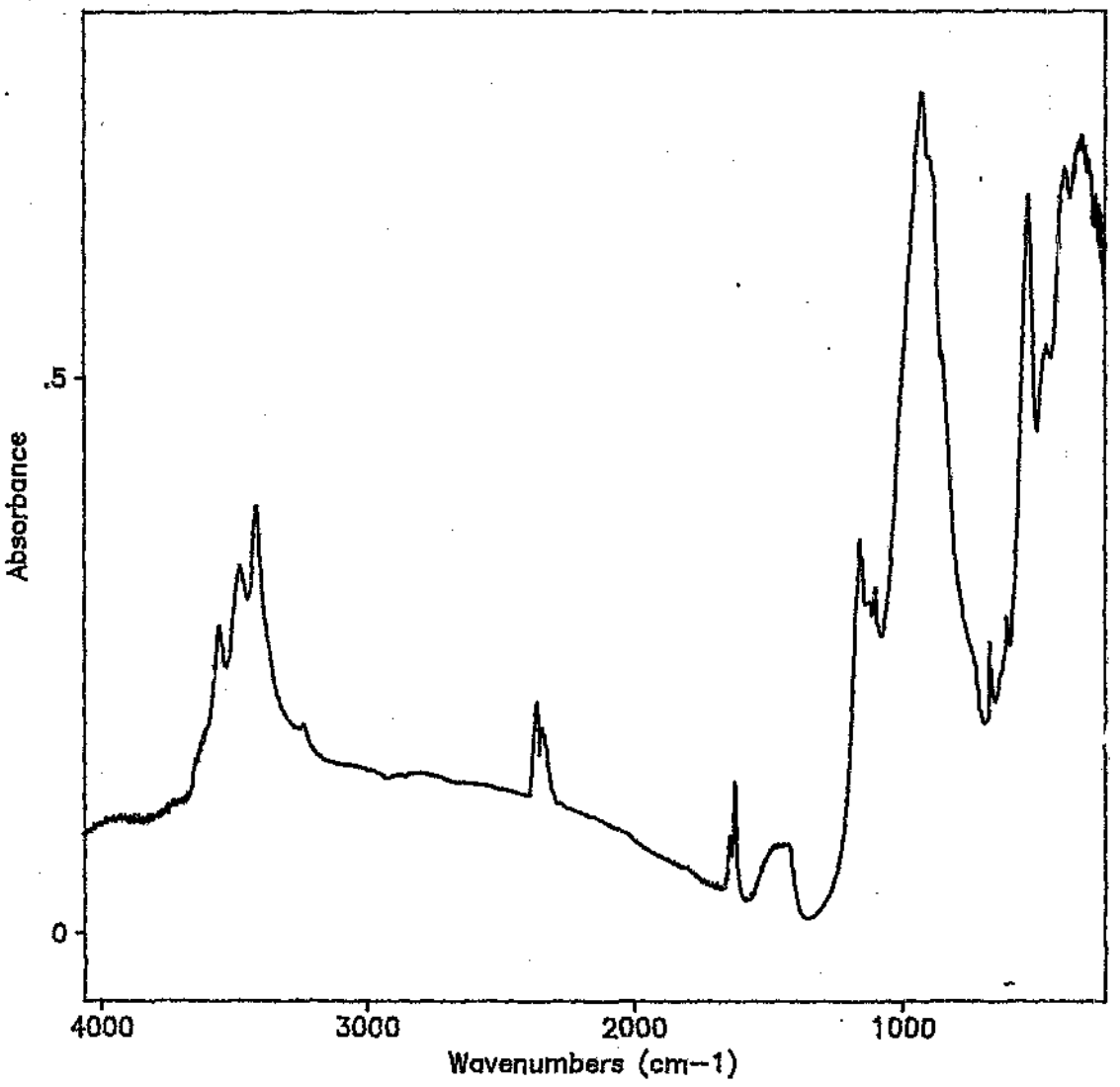
Graph 8.1. AH_3 Spectrum



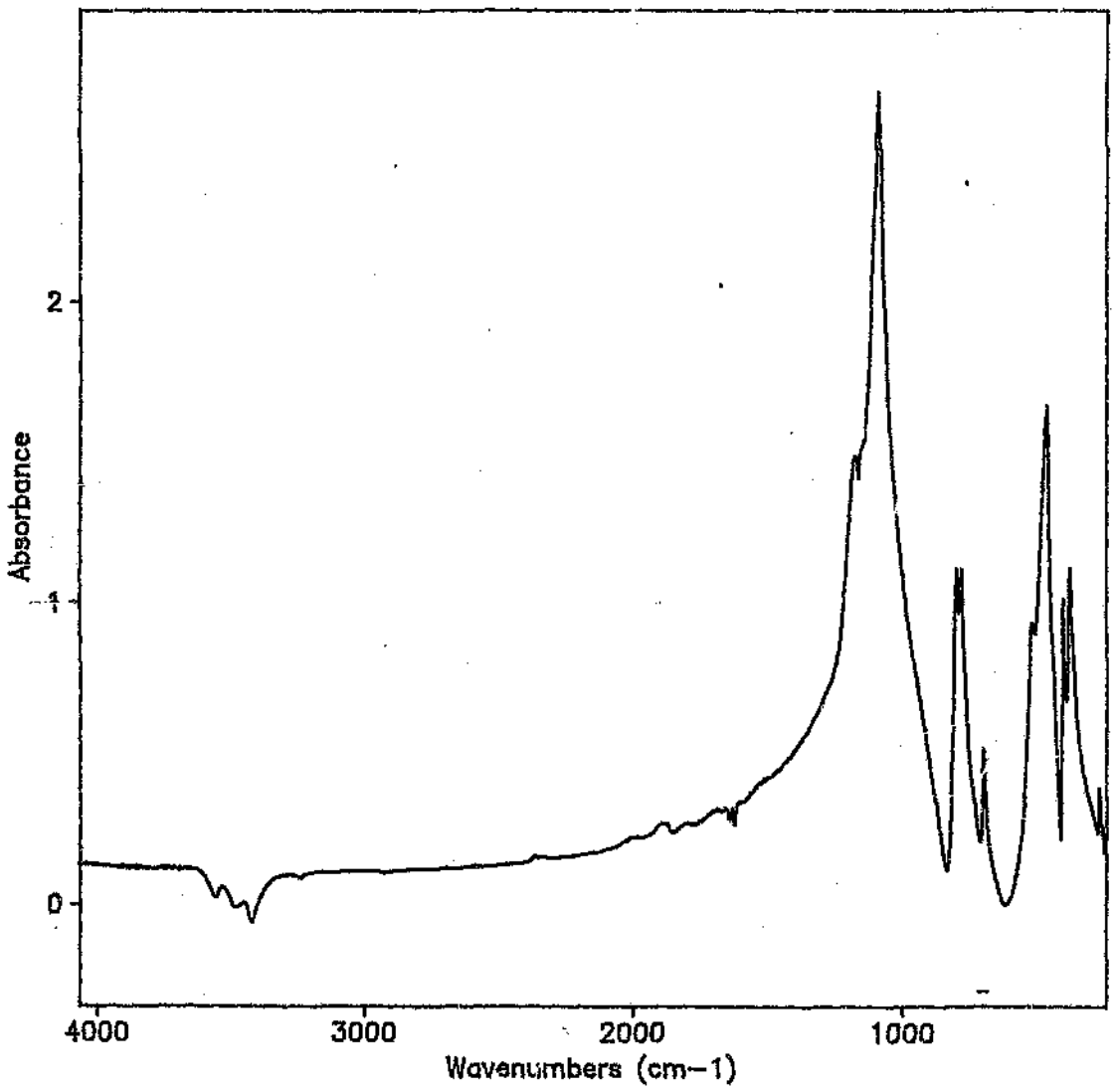
Graph 8.2. Bentonite Spectrum



Graph 8.3. Cement Spectrum



Graph 8.4. Silica Spectrum



The next procedure involved the making up of five identical fibre-reinforced cement boards as described in Chapter 8.2. Each board contained:

Table 8.2. Concentration of Additives in Boards 1 to 5

BOARD NUMBERS 1 TO 5	
Additive	**Concentration (%)**
AH_3	4
Bentonite	1
Cement	34.8
Silica	52.2
Cellulose	8

These boards were sealed in plastic and left to cure for two weeks. Thereafter, they were taken out of the plastic and left to dry at room temperature for another day. They were then placed in an oven with an extractor fan at 100°C until they were completely dried out. The fan in the oven allows the moisture contained within the boards to be drawn off quickly, and also helps reduce the humidity in the oven.

These boards were used for a number of different experiments. The first set of experiments involved the qualitative analysis of the fibre-reinforced cement boards. It was necessary to look at the whole spectrum of the fibre-reinforced cement boards, and then identify as many relevant peaks as possible by matching up the spectra of the pure components previously discussed. Since this research only involved the investigation of AH_3, the peaks representing this additive were of

great interest and importance.

