PROCESSING OF CEMENT FLUE DUST

A thesis submitted in partial fulfilment for the degree
of Doctor of Philosophy in Chemical Engineering at the
University of Aston in Birmingham, England.

Jaw-Huei Khor,
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Summary

Studies were made of the feasibility of calcining alkali rich flue dusts derived from two U.K. cement works, viz, Northfleet and Westbury, in fluidised beds to produce a material which is suitable for intergrinding with normal cement clinker and an alkali by-product which is saleable as fertiliser. To avoid adverse effects on cement quality, most of the KCl and a proportion of the K_2SO_4 in the dusts must be volatilised and the residual free lime of the clinker product must not exceed about 10%. Theoretical considerations indicated that for the calcining conditions envisaged, almost complete KCl volatilisation was feasible but K_2SO_4 volatilisation was limited by the saturation vapour pressure.

Experiments were carried out in 100mm and 150mm diameter fluidised beds heated partly by an external propane burner and partly by direct injection of fuel oil. The fluidised bed was operated at a fluidisation velocity of 3-4 m/s and the gases were air-quenched in a swirl vessel and the condensed alkali fume was collected in bag filter or electrostatic precipitator, after removal of carry-over material in a cyclone.

It was established that over the ranges of temperature (1120-1260°C) and residence time (14-59 min.) investigated, KCl volatilisation was almost complete and virtually independent of either parameter. The K_2SO_4 volatilisation was in agreement with the vapour pressure limiting postulate and a typical residual free lime of 5-6% was obtained, and a by-product containing typically over 90% alkalis was recovered satisfactorily. These results were corroborated by tests on independent 300mm and 450mm fluidised bed experiments.

It is predicted that large-scale processing of Northfleet flue dust is feasible but that Westbury flue dust needs $CaCl_2$ addition or treatmemt under reducing conditions to enhance K_2SO_4 volatilisation. A preliminary evaluation of the process for calcining Northfleet dust and comparison with various options reviewed in the literature survey are also presented.

Key Words: Cement dust, Fluidised bed, Alkali volatilisation

CLAIMS OF CONTRIBUTION

1. Exploration of new technology, viz, the application of high temperature fluidised bed, to convert cement flue dust wastes into useful low grade clinker and fetiliser.

2. Methodical examination of flue dust problems and presentation of substantial flue dust data.

3. Critical review of available literature, including a considerable amount of hitherto unpublished works from cement industry, of the state-of-art of flue dust processing and previous work.

4. Derivation, from known principles of gas-solid fluidisation and alkali vapour pressure data, of a relationship between the amount of alkali sulphate removal and the fluidised bed operating conditions.

5. Development of experimental systems and techniques, with particular reference to the fluidised bed exhaust gas treatment, to evaluate the feasibility of the process operated at industrially viable conditions.

6. Presentation of comprehensive experimental data, with attempted explanations, of high temperature fluidised bed operation and cement dust calcining characteristics as well as useful correlations for scale-up.

7. Evaluation of comparative technology and suggestions of possible refinement to the fluidised bed process developed.

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NOTATION

(Symbols and constants defined and used locally are excluded).

A_t	Cross-sectional area of fluidised bed	$[m^2]$
Bi	Biot's number ($= h_p . d_p / 2k_s$)	[-]
c_p	Specific heat at constant pressure	$[\text{kcal kg}^{-1}\ {}^\circ C^{-1}]$
C_D	Drag coefficient	[-]
d_p	Particle diameter	[mm or m]
E(t)	Particle residence time distribution function	[-]
F(t)	Particle hold-up	[-]
F_e	Rate of material carry-over	$[\text{kg h}^{-1}]$
F_i	Rate of feed input	$[\text{kg h}^{-1}]$
F_o	Rate of calcined produce output	$[\text{kg h}^{-1}]$
g	Acceleration of gravity	$[= 9.81\ \text{m s}^{-2}]$
Ga	Galileo number ($= d_p^3 . \rho_g(\rho_s - \rho_g) g/\mu^2$)	[-]
G_i	Rate of gas input	$[\text{kg h}^{-1}]$
G_o	Rate of gas output	$[\text{kg h}^{-1}]$
h_p	Heat transfer coefficient between gas and particle	$[\text{kcal m}^{-2}\ \text{s}^{-1}]$
$\Delta H_r'$	Heat of reaction based on dust feed	$[\text{kcal kg}^{-1}]$
$\Delta H_r''$	Heat of reaction based on calcined product	$[\text{kcal kg}^{-1}]$
k	Thermal conductivity	$[\text{kcal m}^{-1}\ \text{s}^{-1}\ {}^\circ C^{-1}]$
L_a	Height of fluidised bed active section	[m]
L_{mf}	Height of fluidised bed at minimum fluidisation	[m]
L_f	Height of bubbling fluidised bed	[m]

m	Mass of component	[kg]
m_f	Mass of fuel input	[kg]
M_g	Molecular weight of fluidising gas	[-]
M_v	Molecular weight of alkali vapour	[-]
Nu_p	Nusselt number for gas-particle heat transfer ($= h_p \cdot d_p/kg$)	[-]
p	Partial pressure	[atm]
p^*	Equilibrium partial pressure	[atm]
p_s	Saturation vapour pressure	[atm]
P	Total operating pressure	[atm]
ΔP_B	Pressure drop of fluidised bed material	[mm W.G.]
ΔP_D	Pressure drop of distributor plate	[mm W.G.]
ΔP_o	Pressure drop of fluidised bed and distributor plate	[mm W.G.]
q	Heat transfer	[kcal]
q_L	Heat loss	[kcal]
Re_p	Reynolds number of particle ($= d_p \cdot U_o \cdot \rho_g/\mu$)	[-]
T	Temperature	[°C]
T_b	Temperature of fluidised bed	[°C]
U_{mf}	Minimum fluidisation velocity	[$m\ s^{-1}$]
U_o	Superficial gas velocity of bubbling fluidised bed	[$m\ s^{-1}$]
U_t	Terminal velocity of a particle	[$m\ s^{-1}$]
W	Weight of fluidised bed inventory	[kg]
x	Mass fraction in solid phase	[-]
y	Mass fraction in gas phase	[-]
y^*	Equilibrium mass fraction in gas phase	[-]

