Polymer stabilisation of P. F. Ash

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"Polymer Stabilisation of P.F.Ash"

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I. Contents

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3. Review of P.F.Ash

6. Laboratory work

8. Additional Laboratory Work

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2. Introduction

2. INTRODUCTION

In many industrial processes, waste materials are produced on a scale that can present a serious disposal problem, and it is of considerable advantage if such materials can be put to some use.

The Civil Engineering industry is perhaps unique in employing vast quantities of inert material and it has, from time to time, found uses for industrial waste products which become available on a scale of millions of tons per annum. Examples of these wastes are the slags produced in making iron and steel, which are widely used in various forms; hard-burnt clinker from furnaces is used as an aggregate for concrete and as hardcore; colliery shale is a frequently used in-fill material and in some countries as a source of expanded aggregate.

The ashes from power stations using pulverised fuel has become readily available for use as a multipurpose material and it is intended that an attempt be made to further investigate this material.

Most of the coal used in modern power stations in this country is fired as pulverised fuel, that is the coal is finely ground and injected into the boiler furnace with a stream of air sufficient for complete combustion of the carbonaceous matter. The particles of coal burn away as they pass through the furnace and the ashes so formed are carried through the boiler where ash of the pulverised fuel - p.f. ash - is collected as a fine cement-like powder. A clinker is also formed on the furnace bottom and this is mechanically broken away from the grate before being transported by a continuous sluicing of water into a large collecting chamber. The latter type of ash is called furnace bottom ash.

P.f.Ash is a waste product for which a number of commercial uses have been developed but it is a constant problem to dispose of the remaining ash economically and without creating a nuisance. Usually the ash is dumped wherever a convenient site can be found but the cost of disposal in this way is not negligible and, since the "output" in this country has risen from 7 million tons in 1965 to 9-10 million tons this year, more and more efforts are being devoted to finding uses for this material which will at least partly offset the disposal costs.

P.f.ash has already found application in several kinds of construction work which offers the possibility of taking up large quantities of the material, e.g. soil stabilisation, grouting, embankment construction, a component of concrete mixes, and as a general fill material.

The full development is limited by the lack of complete information to support the use of the ash in the various applications, by the natural conservatism of the users and partly by the variability of the material. The latter arises from the different kinds of coal being burnt and the

the different conditions of boiler operations.

It is not likely that anything can be done to reduce the variability of the p.f.ash and so this remains an obstacle to the mass utilisation of the material; these effects are made more difficult by the fact that it has not been possible to give an effective specification by which unsuitable samples for a particular application can be rejected.

A number of uses for the ash depend on the fact that the material is a pozzolan - that is without being itself a cementitious compound it has the property of setting in the presence of lime and water, by reacting to form cementitious calcium silicates of low solubility.

The more modern coal fired generating stations pulverise the coal in grinding mills so that up to 80% passes a 200 B.S. mesh sieve, and the crushed coal is suspended in a stream of hot air passing into the combustion chamber where the temperature range is 1500°C ± 200°C. Under these conditions most of the minerals present in the coal are fused and undergo various chemical and physical changes. Between 10% and 25% of the ash formed drops to the bottom of the chamber and forms furnace bottom ash. The remainder of the ash particles are carried through the boiler with the flue gasses where a separation is effected by mechanical collectors or electrostatic precipitatores. The extracted material is p.f.ash.

P.f.ash can be supplied to sites in a dry form in which it must be handled either by tanker or in bags. If it is to be handled in trucks it is 'conditioned' by raising the moisture content to be predetermined level to enable handling to be accomplished without incurring a dust nuisance. Certain stations remove both ashes as a slurry which is transported to nearby lagoons, and lagoon ash is the material excavated from these sites after they have been filled with this slurry and allowed to drain. The material so obtained has a very variable moisture content, rarely less than 20 per cent and usually very much higher which may necessitate drying prior to use. This is usually effected by exposure of the ash to atmosphere.

Some twenty years ago a number of runways and runway type constructions were laid down using p.f.ash stabilised with natural resins, but these forms of constructions were not satisfactory as biological degredation proved to be unsurmountable at that time. Similarly the characteristic of breaking down under hydrolysis, in an alkaline environment, has previously ruled out the use of synthetic resins in a similar stabilisation.

However there has been some important research carried out by the paint industry over the past few years and this work has been directed at combating alkaline attack of the basic material used in the production of paints. The basic material used is an emulsion of Polyvinyl Acetate - PVA - which is a synthetic resin.

Because the paint industry appear to have been successful in their improvements it was thought that an attempt should be made to see if the PVA emulsion produced would have some reasonable effects in stabilising p.f.ashes.

Further, it was felt that if the emulsion gave reasonable strengths, the manufacturers would consider adding more of the resisting agent should greater resistance be required. An emulsion supplied to the paint industry was used in this series of tests and the manufacturer providing the emulsion thought that the percentage of resisting agent could be raised without considerably effecting the price of the emulsion.

Thus it was that the idea for this line of research was started and the following pages record the work carried out to investiage "The Polymer Stabilisation of p.f.ash."

3. Review of p.f.ash

3.1. Physical and Chemical Properties

3.1.1. PHYSICAL AND CHEMICAL PROPERTIES

P.f.ash is available in different forms and the method of transporting the material is governed largely by the condition of the ash.

The size range of p.f. ash, based on particle size measurements, is illustrated in Fig.1 which compares the coarser fraction removed by mechanical precollectors and also shows the wide range of sizes in lagoon ash. Translated into soil nomenclature, precipitator ash falls largely into the category of silt while the coarser cyclone material corresponds closely to a fine sand. The characteristics of lagoon ash are affected by the proportion of furnace bottom ash present.

The size of fine particles can be expressed in a number of ways but particle size measurements are not suitable for routine control tests. Sieve analysis is adequate for the larger fractions but this method is unsatisfactory for the fine fractions and, as many precipitor ashes have more than 75% by weight finer than 300 mesh, a method more refined than sieving is needed.

The method most widely used is based on specific surface which is a measure of the total surface and is expressed in square centimetres presented by one gram of material. Recent standardisation in B.S. 3892:1965 of a modified Rigden method of measurement - based on air permeability - has made it more reliable and reproducible for use with p.f.ash.

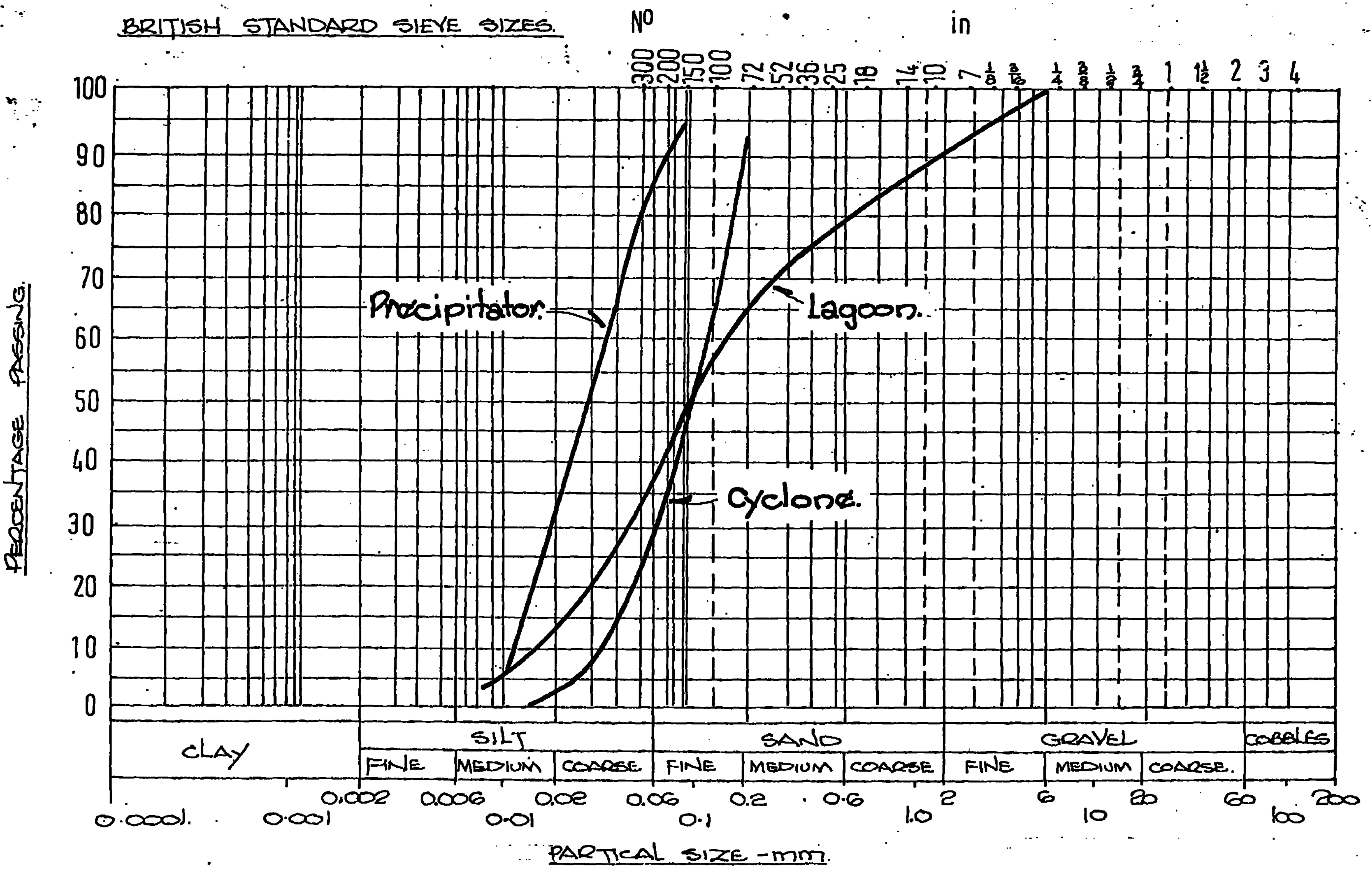


FIG.1. GRADING OF TYPICAL CYCLONE PRECIPITATOR AND LAGOON P.F.A

There is, however, no clear correlation between specific surface and particle size distribution, as a very high specific surface can be produced for a relatively small proportion of very fine particles. Thus figures of specific surface should be assessed in conjunction with a grading analysis. However, it is considered that where an ash is obtained from one source an increase in specific surface usually indicates greater fineness; but where ashes come from different sources this relationship does not necessarily apply, especially with p.f. ash of high carbon content.

It is sometimes necessary to ensure a supply of material of consistent size for certain uses, and, to facilitate this, three grading zones based on specific surface have been defined in BS 3892:1965[3]. They are

Zone A : 1250 up to and including 2750 cm^2/g
Zone B : Above 2750 up to and including 4250 cm^2/g
Zone C : Above 4250 cm^2/g

These are subject to a range not greater than 1500 cm^2/g and based on a mean agreed between purchaser and vender. Of these three zones, Zone A includes most precollector ash and Zone B and C, coarser and finer precipitator ash(2).

The fact that p.f. ash specifications include a figure defining the permissible lower limits of surface area reflects a general belief that the surface area of an ash, and hence its activity. This belief is not entirely true and seems to be based more on the analogy with Portland Cement than on experimental studies of p.f.ash.

Several authors 9.10 have tested the relationship between the activity of an ash and its particle size, but the results varied between poor correlation and no correlation at all according to the parameters chosen as a measure of the particle size, and to the method of measurement adopted.

Most ashes have size distributions which give roughly linear plots on the co-ordinates used in these diagrams, although a few have been recorded as having curved or S-shaped characteristics. From these plots it can be seen that the finer particles are more numerous than the coarse but they contribute much less to the weight.

For examples, more than 60% - numerically - of the particles in one ash have been noted as having diameters of less than 3 microns, but these particles contribute less than 10% of the total weight; conversely, another ash had 1% - numerically - of the particles with diameters greater than 10 microns and this 1% contributed half of the weight of the ash.

This must effect the activity of an ash and this aspect is considered at a later stage.

Prior to 1960 most published investigations of p.f.ash the material had been treated as a homogeneous material of variable properties. The British Coal Utilisation Research

Association have carried out extensive works, published in 1962, investigating the activity of p.f.ash as a pozzolan.(4) The work was also to investigate if an alternative index of ash activity could be deduced as the specifications were expressed in terms of lower limits on the composition of certain components believed to be desirable (SiO_2,AL_2O_3), upper limits on other components supposed to be deleterious (Sulphur, Carbon) and lower limits on fineness etc. The main disadvantages of this approach is that any new uses of the ash, or any new properties which are to be assessed, would require the setting up of further specifications based on other empirical work.

Thorne and Watt analysed ash collected at 13 British generating stations from 4 out of the 5 regions composing the Central Electricity Generating Board. These samples were analysed by colorimetric methods, with their results in Table 1 and can be compared with the stipulated chemical requirements of certain British and American Fly Ash specifications given in Table 2.

The carbon contents of the ashes vary considerably but the ash analyses are otherwise very similar to each other. It can be seen that all except the samples of high carbon content from the Tir John and Llynfi conform to the ASTM and CEGB specifications and most of the samples conform to the requirements of all four specifications. It is also noted that, although the Hams Hall sample was known to have exceptionally high activity[6], its analysis does not appear to depart from the general pattern of the other samples.

3.1.1. TABLE.1

TYPICAL ANALYSES OF p.f. ASHES

FLY ASH.	ANALYSIS PERCENTAGE.												
	SiO_2	Al_2O_3	Fe_2O_3	CaO	MgO	Na_2O	K_2O	TiO_2	Mn_3O_4	SO_3	P_2O_5	C	H_2O	Total
CLIFFQUAY	45.4	25.5	13.5	3.2	2.2	0.8	2.6	1.0	0.1	1.2	0.3	3.7	0.3	99.8
STELLA SOUTH	46.1	27.5	11.8	3.7	2.4	0.2	2.2	1.0	0.1	2.5	tr.	0.8	0.3	99.6
RYE HOUSE	43.6	24.6	11.3	7.7	2.9	0.7	2.3	1.0	0.2	1.2	0.6	2.4	0.1	98.6
TIR JOHN	9.6	5.4	1.0	0.3	0.3	0.3	0.7	0.2	0	0.5	0.1	73.7	1.2	93.3
CASTLE DONINGTON	45.9	24.4	12.3	3.6	2.5	1.0	3.2	0.9	0.1	0.9	0.6	4.1	0.1	99.6
SKELTON GRANGE	47.2	26.7	11.9	3.4	1.9	0.9	3.8	0.8	0.1	1.0	0.2	2.1	0.1	100.1
FERRYBRIDGE	48.7	27.9	9.5	2.4	1.6	1.5	4.2	0.9	tr.	1.2	0.2	1.5	0.3	99.9
CROYDON 'B'	42.8	26.1	9.3	2.4	1.4	0.6	3.6	0.8	0.1	0.6	0.3	11.7	0.3	100.0
CARMARTHEN BAY	41.4	23.9	12.9	2.5	1.8	0.8	3.7	0.7	0.1	0.7	0.2	10.0	0.2	98.6
USKMOUTH	44.2	26.5	8.6	1.9	1.6	0.6	3.8	0.9	0.1	0.8	0.5	8.9	0.2	98.6
DUNSTON	47.7	28.6	8.3	2.1	1.9	0.4	2.6	1.1	0.1	1.4	0.2	3.1	0.6	98.3
LLYNFI	41.4	24.0	6.4	1.3	1.4	0.5	3.3	0.8	0.1	0.2	0.7	18.7	0.2	99.0
HAMS HALL	48.6	28.0	8.1	3.4	1.9	1.9	3.1	1.0	0.1	1.3	0.6	0.6	0.2	98.8
SKELTON GRANGE 1cwt	46.5	26.6	12.0	2.7	1.7	1.2	3.8	0.9	0.1	1.1	0.4	2.3	ND	99.3
FERRYBRIDGE 1cwt	47.4	27.5	10.3	2.1	2.0	1.7	4.0	0.9	0.1	1.8	0.3	0.9	ND	99.0
DUNSTON 1cwt	50.7	34.1	6.4	1.7	1.7	0.3	1.8	1.2	tr.	0.6	0.2	2.0	ND	100.7
TOLERANCE.	0.7	0.5	0.5	0.2	0.2	0.1	0.1	0.1	<0.005	0.2	<0.05	0.2	0.1	

3.1.1 TABLE (2)

Chemical Requirements of Various Published p.f. Ash Specifications

Component	ASTM C350-54T	Bureau of Reclamation	U.S.Corps of Engineers	C.E.G.B.
SiO_2%	40.0 min	$SiO_2+Al_2O_3+Fe_2O_3$ not less than 75.0%	40.0 min	35.0 min
Al_2O_3%	-		15.0 min	-
MgO%	3.0 max	3.0 max	3.0 max	4.0 max
SO_3%	3.0 max	4.0 max	3.0 max	3.0 max
Ignition loss %	12.0 max	5.0 max	5.0 max	12.0 max

3.1.2 DISAGGLOMERATION

The results of works carried out by Watt in 1959 suggested that most p.f.ash particles were not homogeneous separate particles, but agglomerates. Thorne and Watt in 1962 further investigate disagglomeration by extracting p.f.ashes with water. The agglomerated particles in most ashes were rapidly broken down by this treatment to give products whose constituent particles, 1-50 microns in diameter, were seen under the microscope to be similar to the single particles found in the original p.f.ash.

Besides this easily decompossible type of agglomerated particles there was another kind of particle which was not broken up by water, nor even by dilute alkalis, but which was attacked by dilute inorganic acids; the attack proceeded by progressive etching of the particles and continued until the greater part of the agglomerate was dissolved and the rest converted into a featureless residue, without at any time passing through a stage in which the agglomerates were reduced to their constituent particles.

However only the ash from Stella South was found to contain more than about 1% of agglomerates of this kind, and they were neglected, therefore, as insignificant components of all other ashes.

For all the ashes except Stella South the method of water extraction was found to be a sufficient means of disagglomeration and it was adopted as a standard procedure and applied to all ashes before any other examination was made. This allowed the study of the nature and properties of the ash more basically and in greater detail than in previously published work.

X Ray examination of the materials recovered from the aqueous extracts by evaporation of the water has shown them to consist mainly of calcium sulphate and calcium carbonate - the latter being derived presumably from atmospheric carbonation of the calcium oxide which must have been present originally.

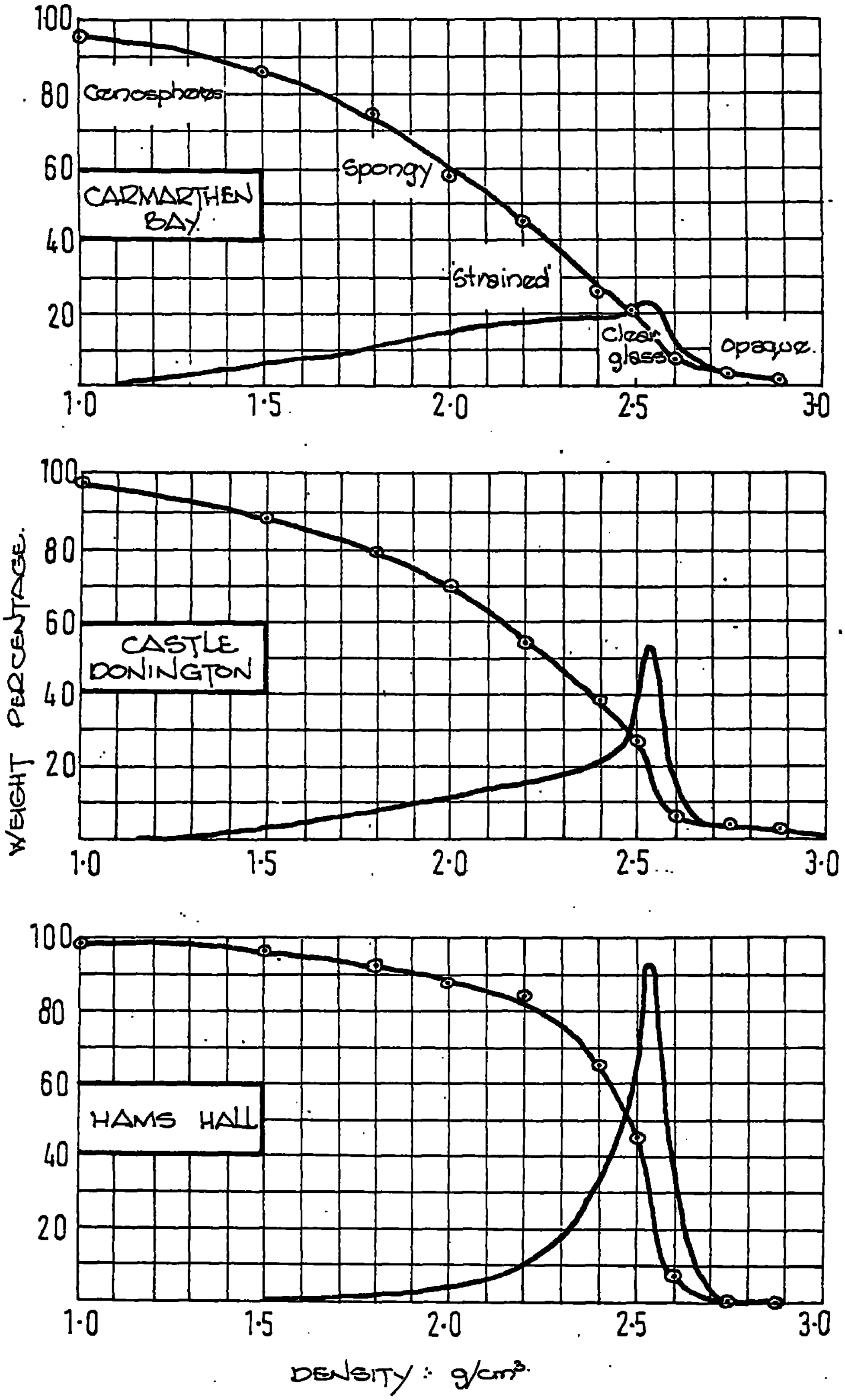
3.1.3 INVESTIGATION OF COMPONENT PARTICLES

Thorne and Watt[4] carried out investigations into the component particles of ashes using both magnetic and density separations. They found that magnetic separation was highly specific and therefore limited, although it was simple and easily applied, so that density separation formed the basis of their investigations. The method used was an adaption of the float-and-sink method which depended on the use of liquids of various densities to separate by settling under gravity.

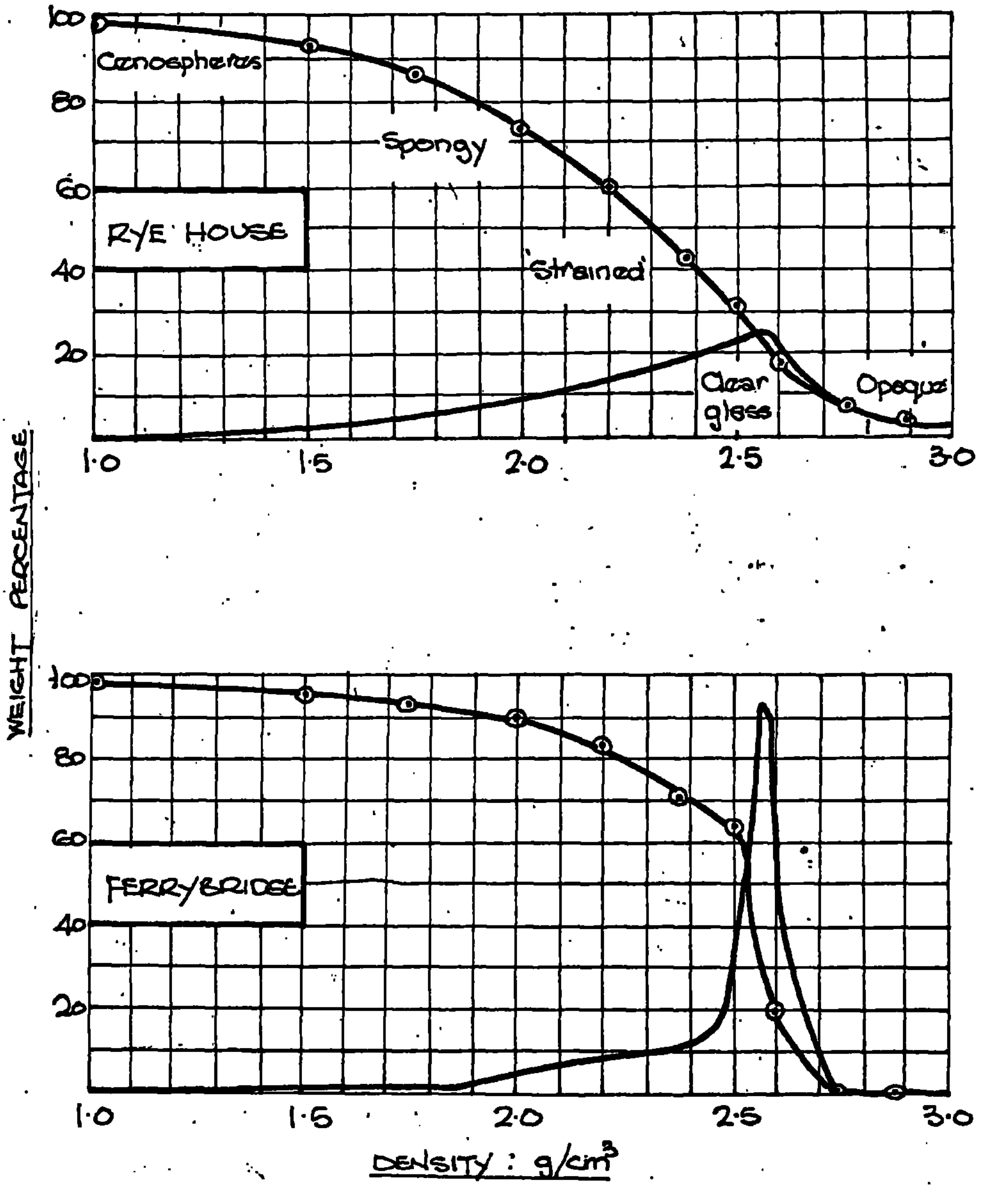
3.1.3.1 Density Separations

Systematic density separations were carried out on five ashes[4] and figures (2 and 3) show the results of this work as curves indicating the relationship between the density of the separation liquid and the percentage fraction of ash sinking in the liquid of this density.

The gradient of density was also measured and plotted



3.1.3.1. FIG. 2. DENSITY DISTRIBUTION OF THREE FLY ASHES.



3.1.3) FIG. 3 DENSITY DISTRIBUTION OF TWO p.f. ASHES -300 MESH.

as a fraction of density. At a density of 2.5 to 2.6 g/cm^3 the ashes were all found to give a peak in the differential curve. This varied in height according to the nature of the ash but was very constant in position from ash to ash. The fractions separating in this region were composed mainly of clear glass spheres and were distinguished sharply from the rest of the ash.

Particles of other kinds were not found to have such highly characteristic densities although it was regularly found that fractions of similar densities separated from different ashes had generally similar characters and contained the same kinds of particles.

The results of these separations were grouped into three regions and are discussed below.

3.1.3.2 Peak Region: density 2.5 - 2.6 g/cm^3

The 2.5 - 2.6 g/cm^3 density peaks were dominant in Hams Hall and Ferrybridge ashes; nearly 40% of these ashes separated out within these limits. In Castle Donington ash the peak was less dominant but still included about 17% of the ash.

Since the position of this peak was found to be so constant from ash to ash it was investigated as to whether the particles corresponding to these peaks were equally constant in properties and composition. All five ashes fractions separating in this region of density were analysed and the results calculated to give a total of 100% for the oxides shown in Table 3.

3.1.3.2 TABLE (3)

Analysis of 2.5 - 2.6 g/cm^3 fractions
Separated from five p.f. ashes

p.f.Ash	Method of Analysis	Constituents, %						
		SiO_2	Al_2O_3	Fe_2O_3	CaO	MgO	Na_2O	K_2O
Rye House	Spectrographic	63	25.5	3.9	2.9	1.4	1.0	2.6
Ferrybridge	Spectrographic	54	30	7	1.3	1.9	1.8	4.6
Carmarthen Bay	Colorimetric	52.1	32.4	6.1	2.0	1.7	0.9	4.6
Castle Donington	Colorimetric	55.6	28.5	6.5	1.9	2.2	1.2	3.9
Hams Hall	Colorimetric	52.6	31.5	5.4	3.5	1.8	1.7	3.6

The analytical results show that the composition of the fractions from the last four of these ashes lie within a rather narrow range; the silica contents, in particular, differ by not more than 4%. The silica and alumina together make up about 84% of the fractions compared with 72 - 80% for the original ash. Most of this difference arises from the iron removed by the magnetic separation although some was probably the calcium removed by the preliminary water extraction.

3.1.3.3 Region above Peak: density greater than 2.6 g/cm^3

In all the p.f.ashes examined the fraction of density higher than that of the 2.5 - 2.6 g/cm^3 peak are a relatively small part of the whole-between 0.2 and 6.7%.

Fractions of the highest density contain material which is obviously rich in iron but these fractions are only a very small part of the total, generally much less than 1% and are not likely, therefore, to contribute much to the general properties of the ash. In the main these high iron components seem to represent particles which are similar in composition and properties to those forming the magnetic and reduced magnetic fractions which have escaped separation.

Only two fractions of density greater than 2.6 g/cm^3 were available in sufficient amount for analysis and the results of both of these showed the decrease in silica content which would be expected from the higher density. In the Rye House fraction the decrease in silica content was accompanied by an increase in the content of calcium; in the Ferrybridge fraction there was a general increase in both calcium and iron.

3.1.3.4 Region below peak: density less than 2.5 g/cm^3

The material separating at densities below 2.5 g/cm^3 was an important part of the whole for all the p.f.ashes examined by Thorne and Watt. The amounts separated in this region varied from 36% of the total for the Ferrybridge ash to more than 55% for the Carmarthen ash. At densities immediately below the peak and down to about 2.4 g/cm^3 the particles were found to be clear glass spheres. Generally the particles in this range of density were larger than those in the peak region and many of the particles contained bubbles.

At the next interval of density below this - 2.2 to 2.4 g/cm^3 - the particles showed no marked change in character but many more contained bubbles and showed a spongy texture. Below this again, in the range 2.0 - 2.2, the tendancy increased but was noted that even in this region small glass spheres were occasionally seen and strained glass spheres were of common occurence.

At densities still lower than this - apart from unburnt coal particles - only spongy particles were found. These increase in sponginess as the density decreased until at the lowest density examined - below 1.0 - real cenospheres predominated.

Cenospheres do not seem to be as common in p.f.ashes, however, as some literature would suggest, and they did not form an important part of any of the ashes in this investigation.

3.1.4 ANALYSIS OF DENSITY FRACTIONS

The composition of these fractions were determined by analysis and the results recorded in Table (4). Considering the Carmarthen, Castle Donington and Hams Hall ashes for which the more reliable colometric analyses are available, it can be seen that the differences in composition both between comparable fractions of different ashes and between fractions of different

3.1.4. TABLE 4.

COMPARATIVE ANALYSES OF FRACTIONS OF VARIOUS DENSITY SEPARATED FROM THREE ASHES

p.f. ASH	FRACTION DENSITY RANGE g/cm^3	ANALYSIS %							TOTAL FLUXING OXIDES %	SiO_2/Al_2O_3 RATIO
		SiO_2	Al_2O_3	Fe_2O_3	CaO	MgO	Na_2O	K_2O		
CARMARTHEN BAY	2·6-2·5	52·2	32·4	6·1	2·0	1·7	0·9	4·6	16·3	1·61
	2·5-2·4	55·6	31·0	4·6	1·3	1·6	1·0	4·9	13·4	1·79
	2·4-2·2	54·6	33·1	4·1	0·7	1·5	0·8	5·1	12·2	1·65
	2·2-2·0	54·6	32·8	4·0	1·0	1·5	0·7	5·4	12·6	1·66
	2·0-1·8	55·2	32·8	3·7	1·0	1·3	0·9	5·2	12·1	1·68
	1·8-1·5	55·6	32·6	3·4	0·6	1·2	1·0	5·6	11·7	1·71
	1·5-1·0	55·8	32·6	3·3	0·7	1·3	0·8	5·5	11·6	1·71
CASTLE DONINGTON	2·6-2·5	55·6	28·6	6·5	1·9	2·2	1·2	3·9	15·7	1·95
	2·5-2·4	56·3	30·7	4·9	0·7	2·0	1·1	4·2	12·9	1·84
	2·4-2·2	56·9	29·8	4·7	1·3	2·0	1·2	4·0	13·2	1·91
	2·2-2·0	57·9	28·0	5·4	1·3	2·1	1·2	4·0	14·0	2·00
	2·0-1·8	55·1	31·8	4·5	1·1	1·8	1·0	4·7	13·1	1·73
	1·8-1·5	55·6	31·7	4·6	0·9	1·8	1·0	4·4	12·7	1·75
	1·5-1·0	56·0	31·8	4·2	1·2	1·6	1·0	4·7	12·7	1·75
HAMS HALL	2·6-2·5	52·5	31·5	5·4	3·5	1·8	1·7	3·6	16·0	1·67
	2·5-2·4	55·7	30·6	4·5	2·4	1·4	1·6	3·8	13·7	1·82
	2·4-2·2	54·5	32·1	4·3	2·4	1·5	1·5	3·7	13·4	1·70
	2·2-2·0	53·4	33·8	4·3	1·8	1·4	1·4	3·8	12·7	1·66
	2·0-1·8	52·8	34·9	3·8	2·0	1·1	1·5	3·9	12·3	1·51
	1·8-1·5	53·0	35·5	3·0	1·4	1·3	1·6	4·1	11·4	1·49
	1·5-1·0	51·9	35·7	4·0	1·1	1·7	1·5	4·1	12·4	1·45

densities separated from the same ash are by no means large.

Within each ash, however, the composition of the fractions show a fairly definite trend and both SiO_2 and Al_2O_3 increase as the density of that fraction decreases. This is best shown by the results for the Ham Hall ash in which the sum (SiO_2 + Al_2O_3) increases uniformly from 81.5% for the 2.5 - 2.6 g/cm^3 fraction to 86.1% for the 1.0 - 1.5% g/cm^3 fraction. Similar but less regular increases can be found in the other two ashes.

The characteristic difference in texture between spongy particles and clear glass particles might be expected to arise from differences in composition so that the temperatures which were high enough to bring about the complete fusion required for the formation of clear glass spheres were sufficient only for the partial melting represented by the bubbled structure of the spongy particles; or the two kinds of particles might have similar composition but different physical history, in that the clear glass particles may have been exposed to higher temperatures or to longer periods of heating.

The differences between the analytical figures for the fractions given in Table (4) are small and these figures can be recalculated on the basis that $SiO_2+Al_2O_3+Fe_2O_3+CaO+MgO+Na_2O+K_2O \simeq 100$. When this is done it is observed that in all the ashes there is a tendancy for the content of the fluxing oxides (Fe_2O_3, CaO, MgO Na_2O, K_2O) to decrease as the density fraction decreases.