By adding small, increasing quantities of AH_3 to the fibre-reinforced cement boards, the peak at 3618cm^{-1} can be shown to be sensitive to concentration. This particular peak seemed to be suitable for determining the concentration of AH_3 in the final product. The following table illustrates how this was done:

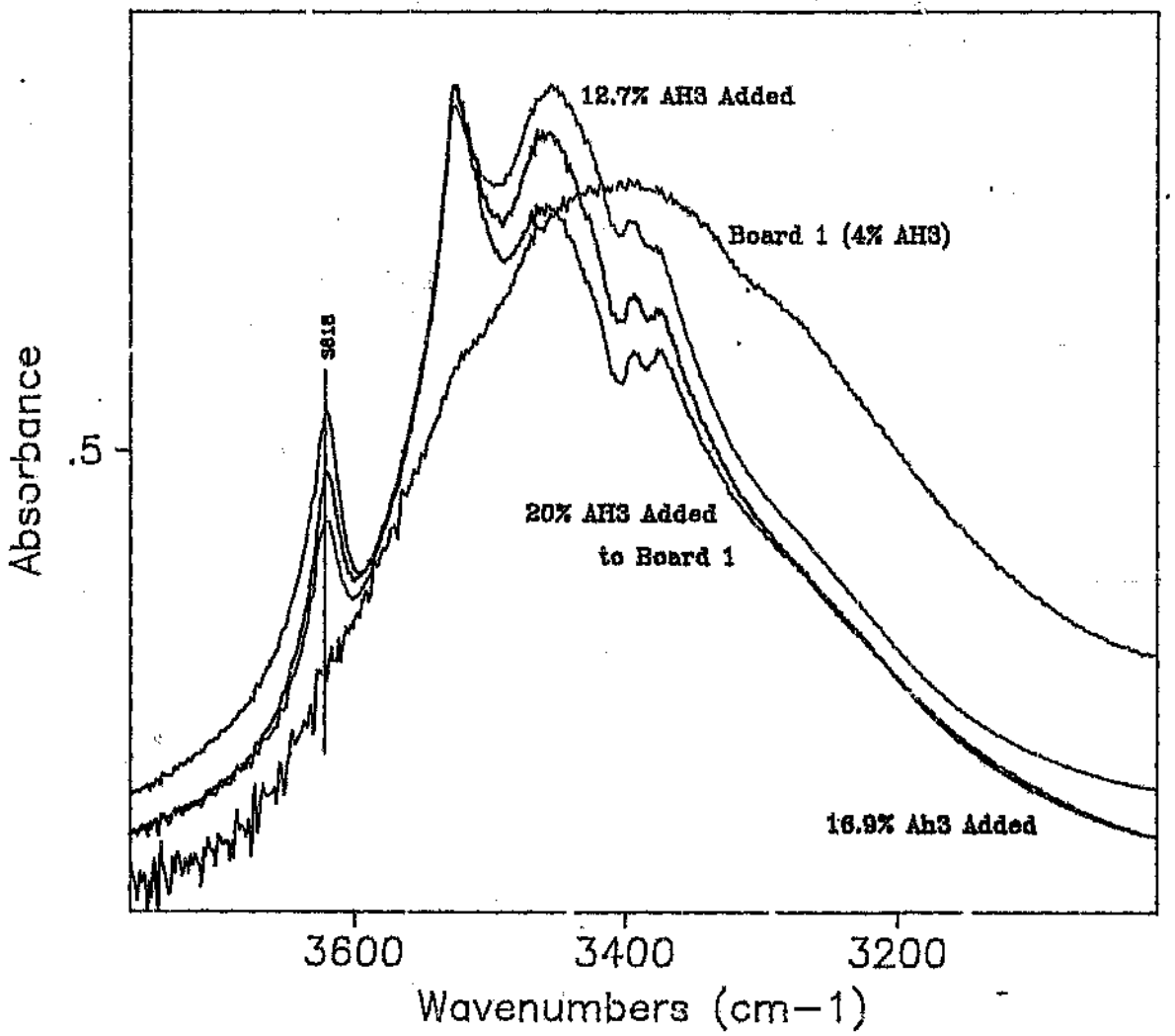
Table 8.3. Concentration Calculation of AH_3 added to Board 1

Exp. No.	Description	Mass of Board Material Excluding AH_3 (mg)	Mass of AH_3 added to the Board Material (mg)	% AH_3 added to the Board Material
2.1	Board 1	7.68	0.32	4
2.2	Exp. 2.1 + 2.6mg pure AH_3	7.68	1.92	20
2.3	Exp. 2.1 + Exp. 2.2	15.36	2.24	12.7
2.4	Exp. 2.3 + 0.4mg AH_3	6.98	1.42	16.9

One percent of each mixture was added to KBr to make up and press a 200mg disc.

The relevant spectra are shown in Graph 8.5. The sensitivity of the absorption peak at 3618cm^{-1} to changes in concentration of AH_3 is clear.

Graph 8.5. Graph showing increasing concentrations of AH_3 added to Board 1.



It can thus be assumed that the presence of a peak at 3618cm^{-1}, and resembling the peak identified as being due to the presence of AH_3, is qualitative proof of the presence of AH_3 and the intensity of the peak is an indication of the concentration in the sample.

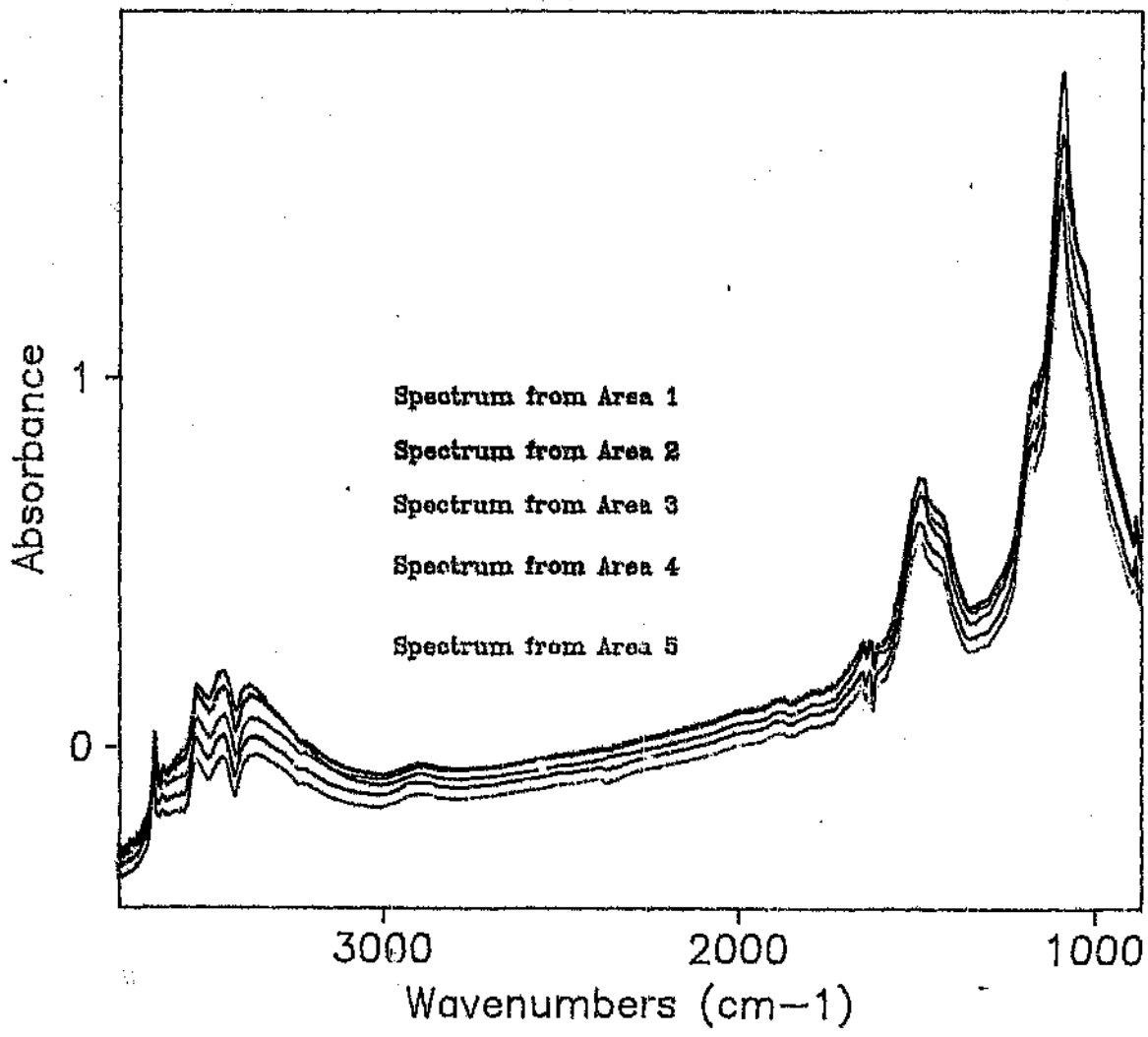
The next set of experiments involved the testing of the board material to make certain that the additives were evenly distributed. To do this, five different areas of a particular board were sampled, and their respective spectra compared. Four discs were pressed from each area of Board 2. The following table illustrates this:

Table 8.4. Percentage Calculation of Board 2 in KBr to Show Even Distribution of additives

Exp. No	Description
3.1.1-3.1.4	1% Board 2 in KBr from Area 1
3.2.1-3.2.4	1% Board 2 in KBr from Area 2
3.3.1-3.3.4	1% Board 2 in KBr from Area 3
3.4.1-3.4.4	1% Board 2 in KBr from Area 4
3.5.1-3.5.5	1% Board 2 in KBr from Area 5

All the spectra from each area were averaged. The resultant spectra are shown in Graph 8.6. The consistency of the shape and intensity of the peak at 3618cm^{-1} confirms that this component of the board is evenly distributed throughout the board.

Graph 8.6. Spectra Showing Consistent Distribution of Additives in Board.