Subscripts

a	Alkali
g	Gas
i	Input condition
o	Output condition
s	Solid
v	Vapour

Greek Symbols

ϵ_{mf}	Void fraction of minimum fluidisation	[-]
ϵ_p	Porosity of pellets	[-]
Ψ	Degree of alkali volatilisation	[%]
λ	Latent heat of vaporisation	[kcal kg^{-1}]
λ_f	Latent heat of fusion	[kcal kg^{-1}]
μ	Viscosity of gas	[N s m^{-2}]
ρ	Density	[kg m^{-3}]
τ_s	Mean residence time of solid	[min]
ϕ_s	Sphericity of paricle	[-]
Σ	Summation	[-]

Abbreviations

BCI	Blue Circle Industries
CMF	Cement Makers Federation
L.O.I.	Loss-on-Ignition
O.P.C.	Ordinary Portland Cement
P.F.A.	Pulverised Fuel Ash
S.E.M.	Scanning Electron Microscope

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CHAPTER 1

INTRODUCTION

1.1 The Need for Processing of Cement Flue Dust

In the manufacture of Portland Cement, large quantities of dusts are produced. The major source of dust emission is the rotary kiln used for heat treatment or "calcination" where, depending on process conditions, as much as a third or more of the raw material input may become entrained in the flue gases leaving the kiln, although the usual levels encountered are lower. This entrained material, which is generally referred to as flue dust or kiln dust, consists of fine particles of feed which have been calcined to varying degrees and become enriched with various relatively volatile components from the raw material and fuel used, notably the alkalis*.

Normally, provided the quantity or alkali content of flue dust is not excessively high, the dust, which is usually collected in an electrostatic precipitator or a bag filter, may be returned directly to the kiln. However, when both the quantity of dust and the alkali content are high, direct recycling is often precluded. This is because, as will be

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* In cement industry reference to alkalis generally implies potassium and sodium oxides (i.e. K_2O and Na_2O). In flue dust, as will be seen later, the majority of K_2O and Na_2O are present in combination with Cl and SO_3. Therefore, unless otherwise stated, the term 'alkalis' will be used in the present thesis to denote collectively K_2O, Na_2O, Cl and SO_3 in various forms while K_2O and Na_2O will be referred to specifically as the 'alkali oxides'.

explained more fully later, an excessive recirculation of alkalis can adversely affect the operation and performance of a cement kiln as well as the quality of the cement clinker produced. A method of dust treatment which is occasionally used for recycling high alkali dust involves leaching out the soluble alkalis and returning the treated dust to kiln. However, this method has several limitations, and is not in use in the U.K. Various alternative methods of dust utilisation and processing suggested so far are either still in their early stages of development or simply too costly. Consequently, flue dust which is unsuitable for direct recycle is presently having to be dumped. In the U.K., it is estimated that over ½ million tonnes of flue dust are dumped each year while elsewhere, such as the U.S.A. for example, as much as 6 million tonnes of flue dusts are reported to be discarded annually.

1.2 Statement of the Problem

This study was instigated by the problem of flue dust disposal facing 2 major cement works in the U.K., both of which are operated by Blue Circle Industries (BCI), formerly known as 'The Associated Portland Cement Manufacturers', which is one of the world's largest cement manufacturing organisations. The first works, which is located in Northfleet (Kent), is the world's largest wet process plant with a production capacity approaching 4×10^6 t.p.a. The second, which is also a wet process plant, is located in Westbury (Wiltshire) and has a production capacity of nearly 650,000 t.p.a. Both the works utilise raw materials which contain fairly high concentrations of alkalis and, as a consequence, the alkali contents of the dusts produced are also high, totalling typically about 18% by weight in both cases. Apart from a small quantity of dust (~15,000 t) being sold as an asphalt filler at Northfleet Works and about 6,500 t being recycled intermittently at Westbury, the bulk of the dusts, which amounted to approximately 200,000 t and 60,000 t respectively in 1975, were dumped.

Besides being wasteful of both raw material and energy, the dumping of the dust can incur considerable expenses and cause further environmental problems: in order to prevent the fine dust particles from becoming airborne after dumping and to ensure that the alkalis leached out by rain water do not present any pollution problem, flue dust is usually wetted and dumped on areas where the underlying structure is impermeable, such as clay deposits. At Northfleet, the dust was prewetted in mixers prior to tipping at a site several miles away (at 'Broadness Marsh'). The cost involved, exclusive of the value of raw material and energy that has already gone into making the dust, amounted to about £1 per tonne of dust dumped (in 1975). At the present rate of dumping, it is estimated that the tipping areas will become exhausted by 1980. At Westbury, there was no prewetting facility and the dry dust was pumped into settling ponds near the works. This dump was starting to encroach on fresh clay reserves, and hence contaminating and reducing the future supply of kiln feedstock.