This change is not altogether regular but the content of fluxing oxides appear to decrease by about 3% in passing from the fractions of highest density to those of the lowest, representing about 20% of the amount of fluxing oxides present.

A change in composition of this magnitude might bring about a sufficient difference between the viscous properties and fusion points of the glasses composing the high density and the low density fractions to account for the observed differences between the spongy and the solid glassy particles they contain.

In the Carmarthen ash the decrease in the content or fluxing oxides is accompanied by an increase in the silica content, with little change in the amount of alumina present. In the Ham Hall and Castle Donington ashes, the silica contents appear to vary in a random way and display no systematic relationship with density, but the alumina contents show a fairly marked tendancy to increase as the densities or the fractions decrease. This increase in the alumina content is accompanied by a decrease in the SiO_2/Al_2O_3 ratio, and this would tend to raise the fusion point of the particles. It is to be noted that the SiO_2/Al_2O_3 ratio for Hams Hall ash is consistently lower in each density range below 2.2 g/cm^2 than for the other ashes. This suggests that the fractions of this ash has a higher fusion point than the corresponding fractions of the other ashes and this in turn implies that the Hams Hall furnace runs at a higher temperature than the others and that the very high proportions of glass spheres found in the ash arise mainly from this circumstance.

3.1.5 POZZOLANIC PROPERTIES OF THE DENSITY FRACTIONS

A principal purpose of the separation of p.f.ashes into fractions was to provide samples consisting predominantly of one kind or another of particles whose pozzolanic activities could then be compared by crushing strength tests on lime mortars. The ashes varied widely in composition and particles which were dominant in one ash were sometimes present in another in such small quantities as to make it impracticable to prepare a sample large enough even for a small scale test.

Density separations were carried out on 20 gram samples at densities of 2.74, 2.5 and 2.0 g/cm^3 using a certifuge. These intervals of density were chosen to divide the ash into regions in which the four main types of particles predominated i.e. high density high-iron particle above 2.74 g/cm^3, clear glass sphere type particles 2.75 - 2.5 g/cm^3 strained glass particles 2.5 - 2.1 g/cm^3 and spongy particles below 2.1 g/cm^3. All fractions were analysed spectrochemically and crushing strengths were determined using an 11 day accelerated cure. The results of this work are presented in Table (5).

3.1.5.1 General relationships between fractions of different densities

3.1.5.2 Fractions of density greater than 2.74 g/cm^3

Fractions of this density from all ashes gave low, but

3.1.5 TABLE 5

ANALYSES MORTAR CRUSHING STRENGTHS ETC, OF FRACTIONS OF VARIOUS DENSITIES SEPARATED: FROM FIVE p.f ASHES.

p.f. ASH	DENSITY RANGE OF FRACTION g/cm³	WT PERCENT OF FRACTION	DENSITY OF MORTAR CUBE g/cm³	WATER CONTENT OF CUBE		p.f ASH CONTENT OF CUBE g	MEAN CRUSHING STRENGTH lb/sq in	SPECTROGRAPHIC ANALYSIS OF FRACTIONS PERCENT								
				WEIGHT %	VOLUME %			SiO_2	Al_2O_3	Fe_2O_3	CaO	MgO	Na_2O	K_2O	IGNITION LOSS	TOTAL
R/B HOUSE	above 2.74	15	2.44	10.3	25	0.241	1850	10.5	6.8	58.1	19.5	10.6	-	-	-	100.5
	2.74 - 2.5	19	2.17	13.6	29	0.207	6750	47.6	21.5	8.4	10.2	2.7	0.6	1.4	-	92.4
	2.5 - 2.1	31	2.00	15.8	32	0.185	5100	49.4	23.6	5.2	2.9	1.4	0.7	2.3	2.4	87.9
	below 2.1	35	1.75	16.6	29	0.161	4350	49.2	28.7	4.1	1.7	1.3	0.6	2.6	5.2	93.4
CASTLE DONINGTON	above 2.74	12	2.44	10.3	25	0.241	1700	14.2	7.8	50.5	14.2	7.2	-	-	-	93.9
	2.74 - 2.5	15	2.19	13.3	29	0.209	6900	52.0	23.8	11.7	3.3	2.6	0.8	2.7	-	96.9
	2.5 - 2.1	38	2.05	15.7	32	0.190	6600	55.6	26.6	7.6	1.7	1.8	0.8	2.9	5.7	102.7
	below 2.1	35	1.72	18.0	32	0.155	2300	49.9	25.4	5.7	0.9	1.7	0.7	3.3	7.5	95.1
SKELTON GRANGE	above 2.74	10	2.43	9.7	24	0.242	1700	17.7	10.4	58.6	8.5	3.2	-	-	-	98.4
	2.74 - 2.5	13	2.17	13.2	29	0.207	7800	50.6	24.5	11.0	5.0	2.0	0.7	2.9	-	96.7
	2.5 - 2.1	40	2.07	13.8	29	0.197	7950	56.3	28.0	6.1	1.8	1.7	0.8	3.5	2.4	100.6
	below 2.1	37	1.72	18.6	32	0.155	3200	51.8	25.6	7.5	0.9	1.8	0.6	3.6	4.3	96.1
FERRYBRIDGE	above 2.74	5	2.45	11.0	27	0.241	3800	20.6	12.4	58.6	6.1	2.3	-	-	-	100.0
	2.74 - 2.5	52	2.19	12.6	28	0.211	8600	56.4	27.4	8.7	2.1	1.7	1.4	4.3	-	102.0
	2.5 - 2.1	29	2.12	13.5	29	0.202	8350	54.2	26.0	6.2	1.7	1.7	1.3	4.2	3.5	98.8
	below 2.1	14	1.68	17.4	29	0.153	3800	51.6	28.7	6.5	1.2	1.7	1.3	4.5	7.7	103.2
HAMS HALL	above 2.74	5	2.28	15.1	34	0.218	1400	22.7	15.1	41.8	8.6	3.5	-	-	-	91.7
	2.74 - 2.5	44	2.19	14.5	32	0.207	7700	52.5	28.1	8.8	3.2	1.7	1.3	2.8	-	98.4
	2.5 - 2.1	35	2.13	12.5	27	0.204	7500	54.2	28.0	5.4	2.2	1.4	1.3	2.9	1.1	96.5
	below 2.1	16	1.81	14.3	26	0.171	3850	49.7	30.8	6.9	1.3	1.2	1.4	3.2	3.1	94.5

not negligible, strengths. It is known from the detailed density separations of these ashes that these fractions still contained some glassy spheres; this is shown also by the analysis of the fractions, which show $SiO_2+Al_2O_3$ contents of 17-38 - and it is probable that the strength of these fractions arise mainly from this. There is a rough parallel between the $(SiO_2+Al_2O_3)$ contents and the strengths observed, except for the Hams Hall fraction. The lower strength of the mortar from this fraction is almost certainly a consequence of the lower density of the cubes (2.28 g/cm^3 compared with 2.44, 2.43 and 2.45 respectively for fractions of similar density from the other ashes) and the correspondingly lower content of ash.

3.1.5.3 Fractions of density 2.74 - 2.5 g/cm^3

For all ashes except the Skelton Grange, the fractions in this range of density were found to give higher strengths than any others, but for most ashes the difference between these fractions and those of next lowest density was not very marked. It would be expected that the strengths of these fractions would be higher than those for the corresponding whole ashes, but in fact this was so only for the Castle Donington and Skelton Grange ashes. It was thought at first that this might be due to some effect of the bromoform used in the density separations which might have altered the nature of the surfaces of the reactive particles and reduced their reactivity, but this was tested directly by wetting a whole sample of Rye House with bromoform, evaporating it off and comparing the strength of a mortar made from the resulting product with one made from the untreated Rye House ash. No significant difference was found and it was concluded that the bromoform treatment had not affected the activities of the fractions. It seems likely that the crushing strength of the mortar made from the most active fraction of the ash is lower than that of a mortar made from the whole ash because of some difference between the packing properties of the particles of the fraction and the particles of the whole ash.

3.1.5.4 Fractions of density 2.5 - 2.1 g/cm^3

The crushing strengths of the mortars prepared from these fractions were generally only a little lower than those from the 2.74 - 2.5 fractions, except for the Rye House ash for which the fraction of lower density had much lower strength. Before this can be accepted as a conclusive statement of the relative strengths of the mortars from the fraction at the two ranges of density, several modifying factors must be taken into account. In the first place, although no actual determinations have been made of the size distributions of the particles, those in the fractions of lower density appeared to be generally larger than those in the 2.74 - 2.5 g/cm^3 fractions and hence will have lower specific surfaces; since accelerated cure tends to reflect differences in the rate of development of the strength of the mortar rather than differences in their final strengths, this would be expected to increase the relative crushing strengths of the mortar made from the fractions of higher density, and to show the lower density fractions at a disadvantage. Secondly, the lower density contains some carbon and if allowance were made for this the strength of their mortars would probably be increased, although not by a large factor. Thirdly, the mortar cubes from the fractions of lower density will have lower strengths because they contain less fly ash, and hence, since the proportions of the solid components of the mortar are fixed, less sand and lime. The effect of this on the strength is likely to be larger than that of either of the two other factors mentioned.

3.1.5.5 Fractions of density less than 2.1 g/cm^3

Mortars made from these fractions all gave crushing strengths much lower than those from the fractions of highest density. The cube densities for these mortars were very low.

3.1.6 SELF HARDENING PROPERTIES

When a p.f.ash is wetted and compacted it slowly hardens and developes a crushing strength over a period of days or weeks. This property was investigated by Thorne and Watt[12] in four Scottish ashes and particular attention was paid to the water soluble components of the ashes.

It was suggested during this investigation that both lime and calcium sulphate were active in the pozzolanic reaction. This was tested by investigating the influence of small amounts of these materials on the strength of an ash, from which all water soluble material had previously been removed by extraction with water.

Firstly, the water extracted ashes were tested by small scale methods to confirm that their self-hardening properties had been removed by the removal of the water-soluble components. This was satisfactorily confirmed and the small strengths recorded were shown to de due to traces of water soluble material still remaining in the extracted samples.

The extracted ashes were mixed with small amounts of lime as CaO, calcium sulphate as $CaSO_4.2H_2O$ and potassium sulphate as K_2SO_4, and the strengths of the products were determined by small scale tests. Each compound added was ground to a maximum particle size less than 10 microns which was comparable with the particle size of the water soluble components of the original ashes.

The effects were as follows:-

3.1.6.1 Calcium Sulphate confered some self-hardening properties either by reacting directly with the p.f.ash particles or by enhancing the effect of the traces of water soluble material still remaining in the water extracted samples.

3.1.6.2 Lime produced a hardening reaction superior to that obtained with calcium sulphate. The relative strengths of the ashes when lime was added were very different from those of the original ash. The finest ash benefited most from the lime while the next coarser ash showed worse strengths than the coarsest ashes. This is possibly explained by a low content of lime in the original ash.

3.1.6.3 When lime and calcium sulphate were both added the strengths increments were greater than the summation of the strengths when the materials were added separately.

3.1.6.4 Further experiments were carried out to test whether the action of calcium sulphate in increasing the effectiveness of additions of lime to the p.f.ash arose from its calcium content or from its sulphate content.

These results showed that potassium sulphate improved the action of lime but not so effectively as calcium sulphate. It was concluded that both the calcium and sulphate content of calcium sulphate take part in increasing the effectiveness of free lime and that the small proportions of alkaline metal sulphates present in the original ash played a part in the self hardening action.

3.1.7 REACTIVITY OF P.F.ASH

From these crushing strength experiments it is evident that there are differences between the self hardening properties of the ash which cannot be explained simply by the differences in the content, or even in the composition of the water soluble material. It is likely that differences in the chemical reactivity of the ash particles making up the ash will influence the strengths.

This was tested by the B.C.U.R.A.[4] when ash was allowed to react with a saturated solution of lime for a given period and the solid products of reactions were then extracted with hydrochloric acid. The reaction between line and p.f.ash results in the conversion, to compounds soluble in acid, of some part of the originally insoluble SiO_2, Al_2O_3 and Fe_2O_3. The amount of the soluble material produced in this way - referred to as the 'acid solubles increment' - can be estimated by normal chemical methods and used as a measure of the extent of chemical reaction with lime.

Again, it has been found that the specific surface of an ash, derived from the particle size distribution, correlates with the extent of reaction in the 'acid solubles increment' determinations.

This implies that the rate of reaction simply depends on the area the particles present for reaction and not on any differences in the inherent reactivity of the particles, arising for example from differences in chemical composition.

Deviations from a similar correlation of specific surface with crushing strengths therefore imply that the crushing strengths, under the conditions of lime addition, are not determined simply by the specific surface of the ashes but that some other factor is involved.

This may be the way in which the particles in the ash pack together and it is interesting to note that, if the 28 day strength increments of the ashes, with the additions of lime and calcium sulphate, are plotted against the products of specific surface and the mean gradient of the size distribution curve an approximately straight line is produced.

If the product of specific surface and mean gradient of the size distribution can be used as a means of taking into account differences in packing properties then the hardening properties of an ash must be related to the packing properties. This means that the 'acid solubles increment' and the packing properties of ashes appear to give the best guide to the activity of any p.f.ash.

3. Review of p.f.ash

3.2. P.f.ash as a fill material

3.2.1 ASH AS A FILL MATERIAL

Where p.f.ash can be used as a material for in-fill or as load bearing fill it will be quickly seen that larger quantities can be handled than in all of the other usages, consequently a lot of work has been put into the various aspects of compacting this material.

The low specific gravity of p.f.ash gives dry and bulk densities for compacted ash which are substantially less than those for soils normally used in road construction. Typical values of maximum dry density and optimum moisture content obtained in the B.S. Standard Compaction Test (B.S.1377) are given in Table 6.

3.2.1 TABLE (?)

TYPICAL VALUES OF MAXIMUM DRY DENSITY
AND OPTIMUM MOISTURE CONTENT FOR P.F. ASH

STATION	MAX. DRY DENSITY (lb/ft^3)	OPT. MOISTURE CONTENT (%)
BARONY	88.0	21.2
BRAEHEAD	74.2	27.0
KINCARDINE	80.0	25.0
PORTOBELLO	76.8	27.5
BOLD	86.0	20.5
AGECROFT	77.4	24.0
CHADDERTON	72.0	26.5

Ashes from different stations could be expected to have different characteristics but it has been found that samples of ash taken from a particular station at different times can have different compaction features, as shown in Table 7.

3.2.1 TABLE 7

VARIATIONS IN COMPACTION CHARACTERISTICS OF ASHES FROM THE SAME STATION

STATION	BATCH	MAX. DRY DENSITY (lbs/ft^3)	OPT. MOISTURE CONTENT (%)
BARONY	1	86.9	20.4
	2	88.8	20.6
	3	84.0	22.4
BRAEHEAD	1	69.0	33.0
	2	72.0	29.0
	3	78.0	23.5
KINCARDINE	1	78.5	23.0
	2	78.5	25.0
	3	70.5	29.5
PORTOBELLO	1	70.2	32.3
	2	78.8	25.7
	3	78.3	25.0

The compaction test procedure used for p.f.ash should be that for soils susceptible to crushing given in B.S.1377,1967, where separate samples are recommended for each moisture content investigated. If the same sample is used throughout the text, crushing of the particles can affect the value of the maximum dry density and the optimum moisture content. It should be noted that maximum dry density in the compaction test occurs at air voids percentages ranging from 5 to 15 percent. Soils normally have air voids between 1 and 5 percent at maximum dry density, therefore, a specification for compacted normal soils which limits percentage air voids in roadworks from 5 to 10 percent does not apply to p.f.ash.

Reports on the self hardening[36,37,38] characteristics of ashes tested under laboratory and field conditions show that ashes from different stations have different self-hardening properties and also that ashes sampled from the same station at different times can have different self hardening properties. This latter condition is probably related to effect of variable compactions at optimum moisture content.

Some investigations used unconfined compression tests as a measure of strength while others used triaxical compression tests to distinguish between the cohesion and friction contributions to shear strength. The results of measurements for unconfined compression strengths[36] at times up to six months indicated that only three of the nine ashes tested exhibited any marked self hardening characteristics. These three ashes attained unconfined compression strengths of about 160 lbs/in^2, 330 lbs/in^2 and 530 lbs/in^2 at six months. Four of the remaining six ashes however did not attain such high strengths at six months but acquired two to three times their initial strengths.

In a further series tested it was shown that at 28 days only one of thirteen ashes showed no strength increase while the remainder had acquited unconfirmed compression strengths of from 1.4 to 9 times the initial strength. After six months the ash with no strength increase at 28 days had increased its strength to 1.3 times its initial strength, the corresponding strengths for the remaining twelve ashes being from 1.7 to 15 times the initial strength.

At the University of Glasgow where investigations have been confined to ashes from Scottish stations, the hardening characteristics of ashes taken from the same station at different times have been found to differ.

The first series of tests at Glasgow were made on ashes from Barony, Braehead, Kincardine and Portobello station. Specimens 1½ inch diameter and 3 inches long were prepared at the maximum dry density and optimum moisture content values found from the B.S.Standard Compaction Test (B.S.1377 1961). Unconfined compression and undrained triaxical compression tests were made at intervals of times up to 3.4 years on specimens which were sealed to ensure no loss of water during curing at constant temperature.

	Ash Source											
AGE (DAYS)	BARONY			BRAEHEAD			KINCARDINE			PORTOBELLO		
	Cu	Øu	U.C.S.	Cu	Øu	U.C.S	Cu	Øu	U.C.S	Cu	Øu	U.C.S
1	11	38	45	9	34	34	14	33·5	52	13	35	50
7	29	41	127	29	39	122	14	34	53	17	41	75
28	32	42	144	32	41	140	12	35·5	47	20	43	92
91	38	42	171	35	42	157	15	35·5	58	22	43	101
182	40	42	180	39	41	171	16	37	64	24	43	111
371	42	42	189	43	40	185	18	38	74	25	43	115
749	51	45	246	45	39	189	19	40	81	25	46	124
1230	79	41	346	70	40	300	30	36	117·5	29	44·5	138.

Cu :- DENOTES COHESION (UNDRAINED) LB/IN^2

Øu :- DENOTES ANGLE OF SHEARING RESISTANCE (UNDRAINED) DEGREES

U.C.S DENOTES UNCONFINED COMPRESSION STRENGTH (LB/IN^2)

3.2.2: TABLE 8 VALUES OF COHESION, ANGLE OF SHEARING RESISTANCE AND UNCONFINED COMPRESSION STRENGTH, WITH TIME.

A summary of the values of cohesion Cu and angles of shearing resistance ϕu obtained at each time of testing is given in Table 8. The initial unconfined compression strength values were approximately 50 lbs/sq.in. in all cases and Table 9 records strengths at given ages as ratios of initial strengths.

3.2.2 COMPARISON OF UNCONFINED COMPRESSION STRENGTHS

3.2.2 TABLE (9)

Ratios of unconfined compression strengths at different times to 1 day strengths

AGE DAYS	ASH SOURCE			
	BARONY	BRAEHEAD	KINCARDINE	PORTOBELLO
1	1	1	1	1
7	2.8	3.6	1	1.5
28	3.2	4.1	0.9	1.8
91	3.8	4.6	1.1	2.0
182	4.0	5.0	1.2	2.2
371	4.2	5.4	1.4	2.3
749	5.5	5.6	1.6	2.5
1230	7.7	8.8	2.3	2.8

It can be seen that between one day and 28 days, the Barony and Braehead ashes increase by 3 to 4 times their one day strength, the Portobello ash was twice as strong while the Kincardine ash actually appears to have lost some strength.

3.2.3 SHEAR STRENGTH CHARACTERISTICS

Most of the investigations into the shear strength and self hardening characteristics of p.f.ashes have been made on specimens prepared at the values of maximum dry density and optimum moisture content found in the B.S.Standard Compaction Test. The Laboratory determined maximum dry density cannot be achieved in field compaction, where 90 percent relative compaction is closer to what can be expected.

The initial shear strength and the shear strength attained at any specific time will be affected by the density and moisture content at which the ash is compacted in the laboratory or the field.

Two series of tests were carried out in the University of Glasgow to investigate the effect of initial density and moisture content on self hardening.

In the first series ashes from five Scottish stations were used. Specimens, 1½ inches diameter and 3 inches long, were prepared at the optimum moisture content for each ash but at compactions of 85, 90, 95 and 100 percent of the maximum dry densities found in the B.S.Standard Compaction Test. Undrained trixial compression tests were carried out on the specimens at 1, 3, 7 and 28 days after preparation, to give undrained shear strength values of cohesion and angle of shearing resistance.

The Coulomb expression for shear strength is

$S = Cu + \sigma \tan \phi u$

where S = shear strength (lbs/in^2)

Cu = Cohesion (undrained) (lbs/in^2)

σ = normal pressure on plane of failure (lbs/in^2)

ϕu = angle of shearing resistance (undrained) (degrees)

To enable comparisons of shear strength to be made between the ashes and to take account of the effects of cohesion and angle shearing resistance on shear strength, the shear strength of all ashes were calculated using a value for the normal pressure, σ, of 20 lbs/in^2.

For the condition of one moisture content - the optimum moisture content - it was found that there was no consistent difference in the rate of hardening of any ash as the relative compaction was increased from 85 to 100 percent. If anything, the ashes that were initially denser displayed greater rates of self hardening.

From these tests, only a broad assessment can be made of the influence of the relative compaction on the shear strength of an ash at any time after preparation since all the ashes did not behave identically. If the shear strength at 100 percent relative compaction is taken as the datum, then the approximate shear strengths at various values of relative compaction - with samples prepared at optimum moisture content - are shown in Table 10.

3.2.3 TABLE (10)

Influence of Relative Compaction on Shear Strength

Percentage Relative Compaction	Shear strength as percentage of value at 100 percent Relative Compaction
85	60
90	75
95	90-95

A further series of tests were made on Portobello ash. Undrained triaxial compression tests were made on specimens prepared within the range of moisture content from 15 to 30 percent (optimum 27.5 percent) and range of relative compaction from 78 to 100 percent and tested at 1, 7 and 28 days.

The general conclusions to be drawn from these tests were that for the ash compacted to a given dry density, slightly higher initial shear strengths were obtained for the lower moisture contents.

Also the ash compacted to a given dry density a greater rate of self hardening occurred as the value of the initial moisture content increased, e.g. for an ash at 100 percent relative compaction the increase in shear strength at 28 days was 4 lbs/in^2 at a moisture content of 15 percent as against 22 lbs/in^2 at a moisture content of 30 percent.

3.2.4 FIELD TRIALS ON A P.F.ASH EMBANKMENT

The laboratory results of the influence of relative compaction and preparation moisture content on self hardening characteristics can be compared with the results from a trial embankment reported on by Sutherland and Finlay[37]. This embankment, which was constructed at Portobello Station, was 6 foot and 6 ins high and had a top area of 60 ft by 25 ft. The material used was hopper ash which was brought to the appropriate moisture content at the station before placing. Compaction was by 17½ cwt and 2 ton vibrating rollers, and tests for dry density and moisture content were made at 24 control areas for each of the nine compacted layers making up the finished height of the embankment. The change in shear strength of the ash with time was investigated by taking samples through the depth of the embankment and submitting them to undrained triaxial compression tests. The tests were carried out at construction and at 37, 144, 550 and 1171 days after construction.

A plot of the dry densities and moisture content of the 216 samples taken during construction indicated that the average relative compaction of all the samples was 86.5 percent of the maximum dry density obtained from the B.S.Standard compaction test. The average moisture content was 26.1 percent against the optimum value of 28.9 percent, and the average density was 63.9 lbs/cu.ft.

The average shear strength of the field samples, which had an average relative compaction of 86.5 percent was about 65 percent of the value corresponding to 100 percent compaction and this average percentage applied to the results obtained during the complete test period of 3.2 years.

Both field and laboratory samples nearly doubled in shear strength in the 3.2 years, about 50 percent of the increase in strength occurring within the first month.

C.B.R. Tests made on the surface of the embankment showed an increase from 16 percent at one week after construction to 38 percent in nine months despite the fact that the average moisture content had increased from 26.9 to 38 percent in the same period.

The average percentage air voids obtained at the field embankment was 25.4 percent. The Ministry of Transport type of specification for compaction control calls for not greater than 10% air voids in general embankment construction and not greater than 5 percent air voids in the top 2 feet of the embankment. The normal air voids criterion does not therefore apply to p.f.ash and this is demonstrated by the relatively high shear strength obtained with p.f.ash even at apparently excessive air void values. For the Portobello ash used in the embankment 100 percent relative compaction occurred at about 10 percent air voids.

3.2.5 COHESION AND ANGLE OF SHEARING RESISTANCE.

Further tests[34] carried out on freshly compacted p.f. ashes gave apparent cohesions in the range 4-10 lbs/in^2 and the angle of shearing resistance in the range 28°- 35° with mean values being of the order of $Cu = 6$ lbs/sq in and $\phi u = 33^{\circ}$. Professor Raymond has found that for almost every ash that he has tested these parametres have increased with time to a greater or lesser degree. The range of values of the apparent cohesions for age hardening specimens is much greater than at zero time reflecting the differing pozzolanic reactivity of different ashes. From tests it has been observed that the strength at any given time shows marked variations between ashes and that the pattern of gain in strength appeared to vary. However, significant gains in strength were noted throughout these tests.

Compacted partially saturated p.f.ash used to support structural loads will thus be in the weakest condition immediately after laying. In many practical applications the interval between laying and load bearing will be sufficiently long to allow appreciable hardening to take place, but in other cases immediate strength forms an important though conservative design condition. The results discussed above and most reported data on p.f.ash properties relate to specimens made up at optimum moisture content and compacted to standard maximum dry density.

Problems of compacting are discussed later but it is confirmed that even with very careful control the Proctor maximum dry density is not achieved in the field, and a figure of 90 percent of this value is a more realistic one.

Systematic studies on the effect of relative compaction suggest that so far as immediate strength is concerned the apparent cohesions of specimens made up at densities which are 90 percent of the maximum are about two thirds the values obtained on the denser specimens; the angle of shearing resistance is reduced by about one fifth.

3.2.6 COMPACTION OF P.F.ASH IN THE FIELD

Since the shear strength of any given p.f.ash is related to the state of compaction, correct handling in the field is of particular importance when ash is used as a structural fill.

Field research and site experience during recent years[33] have shown the following types of plant to be suitable for compacting p.f.ashes:

3.2.6.1 tandem vibrating roller with a minimum dead weight of 17 cwt.

3.2.6.2 towed vibrating roller with a minimum dead weight of 30 cwt.

3.2.6.3 pneumatic tyred rollers

3.2.6.3 trench impact rammers with large shoes.

Large, medium and even small smooth wheeled rollers have not in general given good performances on fine p.f.ash because the material tends to form a wave in front of the forward roll which finally brings the roller to a standstill, and Sheepsfoot rollers tend to overstress and excessively disrupt the rolled surface. Prior to compaction the p.f.ash must be spread in thin layers and given an initial compaction with the spreading plant. Site experience has shown that the flat tracked spreading plant gives a very good surface on which the compaction plant can operate.

Naturally, the type and number of units of equipment employed on any one job will depend on the daily quantity of p.f.ash supplied to the site. In the following examples, however, good compaction was achieved using the actual combination quoted.

3.2.6.5 Confined areas - e.g. wedge fill behind bridge abutments

Approx. 300 loose cu yds of p.f.ash per day	Spreading - Drott skid shovel Compaction - 1 No.Vibroll 32RD tandem vibrating roller. Allam impact rammer or similar for compaction adjacent to the vertical filter drain.
Approx. 500 loose cu yds of p.f.ash per day	Spreading - As above but 2 No vibrating rollers required.

3.2.6.6 Open areas e.g. large embankments

Approx. 3000 loose cu yds of p.f.ash per day	Spreading - 1 No.Caterpillar D8 bulldozer Compaction - 2 No.Caterpillar 955 Traxcavators, towing vibroll 54T vibrating rollers. 1 No.Caterpillar D4 bulldozer towing a 10 ton Pullen wobbly wheel roller.

On other sites Vibroll 72T vibrating rollers have been towed by smaller plant such as D4 bulldozers, County Crawler tractors and wheeled tractors. For estimating purposes 1½ loose cu.yd. of p.f.ash compacts to 1 compacted cu.yd. and 1 compacted cu.yd. of p.f.ash weighs about a ton.

3.2.7 GENERAL SPECIFICATION FOR ASH AS FILL MATERIAL

When p.f.ash is to be specified for use as structural fill material the following specification has been drafted by the technical officers of the C.E.G.B. and their marketing agents as a guide.

3.2.7.1 The p.f.ash shall be supplied from approved power stations of the C.E.G.B.

3.2.7.2 Once the p.f.ash is spread, it shall be compacted immediately.

3.2.7.3 Each layer shall be such that when compacted it does not exceed 6 inches in thickness.

3.2.7.4 The minimum dry density after compaction shall be 90 percent of the mean of the maximum dry densities obtained from a number of samples by the British Standard compaction test. This may be subject to adjustment as agreed from the results of field tests.

3.2.7.5 The compaction shall be carried out by suitable approved plant to achieve the specified dry density.

The limitation of layer thickness after compaction to

6 inches follows the general standard suggested by the Ministry of Transport and the Road Research Laboratory for conventional soils. In some cases low dry densities have been directly attributable to compacting in thick layers.

3.2.8 USE OF FILTER LAYERS

When p.f.ash is used behind abutments and retaining walls it is important that provision of a drained vertical filter layer is made between the p.f.ash and the wall, as this will allow the shear strengths of the ash to develop.

When an embankment is constructed on ground having a high water table, it is advisable to put down a layer of clinker, hard core or free draining granulal fill prior to laying the p.f. ash. The layer should be thick enough to prevent the ground water rising into the p.f.ash, since when this happens proper compaction of the lower layers becomes difficult and a zone is formed, which on the evidence of in-situ tests, remains softer than the rest of the bank. Though this may be of little importance in an embankment of some thickness, it may be of significance in relatively thin banks designed to sustain structural loads.

3.2.9 ACTIVE PRESSURE ON P.F.ASH RETAINING STRUCTURES

The relatively high shear strength of compacted moistened p.f.ash together with its low bulk density when compared with other soils suggested its use as the wedge of selected filling behind earth retaining structures.

Considering the active pressure on a bridge retaining wall 20 ft high having a vertical back and supporting p.f.ash, the surface of which is horizontal. At 90% relative compaction a typical p.f.ash might have the following shear parameter:

$$\phi = 26.5 \text{ deg.}$$

$$C = 4.0 \text{ lb/sq.in.}$$

Assume the bulk density =83 lb/cu.ft. (1 ton/compacted cu.yard)

Since a filter drain will be constructed immediately adjacent to the wall, the wall adhesion Cu 0, and it is reasonable to assume that due to traffic vibration the angle of wall friction $\delta = 0$.

Then $p_{an} = Z \text{ fan}^2 (45 - (\frac{\phi}{2})) - 2 c \tan (45 - \frac{\phi}{2})$

where pan = horizontal component of active pressure at = a depth Z from the top of the wall.

Putting $Z = H = 20$ and using the values given

$$p_{an} = -83 \text{ lb/sq.ft.}$$

The negative pressure indicates that the material will be free standing and the value of the "free standing height" can be calculated for a given set of conditions.

This analysis refers to the state of stress immediately on laying. Due to increase in shear strength of p.f.ash with time, an analysis made allowing for conditions some time after laying would be even more favourable.

When the total pressure on the wall is small or negative in value the Civil Engineering Code of Practise (Earth

Retaining Structures) suggests that design be carried out on the assumption that the horizontal pressure at any depth is equal to that from a fluid having a density of 30 lb/cu.ft.

i.e. pan $=$ 30Z lb/sq.ft

This figure is possibly unduly conservative when designing walls to retain p.f.ash and in the bridge design for the M.1 extension - south section - with the sanction of the Ministry of Transport, a minimum horizontal pressure equivalent to that from a fluid with a density of 15 lb/cu.ft. has been used. In cases where an appreciable proportion of the bank surface is exposed, to permit percolation, seepage towards the drainage layer may cause additional active thrust on the wall and the code suggests that this be taken as half the full hydrostatic head to which the wall could be subject if the drainage were unable to accommodate the seepage and backed up to the full height of the wall i.e. $0.5 \gamma wH$. In this case the submerged density is used in calculating the active pressure and it may be noted that in the example given, the maximum pressure at the base of the wall allowing for seepage is 15 H lb/sq.ft.

3.2.10 FOUNDATIONS ON P.F.ASH

Compacted partially saturated p.f.ash is a material possessing both cohesion and a marked angle of shearing resistance and can be expected to have a high bearing capacity. Terzaghi's equation for the general shear failure of shallow foundations can be used to investigate the bearing capacity of strip footing founded on p.f.ash.

Ultimate bearing capacity

$$= q_f$$

$$= cN_c + \gamma \quad D_f N_q + \gamma \quad (B/2) \; N_\gamma$$

Where N_c, N_q and N are parameters dependent on the angle of shearing resistance of the soil

B = width of footing

Df = depth of footing

Designing again for p.f.ash immediately after laying at 90 percent relative compaction and assuming a 3 ft wide footing founded at 3 foot below the surface we have:-

$C = 4$ lb/sq.in $\quad \phi = 26.5$ deg

$\gamma = 83$ lb/cu.ft $\quad$ Df $= 3$ feet

B = 3 feet

Using tabulated values of the bearing capacity coefficients:-

$$\text{Mean } q_f = 4 \times 144 \times 28 \quad 83 \times 3 \times 14 \quad 83 \times \tfrac{3}{2} \times 12 \text{ lb/sq.ft}$$

$$= 7.2 \quad + \quad 1.55 + 0.67 \text{ tons/sq.ft}$$

$$= 9.42 \text{ tons/sq.ft}$$

Using a factor of safety at 3 this gives a safe bearing capacity of 3.15 ton/sq ft and this value can again be expected to increase with time. It would appear reasonable therefore to design narrow footings founded on thick beds of well compacted p.f.ash to carry design loads of the order of 3 tons/sq ft without risk of undue settlement.

3. Review of p.f.ash

3.3 P.f.ash in concrete

3.3.1 P.F.ASH IN CONCRETE

A pozzolan is defined as a substance which has no cementing property of its own but develops cementitious properties with lime and water. The word pozzolan is derived from the town of Pozzuoli in the Bay of Naples which was one source of highly cementitious volcanic tuff known to the ancients. The development of pozzolanas made the engineering and architectural achievements of the Romans possible, particularly such structures as the 142 ft diameter dome of the Pantheon, the massive vaults of the Colosseum and many other Roman buildings. The remarkable state of preservation of these buildings demonstrates the effectiveness of the material employed. The ability of these pozzolan - lime mixtures to harden under water was also well known to the Romans and their extensive harbour-works, still remaining undersea, testify to the resistance of these materials to aggressive waters. P.f.ash is regarded as a pozzolan.

The pozzolanic reaction is very temperature sensitive, and a temperature rise from 12°C to 25°C can increase the tensile strength of lime pozzolana[11], autoclaving of pozzolanas also produces significant increases in strength.