Having shown that AH_3 can be identified within the spectrum of the fibre-reinforced cement boards, it was necessary to carry out the quantitative analysis.

The first step was to calibrate the absorbance spectra against known concentrations of AH_3. The standards are used to set up calibration curves so that the concentrations of the components of the same species in boards of unknown composition can be determined.

The first set of standards was made up using the **Dilution Method** using a board with no AH_3 as a source of diluent material. The method is summarised as follows:

Table 8.5. Dilution Method

Exp. No.	Description of Standard	Concentration Percentage
4.1	100mg AH_3 made up to 500mg with Board Material	20%
4.2	250mg of 1 made up to 500mg with Board Material	10%
4.3	250mg of 2 made up to 500mg with Board Material	5%
4.4	250mg of 3 made up to 500mg with Board Material	2.5%
4.5	250mg of 4 made up to 500mg with Board Material	1.25%

2mg of each mixture described above was added to 198mg KBr and a disc was pressed and its spectrum recorded.

Qualitatively, an increase in the intensity of the peak at 3618cm^{-1} is noticed each

time a higher percentage of AH_3 is added to pure board.

However, when the peak intensities were compared to the concentrations, the resulting analytical curve was unsatisfactory. This could be due to the non-uniformity of distribution of AH_3 in the standards which would influence the accuracy of each standard derived from the preceding one. Another set of standards was made up to eliminate the possible source of error.

At this stage of the research, it was decided to manufacture boards in the laboratory at Everite each of which contained different concentrations of the additives. The Silica:Cement ratio was kept at a constant 60:40. This series is summarised below:

Table 8.6. Concentration of Additives in Boards 6 to 22

BOARD NUMBER	% ADDITIVE				
	CELLULOSE	SILICA	CEMENT	AH_3	BENTONITE
6 & 7	8	54	36	1	1
8 & 9	8	53,4	35,6	2	1
10 & 11	8	49,8	33,2	8	1
12 & 13	8	47,4	31,6	12	1
14 & 15	8	52,5	35	4	0,5
16 & 17	8	51,6	34,4	4	2
18 & 19	8	50,4	33,6	4	4
20 & 21	8	52,2	34,8	3	2
22	8	54,6	36,4	0	1

These boards were placed in the oven with an extractor fan the day after they were made. (The curing of the boards will be discussed later).

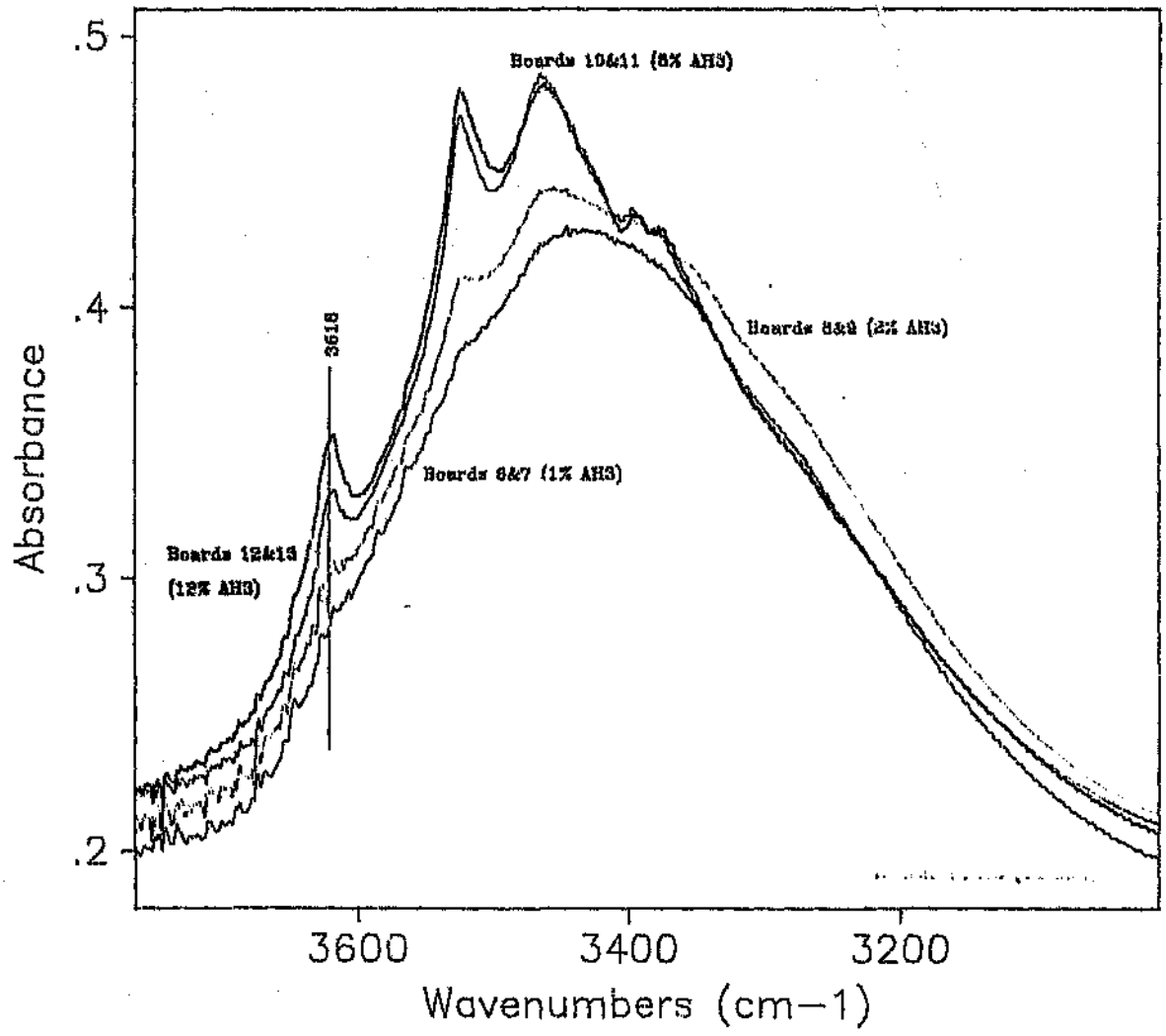
Four different holes were drilled in each fibre-reinforced cement board and the resultant fine board material from each area was placed in test tubes. 1% of the board material was added to KBr and discs were pressed. Their respective spectra were recorded. The following table shows the experiments carried out:

Table 8.7. Experiments carried out Using Boards 1 to 22

Exp. No.	Board No.	% AH_3 in Board	Spectra Averaged to form one Spectrum
5.1.1-5.5.4	1 to 5	4	Boards 1 to 5
5.6.1-5.6.4	6	1	Boards 6 and 7
5.7.1-5.7.4	7	1	
5.8.1-5.8.4	8	2	Boards 8 and 9
5.9.1-5.9.4	9	2	
5.10.1-5.10.4	10	8	Boards 10 and 11
5.11.1-5.11.4	11	8	
5.12.1-5.12.4	12	12	Boards 12 and 13
5.13.1-5.13.4	13	12	
5.14.1-5.14.4	14	4	Boards 14 and 15
5.15.1-5.15.4	15	4	
5.16.1-5.16.4	16	4	Boards 16 and 17
5.17.1-5.17.4	17	4	
5.18.1-5.18.4	18	4	Boards 18 and 19
5.19.1-5.19.4	19	4	
5.20.1-5.20.4	20	3	Boards 20 and 21
5.21.1-5.21.4	21	3	
5.22.1-5.22.4	22	0	Board 22

The area under the peak at 3618cm^{-1} increased as the concentration of AH_3 in the boards increased. This is illustrated in Graph 8.7.

Graph 8.7. Spectra of Boards 1 to 22



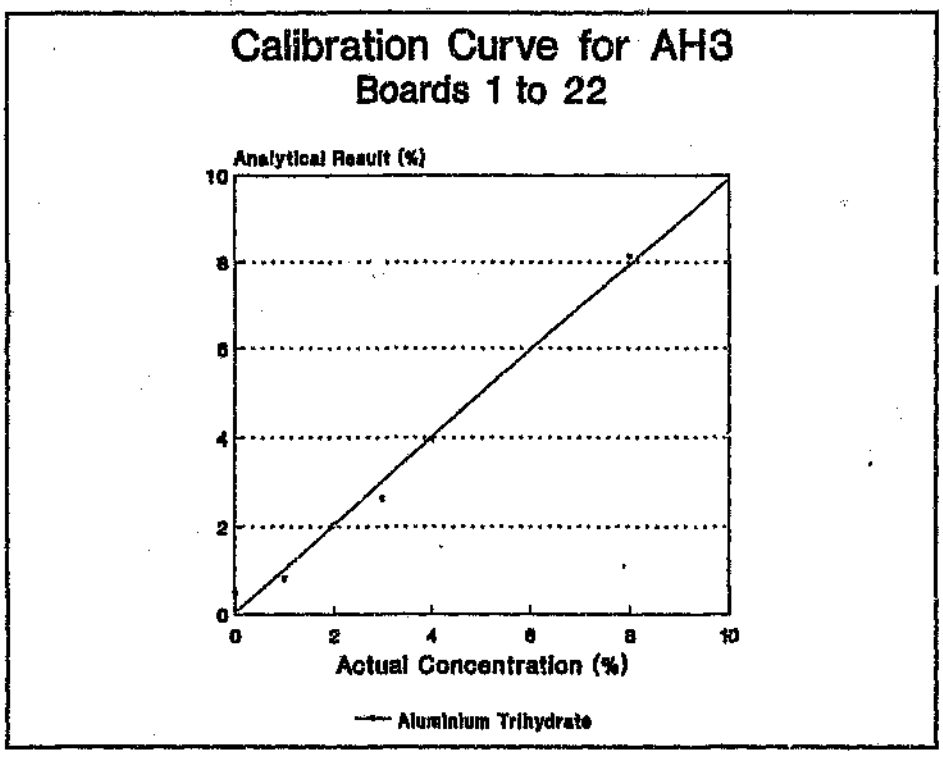
A calibration curve was established using the spectra of boards 1 to 22 as standards. A region (described in the Chapter 8.6 on page 107) of 3629cm^{-1} to 3604cm^{-1} was used to identify increased area of the peak which relates to increased concentration.