Although alternative disposal sites may be available at both Northfleet and Westbury, subject to permission being granted by the appropriate Local and Water Authorities, the need to get access to such sites and minimise any impact to environment, coupled with increased haulage distance and, in the case of Westbury, investment in prewetting facilities, will inevitably increase the cost of disposal significantly. Furthermore, in view of growing public concern and increasingly more stringent legislative control over waste disposal in general, the dumping of flue dust cannot be regarded as a permanent, long-term solution; other means of dust disposal which are environmentally and financially more desirable need to be developed.

1.3 Outline of the Alternative Solutions

1.3.1 Possible Approaches Under Consideration

The problem of Northfleet and Westbury can, in principle, be solved at source by utilising raw materials and fuels of lower alkali contents. However, changing raw materials or fuels is rarely feasible in practice. Alternatively, the alkali concentration of flue dusts may be reduced at source by installing an 'alkali by-pass' in the kiln system, which would enable part of the alkalis to be condensed and collected separately. However, an alkali by-pass is only effective when the kiln gases can be drawn off at a relatively high temperature (~1000°C) as in the case of a dry or semi-dry process kiln. In a wet process kiln, such as those producing the dusts considered here, the gases generally leave the kiln at temperatures below 300°C when all the alkalis have already condensed on the dust particles.

The feasibility of dumping dust at sea has also been considered. However, owing to concern over potential toxicity to marine life and the possibility of dust settling hard on the sea bed and killing plant life, the Ministry of Agriculture, Fisheries, and Food has indicated that dumping may only be permissible in deep waters and has suggested an area 200 miles off the coast of Ireland (Bewley, 1974). Because of the costs and various uncertainties involved, this approach was not pursued any further.

Other approaches which are considered to be more plausible are as follows:

- Sell dust directly,
- Treat dust for recycle,
- Process dust separately.

Various options are associated with each of these approaches, Figure 1.1, which will be reviewed in detail later.

1.3.2 The Proposed Fluidised Bed Calcination Process

The particular option under this study is the calcination of flue dust pellets in a fluidised bed. The process envisaged is as shown in Figure 1.2 and involves three major steps:

- Preparation of a suitable dust feed (by pelletisation and drying),

- Calcination of the feed in a direct-fired fluidised bed operating at high temperatures (1200°C),

- Recovery of the alkalis from the fluidised bed exhaust gases.

Basically, the aims are to volatilise a proportion of the alkalis and convert the remaining dust into a relatively alkali-free calcined material which can be incorporated into ground cement with the normal works clinker without adversely affecting the quality of the resultant cement. The volatilised alkalis are intended to be recovered as a saleable fertiliser.

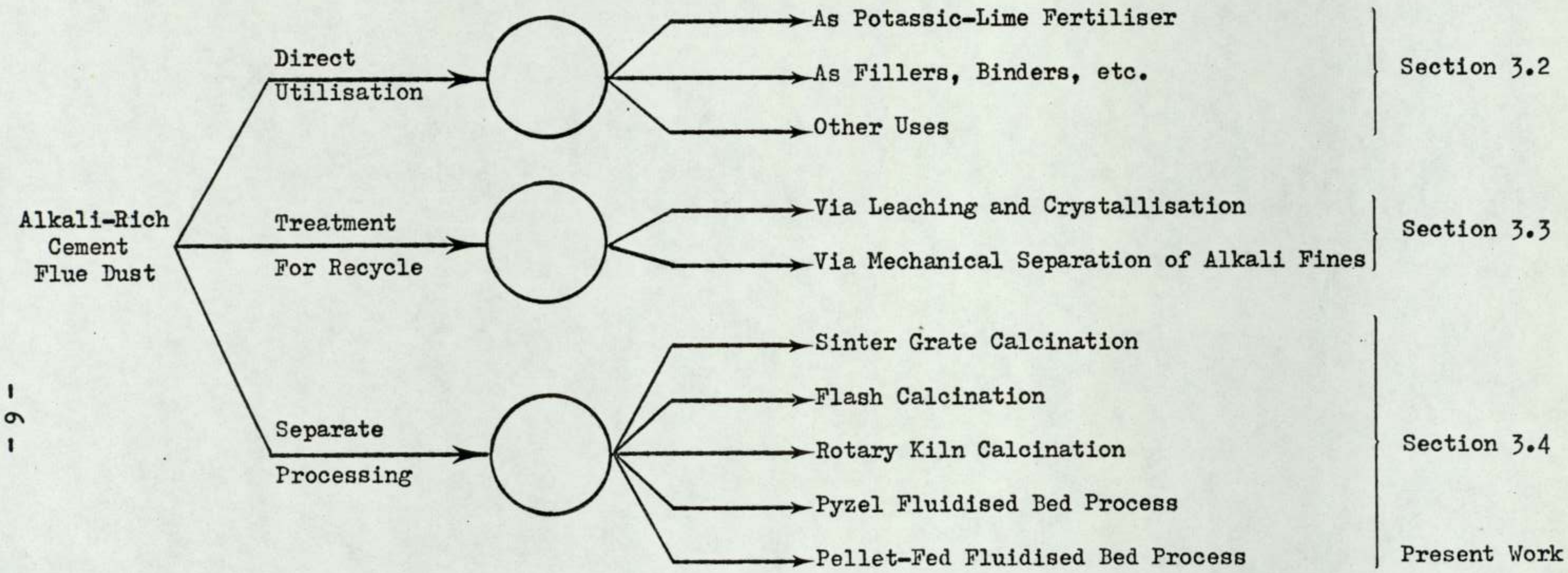

FIGURE 1.1

Options for Utilisation, Treatment and Processing of Alkali-Rich Cement Flue Dust