The reactions of p.f.ash and cement stem largely from the fact that the hydration of portland cement releases considerable amounts of lime. Mixtures of p.f.ash and cement therefore undergo a twofold hardening process, one due to the cement alone and the other due to the reaction between the released lime and the p.f.ash. The second reaction proceeds more slowly than the first but continues for a considerable period; this is a characteristic of pozzolanas.

Ordinary portland cement can be regarded as consisting principally of two calcium silicates: tricalcium silicate 3 $CaO\ SiO_2$ with, generally,a smaller proportion of dicalcium silicate 2 $CaO\ SiO_2$. If it can be regarded as consisting solely of the tricalcium compound, then the hydration reaction can be expressed as:-

$$3\ CaO\ SiO_2 \quad water \quad Ca(OH)_2 \quad x\ CaO.y\ SiO_2\ aq.$$

This action does not stop when thesolution is saturated with calcium hydroxide but hydration continues and the further lime liberated by the reaction is deposited as crystals of calcium hydroxide[4]. The amount of lime so liberated is considerable and may amount to some 10 to 15 percent by weight of the anhydrous cement[12]. In addition to this, free CaO occurs in the cement before hydration, commonly to the extent of 0.5 percent, but occasionally very much higher.

The free lime present in portland cement concretes as a result of the above reactions is the source of a number of weaknesses. It makes little or no contribution to the strength of the concrete and is readily subject to chemical attack, as lime is soluble in water particularly when free CO_a is present. The presence of a pozzolana reduces the rate at which lime can be extracted and the proportion dissolved of the total lime present in the cement, owing to the combination of the free calcium hydroxide in the lime - pozzolana reaction.

3.3.2 CONCRETE CORROSION

Soluble sulphates attach concretes very readily and magnesium sulphate is particularly virulent. The alkaline metal sulphates react with both the free calcium hydroxide and the hydrated calcium aluminates. Magnesium sulphates in addition to attacking these compounds also decompose the tri and dicalcium cilicates[15]. The disruptive effect on concrete of the sulphate/calcium hydroxide reaction can be gauged from the fact that the gypsum (Ca $SO_4.2H_2O$) which is produced has more than double the solid volume of the calcium hydroxide from which it was formed[11].

The end product of magnesium sulphate attack is more complex and there is evidence that the magnesium hydroxide first formed reacts with the silica gel to form a hydrated magnesium silicate. This substance, in contrast to silica gel, has no binding power.

The favourable influence of pozzolonas on resistance to sea water and magnesium sulphate has been attributed primarily to the increased amount of silica gel that is formed when the sulphate acts not only on the hydrated silicates formed from the cement but also on those arising from the reaction of lime with the pozzolana.

The temperature effect on the cement pozzolana reaction is also of great importance. At higher temperatures lime and silica combine to form tobermorite, a mono calcium silicate hydrate ($CaO.SiO_2.H_2O$). The autoclaving process, using steam at about 11 atmospheres pressure - corresponding to a temperature of approx. 185°C - greatly accelerates this reaction which is the basis of many manufactured concrete products, particularly aerated building blocks. This treatment makes concretes almost completely resistant towards sodium and calcium sulphate and also greatly increases resistance to magnesium sulphate.

3.3.3 PHYSICAL EFFECTS

The physical effects of p.f.ash on concrete mixes are many. By virtue of its large content of spherical particles, p.f.ash is a useful workability aid[22] and fields of application include:-

Lean mixes; where the introduction of p.f.ash can be used to give a 1:20 mix the workability of a 1:7 mix without unnecessary increase in strength and this will also reduce the tendency to segregation.

Pumped concretes; where the increased workability gained from the addition of high specific surface ashes increases the distances that concrete can be pumped. At Pembroke Power Station the use of p.f.ash enabled concrete to be pumped distances of up to 1,700 feet.

A higher standard of surface finish in both precast and insitu concrete is being reported from concrete mixes which include p.f.ashes as a workability agent.

3.3.4 CEMENT REPLACEMENT

The effect of replacing part of the cement content of concrete by p.f.ash has a marginal effect on the overall density. This can be readily understood when it is realised that cement rarely exceeds 15% of the total concrete weight in mass structures. Replacement of 20% of cement by p.f.ash would cause a 3% reduction in total concrete weight. As the particle density of p.f.ash is about 70% that of cement, then the density reduction of such concrete would be around 1% by weight.

The settling and initial stages of hardening in concrete are accompanied by temperature rises. This is not normally a problem as the heat generated is dissipated quite readily, but in mass concrete structures of large dimensions, e.g. dams and thick retaining walls, the heat cannot be dispersed as quickly as it is generated. This often leads to quite large temperature rises, producing thermal stresses and dangers of cracking in fresh concrete. As the temperature rise depends on the type and quantity of cement in the mix, methods of control usually involve low heat cements.

P.f.ash assists this problem because it results in a reduction of the total cement, and it has sometimes been found that the depression in temperature rise is greater than expected from the proportion of cement reduction.

A method of designing p.f.ash concretes[24] was produced to reuse the methods of Road Note 4 for normal concretes which contains the logic necessary for a mix designer to adjust the resulting trial mixes and which was versatile in accommodating specification limits.

From the point of view of concrete strength of workability there appears to be no optimum quantity of p.f.ash nor an optimum value of (W/c)w. Economy will require the highest permissible quantity of ash whereas a specification or other considerations may limit the ash/cement ratio. Smith works on the basis that if there is no information available on the ash then the most reasonable value for cementing efficiency is 0.25. The results of trial mixes will show the actual value for the ash.

A series of tests have been carried out on ashes to discover what efficiency should be assumed in preliminary design using an unknown ash and what the range of efficiencies was likely to be.

Thus before a rational method of p.f.ash concrete design could be found it was necessary to discover the effect which the p.f.ash would have on the strength of concrete containing it. As strength is linked with water content a first series of tests was directed at discovering the effect of p.f.ash on the "effective water/cement ratio" of the concrete. This ratio is numerically equal to the water/cement ratio of a cement concrete of the same strength, at the same age as the p.f.ash-cement concrete under consideration.

3.3.5 CEMENTING EFFICIENCY

To give some basis for the comparison for the test results with known properties of the ashes used, each ash was assumed to have a 'cementing efficiency' k such that a weight

F of p.f.ash would be equivalent to a weight kF of cement. Thus for a concrete containing weights W of water, c of cement and F of ash the effective water/cement ratio is

$$(W/c)_s = \frac{W}{C+kF} = \frac{W}{C}\left[\frac{1}{1+(kF/C)}\right]$$

In a series of tests carried out at the University of Glasgow the Portland cement ranged in quality from ordinary to rapid hardening, and the aggregate used was combined washed sands and separate sizes of $\frac{3}{4}$", $\frac{1}{2}$", $\frac{3}{8}$" and $\frac{1}{4}$" crushed whinstone. The absorption of the combined materials was negligible.

The first series of tests were intended to show whether or not the factor k would be useful in measuring the effect of the presence of p.f.ash on the effective water/cement ratio of a concrete.

To calculate the value of k for each ash a control line of strength against water/cement ratio was plotted from the results of tests on control concretes containing no ash. The abscissae of these lines were effective water/cement ratios. The ordinates of these lines are the Road Research Note 4 values[26] for strength, each multiplied by a factor which makes the curve the best fit to the points plotted for the control concretes alone.

The strengths reached by concretes containing ash were then used to find the effective water/cement ratio of these concretes against the control curve. The factor k can then be calculated using the effective water/cement ratio and the mix proportions using the relationship.

$$(W/c)s = \frac{W}{C}\left[\frac{1}{1+\frac{kF}{C}}\right]$$

Using a value of 0.25 for k the effective water/cement ratio of each concrete has calculated from the above equation and the value of (W/C)s used to find design strength on the control line.

Three apparently different ashes were used in this series of tests and the details are given below. At the age of 28 days k was found to be virtually unchanged from the seven day value.

3.3.5 TABLE 11

Ash Source	Specific Surfaces*	Carbon Percent	k	No.of Mixes
Brunswick	4300	3.75	0.255	24
Hackney	5250	9.14	0.264	13
Croydon	6050	14.75	0.266	10

* sq. cm/gm by an air permeability method.

A second series of tests was carried out to include p.f.ashes with a wide range of properties and was intended to test the validity of assumptions made in deriving a practical method for use in the design of p.f.ash cement concretes.

The results of the first series of tests showed that a value of 0.25 for k might be a reasonable one on which to base a rule for the design of a p.f.ash concrete to reach a desired strength.

To allow for the effect of p.f.ash on concrete workability it was found reasonable to assume that the workabilities of a p.f.ash concrete and a normal concrete could be the same if each had the same volume ratio of cement sized particles to water, and the same volume ratio of cement sized particles plus water to total aggregate. This does not hold true for normal fine powders but is approximately true for p.f.ash probably because of the spherical nature of the particles.

3.3.6 THE DESIGN OF CONCRETE MIXES WITH P.F.ASH

The basis of the design method is set out below[24].

A choice must initially be made of the orthodox concretes. The final p.f.ash concrete will be designed to reproduce the strength of one of these and the workability characteristics of the other.

3.3.6.1 In the first concrete, strength considerations will require a water/cement ratio of (W/c)s.

3.3.6.2 In the second concrete, workability considerations will require an aggregate/cement ratio of N when the water/cement ratio is (W/c)w. It should be noted that the value chosen for (W/c)w has an effect on the optimum quantity of ash in the p.f.ash concrete. The ash quantity decreases with an increasing value of (W/c)w.

For this reason (W/c)w should be as low as possible. The suggested practical minimum value is 0.4 although the designer is free to choose any value.

The p.f.ash concrete must have the same strength as the first orthodox concrete. It will therefore have the same value of W/c)s.

3.3.6.2.A $$(W/c)s = \frac{W}{C+kF} \quad \text{i.e.} \quad W/c = (W/c)s\,(1 + (kF/c))$$

= actual weight of water to cement in p.f. ash concrete.

For the workability, the p.f.ash concrete is to be designed to have the same volume ratio as the second orthodox concrete.

In order to have equal volume ratios of water to cement and water to cement plus ash in the two concretes, then

3.3.6.2.B $$(W/c)w = \frac{W/c}{1+(3.15\ F/GC)}$$

where 3.15 is taken as the specific gravity of cement particles and G is the specific gravity of ash particles.

Substituting for W/c from equation 3.3.6.2.A. and rearranging gives the optimum ratio of F/c to be used in the p.f.ash concrete.

3.3.6.2.C $$F/c = \frac{(W/c)s-(W/c)W}{(3.15/G)\ (W/c)w-k\ (W/c)s}$$

In order to have equal volume ratios of aggregate to cement mortar and of aggregates to p.f.ash cement mortar the aggregate/dement ratio of the p.f.ash concrete is given by

$$A/c = \frac{N}{1+3.15(W/c)w}\left[1 + (3.15\ F/GC) + (3.15\ W/c)\right]$$

but from equation 3.3.6.2.B

$$1 + (3.15\ F/GC) = \frac{W/c}{(W/c)w}$$

3.3.6.2.D. i.e. $$A/c = N \frac{W/c}{(W/c)w}$$

3.3.7 DESIGN PROCEDURE

The design procedure to be followed in the design of a p.f.ash concrete is set out below; weight ratios without subscripts are those pertaining to the p.f.ash concrete.

3.3.7.1 Select (W/c)s, the water/cement ratio of an orthodox concrete of the required strength.

3.3.7.2. From a knowledge of the aggregate characteristics and behaviour decide the aggregate/cement ratio, N, which in a normal concrete of water/cement ratio (W/c)w would give the required degree of workability.

3.3.7.3 Calculate the optimum ratio of p.f.ash to cement in the p.f.ash concrete

$$F/c = \frac{(W/c)s - (W/c)w}{(3.15/G)\ (W/c)w - k\ (W/c)s}$$

For most ashes the specific gravities lie between 1.9 and 2.3 it is suggested that G be taken as 2.1. Using this value and taking (W/c)w as 0.4 and k as 0.25 the optimum ratio becomes

$$F/c = \frac{(W/c)s - 0.4}{0.6 - 0.25\ (W/c)s}$$

3.3.7.4 Calculate $W/c = (W/c)s\,(1 + 0.25\,F/C)$

3.3.7.5 Calculate for the p.f.ash concrete

$$A/c = N \frac{W/c}{(W/c)w}$$

If $(W/c)w$ is taken as 0.4 then

$$A/C = N \frac{W/C}{0.4}$$

where N is the aggregate/cement ratio of a normal concrete of water/cement ratio of 0.4.

3.3.7.6 The p.f.ash concrete mix proportions are thus

Water: p.f.ash: cement: aggregate = W/C: F/C: 1: A/C

This method of design approaches closely the conventional methods of orthodox concrete design and only the values of k appear to be in doubt. M.H.Miles of the Scientific Services Department, S.W.Region C.E.G.B. had carried out an extensive work using this method of design but could not confirm the general constancy of k values for ages up to 56 days.

Table 12 shows a significant increase between 3 and 28 days values for k.

3.3.7.6. <u>TABLE (12)</u>

VALUES OF k FOR THREE AND TWENTY EIGHT DAYS

Sample Number	Drakelow 'C'		Hams Hall C		High Marnham	
	3	28	3	28	3	28
1	0.22	0.63	0.23	0.66	0.28	0.78
2	0.17	0.34	0.26	0.33	0.26	0.40
3	0.20	0.42	0.17	0.65	0.19	0.56
4	0.17	0.11	0.28	0.52	0.25	0.28
5	0.20	0.73	0.30	0.47	0.07	0.24
6	0.17	0.48	0.19	0.51	0.27	0.52
7	0.24	0.26	0.23	0.44	0.14	0.41
8	0.17	0.27	0.30	0.44	0.29	0.39
Mean	0.19	0.40	0.24	0.50	0.22	0.45

overall mean k 3 days 0.22
" " " 28 days 0.45

This increase in k is to be expected if the 'cementing efficiency' in any way reflects pozzolanic activity. The latter is generally accepted as developing slowly at first in p.f.ash concretes but is appreciable in some cases before 28 days.

4. Materials used in laboratory work

4. MATERIALS USED IN LABORATORY WORK

The materials used during the main parts of the experimental work fell into three groups:

4.1 P.F.Ashes

4.2 Polyvinyl Acetate Emulsions

4.3 Coalescing Agents

and these are described in the following sections.

4.1 P.F.ASHES

One source of ash was used for the main sections of the report and this was the High Marnham Power Station.

Lying some ten miles west of Lincoln, High Marnham is just inside the easterly boundary of Nottinghamshire and lies on the banks of the River Trent. Coal is supplied by the North Notts Area of the National Coal Board and is transported by train.

The station is about eight years old and can be regarded as a modern coal fired power station unlike the other two sources of p.f.ash used in Sections 6.1 and 6.8 of the laboratory work.

The two other supplies of ash came from North Tees 'B' station and the ICI Power Station at Billingham. Both of these stations are in the South of Durham County with the latter station being the oldest and obviously the least efficient - judging by the combustible matter content of the three ashes.

Table 13 compares the sieve analyses and Table 14 the physical characteristics of samples taken from the three ashes used in the final

4.1 TABLE (13)

SIEVE ANALYSES OF THREE P.F.ASHES

B.S.SIEVE SIZE	PERCENTAGES PASSING		
	High Marnham	North Tees	ICI Billingham
52	100.0	100.0	100.0
72	99.94	98.4	97.8
120	99.19	86.5	90.6
240	95.09	62.7	72.0
300	93.39	55.4	67.5

4.1. TABLE (14)

PHYSICAL CHARACTERISTICS OF THREE P.F.ASHES

CHARACTERISTICS	HIGH MARNHAM	NORTH TEES	ICI BILLINGHAM
COMBUSTIBLE MATTER	1.0%	5.5%	16.1%
SPECIFIC GRAVITY	2.36	2.09	2.05
SPECIFIC SURFACE Gms/cm^2	6050	6550	6330

The emphasis of modern power stations is on the efficiency of combustion and so the trend is towards the production of a finer ash with a consequently lower conbustible matter content. This is because a greater burning efficiency, for a minimum period in the combustion chamber, is achieved by obtaining the maximum surface area per unit weight of fuel.

Improved methods of grinding or pulverising the coal have resulted in improved burning efficiency and it is probably now possible to gauge the approximate age of the station by an inspection of the ash produced.

4.2 POLYVINYL ACETATE EMULSION

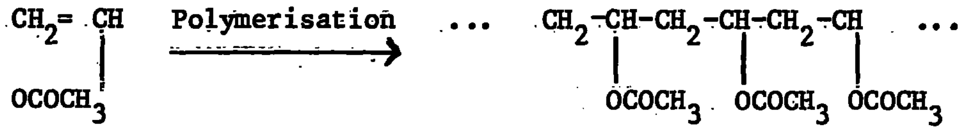
Polyvinyl Acetate Emulsions are dispersions of finely divided particles of polyvinyl acetate-(PVA)-in water. The term "emulsion" which normally refers to a dispersion of one liquid in another, is therefore incorrectly applied because the particles of PVA are in a semi-solid state.

The designation "latex" is sometimes used in describing PVA emulsion since they bear a superficial resemblance to the aqueous dispersions of natural and synthetic rubbers.

However, on account of its wide acceptance, the term "emulsion" has been adopted.

PVA is made from vinyl acetate, a colourless volatile liquid which is usually obtained either by reacting acetylene with acetic acid, or acetaldehyde with acetic anhydride.

Vinyl Acetate, $CH_2 = CHOCOCH_3$, contains the unsaturated vinyl group, $CH_2 = CH -$ which renders it highly reactive and capable of combining with itself or other vinyl compounds. When in the form of single molecules, vinyl acetate is referred to as a monomer; combinations of two or three molecules are known as dimers or trimers respectively, while the term polymer denotes a macromolecule e.g. polyvinyl acetate, which is composed of many monomer units bonded together.



$$\underset{OCOCH_3}{CH_2 = \underset{|}{CH}} \xrightarrow{\text{Polymerisation}} \ldots\ CH_2-\underset{OCOCH_3}{\underset{|}{CH}}-CH_2-\underset{OCOCH_3}{\underset{|}{CH}}-CH_2-\underset{OCOCH_3}{\underset{|}{CH}}\ \ldots$$

Vinyl Acetate Polyvinyl Acetate

The monomer to polymer transformation is known as a polymarisation and can occur to different degrees, thus leading to the concept of degree of polymerisation.

Vinyl acetate and most other vinyl monomers polymerise to form chain-like macromolecules; as the number of linked monomer units grows, so the molecular weight increases and a gradual transition occurs from the liquid to the solid state.

Since PVA is obtained by the polymerisation of only one monomer ie vinyl acetate, it is classed as a homopolymer. Two different monomers may be polymerised together when they either form two separate homopolymers, a copolymer, or a mixture of all three. A copolymer contains repeating units of both monomers arranged either at random or in definite sequence; it is important to note that its physical and chemical characteristics may differ widely from those of a mixture of the corresponding homopolymers.

The basic reason for not using synthetic resins in the stabilising of p.f. ashes has been the alkalinity of ashes as synthetic resins tend to break down under hydrolysis in an alkaline environment.

4.2.1 RECENT IMPROVEMENT OF PVA

This has been so until a most recent development in the paint industry led to the production of a PVA that resists alkaline hydrolysis, due to the presence of an additive called "Veo-Va 911". Veo-Va 911 is a vinyl ester of a mixture of synthetic saturated tertiary carboxylic acids containing 9-11 carbon atoms.

This ester is very resistant to alkaline hydrolysis and when copolymerised with vinyl acetate it greatly reduces the hydrolysis of the acetate groups.

The PVA finally selected for this work was produced by the Pontyclua Chemical Company Ltd. and referred to as Pontyclun 459 (P 459).

Pontyclun 459 is internally plasticised to the equivalent of 10% dibutyl phthalate on total solids, and in certain applications additional plasticisation with dibutyl phthalate may be necessary while the use of a coalescing agents ensures good film coalescence under adverse conditions.

P459 is a colliod-free vinyl acetate terpolymer emulsion containing the Veo-Va 911 previously discussed and has a total solids content of 55% with a pH value of 4.5 - 6.5.

It was possible to carry out the experiments written up in the following pages as the Pontyclun Chemical Company Ltd undertook to supply all the P459 required, along with a lot of technical assistance. Both the material and technical assistance were most gratefully received.

4.3 COALESCING AGENTS

The two coalescing agents investigated were Hexylene Glycol and Butyl Dioxitol Acetate.

4.3.1 HEXYLENE GLYCOL

Hexylene Glycol is a colourless moderately hygroscopic, dihydric alcohol of mild, sweetish odour.

Outstanding among its properties, which are similar to those of low molecular weight glycols, is its exceptional solvent power for a wide range of materials. Hexylene Glycol is a relatively long chain compound which is compatible with aliphatic and aromatic hydrocarbons. The presence of the two hydroxyl groups in the molecule results in misc ibility with polar substances such as water, fatty acids and the lower alcohols.

4.3.2 BUTYL DIOXITOL ACETATE

Butyl Dioxitol Acetate is a solvent for cellulose nitrate,ester, gum, polyvinyl acetate homo and Co-polymers; soluble vinyl co-polymers, polyester resins used in polyurethane coatings and some alkyds. Its primary use is as a coalescing agent in decorative emulsion paints, particularly polyvinyl acetate and acrylate copolymers, where the addition of approx. 1% weight of solvent to the total weight of the paint is recommended by resin manufacturers. As a slow evaporating solvent Butyl Dioxitol Acetate is also useful in certain printing units and "high bake" enamels and in specialised film coating emulsion formulations.

4.3.3 USE IN LABORATORY WORK

After initial experiments with both agents it was possible to eliminate Butyl Dioxitol Acetate. However Hexylene Glycol was used extensively and successfully through the second part of the series of experiments that are recorded in section 6.

5. Outline of investigation

5.1 OUTLINE OF INVESTIGATION

In order to gain some experience with p.f. ash a brief look was taken at one of the tried uses of this material. Cement replacement in concrete mixes provided the most suitable application and this formed the first part of the investigation.

The largest part of the work carried out in the laboratory was on the stabilising effects of polyvinyl acetate emulsion - PVA - on p.f. ashes, following the recent improvements made with PVA outlined in section 4.2.1.

The early stages of the stabilisation investigation concentrated on obtaining maximum compaction of the ash samples with varying percentages of PVA, and the cylinders were treated in a number of ways before being subjected to unconfined compression tests.

The tendency of the first groups of results showed that the oven cured samples gave higher compressive strengths than the samples stored in polythene bags, and so it was decided that a study should be made of the material produced at optimum moisture content and cured in a drying oven.

Variations of additive percentages at maximum compaction were investigated with fixed periods of oven cure; this led to variations of oven cure with variations of pretreatment of the samples prior to cure.

Two coalescing agents were used to reduce the amounts of PVA at the optimum conditions, and finally a comparison of the material was made using samples prepared from three grades of p.f. ash mixed under specified conditions.

6. LABORATORY WORK

6.1 P.F. ASH IN CONCRETE

6.1 P.F. ASH IN CONCRETE

The largest part of the laboratory work was spent in attempting to find a different approach to p.f. ash stabilisation, but a brief look was taken at one of the known uses of p.f. ash to fain some experience with the material under consideration.

Cement replacement was taken as the best method of starting the project and the first part of section 6 deals with this aspect of the work.

The basic concrete mix was as follows :

⅜" Concrete Aggregate	1950 gms
Concrete Sand	1050 gms
Cement	750 gms
Water	337.5 c.c
A/C ratio	4-1
W/C ratio	0.45

and blue circle ferrocrete was used throughout this series of tests.

Further it was decided that rather than carry out a series of cement replacements it would be better if a few variations of addmix could be used.

The variations were limited to the addition of hydrated lime and to the mixing of a plasticiser in the water. Plaz was chosen as the plasticizer and ordinary hydrated lime was used, both being examples of materials readily available from builders merchants.

For these tests p.f. ash was collected from North Tees and I.C.I. Billingham Power Stations and it had been hoped that a third sample could be collected from Blythe, but this was not possible.

The size analysis of North Tees and I.C.I. Billingham ash can be seen in Table 13 and Table 14, Section 4.1. The latter ash has a considerably higher carbon content than the former.

Details of the mix variations and the reference numbers have been recorded in Table 15 below :

6.1 TABLE (15)

DETAILS OF MIXES

Cube Ref.	Details of Variations to Basic Mix
T1-T2	Basic Mix
T11-T14	20% replacement of cement by p.f.ash
T21-T24	20% replacement of cement by p.f.ash + 10% ash weight of hydrated lime.
T31-T34	20% replacement of cement by p.f.ash + 5 parts per 1,000 of Plaz in water.
T41-T44	40% replacement of cement by p.f.ash + 10% ash weight of hydrated lime.
T51-T54	50% replacement of cement byo.f.ash + 10% ash weight of hydrated lime.

4" cubes were used throughout this series of tests and the 28 day test results are given in Tables 16, 17 and 18 starting with the orthodox mix results.

6.1 TABLE (16)

DETAILS OF ORTHODOX CONCRETE MIX

Cube Ref.	Age at Test	WT. Grams	Density lbs/cu.ft.	Crushing Load - tons	Crushing Strength lbs/in^2
T1	28 days	2717	161	57.0	8000
T2	"	2741	161	58.75	8240

6.1 TABLE (17)

DETAILS OF I.C.I. ASH CONCRETE

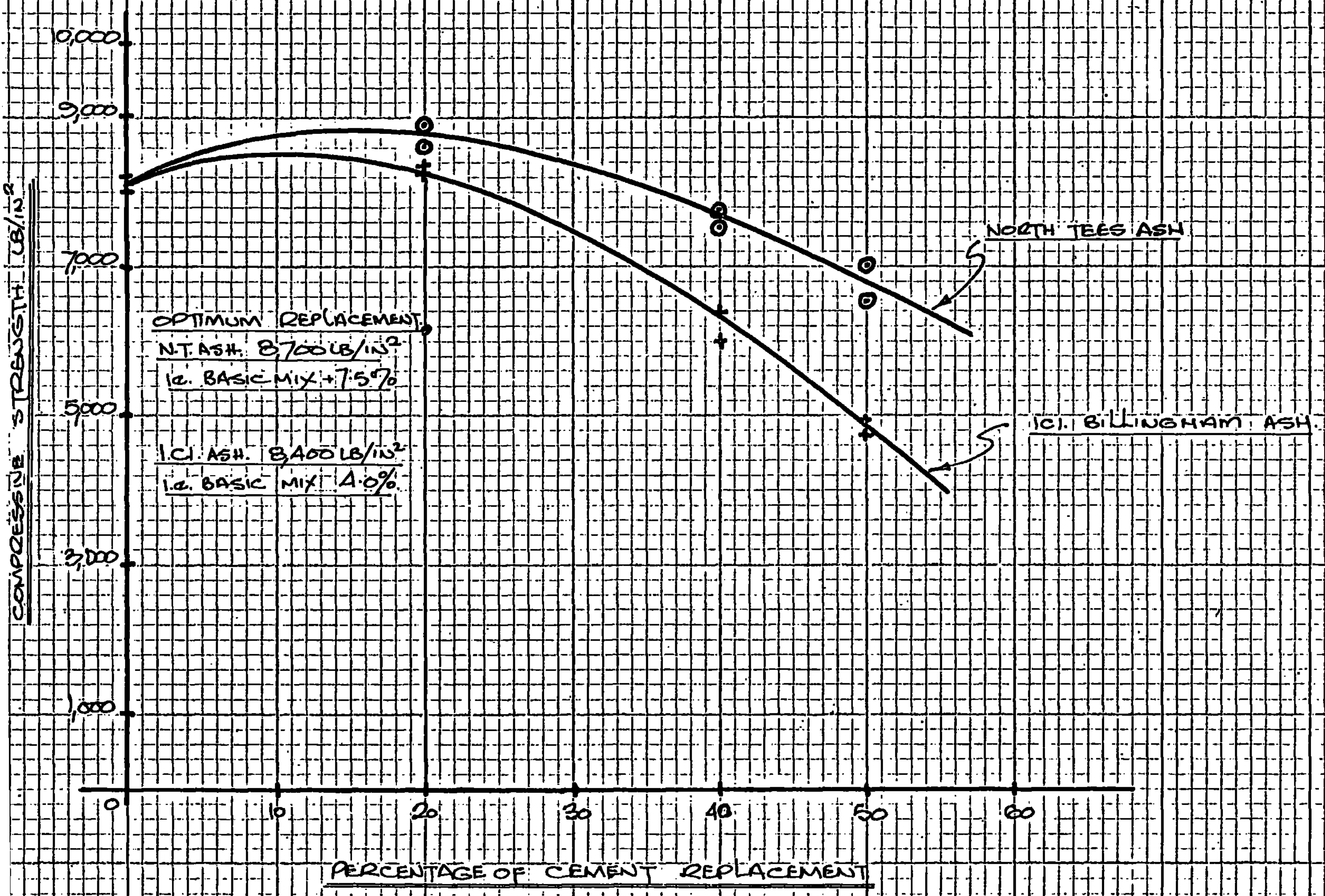
Cube Ref.	Age at Test	WT. Grams	Density lbs/cu.ft.	Crushing Load - Tons	Crushing Strength lbs/in^2
T11	28 days	2700	160	43.5	6100
T12	"	2736	163	41.0	5750
T21	28 days	2736	163	60	8430
T22	"	2733	163	59.5	8350
T31	28 days	2745	163	62.5	8750
T32	"	2757	164	63.5	8900
T41	28 days	2708	161	43.5	6100
T42	"	2691	160	46.0	6450
T51	28 days	2629	157	35.0	4900
T52	"	2689	160	34.0	4770

6.1. TABLE (18).

DETAILS OF NORTH TEES ASH CONCRETE

Cube Ref.	Age at Test	Wt Grams	Density lbs/cu.ft.	Crushing Load - Tons	Crushing Strength lbs/in^2
T13	28 days	2735	163	55.5	7800
T14	"	2678	160	54.75	7650
T23	28 days	2765	165	63.5	8900
T24	"	2745	163	61.0	8550
T33	28 days	2758	164	64.5	9050
T34	"	2714	161	67.0	9400
T43	28 days	2726	163	55.0	7710
T44	"	2679	163	53.5	7500
T53	28 days	2698	161	47.0	6600
T54	"	2715	161	50.0	7000

GRAPH N° I
NORTH TEES GAS
AND I.C.I. ASH USED FOR
CEMENT REPLACEMENTS
TABLES 16, 17 & 18



OPTIMUM REPLACEMENT
N.T. ASH. 8,700 LB/IN²
i.e. BASIC MIX + 7·5%

I.C.I. ASH. 8,400 LB/IN²
i.e. BASIC MIX 4·0%

6. Laboratory work

6.2. Investigation of Dry Density

6.2. INVESTIGATION OF DRY DENSITY

The main part of the work carried out in the laboratory was on investigation of the stabilising effect of the selected polyvinyl acetate emulsion under varying conditions of cure and with the addition of coalescing agents.

The p.f.ash used during this series of tests came from the High Marnham Power Station and, as a number of different samples were used, it was ensured that each group of tests were carried out with ash from individual samples. Compliance was also made with the restrictions of B.S.1377. 1967 as outlined in 3.2.1.

The ash was initially regarded as a cohesive soil and a standard method of testing was used to determine the maximum compaction at optimum moisture content. The dry densities were compared using differing percentages of the emulsion.

The test used throughout this work was based on the standard Proctor Test, and the main differences were that a 2 inch diameter and 3 inch deep mould was used with compaction being carried out using a ½ inch diameter bar 18 inches long. The ash was compacted in three equal layers and each layer received 30 blows with the mild steel rod as rammer. A blow was defined as one tamp with the mild steel bar "dropped" from about three inches above the layer with a small amount of force being used to assist compaction of the sample. The mould was filled with ash as described above and, after compaction, was carefully struck off level with the top of the mould.

The Proctor Test was modified in this way to try and make most use of the amounts of p.f.ash that could be conveniently transported, and, whereas it might not exactly correspond to Proctor Test results, it was carefully maintained as a standard form of testing.

Throughout these series of tests the moisture content has been determined considering the total moisture as the amount of water and polyvinyl acetate emulsion, with the moisture contents and emulsion dilutions being expressed as percentages. Emulsion dilutions are expressed as a percentage of the total moisture.

Dry densities were calculated according to the formulae:-

6.2.A $$\gamma = \frac{W}{V}$$

6.2.B $$\gamma_D = \frac{Ws}{V} = \frac{\gamma}{1+m}$$

Where γ = Bulk Density

γ_D = Dry Density

W = Total Weight of sample

V = Volume of sample

m = Moisture content

Using equations 6.2.A and 6.2.B for the moisture contents of 15% and 30% in table 20.

<u>15%</u>

$$\gamma = \frac{100}{155.5}$$

$$= 1.215 \text{ gms/cc}$$

$$\gamma_D = \frac{1.215}{1+0.15}$$

$$= 1.06 \text{ gms/cc} \quad (66\text{lbs/cu.ft})$$

<u>30%</u>

$$\gamma = \frac{234}{155.5}$$

$$= 1.505 \text{ gms/cc}$$

$$\gamma_D = \frac{1.505}{1+0.30}$$

$$= 1.16 \text{ gms/cc} \quad (72 \text{ lbs/cu.ft})$$

6.2 TABLE 19

DETAILS OF MIXES.