The calibration of the curve involved using all the boards except one. The board that was left out was used as an 'unknown' and when its concentration was calculated by the computer using the calibration curve, it yielded accurate results. The procedure was repeated and the 'unknown' board left out was varied in order to be certain that the analysis was accurate. The 'unknown' board was included in the calibration once it was certain that the analysis yielded accurate results. The analytical results were calculated by the software used. The following table shows the results:

Table 8.8. Analytical Results for Boards 1 to 22

Board No.	Actual Concentration of AH_3	Analytical Result
1 to 5	4	4.07
6 and 7	1	0.84
8 and 9	2	2.04
10 and 11	8	8.15
14 and 16	4	3.73
16 and 17	4	3.77
18 and 19	4	4.25
20 and 21	3	2.63
22	0	0.5

A graph of known concentration of AH_3 in the 'pure' board material versus the analytical result calculated by the computer was plotted using Harvard Graphics.



Graph 8.8. Calibration Curve for AH_3

Once the calibration curve had been established, three boards with different concentrations of the additives were made up in the laboratory at Everite by their staff, and given to me for testing. The concentrations were unknown to me. The boards were left sealed in plastic for a week and then placed in the oven with an extractor fan at a temperature of 100°C.

I took samples from the boards and recorded the spectra. A quantitative analysis using the calibration curve discussed above gave the following results:

Table 8.9. Analytical Result of AH_3 in Unknown Boards

Board Name	Actual Concentration of AH_3	Concentration of AH_3 Calculated by the Spectrometer
A	4	4.23
B	6	6.6
C	4	3.81

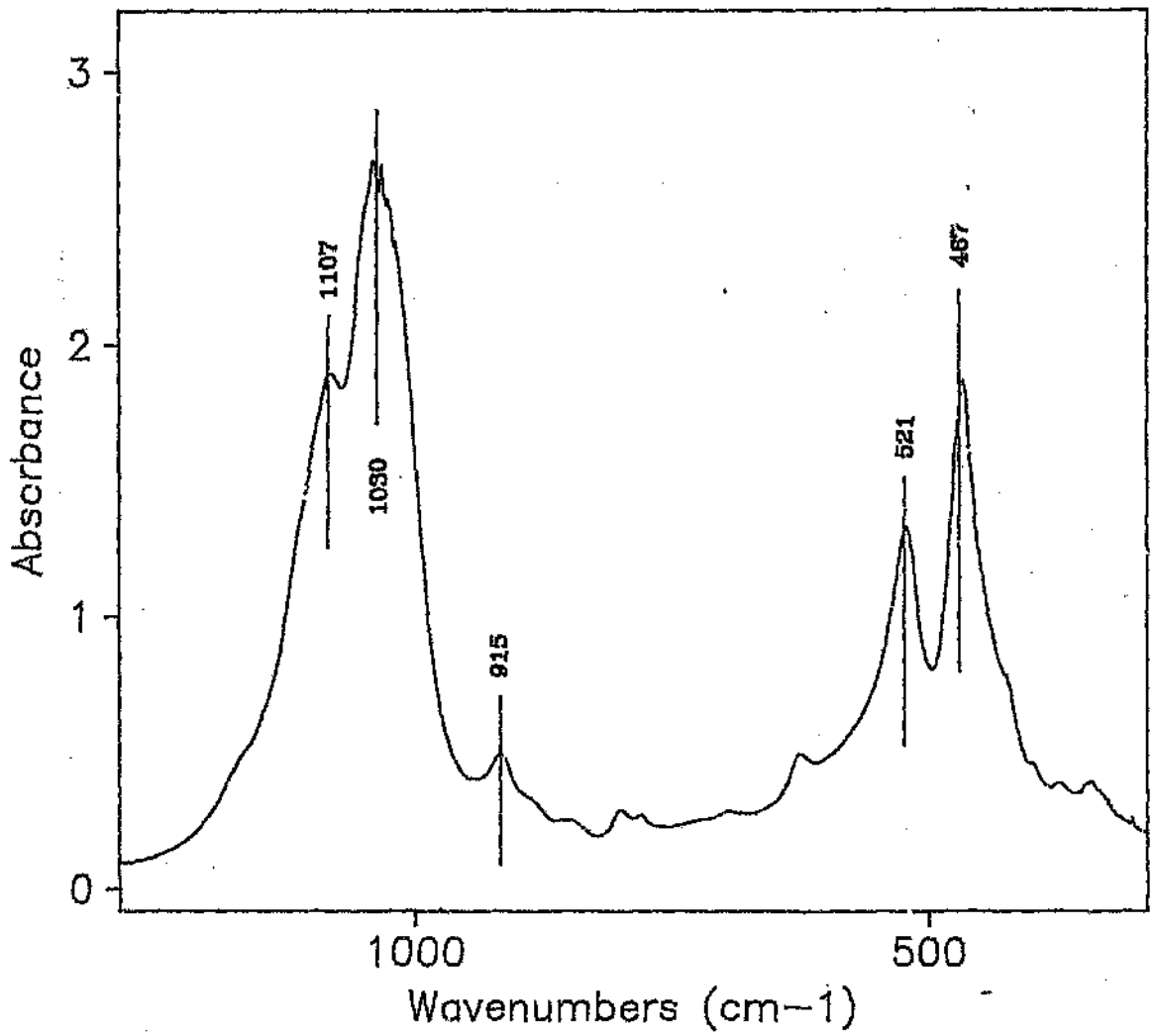
Everite found these results to be within acceptable limits of accuracy for AH_3.

An investigation was carried out to determine whether similar results could be achieved for bentonite but it was found that the bentonite peak is masked by other peaks.

Bentonite is a clay mineral and the bonds between the aluminium and oxygen in the clay are swamped by the aluminium-oxygen bonds in the AH_3. It must be remembered that the concentration of AH_3 in the boards is much higher than that of bentonite. There was no absorption peak that could be regarded as characteristic of bentonite in the board material.

The following graph shows the spectrum of bentonite. The spectrum indicates the presence of montmorillonite mineral by identifying bands at 1107cm^{-1}, 1030cm^{-1}, 915cm^{-1}, 521cm^{-1} and 467cm^{-1}.[14]

Graph 8.9. Bentonite Spectrum Showing Peaks



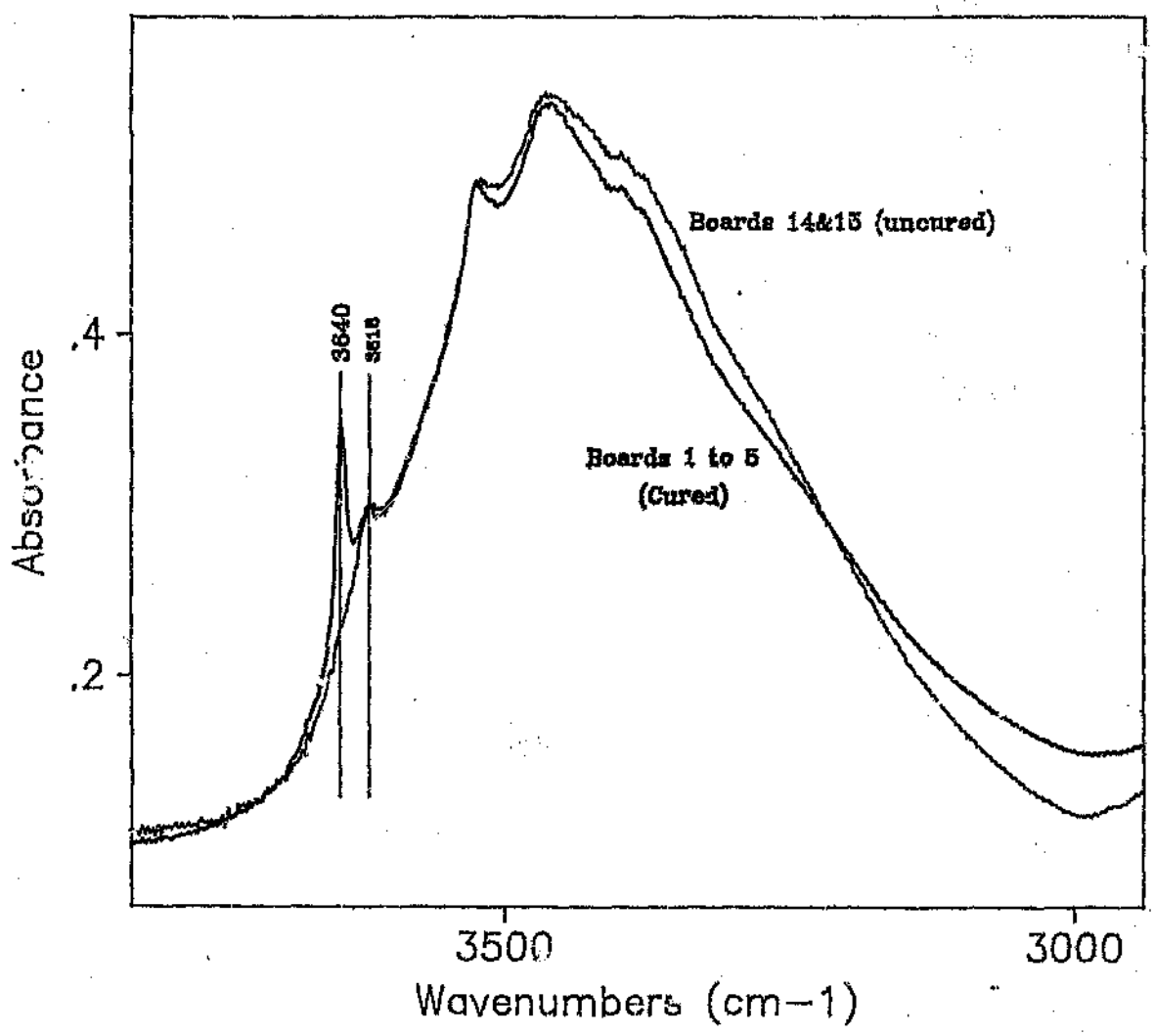
Unfortunately, it is not possible to carry out an analysis on the bentonite since the concentration of bentonite within the board is so small, however fortunately bentonite is a less important component.