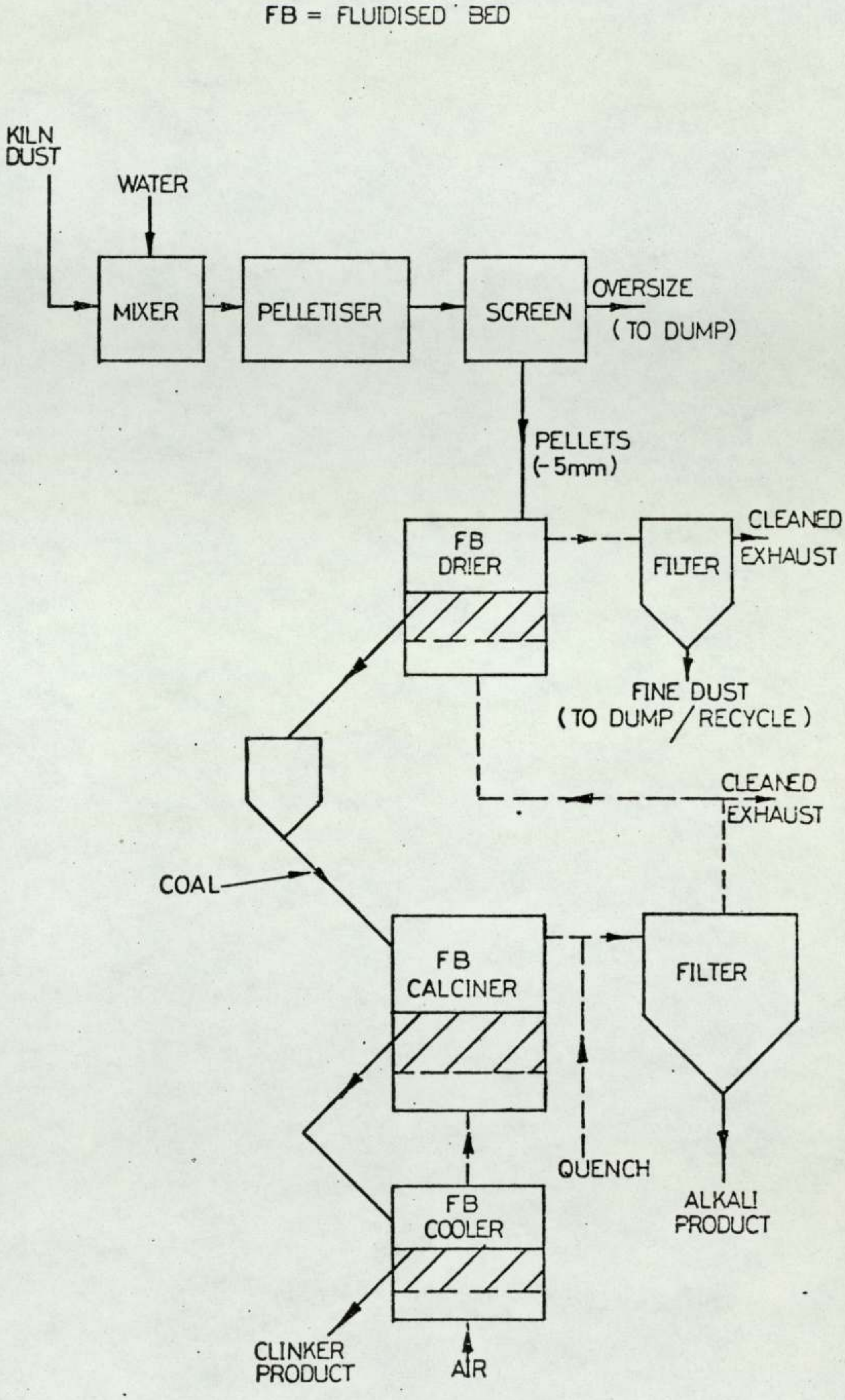

FIGURE 1.2

The Proposed Fluidised Bed Process for Calcining Alkali-Rich Cement Flue Dust

Work on development of the process was initiated towards the end of 1973. Preliminary tests carried out on Northfleet flue dust indicated that the process was technically feasible provided that a suitable method of handling the fluidised bed exhaust gases could be developed. In late 1974, an extensive experimental programme aimed at providing the data necessary for the design and evaluation of the process was instigated. The programme was divided into 2 areas of investigation: one covering the methods of feed preparation and the other on the calcination characteristics and performance of the fluidised bed, including the development of the gas handling system.

1.4 Objectives and Scope of the Present Study

1.4.1 Objectives of this Work

The objectives of this work are to determine the calcination characteristics of Northfleet and Westbury flue dust pellets in a fluidised bed and to develop a method of treating the fluidised bed exhaust gases in order to recover the volatilised alkalis. Embodied in these broad objectives are the following specific tasks:-

(a) define the precise requirements of calcining Northfleet and Westbury flue dusts and deduce a reasonable theoretical approach to the problem,

(b) develop an appropriate test apparatus and procedure for experimentation,

(c) investigate the operating characteristics and constraints of the equipment and establish the optimum calcining conditions,

(d) determine the relationship between the calcining conditions and the alkali retention and lime combination characteristics of the two dusts and, in particular, establish the design parameters of the fluidised bed,

(e) determine the characteristics of the alkali fume and the operating conditions needed for its efficient collection.