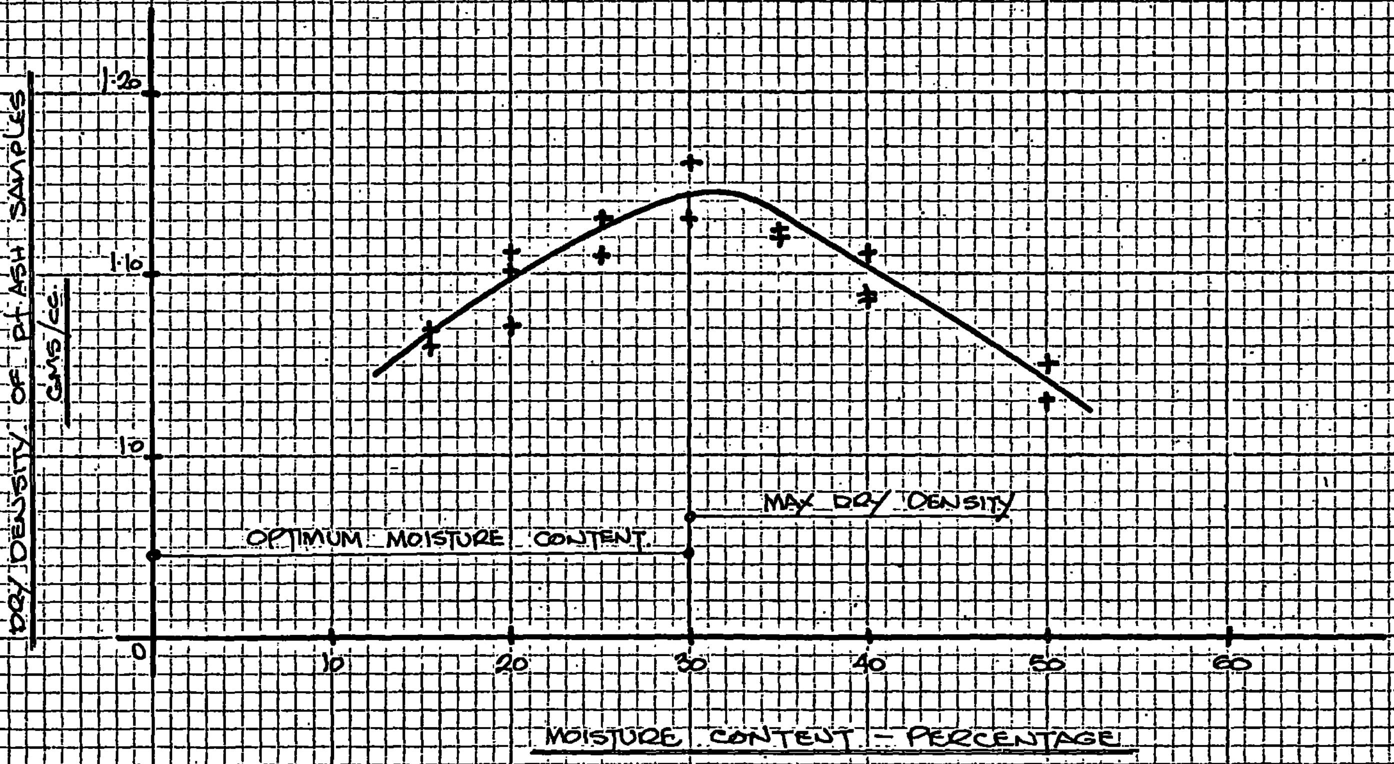
P459 %	M/C %	P.F.ASH Gms	WATER & P459 cc	WATER cc	P459 cc
10	15	1000	150	135	15
10	20	1000	200	180	20
10	25	1000	250	225	25
10	30	1000	300	270	30
10	35	1000	350	315	35
10	40	1000	400	360	40
10	50	1000	500	450	50

6.2 TABLE 20

DETAILS OF SAMPLES.

REF NO.	P459 %	M/C %	WET WT Gms	D.D. Gms/cc
200	10	15	188	1.05
201	10	15	190	1.07
202	10	15	189	1.06
203	10	20	207	1.11
204	10	20	200	1.07
205	10	20	205	1.10
206	10	25	220	1.13
207	10	25	216	1.11
208	10	30	234	1.16
209	10	30	228	1.13
210	10	30	235	1.16
211	10	35	233	1.11
212	10	35	232	1.11
213	10	40	236	1.09
214	10	40	237	1.09
215	10	40	242	1.11
216	10	50	245	1.05
217	10	50	240	1.03

GRAPH N° II
10% P.V.A. EMULSION
TABLE 20.
HIGH MARNHAM ASH



The early and more detailed investigation of Maximum Dry Density was carried out with 10% PVA concentration and the results are shown on Graph No.II. The flat characteristic of the graph drawn indicating zero dry density does not show up the maximum Dry Density to best advantage, but if the range 1.0 to 1.2 gms/cc is plotted against moisture content there is a detectable high point at 30% moisture content.

Graph No.II was taken as a guide to the subsequent investigations of Dry Density and only those moisture contents close to optimum were investigated for 10%, 20%, and 30% concentrations of emulsion.

Results from these three emulsion concentrations were plotted on Graph No.III and again the curves have the rather flat nature; however, it was possible to select the optimum moisture contents. The increase in moisture contents at maximum Dry Density was noted as the concentrations of PVA were raised.

From these early indications it was decided to investigate the unconfined compressive strength of samples prepared at optimum moisture content, and a series of test samples were prepared for three emulsion concentrations with the moisture content values taken from Graph No.III.

6.2 TABLE 21

DETAILS OF 10% MIXES

P459 %	M/C %	P.F.ASH Gms	WATER & P459 cc	WATER cc	P459 cc
10	15	600	90	81	9
10	20	600	120	108	12
10	22½	600	135	121.5	13.5
10	25	600	150	135	15
10	30	600	180	162	18

6.2 TABLE 22

DETAILS OF 10% SAMPLES

REF NO	P459 %	M/C %	WET WT Gms	D.D. Gms/cc
401	10	15	237	1.33
402	10	15	236	1.33
403	10	15	236	1.33
404	10	20	271	1.45
405	10	20	268	1.45
406	10	20	269	1.45
407	10	22½	278	1.46
408	10	22½	277	1.46
409	10	22½	276	1.46
410	10	25	277	1.43
411	10	25	277	1.43
412	10	25	276	1.43
413	10	25	277	1.43
414	10	25	277	1.43
415	10	25	276	1.43

6.2 TABLE 23

DETAILS OF 20% MIXES

P459 %	M/C %	P.F.ASH Gms	WATER & P459 cc	WATER cc	P459 cc
20	20	600	120	96	24
20	25	600	150	120	30
20	30	600	180	144	36
20	35	600	210	168	42
20	40	600	240	192	48

6.2 TABLE 24

DETAILS OF 20% SAMPLES

REF NO	P459 %	M/C %	WET WT Gms	D.D. Gms/cc
416	20	20	253	1.35
417	20	20	253	1.35
418	20	20	251	1.34
419	20	25	267	1.37
420	20	25	265	1.37
421	20	25	270	1.38
422	20	30	269	1.33
423	20	30	268	1.33
424	20	30	267	1.32
425	20	40	253	1.16
426	20	40	252	1.16
427	20	40	254	1.16

6.2 TABLE 25

DETAILS OF 30% MIXES

P459 %	M/C %	P.F.ASH Gms	WATER & P459 cc	WATER cc	P459 cc
30	20	600	120	84	36
30	25	600	150	105	45
30	30	600	180	126	54

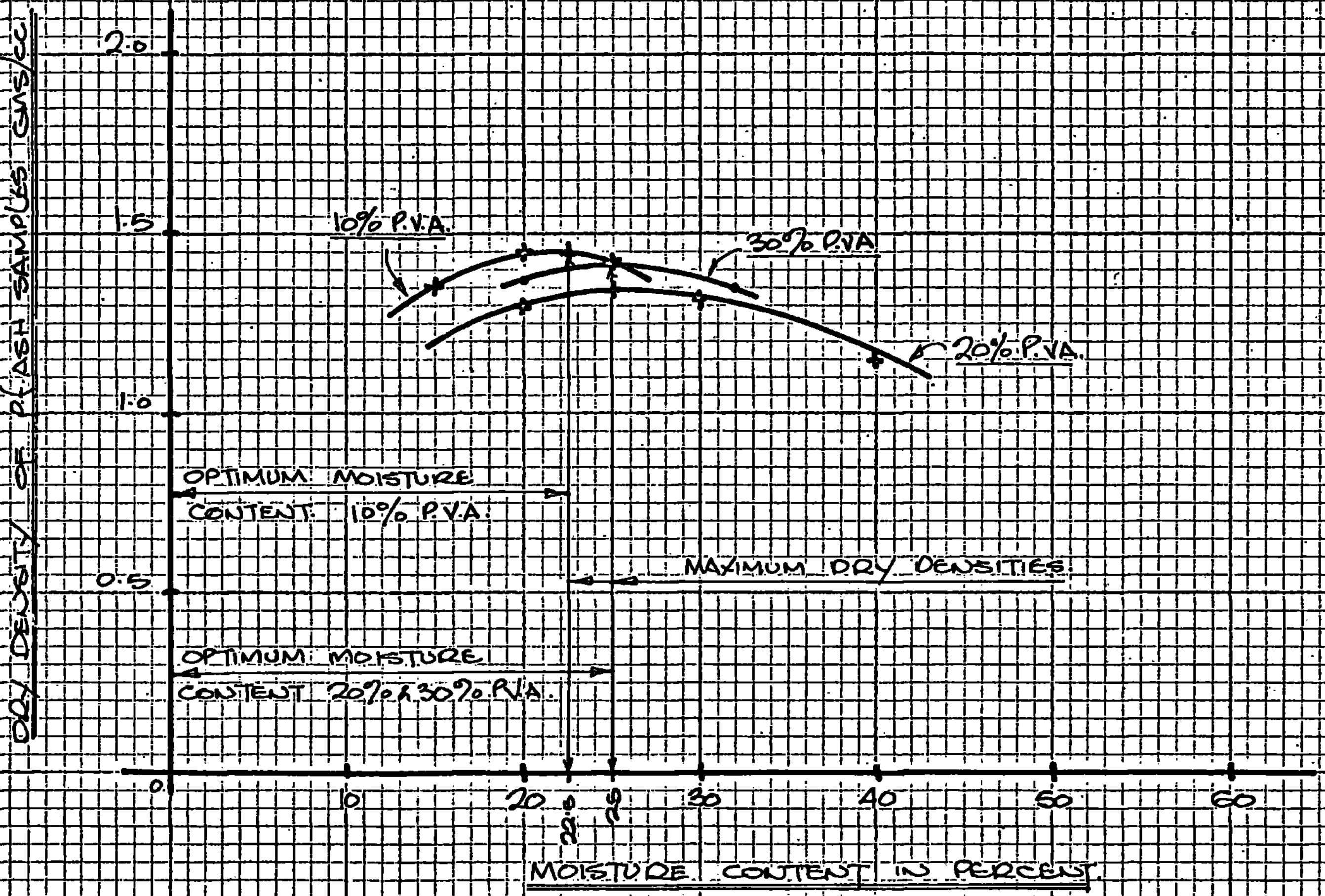
6.2 TABLE 26

DETAILS OF 30% SAMPLES

REF NO	P459 %	M/C %	WET WT. Gms	D.D. Gms/cc
428	30	20	258	1.38
429	30	20	257	1.38
430	30	20	258	1.38
431	30	25	269	1.44
432	30	25	267	1.44
433	30	25	266	1.44
434	30	30	258	1.33
435	30	30	257	1.33
436	30	30	258	1.33

GRAPH Nº III

COMPARISON OF DRY DENSITY
WITH VARIATIONS OF EMULSION
CONCENTRATIONS.
TABLE Nº 22, 24 & 26



6. Laboratory work.

6.3. Samples cured in polythene bags.

6.3 SAMPLES STORED IN POLYTHENE BAGS

Optimum Moisture contents for 10%, 20% and 30% PVA concentrations were taken from Graph II and used to investigate the unconfined compression strengths of the samples.

This group of samples were stored for varying periods in sealed polythene bags in a further attempt to follow the tests carried out on soils.

All compression tests were carried out as unconfined compression tests and were either carried out on the 10 ton Denison or in the unconfined compression test machine.

Table 27 details the three mixes used and tables 28, 29 and 30 give the wet weights and compressive stresses at the noted intervals.

Graph IV summarises results of the crushing tests at 3 days, 28 days and 3 months, and marks an important stage of the work.

It has been hoped that compressive strengths of the p.f.ash samples treated in this way would at least compare with the minimum requirement of 250 lbs/in^2 for soil cement, but the strengths obtained fell quite a long way below this value.

The shape of the samples was possibly not the most advantageous from the strength aspect but any resulting improvement factor would show no great benefit to the strength values.

Despite this low value of strength it must be noted that there was a minimal increase in strength from the 3 day to 3 month tests. This was important because, although the period cannot be regarded as a long one, the damp conditions of the sealed polythene bags did not result in the

PVA breaking down under alkaline hydrolysis.

It was thus decided that an investigation of oven drying should be carried out as an alternative form of curing, and section 6.4 deals with the oven cured samples.

6.3 TABLE 27

DETAILS OF MIXES.

P459 %	M/C %	P.F.ASH Gms	WATER & P459 cc	WATER cc	P459 cc
10	20	1000	200	180	20
20	25	1000	250	200	25
30	25	1000	250	175	75

6.3 TABLE 28

DETAILS OF SAMPLES FOR 3 DAY TEST

REF NO	P459 %	M/C %	WET WT Gms	TEST WT Gms	LOAD Tons	STRESS lbs/in^2
437	10	20	274	274		17.8
438		20	274	271		18.2
439		20	272	271		13.6
440		20	266	265		12.9
441	20	25	266	266		28.0
442		25	268	268		25.2
443		25	268	266		26.0
444		25	268	268		22.6
445	30	25	266	265		29.6
446		25	265	265		30.8
447		25	265	266		30.0
448		25	264	264		22.6

6.3 TABLE 29

DETAILS OF SAMPLES FOR 1 MONTH TEST

REF NO	P459 %	M/C %	WET WT Gms	TEST WT Gms	LOAD Tons	STRESS lbs/in^2
449	10	20	263	259		9.0
450		20	262	260		13
451		20	262	259		14
452		20	260	257		12
453	20	25	272	265		41
453		25	273	268		40
454		25	272	267		40
455		25	273	267		42
456	30	25	268	265		37
457		25	266	264		30
458		25	264	260		34
459		25	266	262		31

6.3 TABLE 30

DETAILS OF SAMPLES FOR 3 MONTH TEST

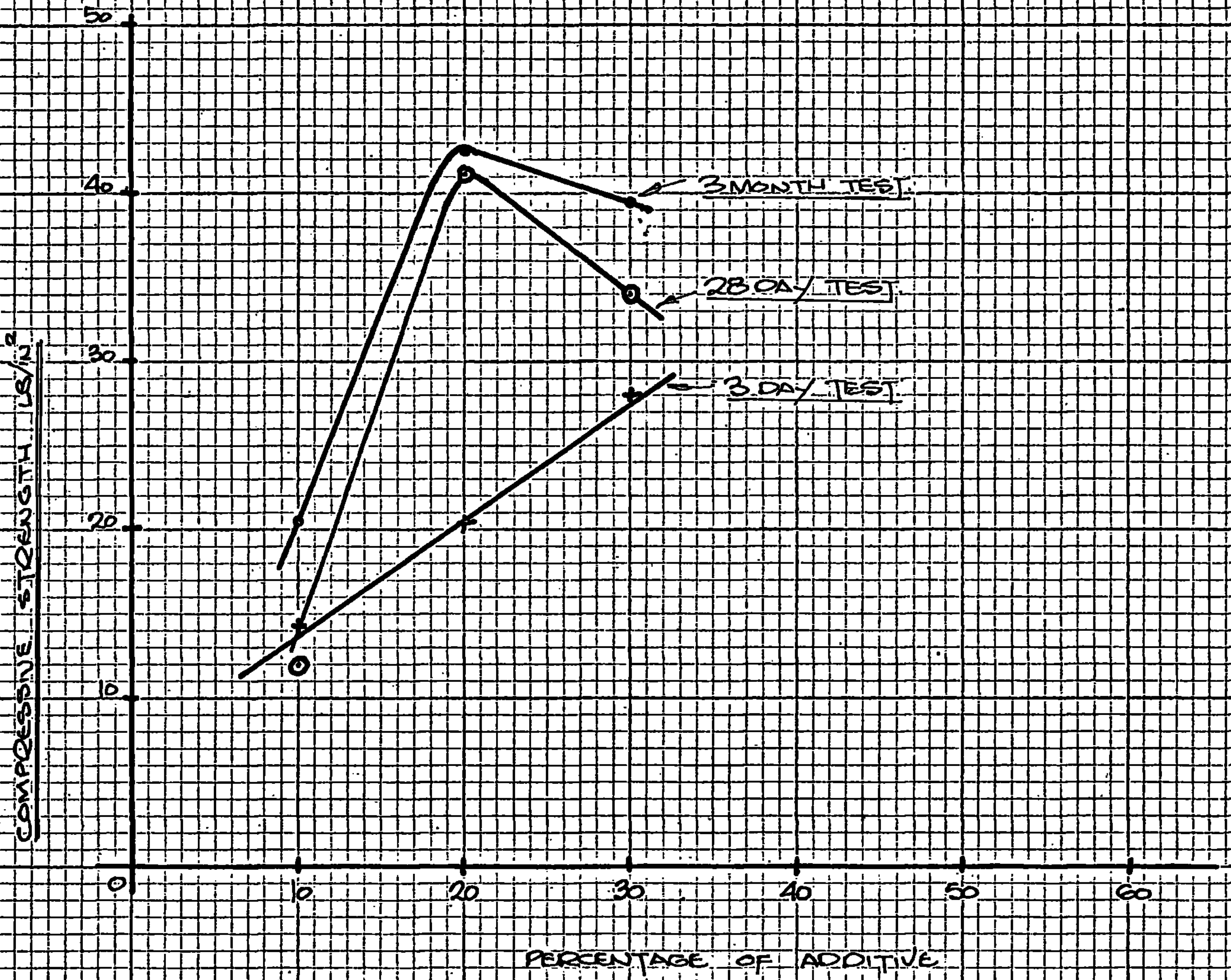
REF NO	P459 %	M/C %	WET WT Gms	TEST WT Gms	LOAD Tons	STRESS lbs/in^2
460	10	20	266	255	0.028	20
461		20	261	251	0.032	23
462		20	265	254	0.022	16
463		20	260	250	0.030	21
464	20	25	270	258	0.055	39
465		25	270	259	0.061	43
466		25	271	259	0.061	43
467		25	271	260	0.064	46
468	30	25	268	257	0.058	41
469		25	267	256	0.050	36
470		25	267	256	0.055	39
471		25	265	256	0.052	37

GRAPH No VI

TEST AGES : 3 DAYS
28 DAYS
3 MONTHS

SAMPLES STORED IN
POLYTHENE BAGS

TABLES No 28, 29 & 30.



6. Laboratory work.

6.4 Preliminary oven cure.

6.4. OVEN DRYING

The indications of Graph IV were generally encouraging despite the low strengths recorded and so the next stage was to try and improve on this aspect of the samples.

The manufacturers of P.459 suggested that some form of heat treatment on the samples at the curing stage would be advantageous. Thus Section 6.4 takes a brief look at the effects of a period of oven cure using a typical materials drying oven regulated to a temperature of 105°C ±5°C.

There was no indication of the length of time in the drying oven and so it was decided that the standard for the initial series would be 24 hours.

Table 31 details the mixes used in this section and Table 32 gives particulars of the samples. The dry weights recorded were the weights of the samples as they were taken out of the oven, but it was noted that when samples were stored for some time, before the compression test was carried out, the dry weights were checked prior to test and were found to agree generally to better than 1%.

The compression tests were all carried out on the 10 ton Denison as the strengths were above the range of the unconfined compression test machine.

The finish of the samples was generally good although the 20% samples had quite a number of surface cracks. These cracks appeared to be restricted to the surface of the samples and were only slightly in evidence on the 30% samples.

6.4 TABLE 31

DETAILS OF MIXES

P459 %	M/C %	P.F.ASH Gms	WATER & P459 cc	WATER cc	P459 cc
10	20	1000	200	180	20
20	25	1000	250	200	50
30	25	1000	250	175	75
40	25	1000	250	150	100
50	25	1000	250	125	125

6.4 TABLE 32

DETAILS OF SAMPLES FOR 24 HOUR TEST

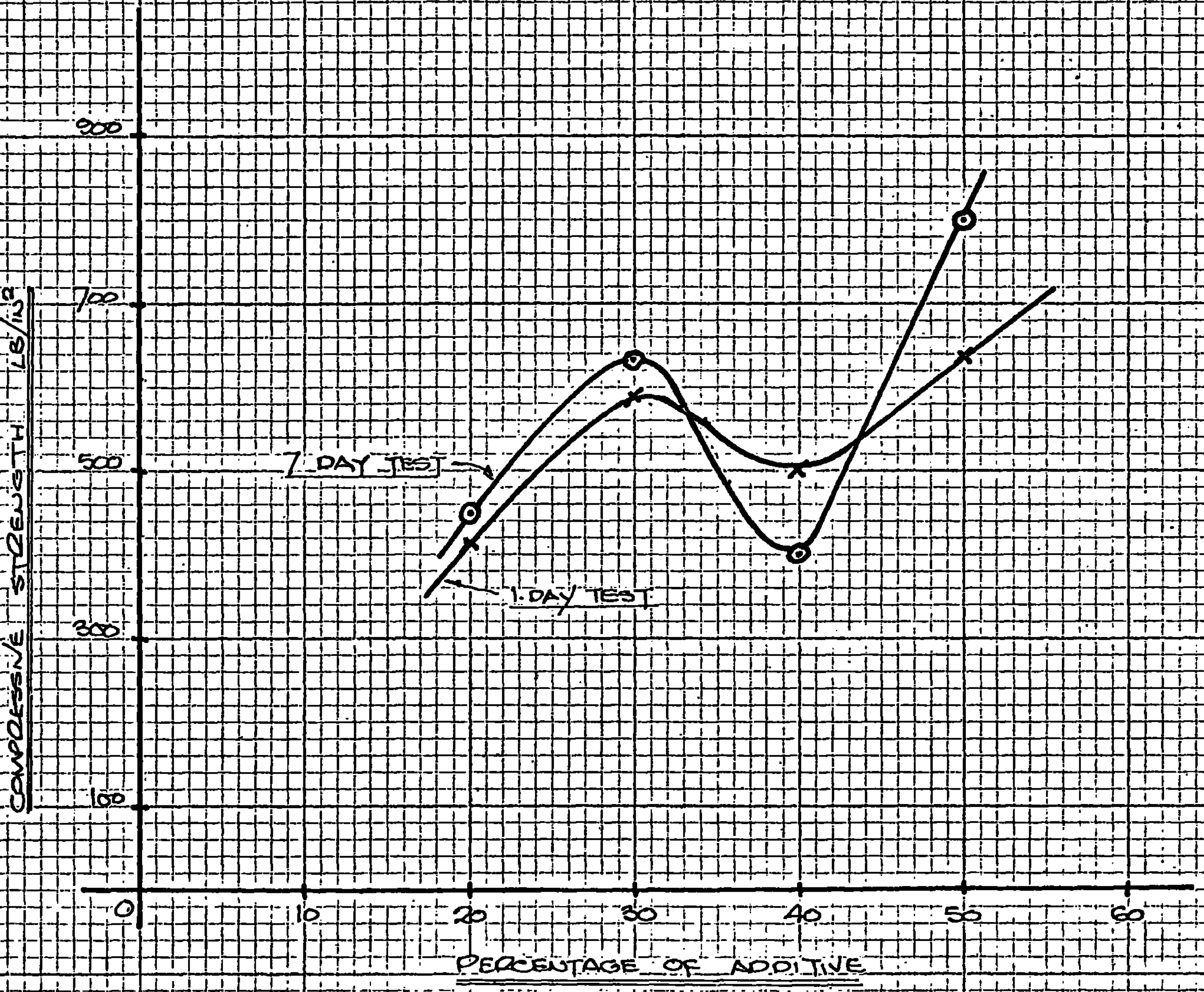
REF NO	P459 %	M/C %	WET WT Gms	DRY WT Gms	LOAD Tons	STRESS lbs/in^2
501	20	25	261	216	0.622	443
502		25	262	217	0.622	443
503		25	262	217	0.566	404
504		25	263	218	NOT TESTED	
505	30	25	264	221	0.812	578
506		25	265	224	0.768	548
507		25	266	223	0.872	623
508		25	266	223	NOT TESTED	
509	40	25	266	225	0.790	543
510		25	264	224	0.70	500
511		25	257	218	0.654	466
512		25	257	219	NOT TESTED	
513	50	25	265	226	0.965	690
514		25	265	225	0.996	710
515		25	262	220	0.690	490
516		25	257	224	NOT TESTED	

6.4 TABLE 33

DETAILS OF SAMPLES FOR 7 DAY TEST

REF NO	P459 %	M/C %	WET WT Gms	DRY WT Gms	LOAD Tons	STRESS lbs/in^2
517	20	25	265	220	0.569	406
518		25	265	220	0.646	461
519		25	265	220	0.683	487
520		25	265	220	NOT TESTED	
521	30	25	266	223	0.895	638
522		25	265	222	0.878	626
523		25	266	223	0.913	650
524		25	264	220	NOT TESTED	
525	40	25	266	225	0.689	490
526		25	266	226	0.572	407
527		25	264	220	0.454	324
528		25	259	223	NOT TESTED	
529	50	25	263	224	1.20	856
530		25	261	225	1.236	883
531		25	259	222	0.916	653
532		25	260	224	NOT TESTED	

GRAPH No V
MOISTURE CONTENT 25%
OVEN CURED - 24 HOURS
TABLES No 32 & 33.



Graph V compares the compressive strengths of the varying percentages of emulsion and as might be expected there is a general increase in strength with greater percentages of additive.

The depression on strength values at 40% emulsion is rather difficult to explain. At first it would appear to be related to some fault in mixing or in forming the cylinders, but there was no apparent difference in the physical appearance of this group of samples and it is peculiar that the effect should be more marked at the seven day test. It is possible that at 40% emulsion there was some form of interference set up in the mix, and it might be that at lower emulsion concentrations the solid PVA particles have no effect on the lubricating action of the 'water', and similarly above 40%, but in the region of 40% emulsion the solid particles, might form some kind of hindrance to compaction.

The other phases of the graph were good in that the 7 day strengths were a slight improvement on the 1 day results and the tendency was to get increased strengths with increased percentages of emulsion.

The graph would be expected to rise at a greater rate above 50% emulsion but it was decided that an upper limit would be set at this percentage additive.

The strength values for this series of around 600 lbs/in^2 showed considerable improvement on the earlier series of samples used in polythene bags, and the surface finish of the dried samples was also good although the 20% samples had surface cracks.

6. Laboratory work.

6.5 Investigation of cure.

6.5 INVESTIGATION OF CURE

The improvement in strength results using oven drying of the samples led to further investigation of the optimum conditions for curing the cylindrical samples.

The increases of strength made it worth looking again at the 10% range and this was followed with 10% increments up to 40% of P459; Table 34 shows the four mixes used throughout this section and for each mix the period of oven cure was varied in three hourly intervals from three to twenty four hours.

It was hoped that, by investigating the strength of a given mix by varying the length of cure, some indications could be seen of the way in which the samples gained a strength so that further improvements could be made.

Other variations were tried in order to find the influence of a period of air cure prior to putting the samples into the drying oven and this led to Graph XIII which indicates the rate of loss of moisture from the prepared cylinders.

6.5 TABLE 34

DETAILS OF MIXES

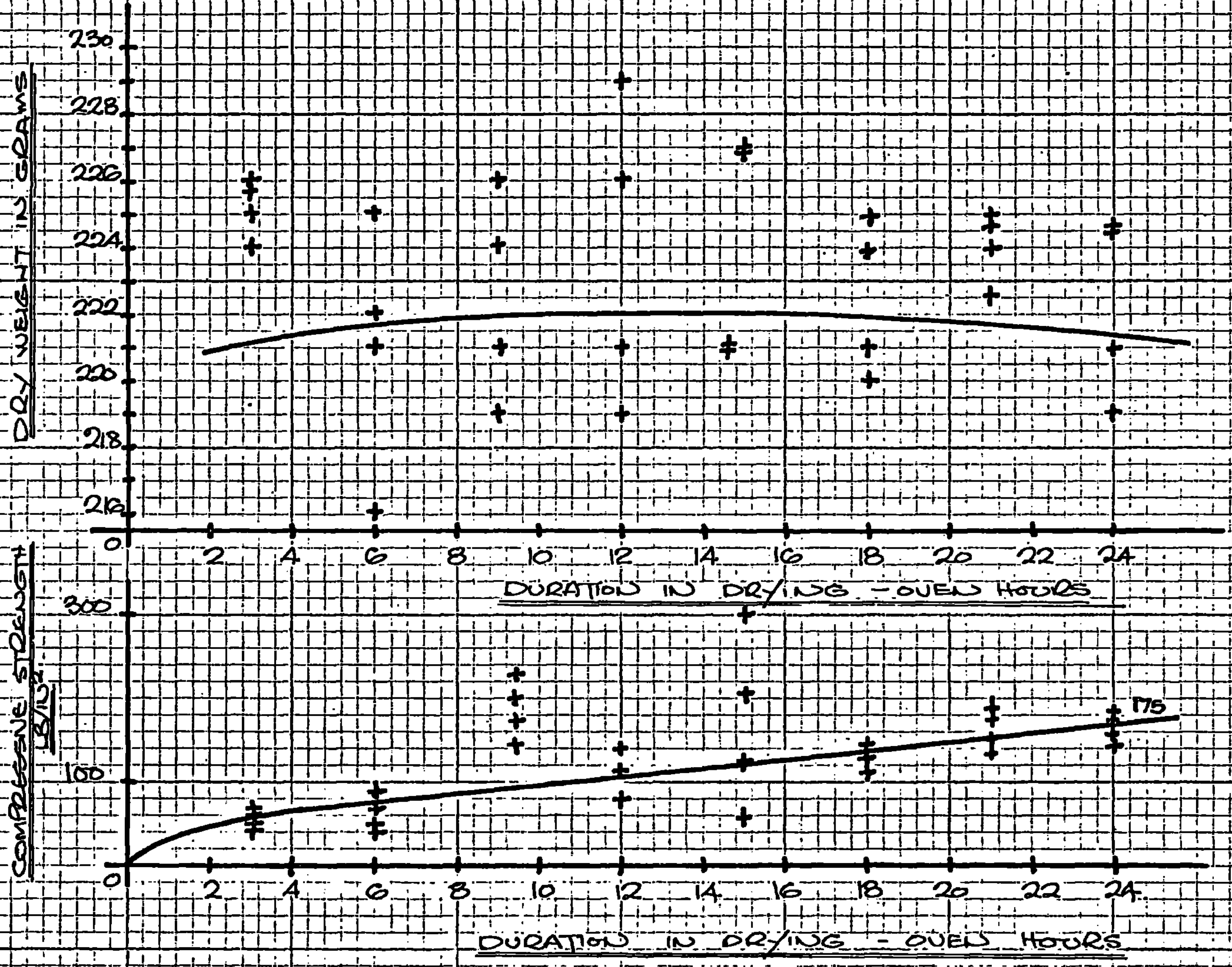
P459 %	M/C %.	P.F.ASH Gms	WATER & P459 cc	WATER cc	P459 cc
10	20	1000	200	180	20
20	20	1000	200	160	40
30	25	1000	250	175	75
40	25	1000	250	150	100

6.5 TABLE 35

DETAILS OF 10% SAMPLES

REF NO	OVEN TIME Hrs	WET WT Gms	DRY WT Gms	LOAD Tons	STRESS lbs/in^2
645	3	264	226	.092	65.6
646		263	225	.108	77.0
647		261	226	.078	55.6
648		261	224	.082	58.5
649	6	267	225	.122	87
650		263	222	.102	72.8
651		261	221	.106	75.6
652		256	216	.074	52.8
653	9	266	226	.294	210
654		264	224	.258	188
655		261	221	.208	148
656		258	219	.248	177
657	12	270	229	.142	101
658		266	226	.198	141
659		262	221	.158	113
660		258	219	.128	91
661	15	270	227	.212	297
662		269	227	.32	228
663		261	221	.188	134
664		261	221	.09	64
665	18	266	225	.091	65
666		264	224	.172	123
667		262	221	.182	130
668		260	220	.152	108
669	21	266	225	.100	135
670		265	224	.262	187
671		266	225	.208	148
672		264	223	.244	174
673	24	267	225	.188	134
674		267	225	.182	130
675		263	221	.175	125
676		260	219	.158	111

GRAPH N° VI
P.ADD. 10%
M/C 20%
COMPRESSION TEST 24 HOURS
TABLE N° 35.