While the results in the table above are reasonably accurate, the concentration of bentonite in Boards A, B and C varied so much that the aluminium-oxygen bonds may have interfered with the observed concentration of AH_3 in the boards.

From the research done during the preliminary investigation, it became evident that the curing of the boards plays an important role in quantifying AH_3 in the fibre-reinforced cement boards.

It must be noted that the standard boards and the unknown boards A, B and C were cured under different conditions. A sharp peak at 3640cm^{-1} is evident in the boards that are cured and not dried out immediately. This peak is due to calcium hydroxide, one of the main products of hydration.[15] Progressive hydration of portland cement is accompanied by an increase of intensity of this absorption band. This is illustrated in the following graph:

Graph 8.10. Absorption Peak at 3640cm^{-1} evident in Cured Boards



To confirm that the peak at 3640cm^{-1} is due to curing, it was necessary to make up a further set of fibre-reinforced cement boards and cure them differently to each other. A quantitative analysis would help in determining whether the concentration of AH_3 in the cement based board material would be affected due to the nature of curing.

It was decided to make up duplicate boards with varying concentrations and place one set in the oven immediately, and allow the other set to cure sealed in plastic for two weeks and then place them in the oven to dry out at 100°C.

The following table illustrates the composition of additive within the boards:

Table 8.10. Concentration of Additives in Boards 23 to 36

BOARD NUMBER	% ADDITIVE				
	CELLULOSE	SILICA	CEMENT	AH_3	BENTONITE
23 & 24	8	54,6	36,4	0	1
25 & 26	8	54	36	1	1
27 & 28	8	53,4	35,5	2	1
29 & 30	8	52,8	35,2	3	1
31 & 32	8	52,2	34,8	4	1
33 & 34	8	51,6	34,4	5	1
35 & 36	8	51	34	6	1

The silica:cement ratio was kept at a constant 60:40. The only additive varying was AH_3.

Unfortunately, the extractor fan in the oven was out of commission. As a result,

the water in the boards that were placed in the oven immediately (in order to prevent any curing) could not be drawn off as quickly as if the fan was working. Thus a small amount of curing did occur for those boards placed in the oven immediately. However, the analysis could still be undertaken since the intensity of the absorption peak at 3640cm^{-1} due to curing of cement in the 'uncured boards' was much smaller than that of the cured boards.

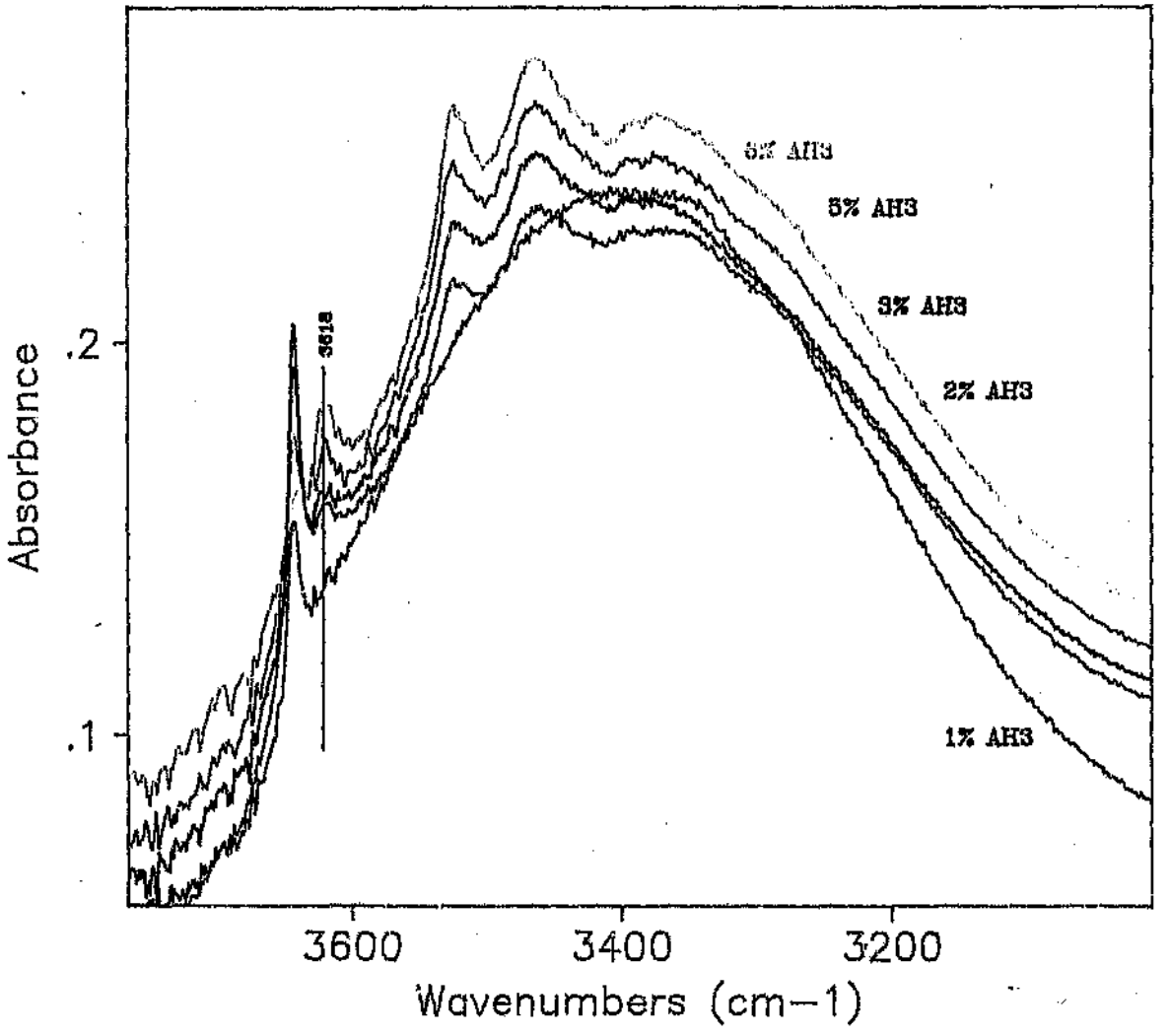
The following experiments were carried out by pressing KBr disks containing 1% board material:

Table 8.11. Experiments using Boards 23 to 36

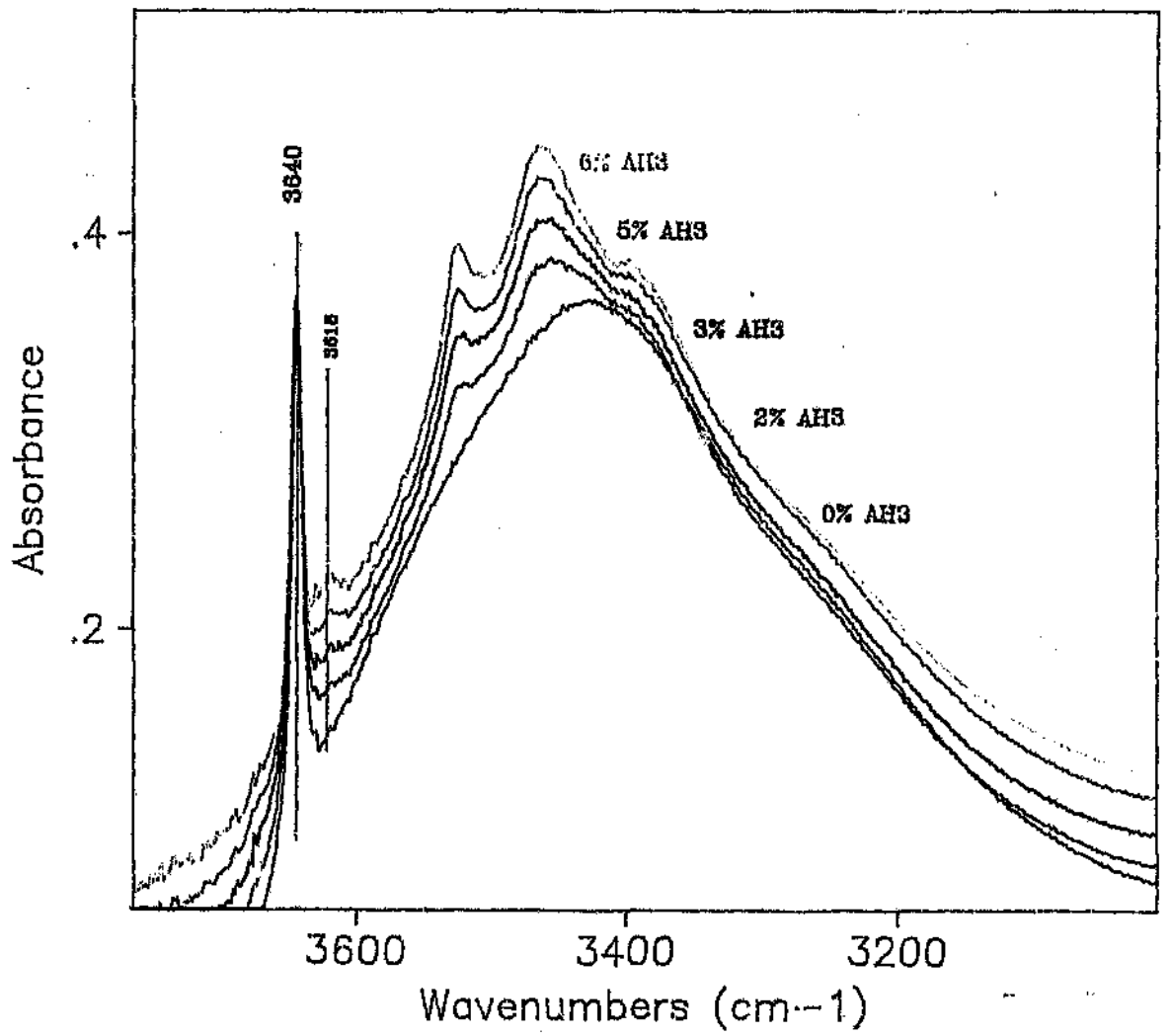
% AH_3	Exp. No. for uncured board	Exp. No. for cured board
0	6.23.1 to 6.23.4	6.24.1 to 6.25.4
1	6.25.1 to 6.25.4	6.26.1 to 6.26.4
2	6.27.1 to 6.27.4	6.28.1 to 6.28.4
3	6.29.1 to 6.29.4	6.30.1 to 6.30.4
4	6.31.1 to 6.31.4	6.32.1 to 6.32.4
5	6.33.1 to 6.33.4	6.34.1 to 6.34.4
6	6.35.1 to 6.35.4	6.36.1 to 6.36.4

The following set of graphs illustrates the increasing intensity of the absorption peak at 3618cm^{-1} indicating an increase of the concentration of AH_3 in the board material. One can also note the increased intensity of the absorption peak at 3640cm^{-1} due to the curing of the boards:

Graph 8.11. Spectra of Uncured Boards 23 to 35



Graph 8.12. Spectra of Cured Boards 24 to 36



The initial quantitative analysis carried out involved calibration using:

1. the **uncured boards**, leaving out one of the spectra in the calibration as an 'unknown' so as to determine the concentration of that 'unknown'. This was done in order to clarify that the peak being used to determine the concentration of AH_3 was the correct one and also to make sure the analytical results calculated by the software being used was correct. By way of an example, Board 29 was left out of the standard, and when determining the concentration of the 'unknown' board, it was found that a concentration of 2.9% of AH_3 was present. Board 29 actually contains 3% AH_3, but an error of 0.1% is acceptable.

2. the **cured boards** for the establishment of a calibration curve and the analysis as explained above.

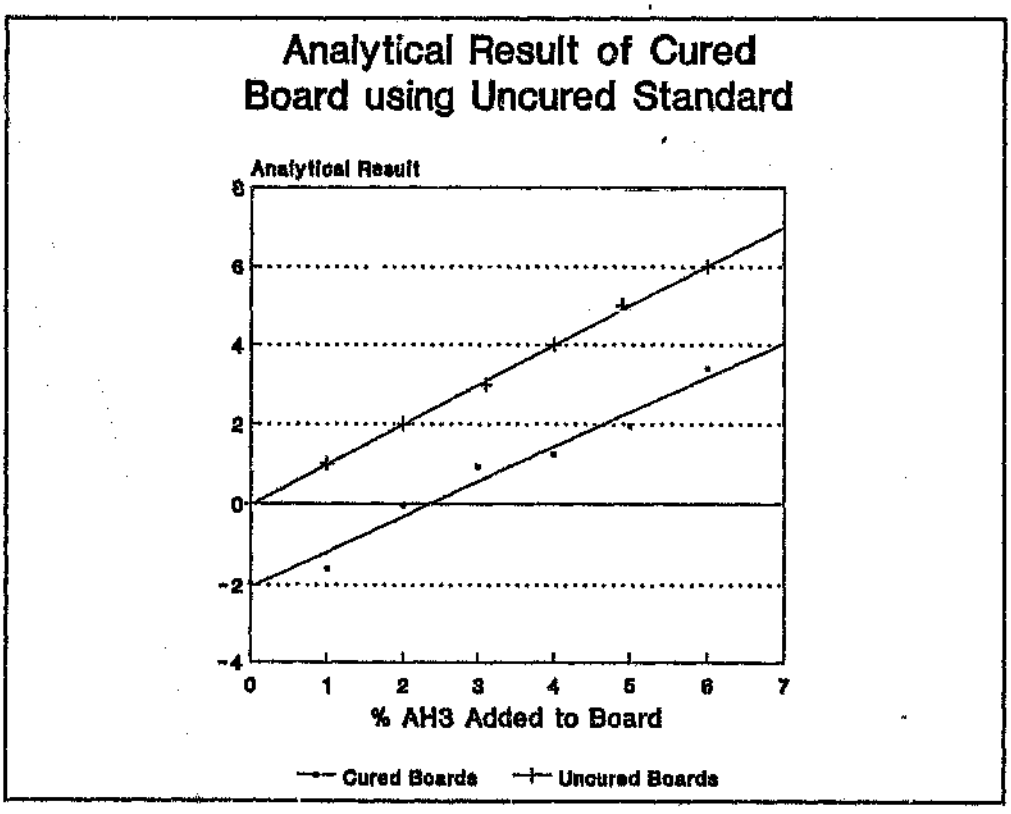
Satisfactory calibration curves were obtained in both cases but the concentrations found according to the two curves were offset by about 2%. This is well illustrated when analysing the 'uncured' board using the calibration curve based on the cured standards and vice versa.

When carrying out this analysis, the following concentrations were calculated for AH_3 contained within the cured boards:

Table 8.12. Concantration of AH_3 Calculated for Cured Boards using Uncured Standard

Board No.	From Experiment No.	Known Concentration of AH_3 in uncured standard	Concentration of AH_3 calculated for Cured Boards using uncured standard
24	6.24.1-6.24.4	0	-1.95
26	6.26.1- 6.26.4	1	-1.59
28	6.28.1-6.28.4	2	-0.024
30	6.30.1-6.30.4	3	0.92
32	6.32.1-6.32.4	4	1.25
34	6.34.1-6.34.4	5	1.94
36	6.36.1-6.36.4	6	3.4

These results show a discrepancy of about 2% AH_3 in the cured boards. The following graph illustrates the point more clearly:



Graph 8.13. Analytical Result of Cured Board Using Uncured Standard

The discrepancy of about -2% for the concentration of AH_3 in all the boards is illustrated in this graph. This is shown by the parallel lines of the cured against uncured boards.

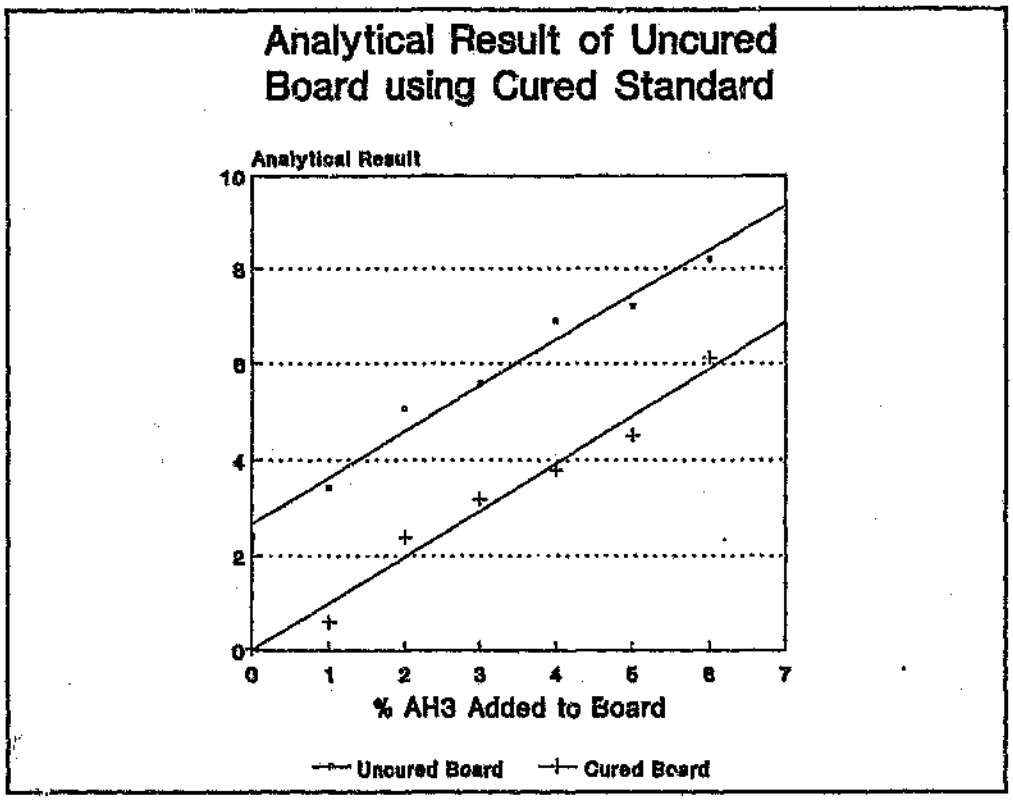
The next analysis involved calibrating the cured boards and determining the concentration of AH_3 contained within the uncured boards. One would expect the reverse concentration to be found in this set of experiments compared to the set as described above.