All the objectives were met. In addition, a preliminary economic evaluation of the process and comparison with various technically feasible options for the case of Northfleet flue dust are presented.

1.4.2 Scope and Presentation of the Thesis

The scope of the thesis and the manner of presentation are as follows: Following this introduction, a general background of cement manufacture and the problem of flue dust recycling, particularly with respect to the problem of alkalis, is given in Chapter 2, which also contains some recent flue dust utilisation data obtained from 19 major cement works in the U.K. In Chapter 3, the alternative approaches to solving the Northfleet and Westbury problems including previous and concurrent work carried out on dust calcination are reviewed together with other literature relevant to the present study. (Much of the literature was derived from internal BCI reports). In Chapter 4, the theoretical aspects of the problem, such as the physico-chemical properties of Northfleet and Westbury flue dusts, the chemical requirements of calcining, and the thermochemistry and kinetics involved are considered. The characteristics of gas-solid fluidisation which are relevant to the design and execution of the experimental work are also briefly dealt with in this chapter.

The construction of the test apparatus, including the modifications required for this work, and the operating procedure adopted are described in detail in Chapter 5. In Chapter 6, the findings of the experiments and the methods of correlating the data are presented. In Chapter 7 a preliminary design and evaluation of the process for calcining 300,000 t.p.a. of Northfleet flue dust is outlined, together with a techno-economical comparison with other options, namely, the Pyzel fluidised bed process, the leaching and crystallisation scheme and the case for converting a surplus capacity cement kiln. Suggestions for possible improvement of the process and future work required are also included. The conclusions of the work are presented in Chapter 8. An extensive bibliography pertaining to flue dust utilisation, treatment, and processing is contained in the reference section.

CHAPTER 2

BACKGROUND

Summary

Ordinary Portland Cement is manufactured by firing a mixture of finely ground calcareous and argillaceous raw materials at temperatures of 1350-1600°C in a rotary kiln. The raw materials (particularly the argillaceous component) and, to a lesser extent, ash particles (when the kiln is coal fired) generally contain a small proportion of various minor constituents such as K, Na, Cl, S, etc. In the hot burning zone of the kiln, a proportion of these constituents are volatilised to form KCl, K_2SO_4, Na_2SO_4, etc. and as these volatile salts move to the cooler region of the kiln, they may condense on the flue dust particles, process material or kiln wall. The alkalis which condense on the dust particles that are subsequently re-deposited within the kiln along with the alkalis which condense on the process material, are carried back towards the hot end of the kiln where the alkalis may be volatilised once again. This phenomenon is usually referred to as the 'internal' alkali/dust cycle.

The alkali/dust which is not involved in the internal cycle is emitted from the kiln and is usually collected in an electrostatic precipitator or a bag filter. The dust quantity involved tends to vary according to the type of process: for a wet process, the quantity is typically about 10% of the clinker throughput, while for a dry or semi-dry process, the quantity is usually about 1%. The dust composition, too, is liable to vary in accordance with the process as well as the chemistry of the raw material and fuel; the dust analyses from 19 major cement works in the U.K. are presented.

In general, provided the alkali contents are not too high, say less than 5-6% K_2O, flue dust can usually be returned directly to the kiln. There are several established methods of recycle including: admixing with the feed, return through scoops inserted in the kiln body, or insufflation: the blowing in of dust from the kiln hood. However, the return of flue dust, particularly in the case of wet process plant, often presents considerable handling problems and when the level of recycle is high, it can also affect the performance of the kiln and gas cleaning equipment. Above all, when both the alkali concentration and dust quantity are high, recycling may lead to an excessive recirculation of alkalis which can adversely affect the kiln performance, e.g., by causing alkali build-ups and impairing the proper functioning of the electrostatic precipitator. Furthermore, as alkali recirculation increases, an increasing proportion of alkalis is retained in the clinker and this can produce many deleterious effects, the most notorious of which is that involving the reaction between the alkalis and certain reactive aggregates which produces an expansive effect and can cause serious cracking damage to the concrete structure. Other adverse effects include the worsening of working and storage properties and strength development.

It is largely because of alkali considerations that flue dusts from Northfleet and Westbury Works are not recycled.

2.1 Introduction

The arising of flue dust and the problem of disposal are closely related to the process of cement manufacture. The purpose of this chapter is to provide some background information on cement manufacture and flue dust arising and review the limitations of the conventional methods of dust recycle, with particular reference to the problem of alkalis. The chapter also contains a survey of flue dust utilisation in 19 major cement works operated by BCI in the U.K.

2.2 Cement Manufacture

2.2.1 Principles of Cement Manufacture

Portland Cement is the generic name for hydraulic cement, i.e., a cement which hardens in the presence of water. There are several varieties of Portland Cement but the bulk of it consists of the 'Ordinary Portland Cement' (O.P.C.), the manufacture of which is covered by British Standard Specification B.S.12 : 1958 Pt. II entitled "Portland Cement (Ordinary and Rapid Hardening)" which states:-

'The cement, whether ordinary or rapid hardening, shall be manufactured by intimately mixing together calcareous or other lime bearing material with, if required, argillaceous and/or other silica, alumina or iron bearing materials, burning them at a clinkering temperature and grinding the resultant clinker so as to produce a cement capable of complying with this British Standard.

No materials other than gypsum (or its derivative), or water, or both shall be added after burning.'