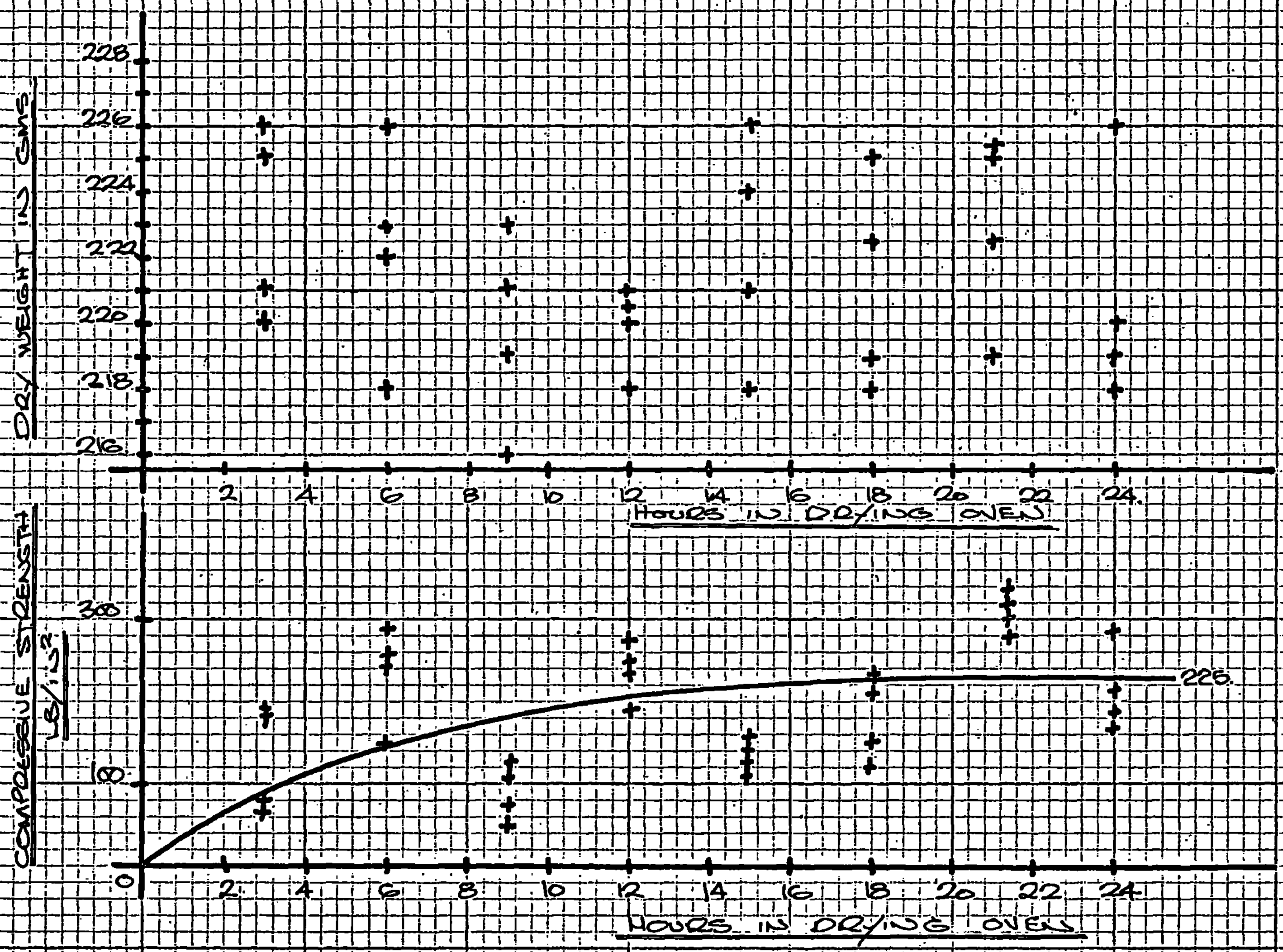


6.5 TABLE 36

DETAILS OF 20% SAMPLES

REF NO	OVEN TIME HRS	WET WT GMS	DRY WT GMS	LOAD TONS	STRESS lbs/in^2
677	3	263	226	.192	137
678		262	225	.176	127
679		256	220	.092	65.5
680		287	221	.112	84
681	6	263	226	.332	237
682		260	223	.340	243
683		250	222	.396	283
684		253	217	.218	156
685	9	258	223	.160	114
686		256	221	.158	113
687		255	219	.127	91
680		250	214	.072	51.4
689	12	257	220	.344	246
690		259	221	.325	232
691		255	218	.265	189
692		257	221	.368	262
693	15	264	226	.207	147
694		261	224	.202	144
695		250	221	.178	127
696		255	218	.144	103
697	18	264	225	.296	211
698		256	219	.174	124
699		259	222	.278	198
700		255	218	.212	151
701	21	264	225	.380	271
702		264	225	.300	214
703		260	222	.324	231
704		256	219	.198	141
705	24	263	226	.402	287
706		256	220	.278	198
707		256	219	.272	194
708		254	218	.288	206

GRAPH No VII
P.ASS. 20%
M/C 20%
COMPRESSION TEST 24 HOURS
TABLE No 36

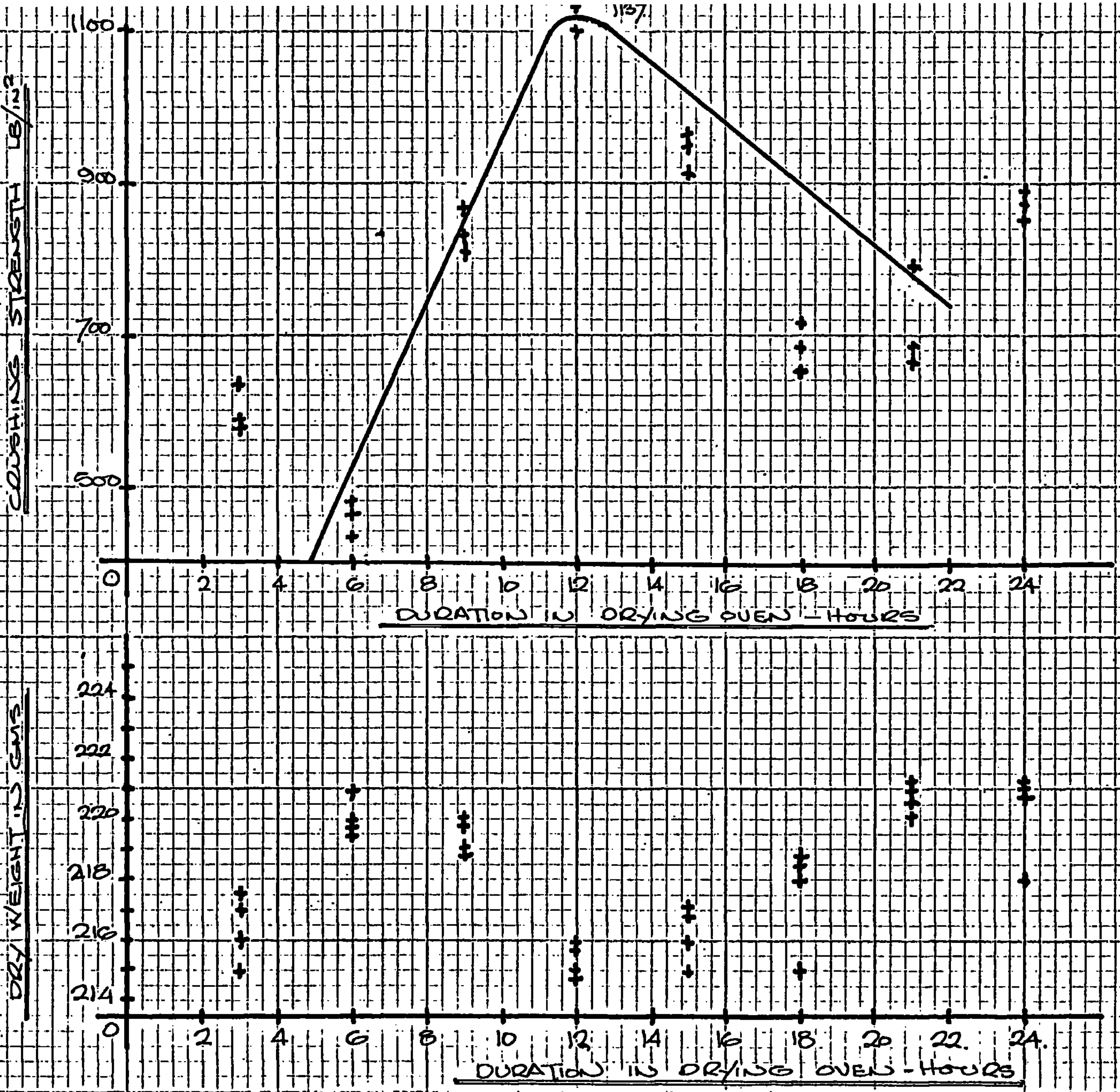


6.5 TABLE 37

DETAILS OF 30% SAMPLES

REF NO	OVEN TIME Hrs.	WET WT Gms	DRY WT Gms	LOAD Tons	STRESS lbs/in^2
709	3	258	217	.804	573
710		259	217	.872	622
711		258	215	.786	562
712		258	216	NOT TESTED	
713	6	263	220	.682	487
714		264	220	.622	444
715		264	221	.658	470
716		263	220	NOT TESTED	
717	9	262	219	1.212	865
718		262	220	1.140	813
719		261	219	1.160	828
720		262	220	NOT TESTED	
721	12	258	216	1.610	1150
722		258	216	1.562	1112
723		257	215	1.613	1150
724		256	215	NOT TESTED	
725	15	258	215	1.346	958
726		258	216	1.302	930
727		259	217	1.363	967
728		259	217	NOT TESTED	
729	18	261	219	1.003	716
730		260	219	.972	693
731		260	218	.912	650
732		257	215	NOT TESTED	
733	21	264	221	.938	667
734		263	221	.944	673
735		263	221	1.08	770
736		262	220	NOT TESTED	
737	24	263	220	1.192	850
738		264	220	1.238	882
739		263	220	1.252	894
740		261	218	NOT TESTED	

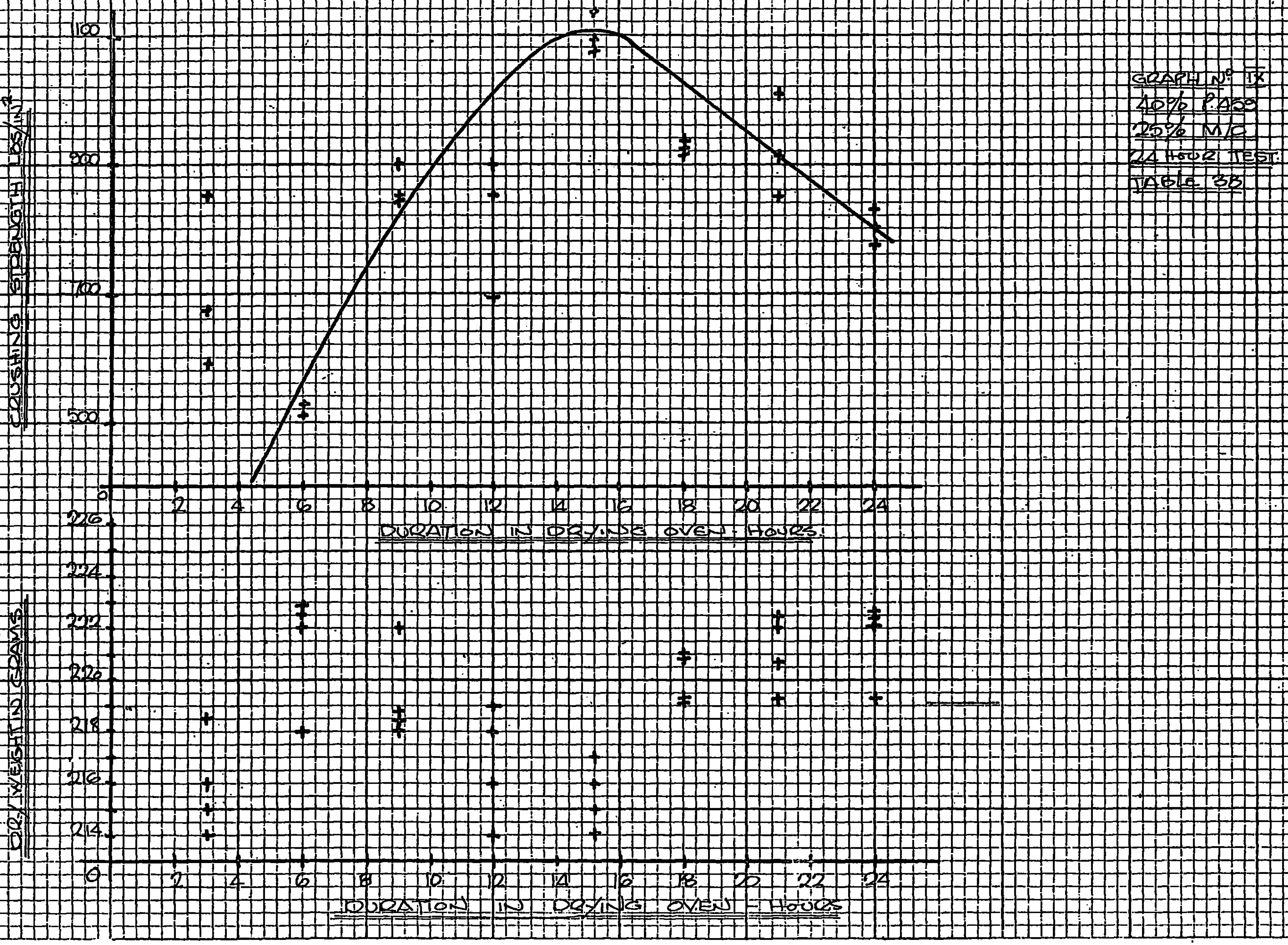
GRAPH Nº VIII
P.459. 30%
M/C 25%
24 HOUR TEST
TABLE Nº 37



6.5 TABLE 38

DETAILS OF 40% SAMPLES

REF NO.	OVEN TIME Hrs.	WET WT Gms	DRY WT Gms	LOAD Tons	STRESS lbs/in^2
741	3	258	219	1.18	840
742		255	216	.962	686
743		253	215	.804	574
744		251	214	NOT TESTED	
745	6	262	223	.725	517
746		262	223	.735	524
747		261	222	.715	508
748		260	218	NOT TESTED	
749	9	261	222	1.265	900
750		258	219	1.180	840
751		258	219	1.180	840
752		256	218	NOT TESTED	
753	12	258	219	1.25	890
754		258	218	1.18	840
755		255	216	.958	684
756		252	214	NOT TESTED	
757	15	257	217	1.59	1130
758		257	216	1.51	1075
759		255	215	1.525	1090
760		254	214	NOT TESTED	
761	18	261	221	1.315	937
762		262	221	1.33	950
763		260	219	1.25	890
764		260	219	NOT TESTED	
765	21	261	221	1.215	865
766		262	223	1.42	1010
767		261	222	1.30	926
768		258	219	NOT TESTED	
769	24	263	223	1.08	770
770		263	223	1.16	825
771		262	223	1.12	800
772		258	219	NOT TESTED	


GRAPH No. IX
40% P.459
25% M/C
24 HOUR TEST
TABLE 38
CRUSHING STRENGTH LBS/IN²
1100
900
700
500
0
2
4
6
8
10
12
14
16
18
20
22
24
DURATION IN DRYING OVEN - HOURS.
DRY WEIGHT IN GRAMS
226
224
222
220
218
216
214
0
2
4
6
8
10
12
14
16
18
20
22
24
DURATION IN DRYING OVEN - HOURS

Graphs VI to IX are plots of the compressive strengths for the given mixes with the period of oven cure being varied with 3 hourly increments.

The graphs fall into two distinct groups with the first two showing gradual improvements up to the total 24 hour oven cure. In both cases the mixes had achieved about 90-95% of the 24 hour cure strength at 12 hour.

The 30% and 40% emulsion samples gave a better indication of the effects of drying with a maximum strength being achieved with about 12 hours of oven cure. This second group of results were more interesting as the strength dropped off slightly with periods of cure greater than 12 hours.

The latter point was particularly noted as it seemed to indicate that damage could be caused to the samples by leaving them for too long under curing conditions.

The reasons for this depression of strength are not clear but it is possible that the P459 gains strength when marginally moist and that after 12 hours in the oven the samples become completely dry.

Whatever the reason for this effect it was decided that a period of 12 hours in the oven would be added to the standard conditions for the following work.

The graphs gave two ranges of strength and so it was decided that the 20% to 30% emulsion range should be investigated with a 12 hour period of oven cure.

6.5 TABLE 39

DETAILS OF MIXES

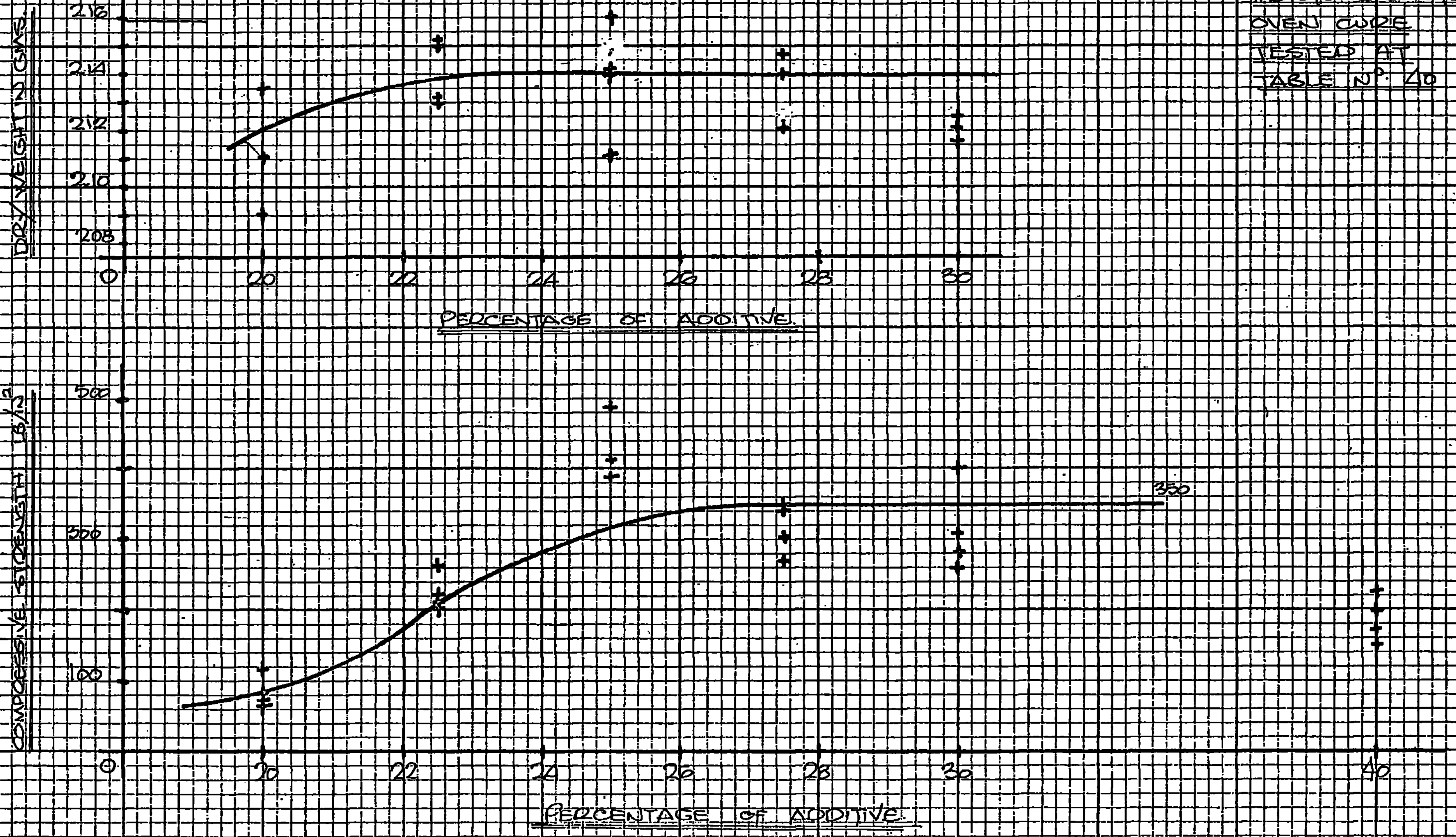
P459 %	M/C %	P.F.ASH Gms	WATER & P459 cc	WATER cc	P459 cc
20	25	1000	250	200	50
22½	25	1000	250	193.75	56.25
25	25	1000	250	187.5	62.5
27½	25	1000	250	181.25	68.75
30	25	1000	250	175	75
40	25	1000	250	150	100

6.5 TABLE 40

DETAILS OF SAMPLES

REF NO	P459 %	M/C %	WET WT Gms	DRY WT Gms	LOAD Tons	STRESS lbs/in^2
805	20	25	253	213	.112	80
806		25	254	213	.160	119
807		25	250	209	.108	77
808		25	252	211	.120	85
809	22.5	25	259	215	.312	222
810		25	260	215	.354	252
811		25	257	213	.324	231
812		25	257	213	.284	202
813	25	25	258	214	.642	456
814		25	260	216	.542	388
815		25	257	214	.542	388
816		25	255	211	.582	415
817	27.5	25	257	215	.512	365
818		25	257	215	.506	361
819		25	256	214	.437	311
820		25	253	212	.370	272
821	30	25	252	212	.360	257
822		25	254	213	.570	408
823		25	253	212	.380	271
824		25	251	211	.432	308
825	40	25	244	206	.312	223
826		25	246	208	.278	198
827		25	243	205	.236	168
828		25	243	205	.264	187

GRAPH No X
MOISTURE CONTENT 25%
OVEN CURE 12 HOURS
TESTED AT 24 HOURS.
TABLE No 40



6.5.1 PRE-CURE SECTION

It was possible that the oven drying was a rather severe form of cure for these particular samples and a brief look was taken at two variations of pre-cure treatment. 12 Hours in the oven seemed to produce good strengths and so it was decided that this should follow the pre-cure period.

One mix was used and the first group of samples were placed in polythene bags for between 3 and 11 hours with 2 hourly increments. The other group of samples were stored in the laboratory at room temperature for between 3 and 11 hours with the same increments of time.

After the pre-cure treatments the samples were subjected to 12 hours of drying to see if there would be any advantage.

One curious effect with the air ~~dried~~ samples was that a colour gradient appeared between the normal grey colour of the 3 hour sample and an almost white sample following the 11 hours of pre-cure.

This mix was also within the range where surface cracks were noticeable and the varying intervals of pre-cure influenced the amounts of the cracks in the dried specimens.

Where samples were stored in polythene bags the amount of surface cracking increased as the length of time in the bags increased.

Similarly the air dried samples of three hours duration showed only slight cracking whereas the 11 hour air cured samples were more noticeably cracked.

Both of these effects were uniform through the range of samples but seemed to run against the trend of the strength cure.

6.5 TABLE 41

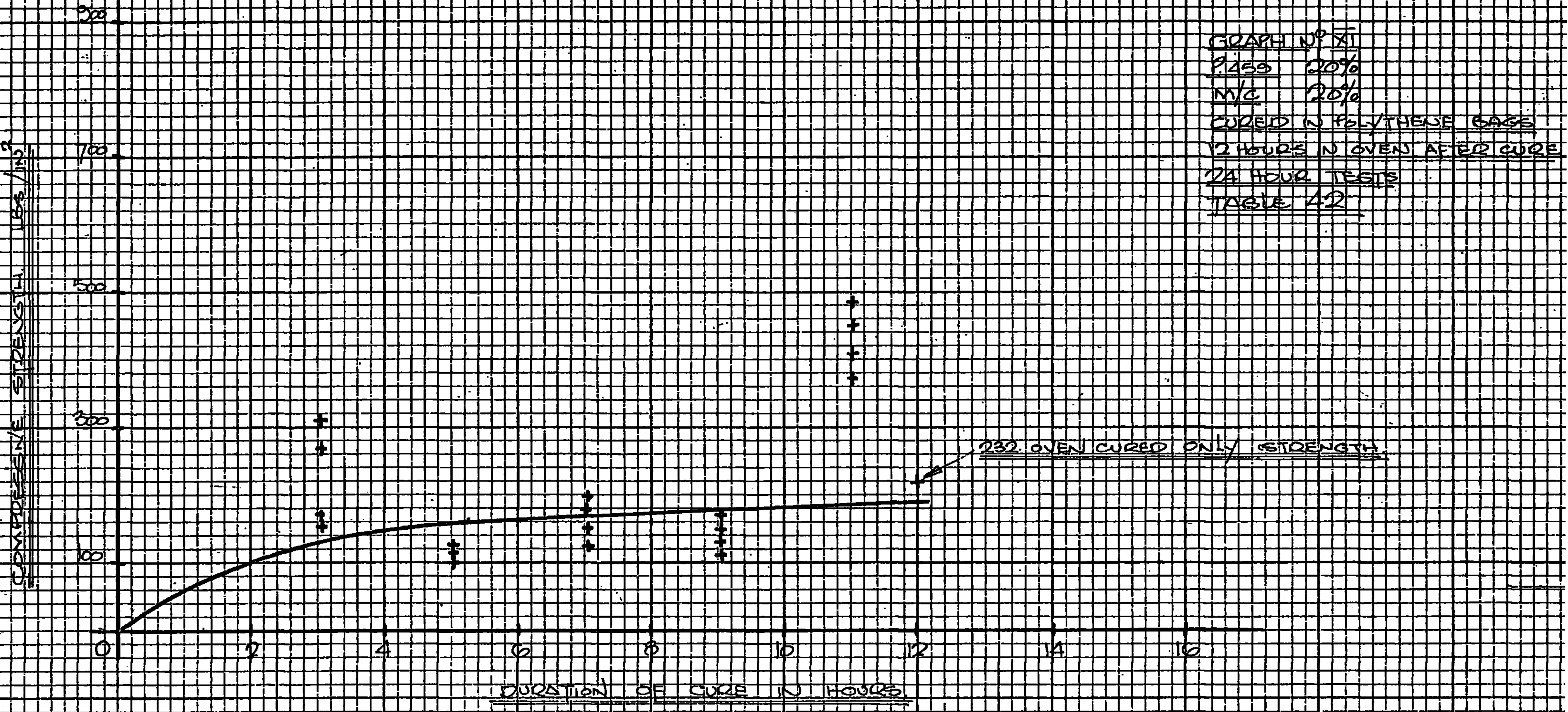
DETAILS OF MIX

P459 %	M/C %	P.F.ASH Gms	WATER & P459 cc	WATER cc	P459 cc
20	20	1000	200	160	40

6.5 TABLE 42

DETAILS OF SAMPLES WITH 12 HOURS OF OVEN CURE AFTER PRELIMINARY CURE IN POLYTHENE BAGS

REF NO	PRELIM CURE Hrs.	WET WT Gms	INTER WT Gms	DRY WT Gms	LOAD Tons	STRESS lbs/in^2
765	3	259	258	221	.442	316
766		258	257	221	.226	161
767		254	253	217	.384	274
768		249	249	214	.216	154
769	5	256	254	219	.186	133
770		253	252	216	.180	128
771		248	248	213	.156	111
772		248	248	213	.160	114
773	7	254	254	218	.280	206
774		256	255	219	.264	188
775		249	249	213	.182	130
776		249	248	213	.222	158
777	9	264	263	225	.172	123
778		262	262	223	.256	183
779		256	255	218	.194	139
780		254	253	217	.215	153
781	11	262	262	225	.656	468
782		264	264	226	.688	492
783		257	256	220	.522	373
784		256	255	219	.568	405

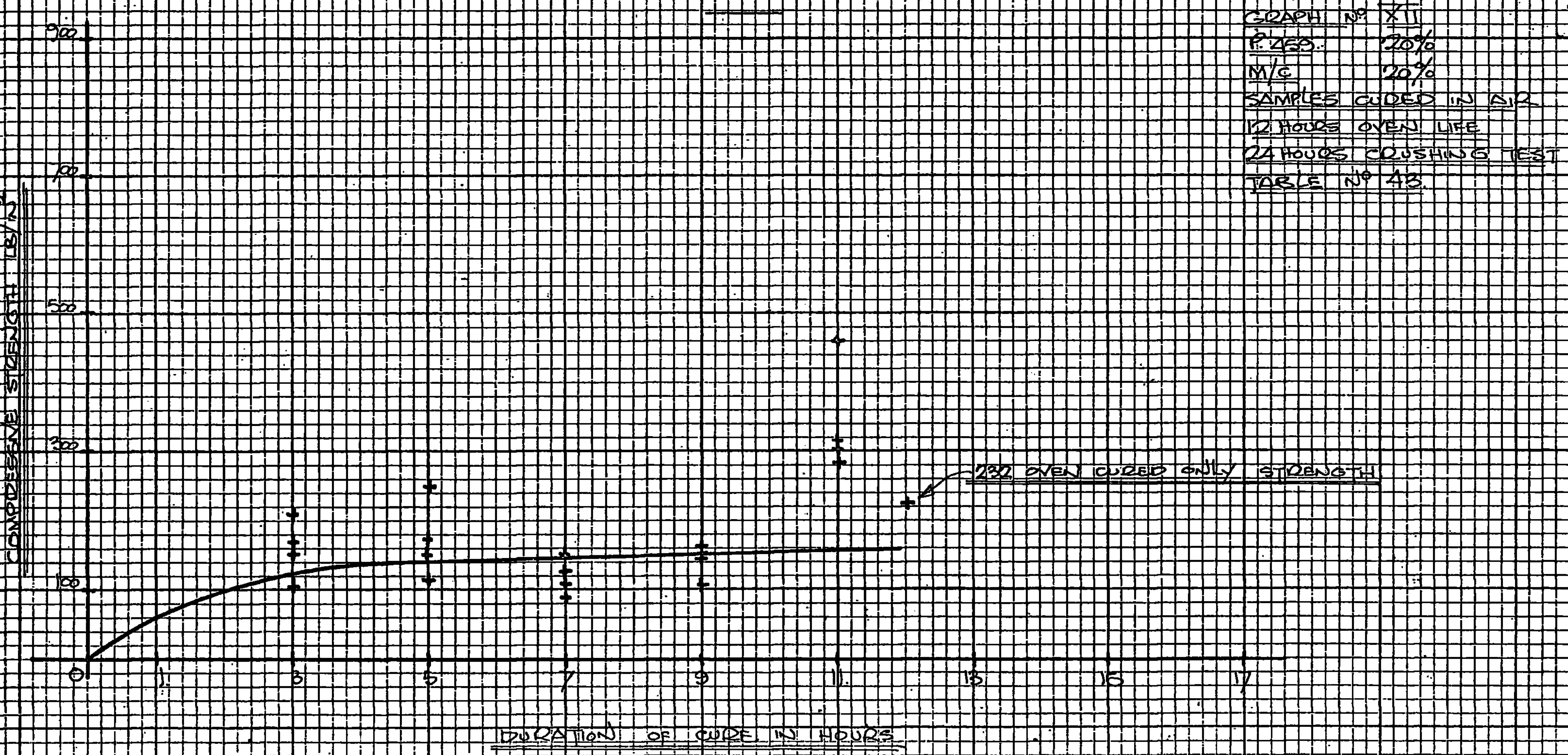


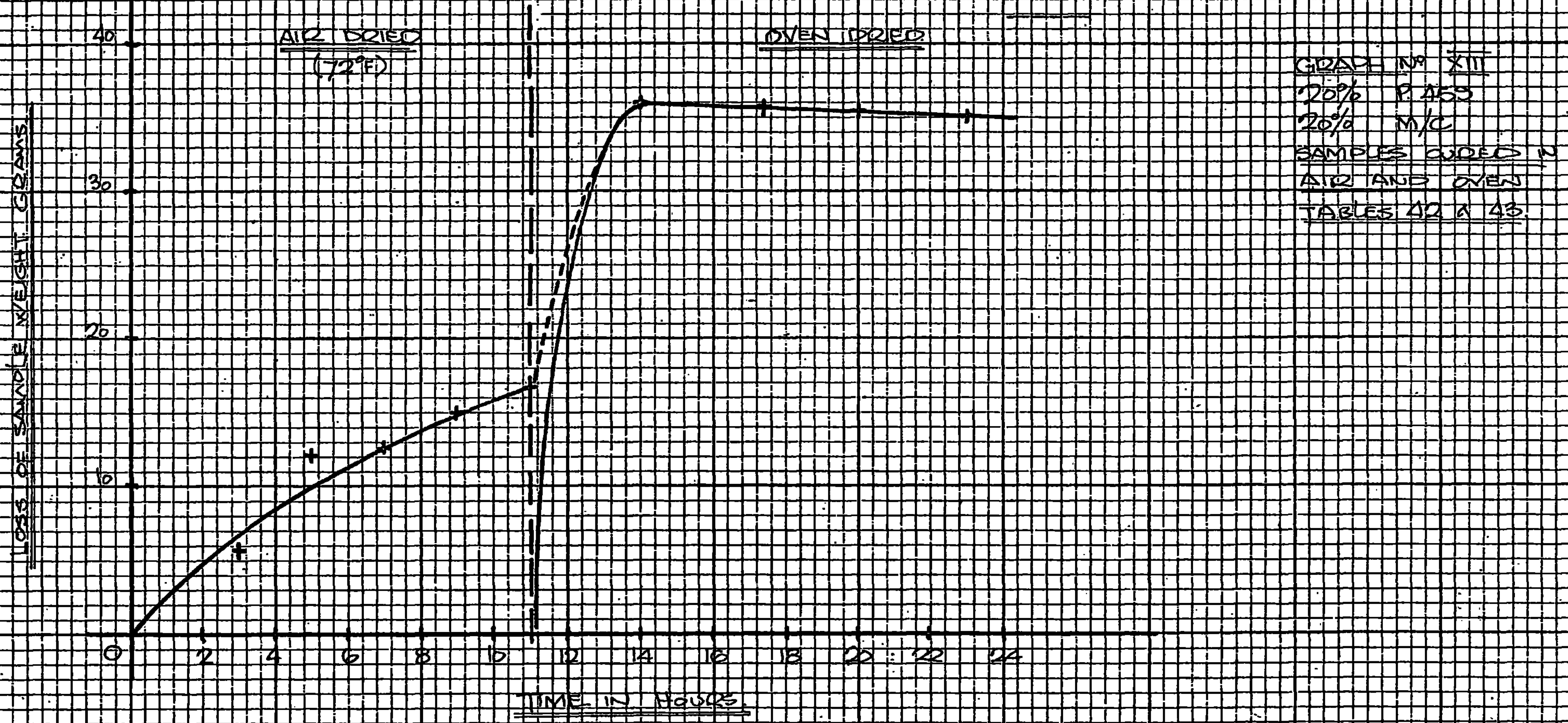
GRAPH No XI
P.459 20%
M/C 20%
CURED IN POLYTHENE BAGS
12 HOURS IN OVEN AFTER CURE
24 HOUR TESTS
TABLE 42

6.5 TABLE 43

DETAILS OF SAMPLES WITH 12 HOURS OF OVEN CURE AFTER PRELIM AIR CURE

REF NO	PRELIM CURE Hrs.	WET WT. Gms	INTER WT Gms	DRY WT. Gms	LOAD Tons	STRESS lbs/in^2
785	3	258	251	220	.152	109
786		254	248	218	.290	207
787		249	244	214	.246	176
788		253	245	217	.228	163
789	5	257	247	219	.256	183
780		258	248	219	.224	160
791		257	245	218	.358	255
792		253	238	216	.170	121
793	7	255	245	218	.234	167
794		253	244	217	.198	141
795		251	240	214	.168	119
796		250	233	214	.136	97
797	9	253	241	217	.232	166
798		248	235	212	.212	151
799		249	237	213	.238	170
800		246	227	212	.156	111
801	11	262	243	224	.648	462
802		258	243	221	.448	320
803		258	243	221	.424	303
804		257	237	220	.412	294


GRAPH No XII
P. 459. 20%
M/C 20%
SAMPLES CURED IN AIR
12 HOURS OVEN LIFE
24 HOURS CRUSHING TEST
TABLE No 43.


GRAPH Nº XIII
20% P.453
20% M/C
SAMPLES CURED IN
AIR AND OVEN
TABLES 42 & 43.
AIR DRIED
(72°F)
OVEN DRIED
LOSS OF SAMPLE WEIGHT GRAMS
40
30
20
10
0
2
4
6
8
10
12
14
16
18
20
22
24
TIME IN HOURS.