When carrying out this analysis, the following concentrations were calculated for AH_3 contained within the uncured boards:

Table 8.13. Concentration of AH_3 Calculated for Uncured Boards Using Cured Standard

Board No.	From Experiment No.	Known Concentration of AH_3 in cured standard	Concentration of AH_3 calculated for Uncured Boards using Cured Standard
23	6.23.1-6.23.4	0	2.43
25	6.25.1-6.25.4	1	3.44
27	6.27.1-6.27.4	2	5.06
29	6.29.1-6.29.4	3	5.59
31	6.31.1-6.31.4	4	6.98
33	6.33.1-6.33.4	5	7.25
35	6.35.1-6.35.4	6	8.1

These results also show a discrepancy around 2% AH_3 in the cured boards. The following graph illustrates the point more clearly:



Graph 8.14. Analytical Result of Uncured Boards using Cured Standard

It must be emphasised that Calcium Alumina Hydrate (CAH) arises from C_3A + H_2O (when adding water to cement)[5].

These findings illustrate the fact that the hydration (curing) of cement gives rise to molecular species with infrared absorption near to that of AH_3. The following mechanism, that might explain this phenomenon, is proposed. When water is added to cement, it is known that the first reaction involves the hydration of C_3A.

It seems reasonable to assume that aluminium-hydroxide bonds are formed and that they will coincide with those of AH_3 or at least affect those of AH_3 at $3618cm^{-1}$, giving a false reading for AH_3 in the board. However, to explain the phenomenon observed, it must be argued that CAH is an intermediate product that disappears with further curing. Further work was done to elucidate the role this plays in the quantitative infrared determination of AH_3 in cementitious boards.

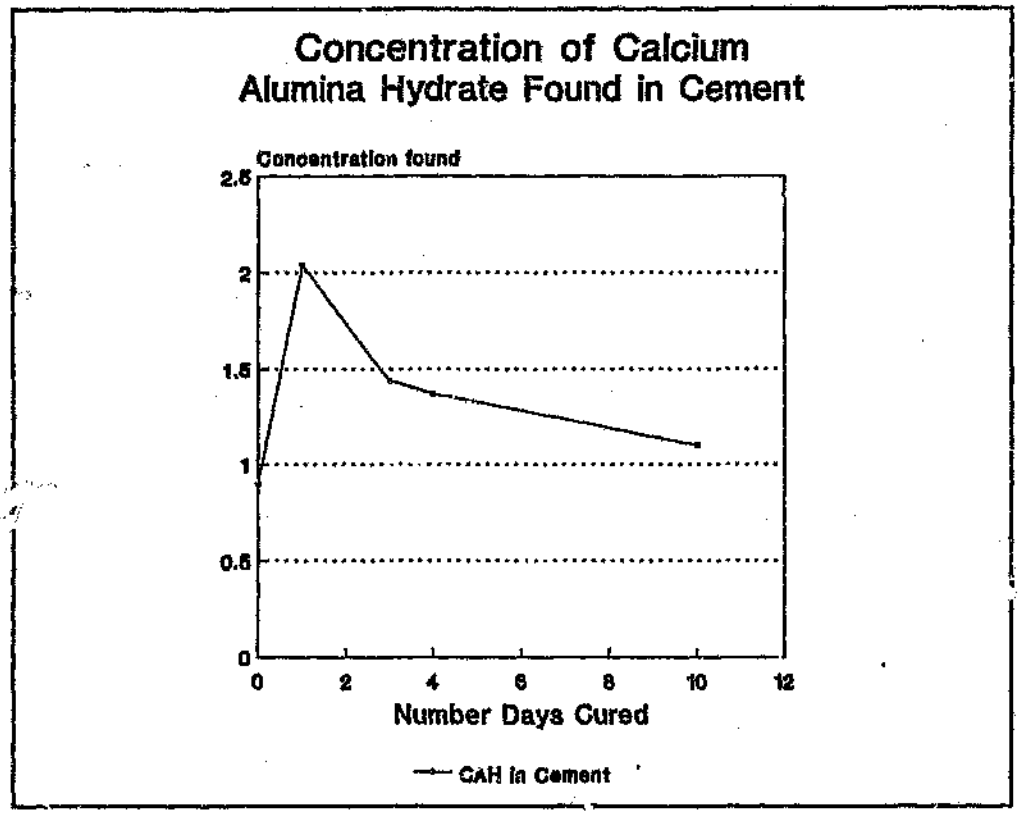
This set of experiments involved mixing pure cement (without AH_3) with water and then recording the spectra of the cement at progressive intervals of the curing. The infrared spectra appear to be quite sensitive in identifying slight hydration at the $3640cm^{-1}$ region band in standard cement samples exposed once to the atmosphere.[16]

The absorption peak at $3618cm^{-1}$ was used to determine the concentration of the supposed formation of CAH after adding water to the cement. The quantitative analysis was calculated by using the standard of the cured boards. The following table represents the experiments carried out and the development of the aluminium hydrate in cement during the early phases of hydration:

Table 8.14. Analytical Result of Apparent AH_3 in Pure Cement

Exp. No.	Description	Analytical Result using Cured Standard (i.e. apparent AH_3 concentration)
7.1.1 to 7.1.6	Cement dried out immediately at 100°C	0.9
7.2.1 to 7.2.6	Cement cured for 1 day and then dried out at 100°C	2.04
7.3.1 to 7.3.6	Cement cured for 3 days and then dried out at 100°C	1.44
7.4.1 to 7.4.6	Cement cured for 4 days and then dried out at 100°C	1.37
7.5.1 to 7.5.6	Cement cured for 10 days and then dried out at 100°C	1.1

The following graph illustrates the plot of the results described in the table above:

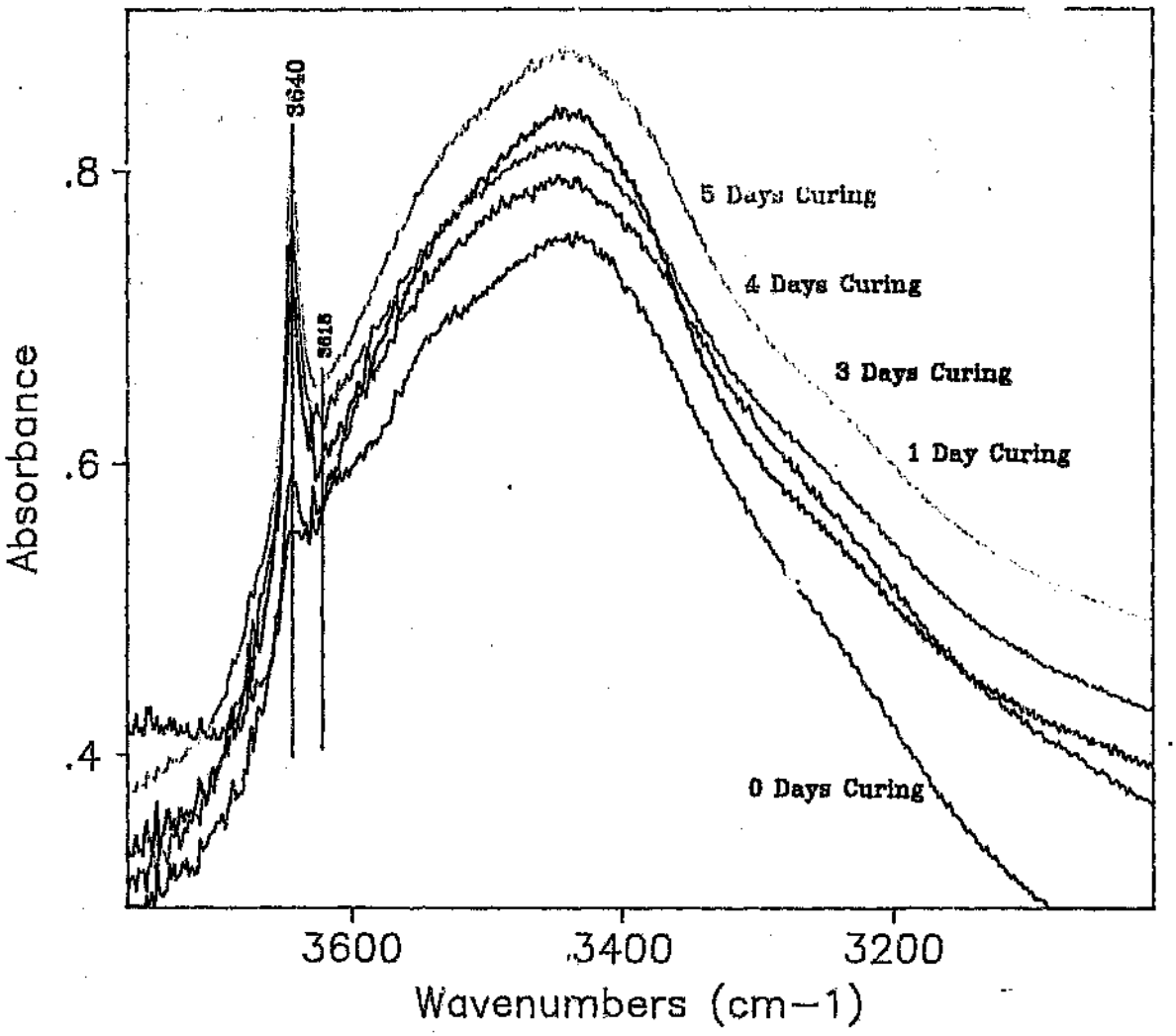


Graph 8.15. Concentration of CAH that Develops During The Early Phases of Hydration

The spectra are shown in Graph 8.16. The graph above illustrates the formation of the aluminium hydroxide bonds that are formed immediately after adding water to cement. The highest concentration for CAH found was after one day of curing. As time goes on, the concentration of the aluminium hydrate diminishes.