The clinker produced consists essentially of a mixture of 4 crystalline compounds as listed below:-

Name of Compound	Chemical Formula	Abbreviated Formula Used in Cement Industry*
Tricalcium Silicate (or Alite)	$3CaO.SiO_2$	C_3S
Dicalcium Silicate (or Belite)	$2CaO.SiO_2$	C_2S
Tricalcium Aluminate	$3CaO.Al_2O_3$	C_3A
Tetracalcium Alumino-Ferrite	$4CaO.Al_2O_3.Fe_2O_3$	C_4AF

In addition to these major constituents, various minor constituents such as alkali oxides, magnesia, sulphur, etc. are also present. The chemical analysis of a typical O.P.C. and the range of variation commonly encountered are shown in Table 2.1. Also included in the table are various factors such as L.S.F., S/R, etc., (see Appendix A for the definitions) which are used as general guides to the properties of the cement. For further details of cement chemistry, the text of Lea (1971) or Bogue (1955) is referred.

2.2.2 Cement Manufacturing Processes

Cement manufacture is a complex chemical process which was developed in the 19th century. Initially, the process was based on shaft kilns but today almost all Portland Cement is made in rotary kilns. Basically,

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* In the cement industry, the following chemical abbreviations are adopted:- $C \equiv CaO$, $S \equiv SiO_2$, $A \equiv Al_2O_3$, and $F \equiv Fe_2O_3$

TABLE 2.1

Chemical Analysis of Ordinary Portland Cement

Analyses	Typical	Range
SiO_2	20.70	18.0 - 24.0
I.R.$^{\otimes}$	0.50	up to 1.5*
Al_2O_3	5.75	4.0 - 8.0
Fe_2O_3	2.50	1.5 - 4.5
Mn_2O_3	0.05	0.03 - 0.50
TiO_2	0.30	0.20 - 0.40
P_2O_5	0.15	0.05 - 0.30
CaO	64.00	2.0 - 66.0
MgO	1.00	0.7 - 4.0*
SO_3	2.75	1.5 - 3.0*
L.O.I.	1.50	up to 3.0*
K_2O	0.60	0.1 - 1.5
Na_2O	0.20	0.1 - 0.9
	100.00	
Quality Factors **		
Free lime	2.0	0.5 - 3.0
L.S.F.	93.4	88 - 102
L.C.F.	90.4	
S/A+F	2.51	1 - 4
A/F	2.30	1 - 4
Compositions (Calculated by the method of Bogue)		
$3CaO.SiO_2$	45.1	
$2CaO.SiO_2$	25.3	
$3CaO.Al_2O_3$	11.0	
$4CaO.Al_2O_3.Fe_2O_3$	7.6	

⊗ Insoluble Residues, mainly SiO_2, Al_2O_3 and Fe_2O_3.

* British Standard Specification Limits

** See Appendix A

there are 4 types of processes: the wet, the semi-wet, the dry and the semi-dry. The names are derived from the way in which the raw material is prepared for the kiln: in the wet process, which is most applicable to raw materials with a naturally high water content, e.g. chalk and clay, the raw materials are ground with water in either wash mills or ball mills to produce a slurry containing typically 30-40% moisture which is then blended and pumped to a rotary kiln, Figure 2.1 (a). In the kiln, which may be fired by coal, oil or natural gas, the feed is progressively dried, decarbonated and, finally, at a material temperature in excess of 1400°C, converted to clinker. The clinker is then cooled and ground, with the addition of about 5% by weight of gypsum, to form cement. The gypsum is added in order to control the setting time of the cement.

The wet process is the oldest of the 4 processes and by far the commonest in the U.K. It has the advantages of simplicity, the ability to remove flint and impurities in some raw materials and the possibility of pumping slurry over long distances from quarry to works. However, due to the large amount of water involved, the process has the highest specific fuel consumption and has been increasingly replaced by the other processes in recent years.

The semi-wet process, Figure 2.1 (b), is designed to give the advantages of the wet process without the associated high fuel consumptions. The raw materials are prepared as previously, but instead of feeding directly to the kiln in a wet state, they are first pumped into filter presses where the majority of the water is extracted leaving a 'cake' containing 18-20% moisture. The cake is then made into small nodules about 25mm in diameter and preheated by the kiln exhaust gases in a preheater before passing to