6. LABORATORY WORK

6.6 COALESCING AGENTS

6.6 TABLE 44

DETAILS OF MIXES

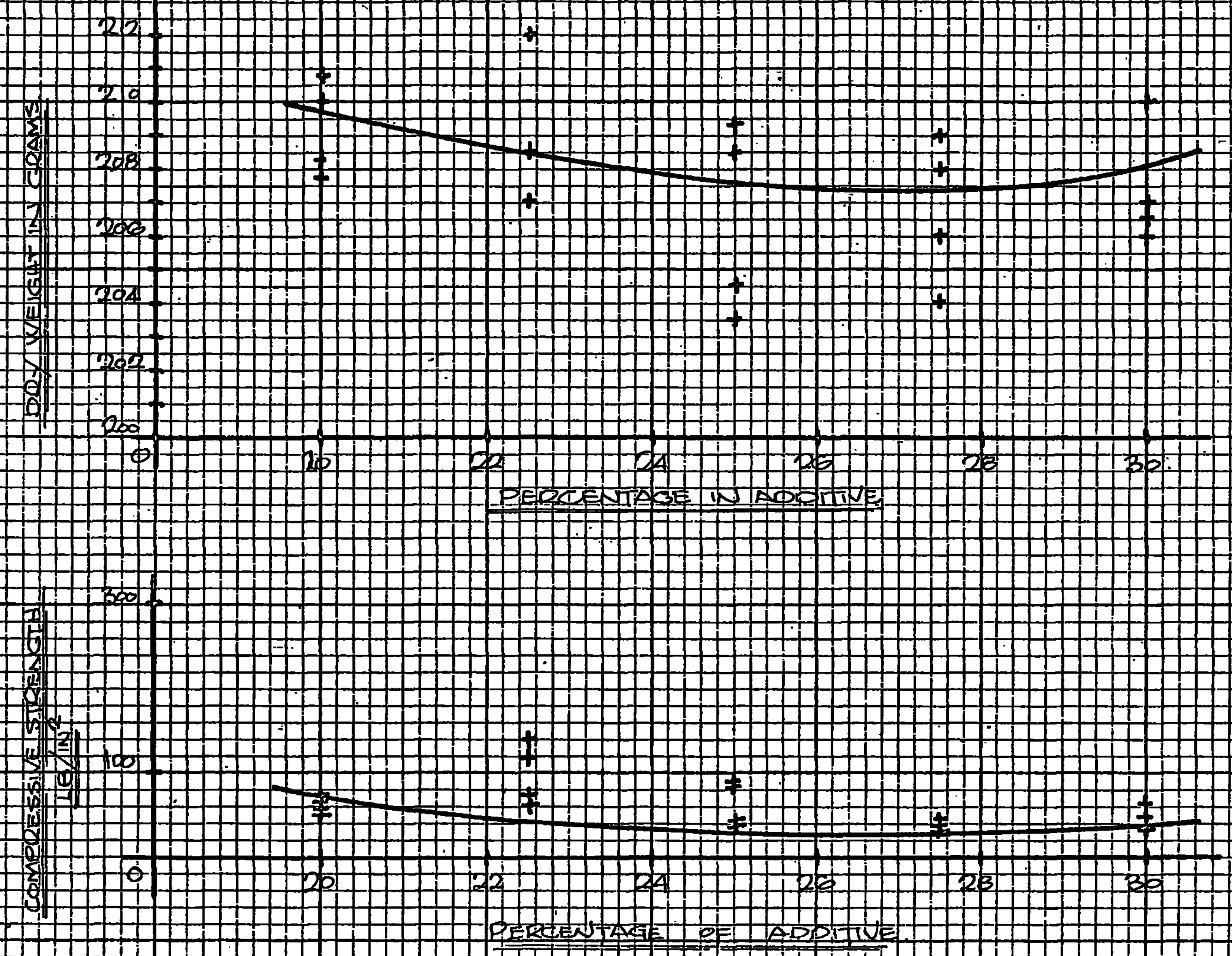
P459 %	M/C %	P.F.ASH Gms	WATER & P459 cc	WATER cc	P459 cc	2%B.D.A. cc
20	25	1000	250	200	50	1.0
22½	25	1000	250	193.75	56.25	1.125
25	25	1000	250	187.5	62.5	1.25
27½	25	1000	250	181.25	68.75	1.375
30	25	1000	250	175	75	1.50

6.6 TABLE 45

DETAILS OF SAMPLES

REF NO	P459 %	M/C %	WET WT Gms	DRY WT Gms	LOAD Tons	STRESS lbs/ins
845	20	21	249	211	.124	88
846	20	21	248	210	.096	68
847	20	21	244	208	.100	71
848	20	21	245	208	.096	68
849	22.5	21	250	212	.190	135
850	22.5	21	250	212	.168	120
851	22.5	21	245	208	.114	81
852	22.5	21	244	207	.110	78
853	25	21	244	208	.090	64
854	25	21	244	209	.088	63
855	25	21	238	203	.050	36
856	25	21	239	204	.062	44
857	27.5	21	243	208	.066	47
858	27.5	21	244	209	.068	48
859	27.5	21	239	204	.042	30
860	27.5	21	241	206	.048	34
861	30	21	245	210	.080	57
862	30	21	242	207	.062	44
863	30	21	242	207	.058	41
864	30	21	240	206	.044	31

GRAPH Nº XIV	
MOISTURE CONTENT	21%
B.D.A.	2%
OVEN CURE	12 HOURS
TESTED AT	24 HOURS
TABLE Nº 40.	



6.6 TABLE 46

DETAILS OF MIXES

P459 %	M/C %	P.F.ASH Gms	WATER & P459 cc	WATER cc	P459 cc	2%B.D.A. cc
20	25	1000	250	200	50	1.00
22.5	25	1000	250	193.75	56.25	1.125
25	25	1000	250	187.5	62.5	1.25
27.5	25	1000	250	181.25	68.75	1.375
30	25	1000	250	175	75	1.50

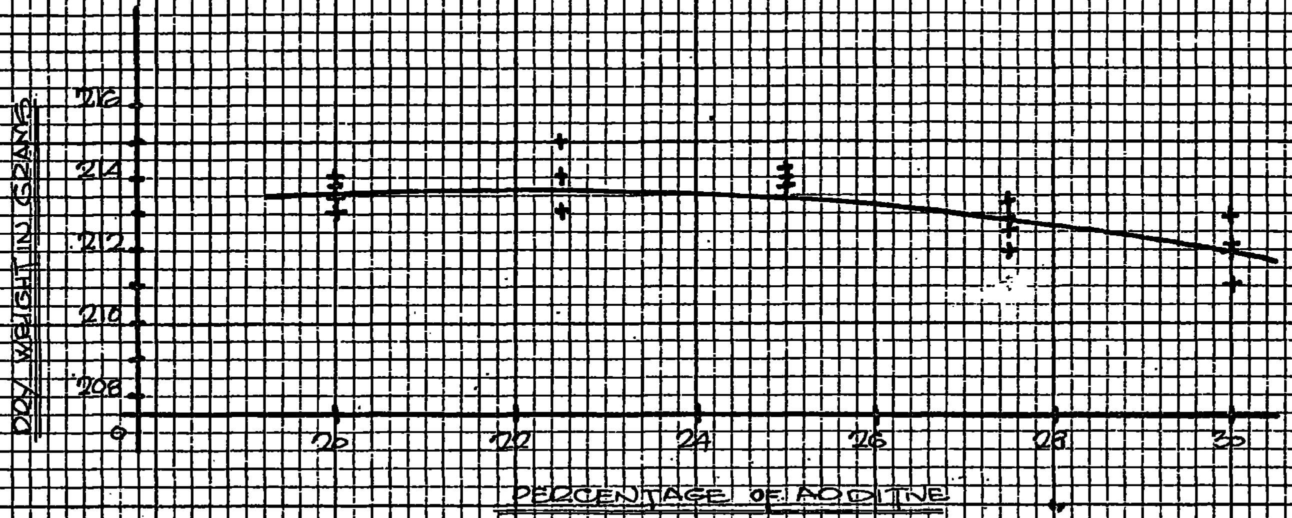
6.6 TABLE 47

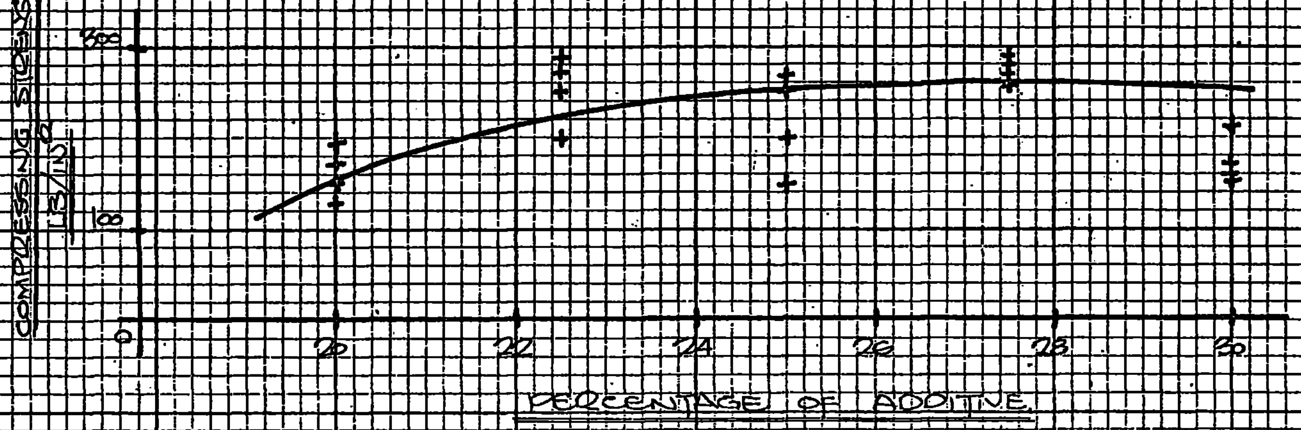
DETAILS OF SAMPLES

REF NO	P459 %	M/C %	WET WT Gms	DRY WT Gms	LOAD Tons	STRESS lbs/ins
885	20	25	258	214	.178	127
886	20	25	259	214	.210	150
887	20	25	259	214	.258	184
888	20	25	258	213	.274	195
889	22.5	25	259	215	.356	254
890	22.5	25	259	215	.392	279
891	22.5	25	258	214	.402	286
892	22.5	25	257	213	.268	191
893	25	25	258	214	.330	241
894	25	25	257	214	.352	251
895	25	25	257	214	.227	163
896	25	25	257	214	.274	195
897	27.5	25	256	213	.358	255
898	27.5	25	255	212	.414	296
899	27.5	25	257	214	.342	244
900	27.5	25	254	212	.380	272
901	30	25	254	213	.304	218
902	30	25	254	212	.264	188
903	30	25	253	212	.252	180
904	30	25	253	211	.264	188

GRAPH No XV

MOISTURE CONTENT	25%
B.D.A.	2%
OVEN CURE	12 HOURS
TESTED AT	24 HOURS
TABLE No 47	





6.6 COALESCING AGENTS

Thus using P459 and oven curing of samples the next stage was to try and improve the action of the PVA emulsion.

Two coalescing agents were selected as the most suitable materials. Hexylene Glycol and Butyl Dioxitol Acetate were the two agents used and the next series of samples were made to investigate the worth of these two agents.

The two agents are different but the conditions in which they are used are similar and although Hexylene Glycol is the more usual coalescing agent there are a number of circumstances in which Butyl Dioxitol Acetate proves superior.

Hexylene Glycol, which has properties similar to those of low molecular weight glycols, has exceptional solvent powers for a wide range of materials. It is a relatively long chain compound which is compatible with aliphatic and aromatic hydrocarbons.

Butyl Dioxitol acetate on the other hand is a solvent for many materials such as cellulose nitrate, extra gum and polyvinyl acetate homo - and co-polymers. Its primary use is as a coalescing agent in decorative emulsion paints, particularly polyvinyl acetate and acrylate co-polymer.

These two coalescing agents were compared in the first series of mixes and on the basis of these results Hexylene Glycol was selected as having a more beneficial effect under these conditions of use.

6.6 TABLE 48

DETAILS OF MIXES

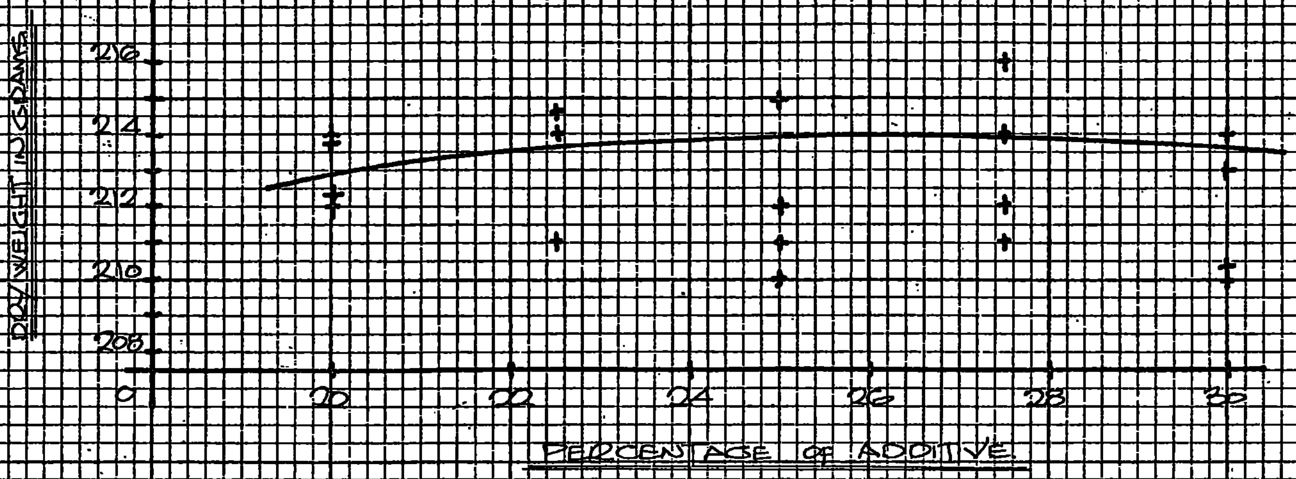
P459 %	M/C %	P.F.ASH Gms	WATER & P459 cc	WATER cc	P459 cc	4%B.D.A.
20	25	1000	250	200	50	2.0
22.5	25	1000	250	193.75	56.25	2.25
25	25	1000	250	187.5	62.5	2.50
27.5	25	1000	250	181.25	68.75	2.75
30	25	1000	250	175	75	3.00

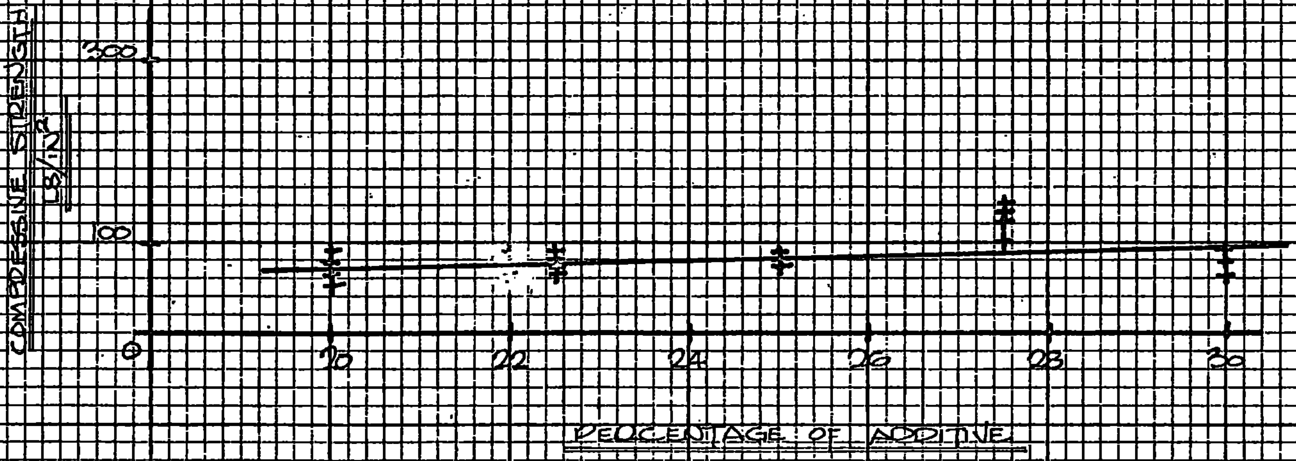
6.6 TABLE 49

DETAILS OF SAMPLES

REF NO	P459 %	M/C %	WET WT Gms	DRY WT Gms	LOAD Tons	STRESS lbs/ins
925	20	25	258	214	.110	78
926	20	25	259	214	.112	80
927	20	25	257	212	.088	63
928	20	25	256	212	.134	96
929	22.5	25	258	215	.120	86
930	22.5	25	259	214	.122	87
931	22.5	25	257	214	.102	73
932	22.5	25	254	211	.100	71
933	25	25	258	215	.124	89
934	25	25	254	211	.114	81
935	25	25	255	212	.106	76
936	25	25	253	210	NOT TESTED	
937	27.5	25	257	214	.190	135
938	27.5	25	259	216	.168	120
939	27.5	25	253	211	.132	94
940	27.5	25	254	212	.164	117
941	30	25	255	213	.136	97
942	30	25	256	214	.134	96
943	30	25	253	210	.132	94
944	30	25	251	210	.106	76

GRAPH Nº XVI
MOISTURE CONTENT 25%
B.D.A. 4%
OVEN CURE 12 HOURS
TESTED AT 24 HOURS
TABLE Nº 49





6.6 TABLE 50

DETAILS OF MIXES

P459 %	M/C %	P.F.ASH Gms	WATER & P459 cc	WATER cc	P459 cc	2%H.G. cc
10	25	1000	250	225	25	0.5
20	25	1000	250	200	50	1.0
30	25	1000	250	175	75	1.5
40	25	1000	250	150	100	2.0

6.6 TABLE 51

DETAILS OF SAMPLES

REF NO	P459 %	M/C %	WET WT Gms	DRY WT Gms	LOAD Tons	STRESS lbs/ins
617	10	19	269	230	.162	116
618	10	19	266	228	.142	101
619	10	19	265	227	.148	106
620	10	19	263	227	NOT TESTED	
621	20	21	261	222	.61	436
622	20	21	261	223	.60	428
623	20	21	262	223	.602	429
624	20	21	262	221	NOT TESTED	
625	30	20	265	228	.512	366
626	30	20	259	223	.530	384
627	30	20	256	221	.432	308
628	30	20	253	218	NOT TESTED	
629	40	22	257	222	.902	644
630	40	22	255	220	.682	486
631	40	22	254	219	.534	381
632	40	22	250	216	NOT TESTED	

6.6 TABLE 52

DETAILS OF MIXES

P459 %	M/C %	P.F.ASH Gms	WATER & P459 cc	WATER cc	P459 cc	2%H.G.
20	25	1000	250	200	50	1.0
22.5	25	1000	250	193.75	56.25	1.125
25	25	1000	250	187.5	62.5	1.25
27.5	25	1000	250	181.25	68.75	1.375
30	25	1000	250	175	75	1.50

6.6 TABLE 53

DETAILS OF SAMPLES

REF NO	P459 %	M/C %	WET WT Gms	DRY WT Gms	LOAD Tons	STRESS lbs/ins
825	20	21	250	213	.122	87
826	20	21	252	214	.134	96
827	20	21	246	210	.092	66
828	20	21	248	211	.086	61
829	22.5	21	248	212	.098	70
830	22.5	21	249	212	.090	64
831	22.5	21	244	210	.060	43
832	22.5	21	243	209	.066	47
833	25.0	21	246	211	.144	103
834	25.0	21	248	213	.154	109
835	25.0	21	245	211	.152	108
836	25.0	21	244	209	.096	68
837	27.5	21	252	215	.244	174
838	27.5	21	249	213	.238	169
839	27.5	21	245	209	.172	123
840	27.5	21	245	209	.202	144
841	30	21	247	212	.152	108
842	30	21	247	211	.132	94
843	30	21	244	209	.112	80
844	30	21	245	210	.142	102

GRAPH No XVII

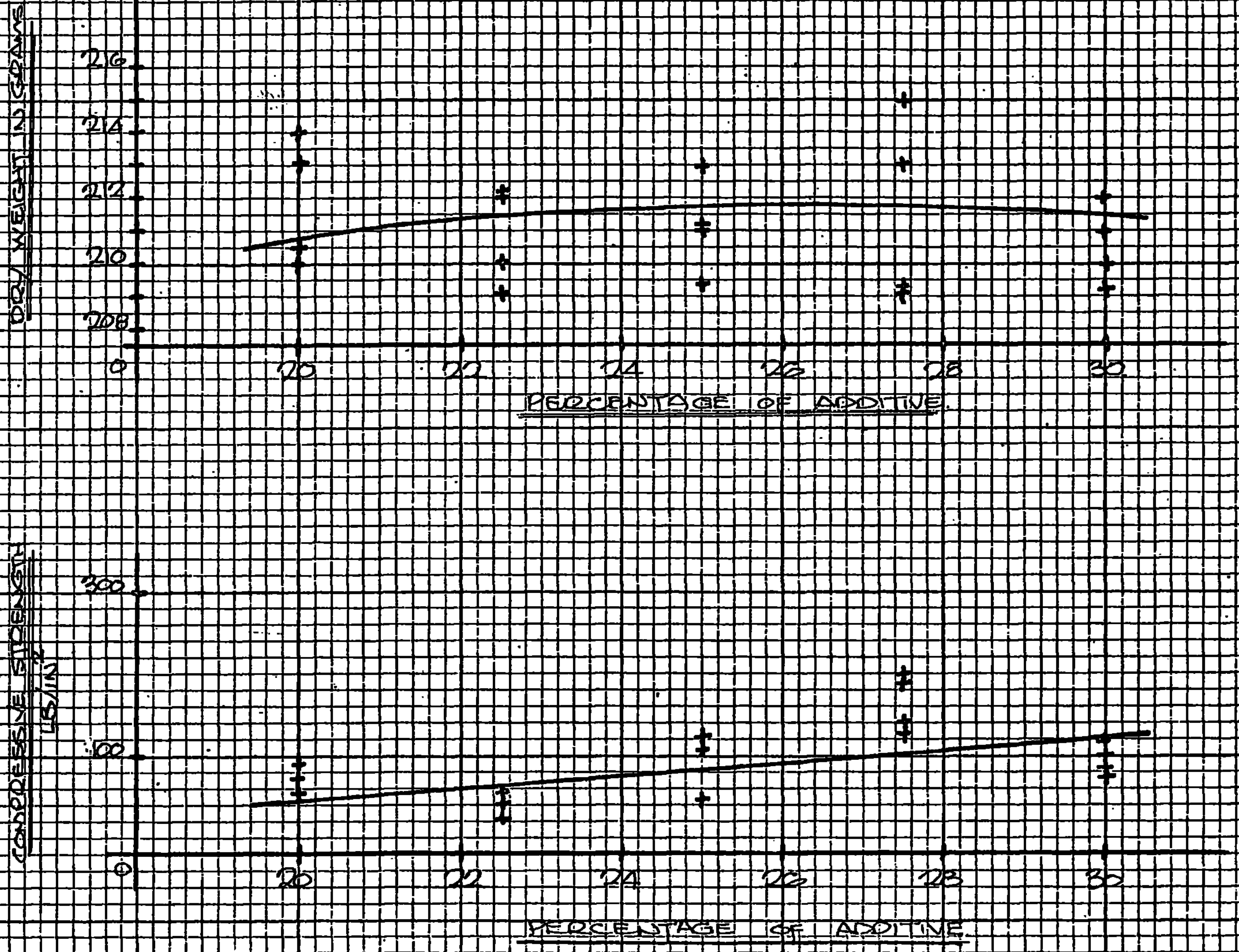
MOISTURE CONTENT 21%

HEXALENE GLYCOL 2%

OVEN CURE 12 HOURS

TESTED AT 24 HOURS

TABLE No 53.



6.6 TABLE 54

DETAILS OF MIXES

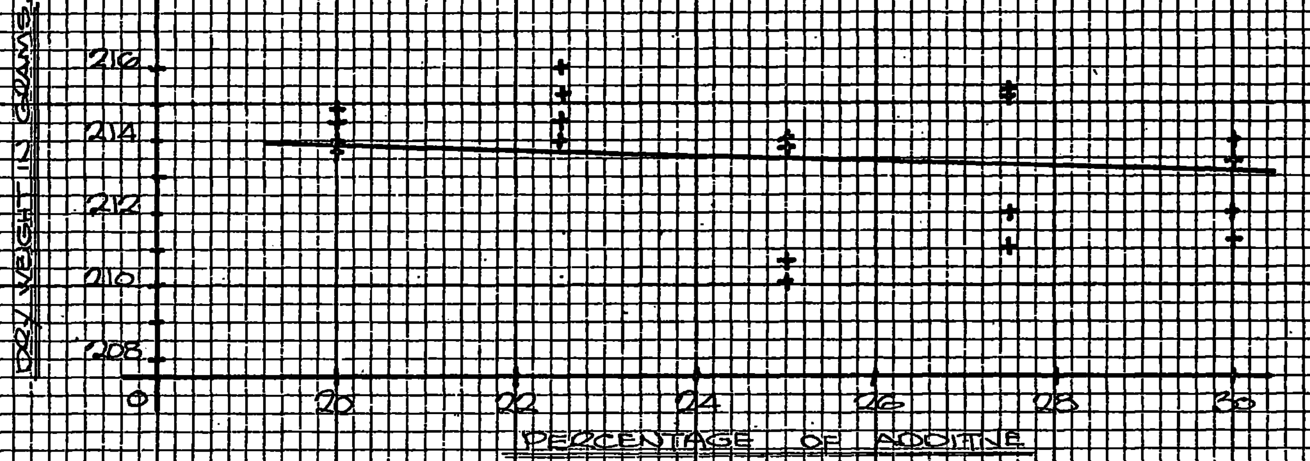
P459 %	M/C %	P.F.ASH Gms	WATER & P459 cc	WATER cc	P459 cc	2%H.G. cc
20	25	1000	250	200	50	1.00
22.5	25	1000	250	193.75	56.25	1.125
25	25	1000	250	187.5	62.5	1.25
27.5	25	1000	250	181.25	68.75	1.375
30	25	1000	250	175	75	1.50

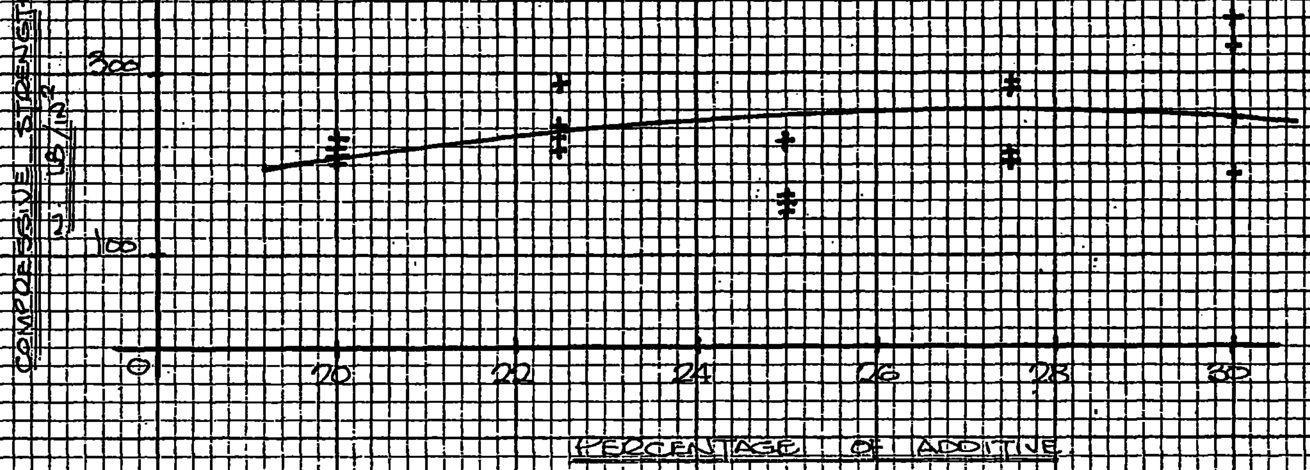
6.6 TABLE 55

DETAILS OF SAMPLES

REF NO	P459 %	M/C %	WET WT Gms	DRY WT Gms	LOAD Tons	STRESS lbs/ins
865	20	25	259	215	.322	230
866	20	25	257	214	.316	226
867	20	25	258	214	.292	208
868	20	25	257	214	.322	230
869	22.5	25	259	216	.310	221
870	22.5	25	258	214	.402	287
871	22.5	25	259	215	.336	240
872	22.5	25	257	214	.325	232
873	25	25	257	214	.213	152
874	25	25	257	214	.324	231
875	25	25	253	211	.264	188
876	25	25	252	210	.228	163
877	27.5	25	257	215	.390	278
878	27.5	25	258	215	.406	290
879	27.5	25	253	212	.282	201
880	27.5	25	252	211	.300	214
881	30	25	255	214	.475	339
882	30	25	255	214	.366	261
883	30	25	252	211	.366	261
884	30	25	248	208	.274	196

GRAPH Nº XVIII	
MOISTURE CONTENT	25%
H.G.	2%
OVEN CURE	12 HOURS
TESTED AT	24 HOURS
TABLE Nº 55	





6.6. TABLE 56

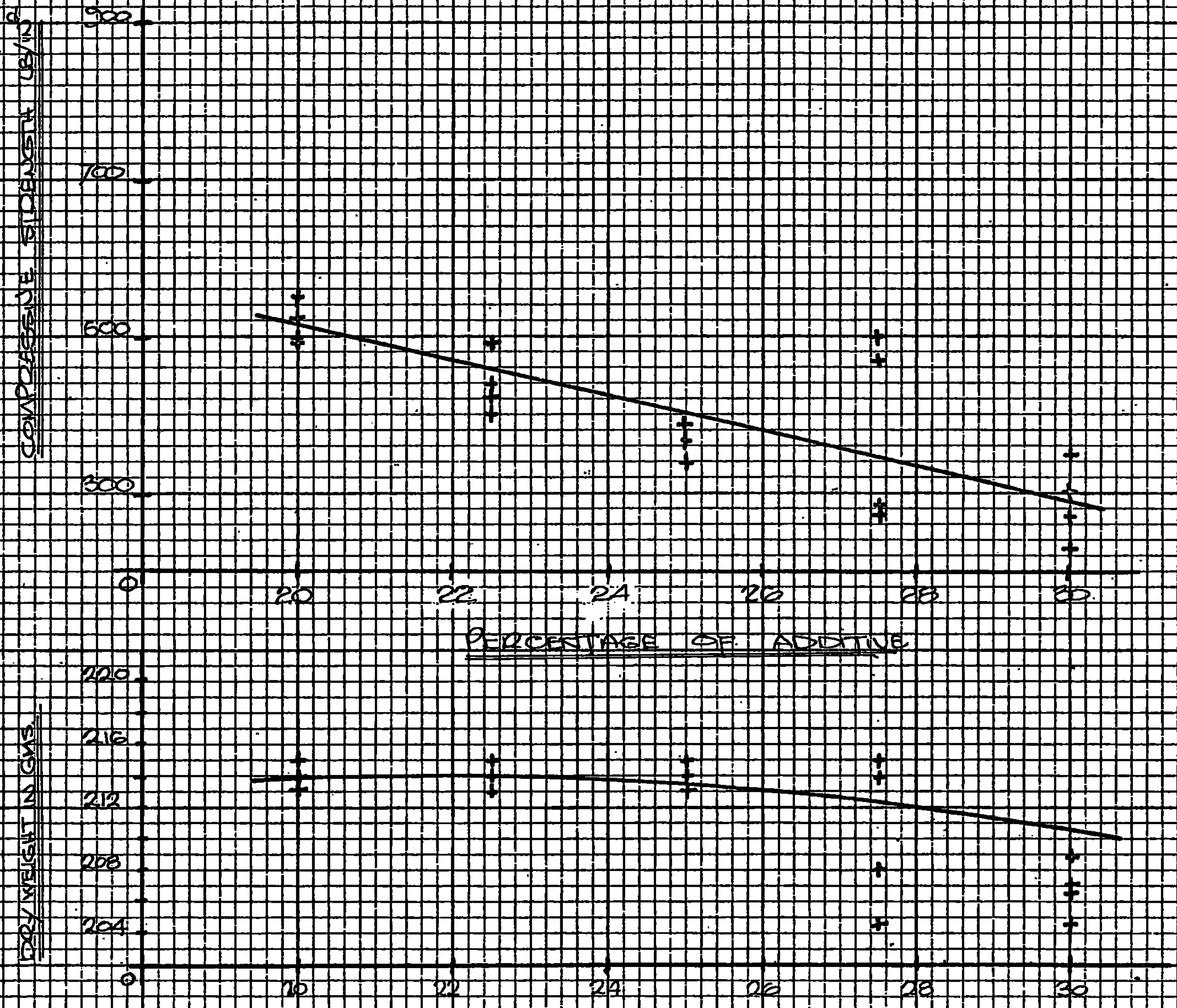
DETAILS OF MIXES

P459 %	M/C %	P.F.ASH Gms	WATER & P459 cc	WATER cc	P459 cc	4%H.G. cc
20	25	1000	250	200	50	2.00
22.5	25	1000	250	193.75	56.25	2.25
25	25	1000	250	187.5	62.5	2.50
27.5	25	1000	250	181.25	68.75	2.75
30	25	1000	250	175	75	300

6.6 TABLE 57

DETAILS OF SAMPLES

REF NO	P459 %	M/C %	WET WT Gms	DRY WT Gms	LOAD Tons	STRESS lbs/ins
905	20	25	259	214	.696	496
906	20	25	259	214	.694	494
907	20	25	260	215	.746	532
908	20	25	258	213	.782	557
909	22.5	25	260	215	.692	493
910	22.5	25	259	214	.598	426
911	22.5	25	258	214	.766	546
912	22.5	25	257	213	.574	409
913	25.0	25	258	215	.528	376
914	25.0	25	258	215	.526	374
915	25.0	25	256	214	.464	330
916	25.0	25	254	213	.206	147
917	27.5	25	258	215	.702	500
918	27.5	25	256	215	.668	475
919	27.5	25	246	205	.402	286
920	27.5	25	250	209	.418	298
921	30	25	252	210	.425	303
922	30	25	251	210	.506	362
923	30	25	248	207	.385	275
924	30	25	245	205	.332	238



GRAPH N° XIX
MOISTURE CONTENT 25%
HEXYLENE GLYCOL 4%
OVEN CURE 12 HOURS
TESTED AT 24 HOURS
TABLE N° 57

6.6.1 HIGHER RANGES OF COALESCING AGENTS

This set of readings did not seem to give the marked differences between Hexylene Glycol and Butyl Dioxitol Acetate and so a further set of samples were prepared with 10% coalescing agent.

The further group of results allowed, graph XX to be plotted for a 25% polyvinyl acetate emulsion solution and a twelve hour cure in the drying over.

The graph for Hexylene Glycol showed an initial depression of strength with the small percentages of coalescing agent but the strengths showed a continual improvement with increases in Hexylene Glycol.

Under similar conditions of test Butyl Dioxitol acetate had a less satisfactory characteristic as from the early strength reading the coalescing agent had an increasingly detrimental effect.

On this basis Butyl Dioxitol acetate was not considered for further experimental work, and all the remaining tests were carried out using Hecylene Glycol as the coalescing agent.

Thus this section adds one more restraint to the group of conditions being applied to the cylindrical samples, and prepares the way for further and more detailed investigations with coalescing agents.