The increase in the intensity of the peak at 3640cm^{-1} (due to the hydration of cement) as the curing progresses is observed in the spectra.

Graph 8.16. Spectra of Cement Curing



It must be noted that the cement hydration research described above was done in order to explain the discrepancy of the results for the concentration of AH_3 believed to be due to the curing of the boards. It was shown that the curing of the cement plays an important role in determining the concentration of AH_3. However, an investigation into the curing of cement using Infrared spectroscopy should be researched further. This was beyond the scope of my Research Report.

Now that it is known that the Infrared spectrometer can be used to determine the concentration of AH_3 in fibre-reinforced cement boards, it is possible that by using particular standards, the concentration of AH_3 in the final product as well as at certain relevant points along the manufacturing process can be determined.

8.6 Selection of Region

When using the quantitative analytical method provided by the software associated with the spectrometer, the known concentrations of AH_3 added to the board were entered in the computer.

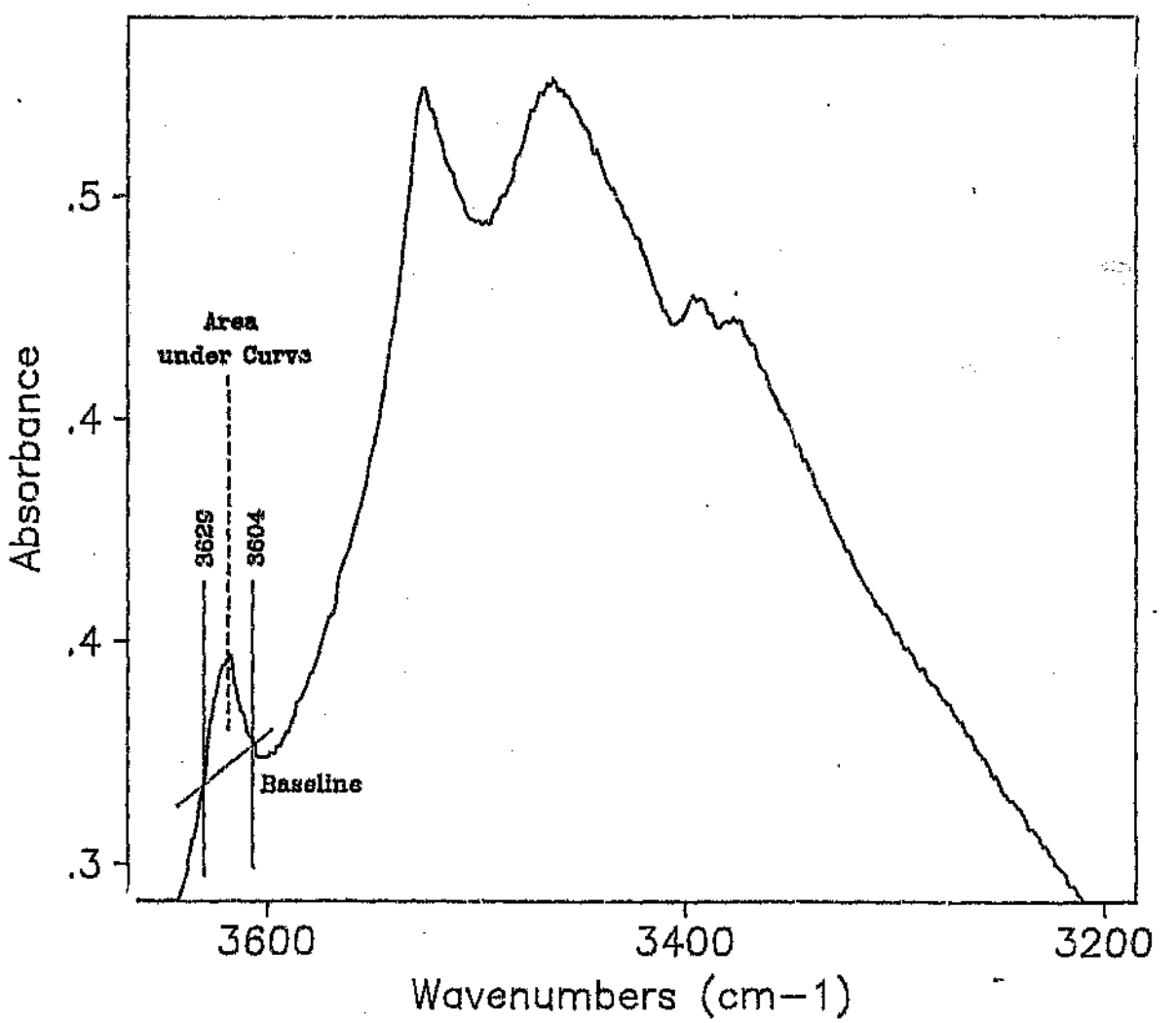
The Region was then selected. The Baseline is automatically calculated using the software. As mentioned in Chapter 6.2, a baseline refers to the peak height related to the spectrum. Because of differences in concentrations and other impurities within a disc, the whole spectrum may move with respect to the y-axis, i.e. the background absorbance changes. This is also due to variations in the opacity of individual discs. The region defines the area of the peak under investigation.

The matrix was then calculated. This calculates the calibration matrix that corresponds to the standards that have been entered. For successful analysis, the standard deviation value (or error) should be as close to zero as possible.

A region of 3629cm^{-1} and 3604cm^{-1} was used for the analysis, as shown in Graph 8.17.

The analytical procedure provided by the software was then used to calculate the concentrations of AH_3 in the 'unknown' standards.

Graph 8.17. Spectrum illustrating Region



9 CONCLUSION

The purpose of this investigation was to identify and quantify aluminium tri-hydrate (AH_3) in fibre-reinforced cement boards to which it is added to limit cracking of the autoclaved boards produced by Everite. It was therefore necessary to run a spectrum of 'pure' AH_3 to obtain its infrared fingerprint and find at which wavenumbers absorption peaks characteristic of the additive appeared. A spectrum of board material containing no AH_3, as additive, was recorded to establish whether there are interfering absorption peaks. Similarly, spectra were recorded using material from boards 'as produced' and material to which various concentrations of AH_3 had been added after manufacture. This was done to establish whether the presence of AH_3 could be determined in the manufactured boards and whether the selected AH_3 absorption peak showed satisfactory sensitivity to concentration.

It was found that at a wavenumber of 3618cm^{-1}, there was evidence of increasing absorption with increasing concentration of AH_3 in the 'pure' board material. Thus, it was shown that the presence of AH_3 could be determined.

With regard to the quantitative investigation, fibre-reinforced cement boards with different known concentrations of AH_3 were made up in the laboratory at Everite, and their spectra were recorded.

The peak at 3618cm^{-1} was used for calibration of the AH_3 concentrations. Once

the calibration curve for AH_3 was drawn up, 'unknown' concentrations of AH_3 in the boards were made up by Everite and a quantitative analysis to determine the concentration of the AH_3 was undertaken. The 'unknown' concentrations of AH_3 in the boards were determined with satisfying accuracy using Fourier Transform Infrared (FT-IR) Spectroscopy, but the consistent curing of the boards (both the standards and the analytical samples) was shown to play a crucial role in the investigation.

A sharp absorption peak at 3640cm^{-1} is evident in the boards that are cured and not dried out immediately. The peak is due to calcium hydroxide, one of the main products of hydration.

In addition, it could be shown that the hydration of cement gives rise to transient molecular species with infrared absorption near to that of AH_3. It seems that aluminium-hydroxide bonds form due to the hydration of cement (probably the C_3A component) which affect those of AH_3 at 3618cm^{-1}, giving a false reading for the concentration of AH_3 in the board material. However, this absorption decreases again as hydration proceeds and it is not present in the board that has been 'cured' and in which hydration has reached an advanced stage.

It can be seen that the curing of the fibre-reinforced cement boards plays a crucial role in determining the concentration of AH_3 within the boards. It is imperative that both the standard boards (those boards used to calibrate the analytical curve) and the boards to be analysed are cured in the same manner. Autoclaving the boards

may provide a reasonable way to ensure that the curing of the boards is similar.

This completed my investigation, but it can be seen that there is scope for further investigation of this process. This could involve taking samples from the sieves, mud water tanks, vacuum box, stirrers and mixers to be analyzed so that a complete analysis of the additive throughout the process could be undertaken. Further investigation of the other additives could also be beneficial to Everite, and very interesting for the researcher.

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