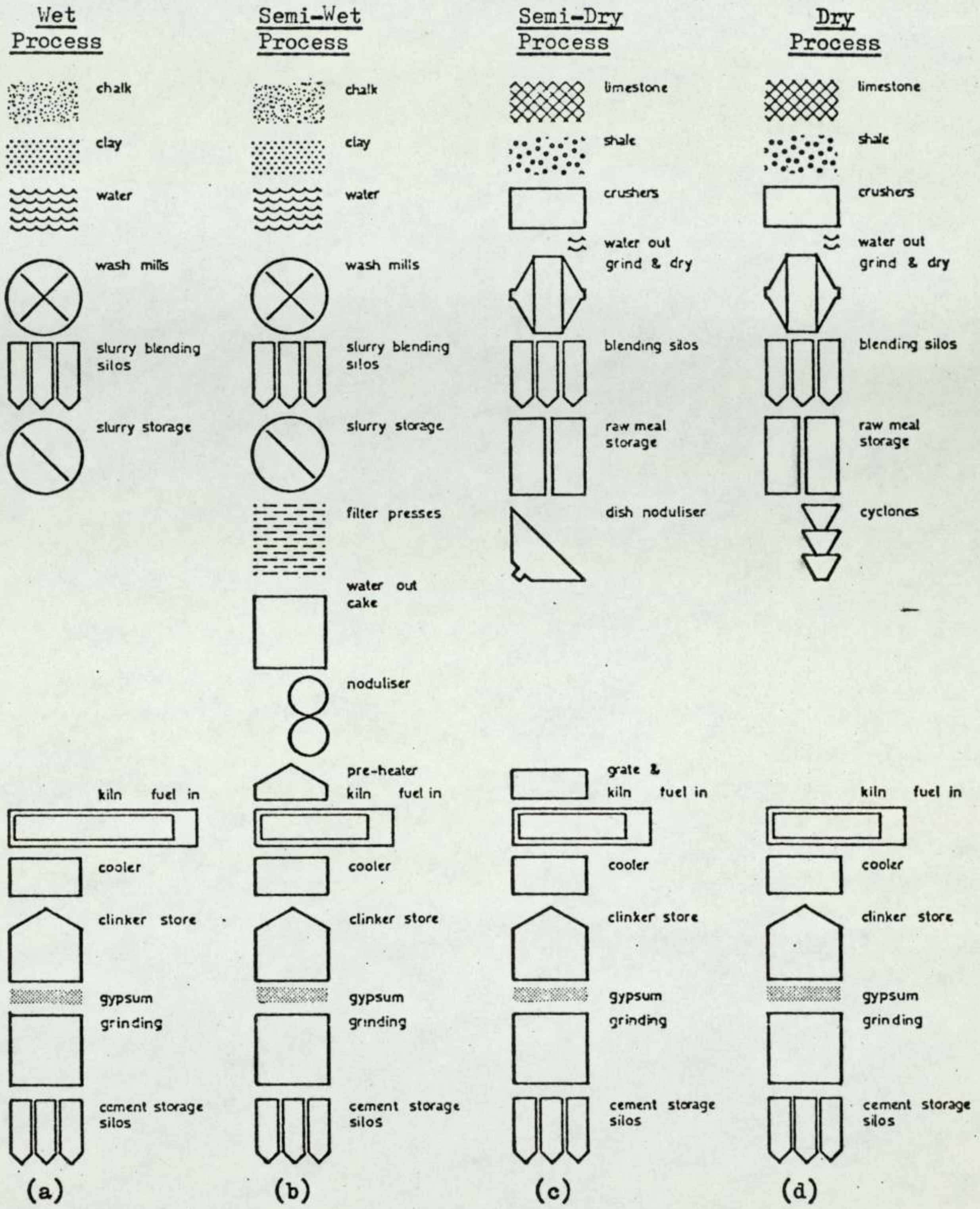


FIGURE 2.1

Rotary Kiln Processes of Cement Manufacture the kiln, which is considerably shorter than an equivalent wet process kiln of the same output. The major disadvantages of the process are the additional cost of filtration and the problem which can sometimes arise from the handling of filter cake. At the moment, there is no semi-wet process works to be found in the U.K. and comparatively few around the world.

Finally, for the dry or semi-dry process, the raw materials are prepared and blended in the dry state. In the case of the semi-process (Figure 2.1 (c)), the powder is made into nodules by the addition of 10-12% water in a slowly rotating dish and preheated on a travelling grate by the hot kiln exhaust gases before passing into the kiln. This process is commonly referred to as the 'Lepol' process by its trade-name and has a fuel consumption similar to that of the modern dry process kiln. There are 2 basic types of dry process kilns: those with preheater or pre-calciner (commonly referred to as "modern dry process"), and those without (generally called "long dry process"). In the modern dry process kiln, the most common of which is the suspension preheater type (S.P.) utilising a series of cyclone preheaters to improve the process efficiency, most of the dust and heat carried out of the kiln is recuperated (Figure 2.1 (d)). The process is still undergoing further improvement and in recent years an increasing proportion of raw meal decarbonation is being effected outside the kiln, e.g., the suspension flash calciner (S.F.) or Mitsubishi fluidised bed calciner process. In the long dry process kiln, which is fast becoming obsolete, the dry raw meal is fed directly to the kiln without passing through any heat/dust recuperators. Consequently the level of dust produced is high and the fuel consumption is only marginally better than that of a good wet process kiln.

For further details of various cement manufacturing processes, 2 recent publications, viz, 'Conservation Potential in Cement Industry' (U.S. Portland Cement Association, 1976) and Duda (1977) are referred, the former also including a survey of various novel processes developed recently.

2.2.3 Choice of Process

In the U.K., approximately two-thirds of cement production is still based on the less energy-efficient wet process (Table 2.2). This is because the majority of cement plants in this country were built before the fifties or in the early sixties when the more energy-efficient dry and semi-dry processes were still in their early stages of development and also when energy consideration was not a vital issue (Davis and McColgan, 1973). In the case of Northfleet Works, which was commissioned in 1971, other factors have dictated the selection of wet process. According to Ironman (1976), it was considered more economical to prepare and transport the high moisture content raw material from its distant quarry to the main plant and the wet milling facilities were also preferred for the necessity to remove large quantities of flint present in the chalk. Another consideration is the alkali content of the raw material. As all preheater systems are susceptible to build-up blockages when exessive alkalis are present, it is generally reckoned that the maximum level of chloride present in the raw material tolerable in a suspension preheater kiln is 0.02% (Davis and McColgan, 1973; Brown, 1976). The levels of chloride present in Northfleet raw material (nearly 0.2%) would be generally considered to be unacceptable for the dry process without further