6.6.1 TABLE 58

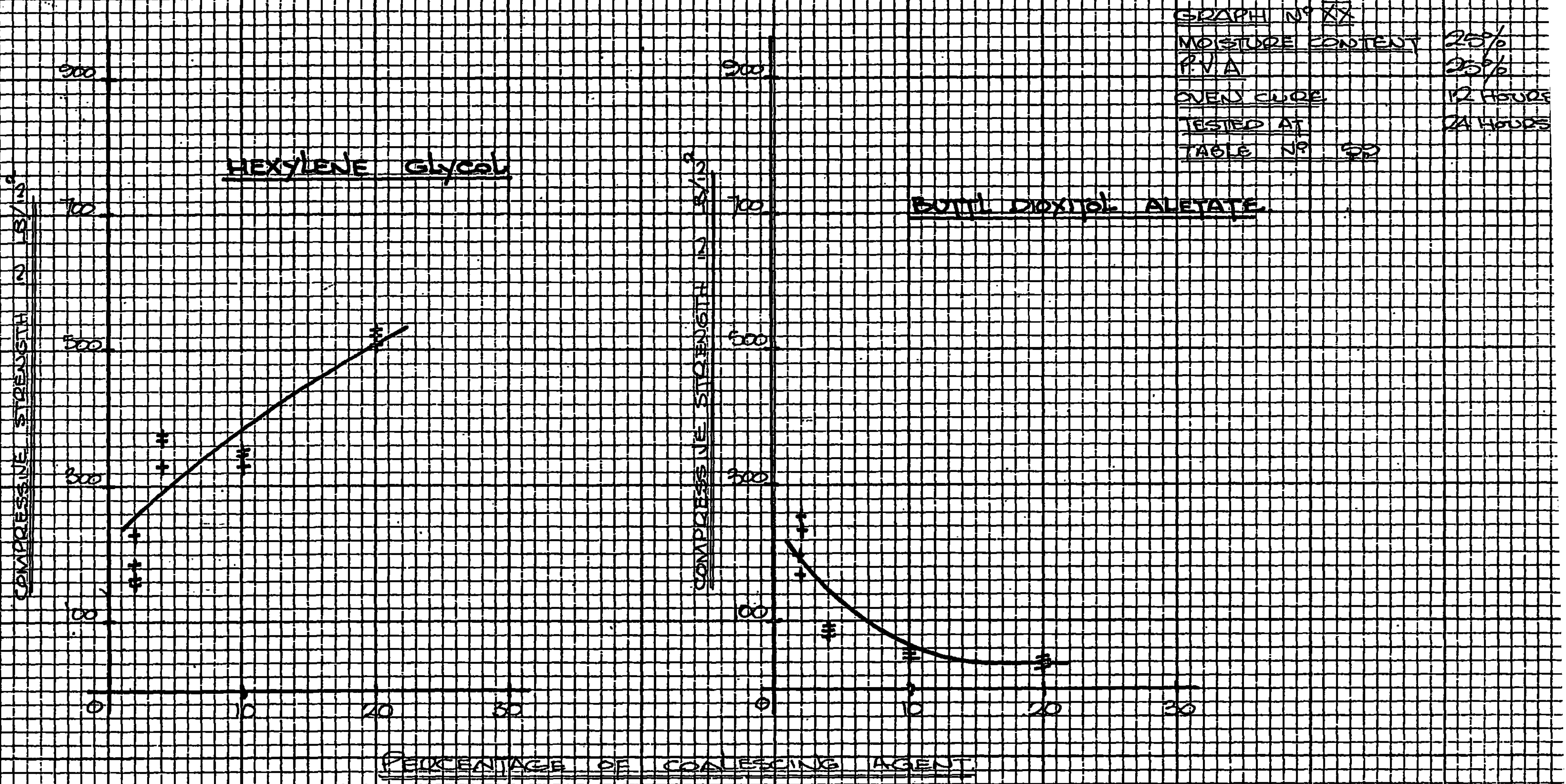
DETAILS OF MIXES

P459 %	M/C %	P.F.ASH Gms	WATER & P459 cc	WATER cc	P459 cc	H.G. 10% cc
25	25	1000	250	187.5	62.5	6.25

6.6.1 TABLE 59

DETAILS OF SAMPLES

REF NO	P459 %	M/C %	WET WT Gms	DRY WT Gms	LOAD Tons	STRESS lbs/in^2
10% H.G.						
985	25	25	258	214	.478	342
986	25	25	256	212	.448	320
987	25	25	255	212	.478	340
988	25	25	253	210	NOT TESTED	
20% H.G.						
989	25	25	258	212	.704	502
990	25	25	258	212	.720	515
991	25	25	257	212	.738	526
992	25	25	260	214	NOT TESTED	
10% B.D.A.						
993	25	25	259	215	.072	51
994	25	25	258	214	.070	50
995	25	25	258	214	.096	69
996	25	25	259	215	NOT TESTED	
20% B.D.A.						
997	25	25	258	215	.046	33
998	25	25	258	214	.072	51
999	25	25	259	216	.048	34
1000	25	25	259	216	NOT TESTED	


GRAPH Nº XX
MOISTURE CONTENT 25%
P.V.A 25%
OVEN CURE 12 HOURS
TESTED AT 24 HOURS
TABLE Nº 22
HEXYLENE GLYCOL
BUTYL DIOXITOL ACETATE.
COMPRESSIVE STRENGTH IN LB/IN²
900
700
500
300
100
0
10
20
30
PERCENTAGE OF COALESCING AGENT

6.6.2 HEXYLENE GLYCOL

Section 6.6.1 allowed Butyl Dioxitol acetate to be ruled out as a coalescing agent and so this last section on the investigation into improvements of the basic material was directed at finding the optimum amounts of Hexylene Glycol.

It was decided that the moisture content would be set at a nominal 20% as it was anticipated that the higher percentages of Hexylene Glycol might put the moisture content of compaction of the samples it also had to be considered that the samples might slump on extraction from the mould.

Optimum conditions were gauged at the mixing stage and the amount of "moisture" added to the ash noted so that the moisture contents could be recalculated on an actual basis.

At this stage of the work the "moisture" added to the ash was water, PVA and Hexylene Glycol and the amounts of coalescing agent were expressed as a percentage of the PVA emulsion added. These conditions were maintained throughout the remainder of this work.

6.6.2 TABLE 60

DETAILS OF MIXES

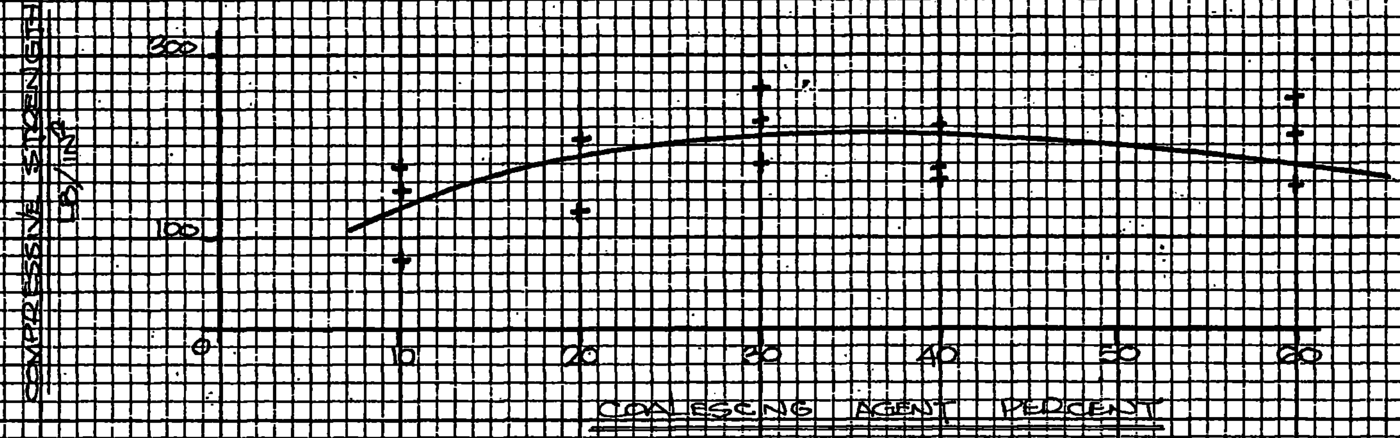
P459 %	M/C %	P.F.ASH Gms	10%H.G. cc	20%H.G. cc	30%H.G. cc	40%H.G. cc	60%H.G. cc
10	25	1000	2.5	5.0	7.5	10	15.0
15	25	1000	3.75	7.5	11.25	15	22.5
20	25	1000	5.0	10.0	15.0	20	30

6.6.2 TABLE 61

DETAILS OF SAMPLES

REF NO	P459 %	M/C %	WET WT Gms	DRY WT Gms	LOAD Tons	STRESS lbs/ins
10% H.G.						
1009	10	19	262	224	.110	78
1010	10	19	263	225	.212	151
1011	10	19	267	228	.252	180
1012	10	19	265	226	NOT TESTED	
20% H.G.						
1013	10	18	264	226	.170	121
1014	10	18	263	226	.124	89
1015	10	18	268	230	.286	204
1016	10	18	267	229	NOT TESTED	
30% H.G.						
1017	10	18	263	224	.200	177
1018	10	18	265	226	.307	267
1019	10	18	265	226	.252	223
1020	10	18	266	227	NOT TESTED	
40% H.G.						
1021	10	18	263	226	NOT TESTED	
1022	10	18	264	227	.164	117
1023	10	18	264	227	.223	163
1024	10	18	265	229	.168	120
60% H.G.						
1025	10	18	262	223	.178	157
1026	10	18	263	223	.242	214
1027	10	18	264	224	.292	258
1028	10	18	264	224	NOT TESTED	

GRAPH Nº	XXI
P.V.A.	10%
M/C	19%
OVEN CURE	12 HOURS
TESTED AT	24 HOURS
TABLE Nº	61



6.6.2 TABLE 62

DETAILS OF SAMPLES

REF NO	P459 %	M/C %	WET WT Gms	DRY WT Gms	LOAD Tons	STRESS lbs/ins
10% H.G.						
1029	15	19	264	225	.244	174
1030	15	19	266	227	.213	152
1031	15	19	262	223	.334	238
1032	15	19	264	225	NOT TESTED	
20% H.G.						
1033	15	19	264	225	.296	211
1034	15	19	265	226	.280	200
1035	15	19	261	224	.232	165
1036	15	19	260	223	NOT TESTED	
30% H.G.						
1037	15	20	259	218	NOT TESTED	
1038	15	20	260	219	.322	230
1039	15	20	258	217	.270	193
1040	15	20	259	219	.322	230
40% H.G.						
1041	15	18	262	224	NOT TESTED	
1042	15	18	263	225	.174	124
1043	15	18	262	225	.184	131
1044	15	18	262	225	.235	168
60% H.G.						
1045	15	18	260	220	NOT TESTED	
1046	15	18	260	220	.182	130
1047	15	18	262	222	.186	133
1048	15	18	260	221	.238	170

6.6.2 TABLE 63

DETAILS OF SAMPLES

REF NO	P459 %	M/C %	WET WT Gms	DRY WT Gms	LOAD Tons	STRESS lbs/ins
10% H.G.						
1049	20	20	263	224	.422	300
1050	20	20	264	225	.466	332
1051	20	20	262	223	.646	460
1052	20	20	262	224	NOT TESTED	
20% H.G.						
1053	20	19	263	225	.526	466
1054	20	19	262	225	.470	416
1055	20	19	262	225	.578	512
1056	20	19	261	224	NOT TESTED	
30% H.G.						
1057	20	20	257	219	NOT TESTED	
1058	20	20	258	220	.430	307
1059	20	20	259	220	.372	266
1060	20	20	260	221	.376	268
40% H.G.						
1061	20	19	260	221	NOT TESTED	
1062	20	19	261	223	.295	210
1063	20	19	261	224	.278	198
1064	20	19	261	223	.288	206
60% H.G.						
1065	20	19	257	218	.314	224
1066	20	19	256	216	NOT TESTED	
1067	20	19	257	218	.374	267
1068	20	19	256	217	.342	244

GRAPH No XXII

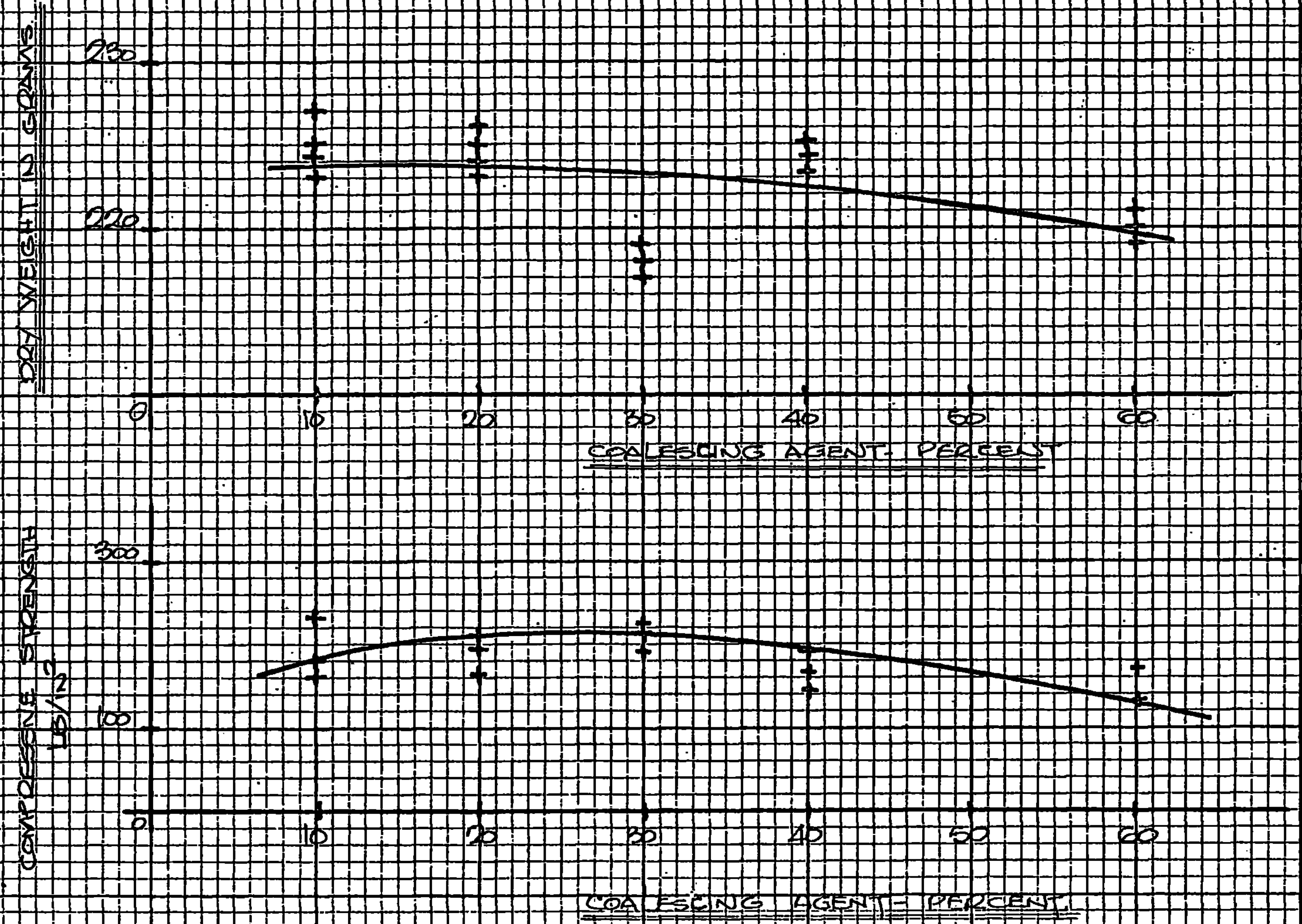
P.V.A 15%

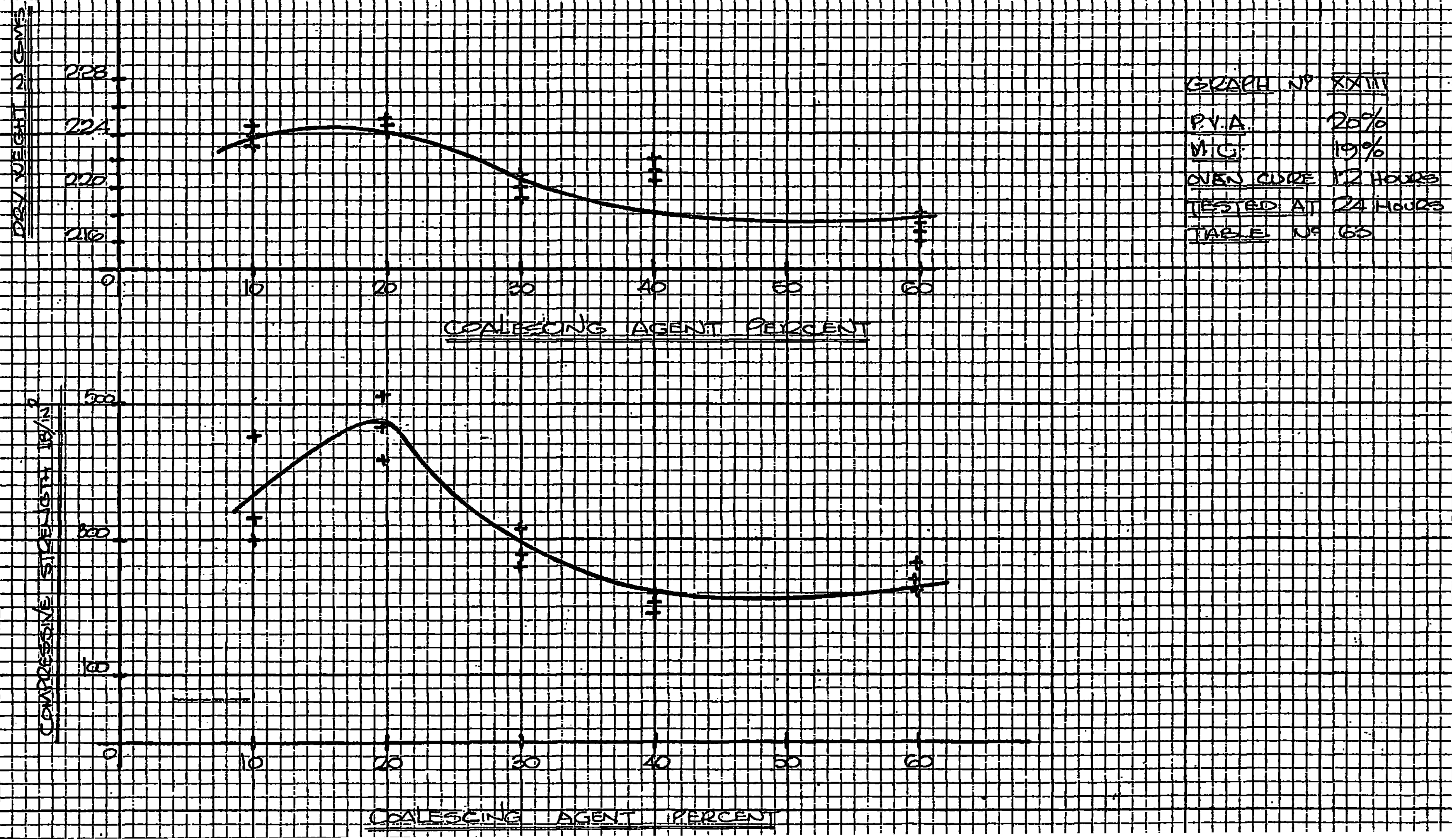
M/C 5%

OVEN CURE 12 HOURS

TESTED AT 24 HOURS

TABLE No 62




GRAPH Nº XXIII
P.V.A. 20%
M.C. 19%
OVEN CURE 12 HOURS
TESTED AT 24 HOURS
TABLE Nº 63
DRY WEIGHT IN GMS
228
224
220
216
0
10
20
30
40
50
60
COALESCING AGENT PERCENT
COMPRESSIVE STRENGTH lb/in²
500
300
100
0
10
20
30
40
50
60
COALESCING AGENT PERCENT

6. LABORATORY WORK

6.7 COMPARISON OF ASHES

6.7 COMPARISON OF ASHES

The various sections of this work have given guide lines for the production of a building block type material, and the penultimate sections deal with the comparison of p.f. ash samples made with ash from High Marnham, North Tees and I.C.I. Billingham Power Stations.

The amount of P459 was fixed at 25% of the water content and for Hexylene Glycol the figure was set at 30% of the amount of P459. Samples were prepared with these additives and compacted at optimum moisture content. The latter feature was found by briefly carrying out the procedure of section 6.2. and the samples were then submitted to a 12 hour period of oven cure.

The three ashes were thus compared by their strength characteristic of twenty four hours using an unconfined compression test, and the results of this series of tests were tabulated and graph XXIV shows the comparison of Dry Density for the three ash.

The dry densities can be seen to decrease from the highest value obtained with the -300 B.S.S. fraction of the High Marnham Ash followed by natural High Marnham ash, North Tees Ash and I.C.I. Billingham ash in that order. The optimum moisture contents increasing in the same sequence.

I.C.I. Billingham gave good strength results for this series and so 10% and 15% emulsion characteristics were added to the 25% values. Graph XXVII gives the comparison of strengths with increases in emulsion characteristics.

6.7 TABLE 64

DETAILS OF MIXES

P459 %	M/C %	P.F.ASH Gms	WATER & P459 cc	WATER cc	P459 cc	30%H.G. cc
25	12.5	1000	125	93.75	31.25	9.375
25	15.0	1000	150	112.5	37.5	11.25
25	17.5	1000	175	131.25	43.75	13.125
25	20.0	1000	200	150.0	50.0	15.0
25	22.5	1000	225	168.75	56.25	16.875
25	25.0	1000	250	187.5	62.5	18.75

6.7 TABLE 65

DETAILS OF HIGH MARNHAM ASH SAMPLES

REF NO	M/C %	WET WT Gms	DRY WT Gms	D.D. Gms/cc	LOAD Tons	STRESS lbs/ins
1069	12.5	268	225	1.49	NOT TESTED	
1070		263	232		.107	76.5
1071		260	229		.072	51
1072		262	232		.120	86
1073	15.0	275	23.9	1.51	.165	118
1074		274	23.8		.174	124
1075		270	23.5		.184	131
1076		270	235		NOT TESTED	
1077	17.5	277	240	1.49	.314	224
1078		273	236		.164	117
1079		270	238		.258	184
1080		274	235		NOT TESTED	
1081	20.0	282	240	1.48	.432	308
1082		283	240		.406	288
1083		281	239		.580	414
1084		277	237		NOT TESTED	
1085	22.5	274	230	1.43	.790	563
1086		275	231		.768	547
1087		278	233		.564	402
1088		278	233		NOT TESTED	
1089	25.0	276	228	1.40	.764	544
1090		275	227		.792	564
1091		273	226		1.10	780
1092		275	227		NOT TESTED	

6.7 TABLE 66

DETAILS OF MIXES

P459 %	M/C %	P.F.ASH Gms	WATER & P459 cc	WATER cc	P459 cc	30%H.G. cc
25	12.5	1000	125	93.75	31.25	9.375
25	15.0	1000	150	112.5	37.5	11.25
25	17.5	1000	175	131.25	43.75	13.125
25	20.0	1000	200	150	50	15.0

6.7 TABLE 67

DETAILS OF SAMPLES MADE WITH HIGH MARNHAM (.300) ASH

REF NO	M/C %	WET WT Gms	DRY WT Gms	D.D. Gms/cc	LOAD Tons	STRESS lbs/ins
1169	15.0	275	242	1.52	0.20	142
1170		270	238		0.188	134
1171		271	240		0.206	147
1172		269	239		0.200	142
1173	17.5	285	247	1.54	0.538	384
1174		280	242		0.326	233
1175		279	242		0.418	298
1176		279	241		0.396	282
1177	20.0	286	243	1.53	0.30	214
1178		286	243		0.323	230
1179		284	243		0.346	246
1180		285	242		0.312	223

6.7 TABLE 68

DETAILS OF MIXES

P459 %	M/C %	P.F.ASH Gms	WATER & P459 cc	WATER cc	P459 cc	30%H.G. cc
25	25	1000	250	187.5	62.5	18.75
25	30	1000	300	225	75	22.5
25	35	1000	350	262.5	87.5	26.25
25	40	1000	400	300	1000	30

6.7 TABLE 69

DETAILS OF NORTH TEES ASH SAMPLES

REF NO	M/C %	WET WT Gms	DRY WT Gms	D.D. Gms/cc	LOAD Tons	STRESS lbs/ins
1093	25	187	155	0.94	.478	340
1094		183	152		.262	187
1095		181	150		.378	269
1096		185	153		.312	222
1097	30	196	157	0.97	.668	477
1098		203	161		.742	529
1099		196	158		.486	346
1100		194	154		.462	330
1101	35	208	161	0.99	.94	672
1102		208	160		1.00	712
1103		208	162		1.15	820
1104		209	162		.88	628
1105	40	207	155	0.97	.995	708
1106		206	155		1.06	755
1107		216	161		1.14	810
1108		214	161		1.16	825

6.7 TABLE 70

DETAILS OF MIXES

P459 %	M/C %	P.F.ASH Gms	WATER & P459 cc	WATER cc	P459 cc	30%H.G.
25	30	1000	300	225	75	22.5
25	40	1000	400	300	100	30
25	50	1000	500	375	125	37.5

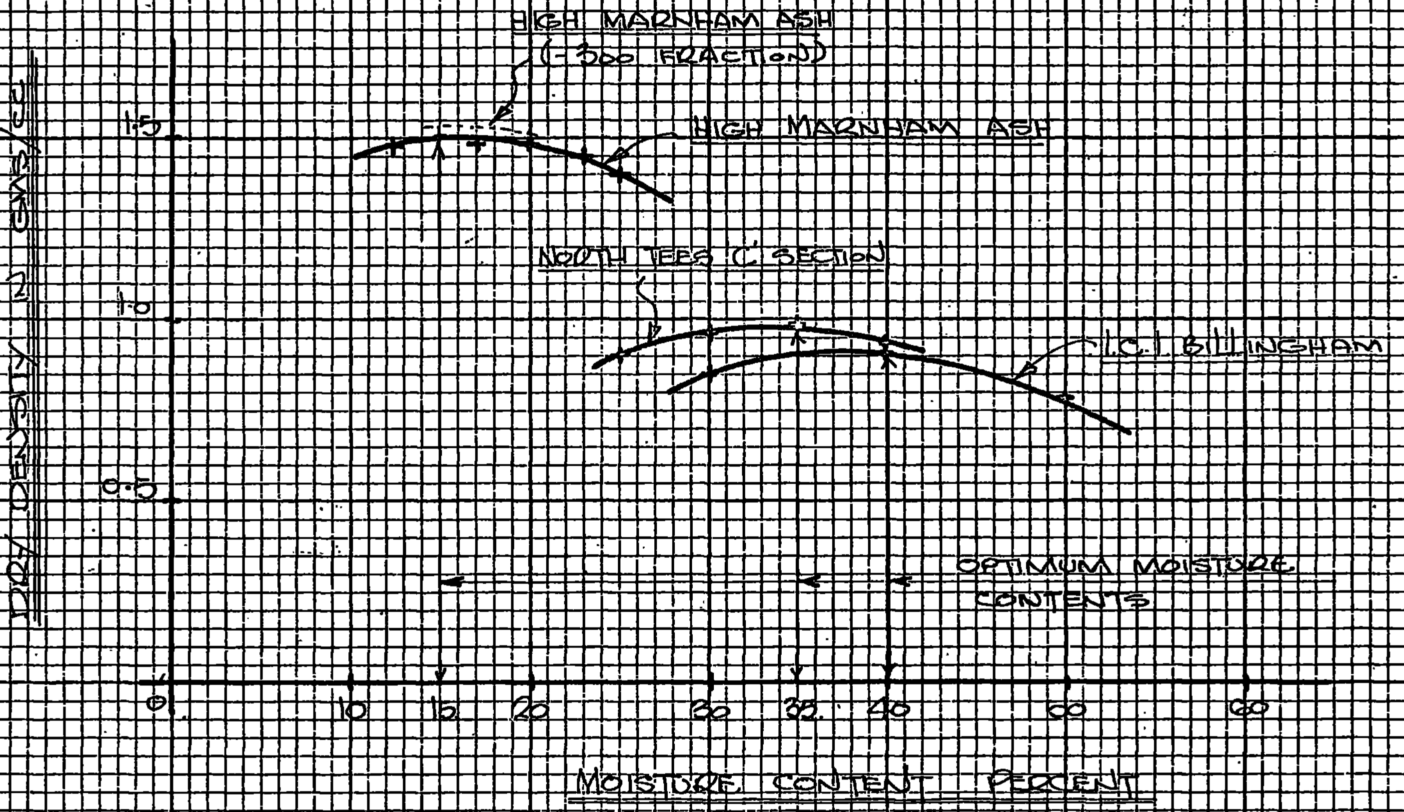
6.7 TABLE 71

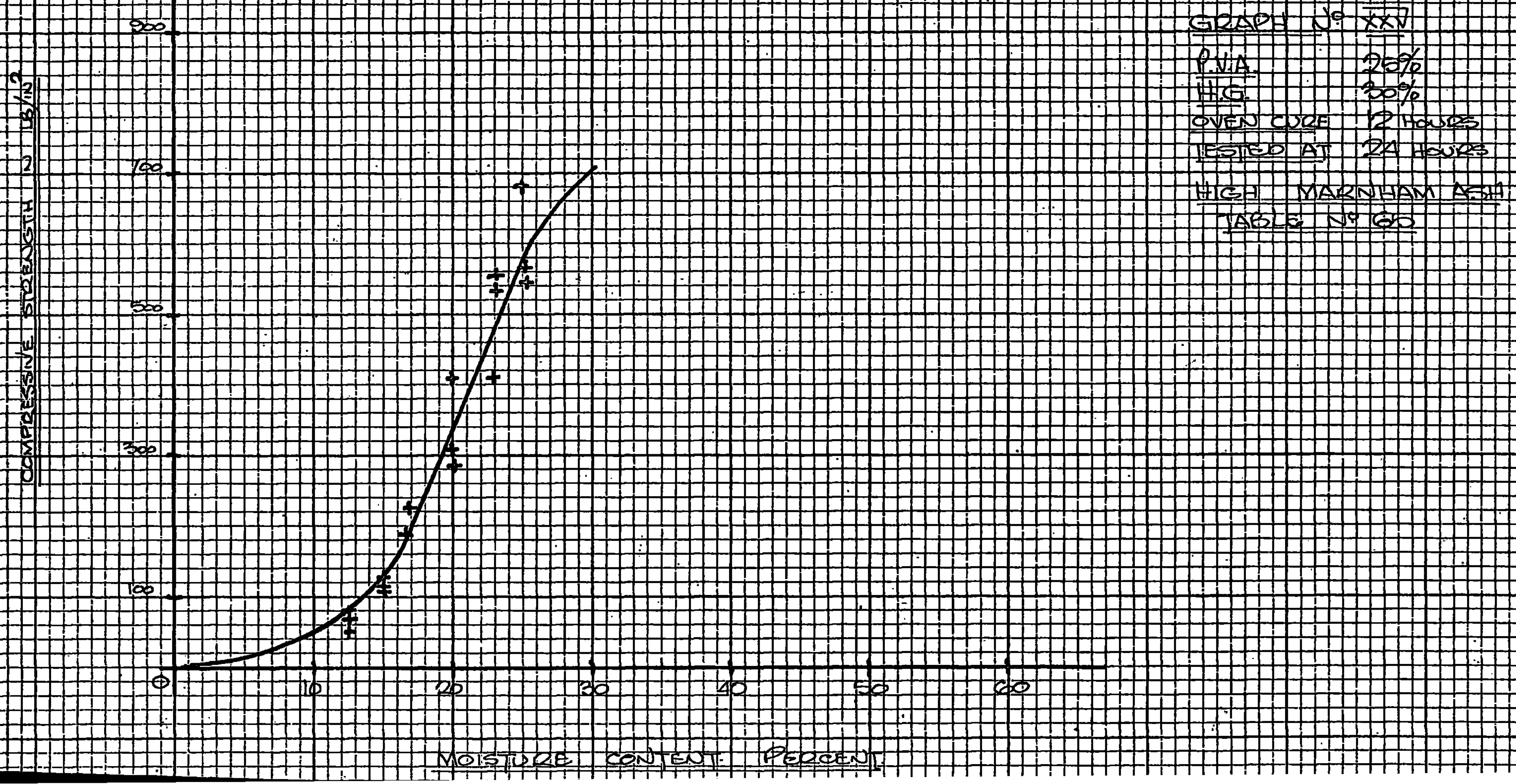
DETAILS OF I.C.I. ASH SAMPLES

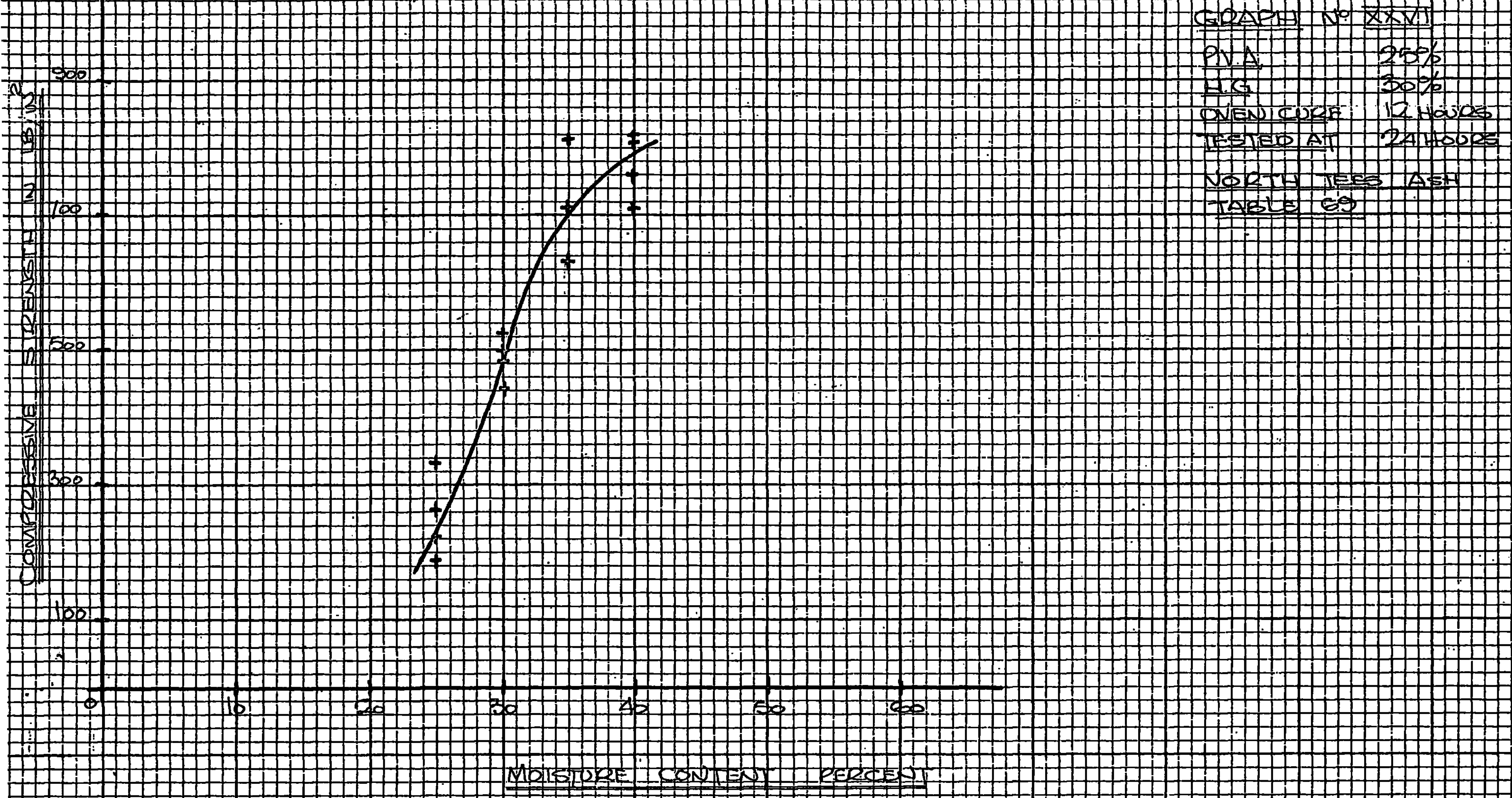
REF NO	M/C %	WET WT Gms	DRY WT Gms	D.D. Gms/cc	LOAD Tons	STRESS lbs/ins
1108	30	176	140	0.87	.280	199
1109		169	135		.218	155
1110		183	145		.230	169
1111		176	141		.264	188
1112	40	200	156	0.94	.930	663
1113		200	145		.942	670
1114		205	154		.946	673
1115		205	154		.802	572
1116	50	205	143	0.89	.816	581
1117		206	145		.796	567
1118		206	145		.922	656
1119		210	149		.932	664

GRAPH No XXIV

P.V.A. 25%
H.G. 30%
OVEN CURE 12 HOURS
TABLES 65, 67, 69 & 71.




GRAPH Nº XXV
P.V.A. 25%
H.G. 30%
OVEN CURE 12 HOURS
TESTED AT 24 HOURS
HIGH MARNHAM ASH
TABLE Nº 60
COMPRESSIVE STRENGTH ᴵ LB/IN²
900
700
500
300
100
0
10
20
30
40
50
60
MOISTURE CONTENT PERCENT


GRAPH No XXVI
PVA 25%
HG 30%
OVEN CURE 12 HOURS
TESTED AT 24 HOURS
NORTH TEES ASH
TABLE 69
COMPRESSIVE STRENGTH LB/IN^2
900
100
500
300
100
0
10
20
30
40
50
60
MOISTURE CONTENT PERCENT

6.7 TABLE 72

DETAILS OF MIXES

p459 %	M/C %	P.F.ASH Gms	WATER + p459 cc	WATER cc	p459 cc	30%H.G. cc
10	30	1000	300	270	30	9
10	40	1000	400	360	40	12
10	50	1000	500	450	50	15

6.7 TABLE 73

DETAILS OF I.C.I. ASH SAMPLES

REF NO	M/C %	WET WT Gms	DRY WT Gms	D.D. Gms/cc	LOAD Tons	STRESS lbs/ins
1141	30	182	143	0.91	0.08	57
1142		184	143		0.12	85.5
1143		183	143		0.112	80.0
1144		185	145		0.106	75.5
1145	40	206	151	0.925	0.214	151
1146		205	149		0.212	150
1147		195	143		0.138	98.5
1148		200	145		0.188	134
1149	50	203	140	0.88	0.188	134
1150		204	140		0.196	140
1151		206	141		0.214	152
1152		206	142		0.210	156

6.7 TABLE 74

DETAILS OF MIXES

p459 %	M/C %	P.F.ASH Gms	WATER + p459 cc	p459 cc	WATER cc	30%H.G. cc
15	30	1000	300	45	255	13.5
15	40	1000	400	60	340	18.0
15	50	1000	500	75	425	22.5

6.7 TABLE 75

DETAILS OF I.C.I. ASH SAMPLES

REF NO	M/C %	WET WT Gms	DRY WT Gms	D.D. Gms/cc	LOAD Tons	STRESS lbs/ins
1153	30	182	144	0.89	.178	127
1154		177	140		.152	108
1155		180	142		.170	121
1156		180	142		.198	141
1157	40	215	160	0.97	.618	440
1159		213	157		.620	442
1159		210	155		.624	444
1160		207	152		.430	312
1161	50	208	145	0.905	.472	336
1162		211	148		.482	344
1163		211	148		.518	370
1164		211	148		.516	368

GRAPH Nº XXVII

P.V.A. VARIABLE %

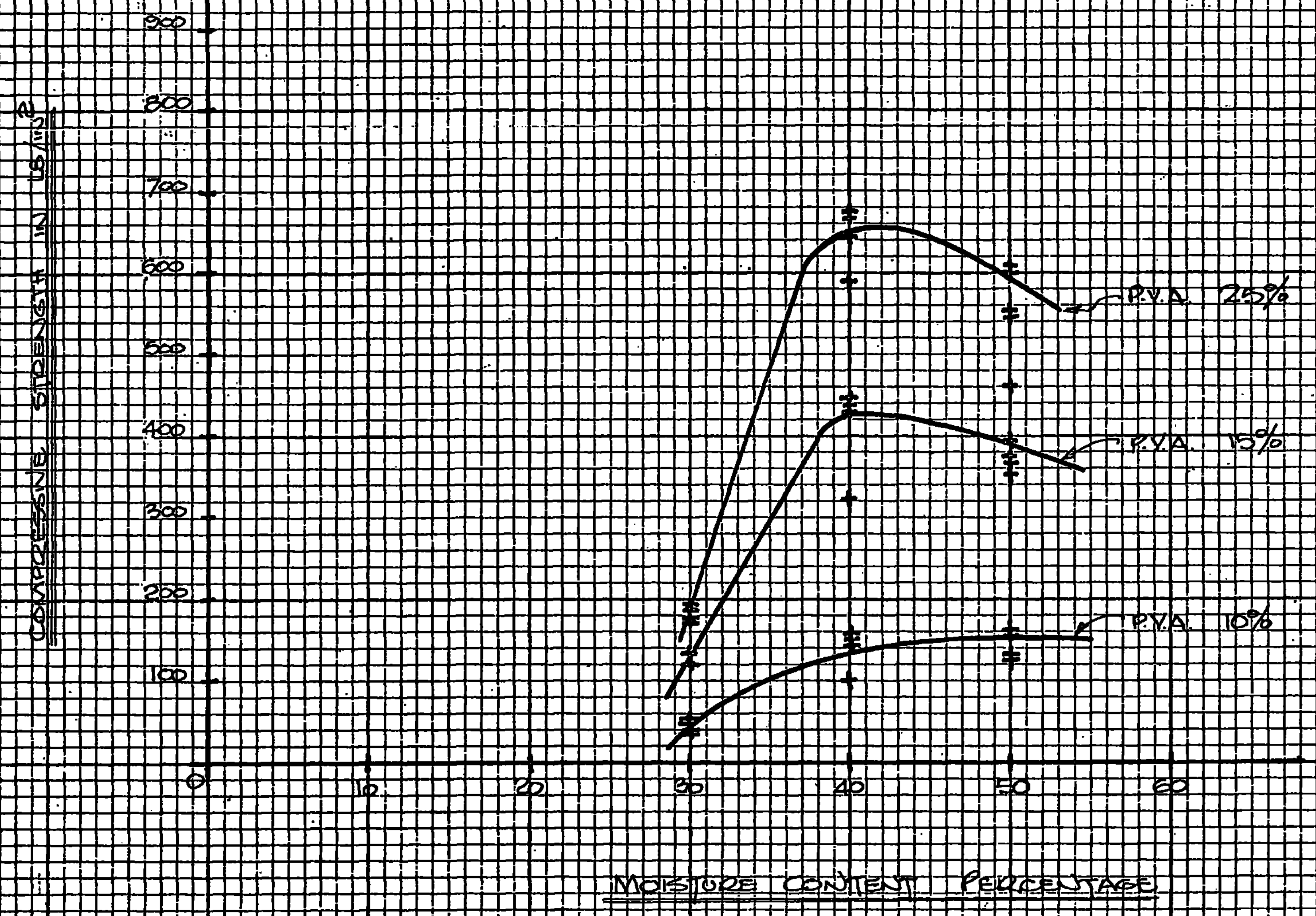
H.G. 30%

OVEN CURE 12 HOURS

TESTED AT 24 HOURS

I.C.I. BILLINGHAM ASH

TABLE Nº 73 & 75



6.7.1 VOIDS IN SAMPLES

USING $\frac{1}{\gamma_d} = \frac{1}{\gamma_s} \frac{M}{100\gamma_\omega}$ ________________ 6.8.1.A

for zero air voids

and $\frac{1 - \frac{Va}{100}}{\gamma_d} = \frac{1}{\gamma_s} + \frac{M}{100\gamma_\omega}$ ________ 6.8.1.B

for times of constant air voids

where γ_d = Dry density of ash samples
m = Moisture content (%)
γ_s = Density of ash particles
γ_ω = Density of water
V_a = Air voids expressed as a percentage of total volume.

from Soil Mechanics for Road Engineers published by D.S.I.R.

6.7.1.1 HIGH MARNHAM ASH TABLE 76

γ_s = 2.36 gms/cc

DRY DENSITY IN Gms/cc					
M/C	% AIR VOIDS				
%	0%	5%	10%	20%	30%
10	1.91	1.81	1.72	1.53	1.34
20	1.60	1.52	1.44	1.28	1.12
30	1.38	1.31	1.24	1.10	0.97
40	1.21	1.15	1.09	0.97	0.85
50	1.08	1.03	0.97	0.86	0.76

At optimum m/c of 15%

Dry Density = 1.51 gms/cc

∴ % AIR VOIDS = 12.5%

NORTH TEES ASH TABLE 77 6.7.1.2.

γ = 2.09 gms/cc

DRY DENSITY IN GMS/CC						
M/C	% AIR VOIDS					
%	0%	5%	10%	15%	20%	30%
10	1.75	1.66	1.50	1.49	1.40	1.23
20	1.49	1.41	1.34	1.27	1.19	1.05
30	1.30	1.23	1.17	1.10	1.04	0.91
40	1.15	1.09	1.04	0.98	0.92	0.81
50	1.03	0.98	0.94	0.88	0.83	0.72
60	0.93	0.88	0.84	0.79	0.75	0.65

At optimum moisture content of 0.35%

Dry Density = 0.99gms/cc

∴ Air Voids = 18%

I.C.I. BILLINGHAM ASH TABLE 78 6.7.1.2.

γ = 2.05 gms/cc

DRY DENSITY IN GMS/CC						
M/C	% AIR VOIDS					
%	0%	5%	10%	15%	20%	30%
10	1.70	1.62	1.53	1.45	1.36	1.19
20	1.45	1.30	1.31	1.24	1.16	1.02
30	1.27	1.21	1.14	1.08	1.02	0.89
40	1.12	1.07	1.01	0.95	0.90	0.79
50	1.01	0.96	0.91	0.86	0.81	0.70
60	0.92	0.87	0.83	0.78	0.73	0.64

At optimum moisture content of 40%

Dry Density = 0.94gms/cc

∴ Air Voids = 16%

6. LABORATORY WORK

6.8 WEATHER TESTS

6.8 WEATHER TESTS

Following the comparison of samples made from three differing grades of ash in Section 6.8. It was thought that the effects of weather on the samples would be worth investigating.

Table 79 and Table 80 list the mixes and details of the cylindrical samples used in the weather test, and a suitable location was selected towards the south end of the Science Laboratory roof. The samples were placed in a galvanised tray with small holes in the bottom to allow self draining of the tray and were placed in this exposed position.

The samples were inspected at five months exposure and the following observations were made :

> High Marnham ash samples had suffered most damage on a visual inspection, and the sample top had lost its sharp edge.
>
> North Tees and I.C.I. Billingham ash samples had suffered no obvious damage to their surfaces and the tops had retained their sharp edges.

Unfortunately the tray had not drained during this test and the effect of this was that the samples had been standing in about one inch of water, and were completely saturated.

This made the weather test a more severe test than had been intended but it was interesting to note that the samples seemed generally better preserved below the water level - on surface appearance only - but the surface of all the samples were all softer than at the production stage.

The samples were not tested for strength at this point but the High Marnham ash samples had probably lost over 50% of their original strength; the loss of strength in the other samples was probably closer to 40%.

6.8 TABLE 79

DETAILS OF MIXES

P459 %	M/C %	P.F.ASH Gms	WATER + P459 cc	WATER cc	P459 cc	30%H.G. cc
HIGH MARNHAM ASH						
25	20	1000	200	150	50	15
NORTH TEES ASH						
25	40	1000	400	300	100	30
I.C.I. BILLINGHAM ASH						
25	40	1000	400	300	100	30

6.8 TABLE 80

DETAILS OF SAMPLES

REF NO	M/C %	P459 %	WET WT Gms	DRY WT. Gms
HIGH MARNHAM ASH				
1129	20	25	278	237
1130			280	239
1131			277	237
1132			280	240
NORTH TEES ASH				
1133	40	25	204	153
1134			207	156
1135			213	159
1136			212	159
I.C.I. BILLINGHAM ASH				
1137	40	25	196	146
1138			200	149
1139			203	152
1140			200	149

7. CONCLUSIONS

7. CONCLUSIONS

7.1 The ash from High Marnham Power Station used through the main sections of the laboratory work can be regarded as a typical ash produced in modern coal fired stations; this cannot be said about the other two samples used in Section 6.1 and 6.7, and a comparison of the three ashes is made in Tables 13 and 14 to illustrate this point.

7.2 In Section 6.1 a brief look was taken at variations on cement replacements using hydrated lime and a mortar plasticiser. The number of cubes prepared was only small and so it will only be possible to make some qualitative observations on the results.

7.3 Unfortunately only samples of North Tees and I.C.I. Billingham ashes were available for testing but these can be regarded as examples of medium grade and coarse ash. When 20% of the cement from the orthodox mix was replaced by ash the resulting concrete had reduced strength as might be expected, but when this same replacement was supplemented by 10% lime the concrete showed improved strengths on the original mix.

7.4 Greater strength improvements were recorded using 20% cement replacement and a plasticiser in the water; under these conditions North Tees ash gave improvements in advance of 12% and I.C.I. ash gave about 10% increase in strength over the basic concrete mix.

7.5 The mixes prepared with 40% and 50% cement replacement, with the addition of lime, gave strength values below those of the orthodox mix, but these values were only down to 80% and 60% of the basic mix strength when 50% of cement had been replaced.

7.6 The concrete cubes prepared with North Tees ash were always an improvement on the corresponding cubes made with ash from I.C.I. Billingham, which is what might have been expected from the physical characteristics of the two materials.

7.7 Of the ashes used in Section 6.7 and 6.1, the ash from I.C.I. would have been deemed unsuitable by all four of the specifications limiting ignition losses listed in Section 3.1.1 Table 2. North Tees ash would have complied with two and been fractionally outside the requirements of the other two bodies. The ash from High Marnham would have complied with all four.

7.8 Thus although no firm, quantitative conclusions can be drawn from Section 6.1 of the work in the laboratory, it is interesting to note that good strengths can be obtained with cement replacements of up to 50% when lime is added; this section proved to be a most useful introduction to the material used throughout this work.

7.9 The largest part of the time spent in the laboratory involved investigations of the stabilisation of p.f. ash with PVA and these started with a series of tests to find the optimum moisture content of the ash from High Marnham Power Station; this was used throughout the main series of tests as a condition under which samples should be prepared.

7.10 From the values of specific gravity noted in Table 4 it was possible to calculate the percentage of voids for the samples prepared in Section 6.7. These ranged from 12.5% for High Marnham, 18% for North Tees and 16% for I.C.I. Billingham. These values for air voids indicate that the standard test used throughout this work could be improved to give values closer to Proctor Test results. However, to effect an improvement would have meant using a larger mould and this would have reduced the range and possibly the number of group experiments that were carried out with the adopted test.

7.11 In Sections 6.2 to 6.7 a point was made of using one particular sample of ash for an individual section of the investigation. In this way it was hoped that any variations from sample to sample would be eliminated but an unfortunate side effect of this step was that each section became more of an individual group of experiments where the strengths of subsequent sections could not necessarily be compared.

7.12 However the work was carried out in such a way that each section provided another parameter for the following tests, leading up to Section 6.7 where all the various parameters were fixed and samples of three ash were compared under identical conditions.

7.13 The ash was being regarded as a cohesive soil and it was natural that an investigation should be based on optimum conditions for the material, thus Section 6.2 set out to find the maximum dry density under conditions of the modified Proctor Test.

7.14 The initial test was carried out with quite a number of moisture contents on either side of optimum - Graph II - but in later sections it was found that optimum could be gauged during mixing. In fact it was found that as the work progressed a greater familiarity with the material allowed reasonably accurate assessments to be made, and these were easily confirmed by slightly increasing and decreasing the moisture contents for a further two mixes.

7.15 The effects of varying percentages of PVA can be seen in Graph III where the moisture content at optimum was found to increase slightly with increased percentages of the additive. This was to be expected as the PVA contained only 45% water so that the increasing percentages of PVA effectively reduced the amounts of water added to the ash.

7.16 After the investigation of compaction it was decided that the strength of the samples would be the guiding criterion with a restriction being placed on the amounts of additive used, and so Section 6.3. was the first occasion when the strength of the material was considered.

7.17 As the material was being considered as a soil it was natural that the first samples should be kept in polythene bags, prior to test.

7.18 The group of samples prepared in tables 28, 29 and 30 led to the plotting of graph IV and as mentioned in 6.3 this was an important stage of the work.

7.19 This was an important step as the strengths were well below those hoped for in the outset of the work but graph IV was encouraging as the three month strengths were a slight improvement on the three day tests. This was possibly one of the most important groups of results as the fears that this PVA would break down in alkaline conditions appear to have been dispelled for this type of emulsion on a short term basis.

7.20 This means that the amounts of Veo-Va 911 added to P.459 at least provide short term assistance to hydrolysis.

7.21 The values of strengths, however, were low even with 30% PVA and so the conditions of cure had to be reconsidered.

The most suitable alternative was the drying oven and Section 6.4 covers an initial investigation of oven cure. The early indications of strengths were good in that the 30% PVA range of strengths was raised from 45lb/in^2 for samples retained for three months in polythene bags was improved to 650 lb/in^2 at seven days when 24 hours of oven cure were used.

7.22 The increase in strength may have been partly due to a misunderstanding of the way in which the PVA gained strength as it does appear to require conditions in which it can dry out, (and, possibly, polymerise), which becomes evident with the results of 6.4.

7.23 Section 6.5 was a more detailed investigation of cure generally based on the drying oven. Firstly the effects of variations of time in the oven were studied for a range of PVA percentages.

7.24 This series of tests showed that oven cure effects were related to time and the samples with 30% and 40% PVA appeared to suffer slight damage with periods of oven cure greater than 12 hours.

7.25 Further it was thought that immediate oven cure might be rather severe and so variations of pretreatment using polythene bags and air drying prior to a twelve hour period in the oven. This section on pretreatment showed that there was nothing to be gained from a more gentle form of cure.

7.26 One effect that was noticed in this section was the colour gradient that appeared through the range of samples with those spending longest in the polythene bags becoming the lightest shade of grey.

7.27 The rate of loss of moisture was plotted in graph XIII. which shows that the loss of weight is approximately proportionate to time, and that the samples are dry after less than three hours in the oven.

7.28 These findings were slightly surprising in that it had been imagined that oven cure might be rather a severe transition. The remaining tests carried out in this section were all carried out with twelve hours of cure on the basis of these results.

7.29 At this point a brief look was taken at an alternative native additive. Two examples of Styrene Acrylate were supplied by the Pontyclun Chemical Co. Ltd. However the samples prepared in Section 8.1 showed that in this particular use these two samples of Styrene Acrylate proved inferior to the PVA so far used.

7.30 In returning to the main investigation using PVA the next step was to see if any further improvements in strength could be made. It was thought that some improvements would be made if a coalescing agent could be used.

7.31 In Section 6.6 two examples of these agents were investigated and of these it was possible to eliminate

Butyl Dioxitol acetate as this produced reductions of strength but Hexylene Glycol had a good effect on the general mix.

7.32 Graph XX compares the effects of varying percentages of coalescing agent using a basic mix with 25% PVA and compacted at a moisture content of 25%.

7.33 Thus the six subdivisions of the laboratory work provided a progression of improvements on the samples prepared in the first instance. The most obvious improvement being recorded in the strength aspect but it must be noted that the general material produced was greatly improved by the addition of the coalescing agent; this was particularly obvious in the surface improvement of the samples.

7.34 The penultimate section of the laboratory work compared the material produced using three different examples of p.f. ash.

7.35 This was carried out by setting the percentages of PVA at 25% of the water plus P459 volume and the amount of Hexylene Glycol at 30% of the P459 to try and obtain a reasonable basis for comparison. All the samples were subjected to a twelve hour period of oven cure following extraction from the mould, and, as was normal practice throughout this work the samples were extracted immediately after compaction.

7.36 A three point determination of the optimum moisture content was carried out for the three ashes and conditions of maximum dry density were used as the basis of the comparison.

7.37 Graphs XXIV, XXV and XXVI give the strength characteristics for the ashes used when the percentage of additive was varied.

7.38 The samples prepared in Section 6.7 under the indicated conditions allowed the materials produced to be compared. The moisture contents of the samples prepared varied by too wide a margin for a direct comparison to be made but the following characteristics were noted about the samples prepared at optimum moisture content.

7.39 High Marnham ash had an o.m.c. of 15.0% which gave strengths in the range of 175 lbs/in^2 and dry density of 1.51 gms/cc with 12.5% air voids.

7.40 North Tees ash had an o.m.c. of 35% which gave strengths in the range 710 lbs/in^2 and a dry density of 0.99 gms/cc at 18% air voids.

7.41 I.C.I. Billingham ash had an o.m.c. of 40% which gave 650 lbs/in^2 and a dry density of 0.94 gms/cc with 16% air voids.

7.41 The surface of the samples was consistent for each group produced and the best surfaces were produced with the High Marnham ash samples. North Tees ash samples had

had a coarser textured surface and the samples prepared from I.C.I. Billingham ash was similar in this respect but had a darker colour due to the high carbon content of the latter ash.

7.42 It was a pity that the I.C.I. ash had such a high carbon content as this will certainly have affected the strengths obtained with this ash, and adds a rather indeterminate factor into the conclusions on strength- other than to agree with the restrictions of table II limiting combustible material content to ashes. As carbon will be a softer material than the other fused particles of the ash the PVA would not be able to bind the softer carbon surfaces as efficiently as those of the harder materials.

7.43 Graphs XXIV, XXV and XXVI are interesting in that only the graph for I.C.I. Billingham ash gave reducing strengths over optimum moisture content.

7.44 This is particularly noteworthy in that the strength of samples compacted with moisture contents greater than optimum might be expected to be reduced due to the incresed voids ratio. In this case the strength will have come from the PVA and this emulsion has more than offset any strength losses above optimum in two of the three cases under consideration.

7.45 The samples produced with North Tees ash have given the best results in all respects including surface finish. At a moisture content of 40% - 25% PVA - this ash gave strengths of 775 lbs/in^2 and a dry density of 0.97 gms/cc or approximately 60 lbs/ft^3.

7.46 These characteristics fall well within the range of a number of materials now marketed as building block material.

7.47 The final test carried out was to find the effect of weather on the samples produced at optimum moisture content in Section 6.7

7.48 As described in Section 6.8., the weather test actually undergone by the samples was more severe than had been intended as the samples had been exposed to the weather in a saturated condition.

7.49 Despite this the samples prepared with North Tees and I.C.I. ashes stood up well to the weathering.

7.50 Thus it seems that contrary to the thoughts at the outset of the work that the finer ash would give the best results it is obvious that the coarser the sample the better will be the results for materials prepared in accordance with Section 6.8. The obvious restriction that should be placed on the ash would limit the carbon content to a maximum of 5% or slightly above this figure.

7.51 In a final reflection it must be noted that this work will certainly not have solved all the problems but it is hoped that some contribution has been made towards "The Polymer Stabilisation of P.F. Ash".

7.52 Sufficient work has been done to show that P.F. Ash can be stabilised into blocks by mixing with a small percentage of polymer additives and curing the formed mixture under suitable conditions. It has been shown that, in general, the crushing strength of the blocks increases with additive percentage, but that strengths and densities comparable with those of currently used light-weight building blocks are achieved with very small amounts of additive. Suitable conditions of mix proportion, compaction and cure have been demonstrated, and the comparative behaviour of three types of ash has been studied.

It is too early to deduce any real conclusion from the limited weathering investigation already carried out, though the behaviour of the specimens to date appears to confirm the view that the coarser ashes perform best. Further investigations would be required to show whether any of the blocks have sufficiently long term stability to be used in a weathering environment, or whether they should be restricted to "dry" situations, as in the case with most other light-weight blocks. Other investigations may show that stabilisation can be achieved with curing conditions at lower temperatures and for shorter periods.

The present work shows that another use has been found for a readily available material, and another possible material of construction can be developed.

8. ADDITIONAL LABORATORY WORK

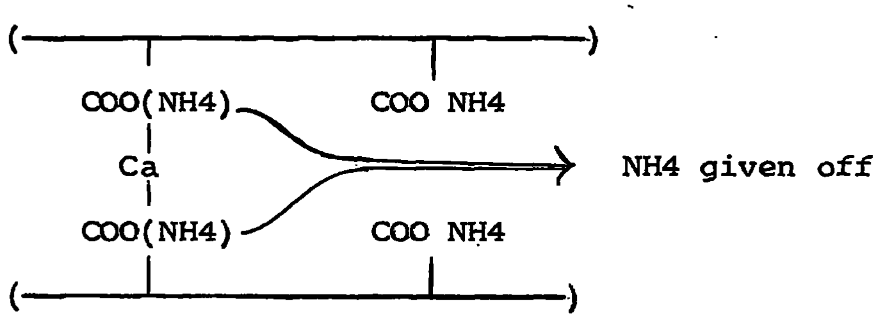
8.1 FURTHER ADDITIVES

8.1 FURTHER ADDITIVES

A slight diversion was taken during the main part of the work with P459 to investigate an alternative form of additive to the polyvinyl acetate being used.

The Pontyclun Chemical Company Limited, who had taken considerable interest in this work, suggested that the use of Styrene Acrylate might give better results than those obtained with the polyvinyl acetate.

This idea had a number of advantages not the least of which was that should there by any calcium in the ash a reaction would be set up with the Styrene acrylate releasing ammonia. This reaction would be of the form :



The unstable styrene acrylate would thus be stabilised according to the above equation and it was hoped that this would provide a better strength material particularly as styrene acrylates give better resistance in alkaline conditions. However this material is considerably more expensive than the polyvinyl acetates.

Table 81 gives details of two mixes that should have given the increased strengths with two samples of styrene acrylates - P516 and E834.

8.1 TABLE 81

DETAILS OF MIXES

ADDITIVE %.	M/C %	P.F.ASH Gms	WATER + ADDITIVE cc	WATER cc	ADDITIVE cc
10	20	1000	200	180	20
20	20	1000	200	160	40

8.1 TABLE 82

DETAILS OF p516 SAMPLES

REF NO	p516 %	M/C %	WET WT Gms	DRY WT Gms	LOAD Tons	STRESS lbs/ins
601	10	20	256	217	0.06	42.8
602	10	20	258	219	0.045	32.2
603	10	20	260	220	0.035	25.0
604	10	20	250	219	NOT TESTED	
605	20	20	254	317	0.05	35.7
606	20	20	253	217	0.045	32.1
607	20	20	249	214	0.04	28.6
608	20	20	248	213	NOT TESTED	

8.1 TABLE 83

DETAILS OF E834 SAMPLES

REF NO	E834 %	M/C %.	WET WT Gms	DRY WT Gms	LOAD Tons	STRESS lbs/ins.
609	10	20	256	218	0.062	44.2
610	10	20	255	217	0.056	40.0
611	10	20	256	217	0.044	31.4
612	10	20	254	217	NOT TESTED	
613	20	20	256	219	0.042	29.9
614	20	20	254	216	0.050	35.7
615	20	20	248	211	0.048	34.3
616	20	20	249	213	NOT TESTED	

The cylinders were made in accordance with the standard procedure developed during this work with the compression tests at seven days and these results can be seen in Table 82 and Table 83.

Tables 82 and 83 show the values of wet and dry weight and also the crushing test results.

The crushing strengths were low in both the samples made with P516 and with E834 and compared only with the strengths of the earlier samples made with P459 and stored in moist conditions. As these samples had been cured in the drying oven it was felt that these two examples of styrene acrylates were unlikely to produce the necessary improvement in strengths.

On the basis of the results in tables 82 and 83 it was decided that the main line of investigation should continue with P459 as the additive.

8. ADDITIONAL LABORATORY WORK

8.2 SAND SAMPLES

8.2 SAND SAMPLES

During one of the visits to the Laboratories it was decided that an investigation should be made into the effects of the additive on sand samples.

This was carried out using the same method of sample production as detailed in Section 6.2 and a period of oven cure of 12 hours with the samples being prepared at a moisture content selected as optimum after a brief investigation of the Dry Density characteristic. In this series "moisture" was described as water plus PVA and a "moisture" content of 10% was used throughout with the varying percentages of PVA expressed as a fraction of the total moisture content.

Details of the mixes are given in Table 86 for the varying percentages of PVA increasing from 20% - 70% and the results of the unconfined compression tests taken at 24 hours are listed in Table 87 and are plotted on Graph No. XXVIII.

One of the main problems in this series of tests was that the sand samples were more difficult to extract from the mould than the samples made with p.f. ash. This meant that a number of the samples were damaged during extrusion but the series under test were generally in good order.

Samples of the sand were sieved and the specific gravity of the ash was measured using a small scale test. However, the latter test was repeated three times so that the value of the mean of these results should be reasonably accurate. The mean value was then used to find the amount of air voids at the 10% moisture content; the air voids calculated on this basis were 15.5%

The strength of these samples would be considerably improved if the compaction could be improved thus reducing the voids ratio to around say 5% which would probably add about 20% - 25% to the strength values of Table 87.

DETAILS OF SAND SAMPLES

B.2 TABLE 84.

SIEVE ANALYSES OF SAND - (2000 gm sample)

APPERTURE SIZE MICRONS	MESH NO. 3.5	PERCENTAGE PASSING
2400	7	98.2
1200	14	93.5
850	12	75.7
600	25	58.8
300	52	26.7
210	72	13.8
150	100	6.1
90	170	0.8
75	200	0.2

B.2 TABLE 85.

SPECIFIC GRAVITY OF SAND

W_5	=	13	36	46
W_1	=	74	74	74
W_2	=	82	96	104
G_5	=	2.68	2.66	2.70

MEAN G_5 = 2. 68

MEAN D.D. of samples = 1. 80 gm/cc

AIR VOIDS = 15. 5%

SAND SAMPLES

8.2 TABLE 86

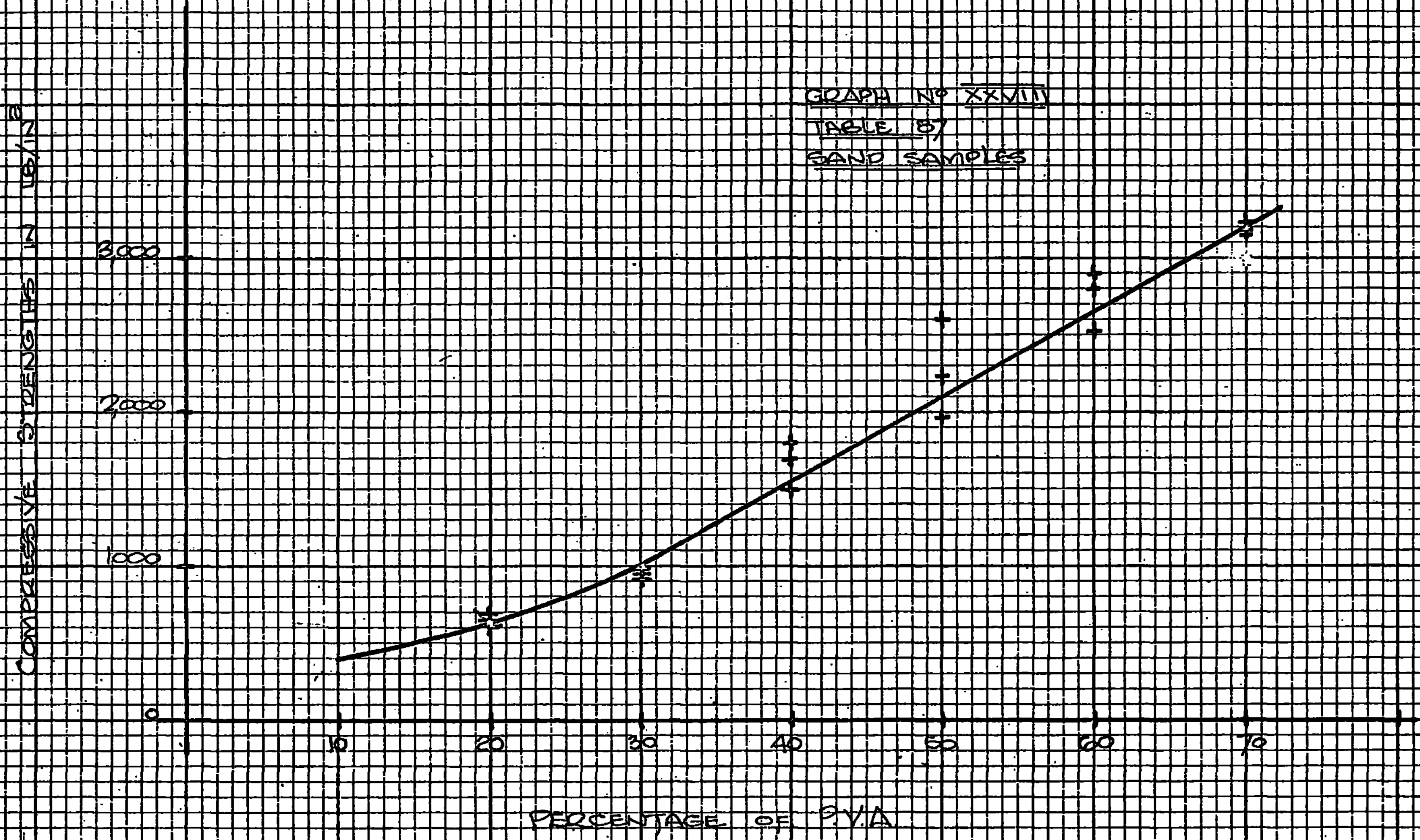
DETAILS OF MIXES.

P459 %	M/C %	SAND Gms	WATER + P459 cc	WATER cc	P459 cc
20	10	1000	100	80	20
30	10	1000	100	70	30
40	10	1000	100	60	40
50	10	1000	100	50	50
60	10	1000	100	40	60
70	10	1000	100	30	70

8.2 TABLE 87

DETAILS OF SAMPLES

p459 %	M/C %	WET WT Gms	DRY WT Gms	LOAD Tons	STRESS lbs/ins
20	10	300	278	0.856	610
		303	280	0.984	700
		303	281	0.866	618
30	10	307	285	1.335	950
		306	285	1.370	975
		306	285	1.380	985
40	10	310	289	2.38	1700
		306	286	2.48	1770
		308	288	2.175	1550
50	10	311	291	2.70	1930
		310	291	3.575	2550
		308	289	3.15	2250
60	10	310	292	3.525	2530
		310	292	4.075	2900
		307	290	3.925	2800
70	10	311	294	3.70	2660
		311	294	4.50	3210
		314	299	NOT TESTED	



GRAPH No XXVIII
TABLE 87
SAND SAMPLES

9. ACKNOWLEDGEMENTS

9. ACKNOWLEDGEMENTS

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