TABLE 2.2

CMF Rotary Kiln Plant Annual Outputs, Process and Age

Number on Map	Name	Nearest Town	Date of Building or Major Extension	Process	Number of Kilns	Clinker Output tonnes/year x 1000
1	Cauldon	Stoke	1957, 1960, 1962	Semi-dry	3	750
2	Cookstown	Cookstown	1968	Semi-dry	1	425
3	Dunbar	Dunbar	1963, 1966	Semi-dry	3	960
4	Holborough	Medway, Maidstone	1923, 1928, 1938	Wet	4	390
5	Hope	Sheffield	1970	Dry	2	1350
6	Humber	Hull	1921, 1925	Wet	3	306
7	Kirton Lindsey	Gainsborough, Scunthorpe	1920 to 1937, 1968	Wet	3	231
8	Magheramorne	Larne	1915, 1920, 1954	Wet	3	310
9	Martin Earles	Medway	1922	Lime	2	-
10	Masons	Ipswich	1912 to 1938, 1966	Wet	2	450
11	Norman	Cambridge	1920	Wet	1	120
12	Northfleet	Northfleet, Tilbury	1969 to 1971	Wet	6	3600
13	Oxford	Woodstock	1929, 1933, 1936	Wet	3	325
14	Plymstock	Plymouth	1961, 1966	Dry	2	533
15	Shoreham	Shoreham	1951	Wet	2	355
16	Sundon	Luton, Dunstable	1905, 1927	Wet	2	110
17	Swanscombe	Swanscombe, Thurrock	1925 to 1929	Wet	3(+1 S/C)	520 (+ 120)
18	Weardale	Consett, Bishop Auckland	1965	Semi-dry	2	795
19	Westbury	Westbury	1962, 1965	Wet	2	620
20	Wouldham	Thurrock	1928 to 1936 on	Wet	2	400
21	Barrington	Cambridge	1927, 1936, 1955, 1964	Wet	4	499
22	Chinnor	High Wycombe	1926, 1957, 1958	Wet	3	264
23	Rochester	Medway, Maidstone	1929, 1933, 1938, 1950, 1951	Wet	3	389
24	Lewes	Lewes	1925	Wet	1	82
25	Rugby	Rugby	1910, 1973, 1946, 1953, 1968	Wet	4	678
26	Southam	Leamington Spa	1905, 1914, 1937, 1958, 1957, 1961	Wet	4	511
27	Ferriby	Hull	1937, 1968, 1975	Semi-dry	2	664
28	Padeswood	Mold	1949	Wet	2	565
	"	"	1966	Dry	1	
29	Pitstone	Aylesbury, Dunstable	1937, 1952, 1954, 1962	Wet	4	925
	"	" "	1969	Dry	1	
30	West Thurrock	Thurrock	1911 to 1958, 1947, 1949, 1958, 1962, 1963	Wet	6	1060
31	Metton	Stamford	1929, 1933, 1939, 1952, 1962, 1967	Wet	6	650
32	Riddlesdale	Burnley, Blackburn	1936, 1937, 1951, 1961, 1967	Wet	5	300
33	Aberthaw	Barry	1914, 1967, 1975	Dry	2	789
34	Rhoose	Barry	1913, 1962	Wet	1	215

modification.

A detailed discussion of this topic is outside the scope of the present work but the various references cited should provide further information for the interested reader.

2.3 Arising of Cement Flue Dust and Data from BCI Works in U.K.

2.3.1 The Alkali/Dust Cyclic Process in Rotary Kiln

The chemical changes necessary to convert cement raw material into cement clinker take place in the rotary kiln. The reactions involved are extremely complex (Lea, 1971), but for the present purpose, only those relating to alkali and dust production are considered.

Alkali oxides (K_2O and Na_2O) are amongst the most widely distributed elements in nature. In cement manufacture, they originate mainly from the argillaceous raw materials such as clay and marl where they are present in finely dispersed feldspar, mica or illite particles. In this country, and indeed in most of Europe, potash predominates over soda by a factor often in excess of 3 and sometimes as much as 10. Typically, the range of alkali concentrations present in mixture of cement raw meal are 0.2-1% K_2O and 0.05-0.7% Na_2O. When coal is used as fuel, there is a further contribution of alkalis from the ash, although the amount is usually less than 10% of the overall alkali input.

According to the investigation of Ritter cited by Goes and Keil (1960), as the kiln charge is heated up, a proportion of alkali oxides becomes volatilised, starting from about 800°C upwards. In the presence of chloride and sulphur oxides, which are normally also present, the various alkali volatiles tend to react to form the more stable alkali salts. According to Brown (1976), for the raw material and fuel normally encountered in this country, the predominant alkali salts formed are KCl, K_2SO_4 and Na_2SO_4. These relatively volatile salts are then carried by the flue gases into the feed end of the kiln where, starting from about 900°C, they condense on the fine dust particles which are also entrained in the flue gases, as well as on the process material and kiln wall. The alkalis that condense on the dust particles which are subsequently re-deposited within the kiln system, e.g. in the preheaters of a dry or semi-dry process kiln and the chain section of a wet process kiln, as well as those which condense on the process material, are transported back towards the hot end of the kiln where volatilisation may occur once again, as illustrated in Figure 2.2. The extent of volatilisation varies according to the nature of the raw material and process conditions but in general, the extent of volatilisation decreases as the heat efficiency of the kiln process increases (Weber, 1963). There is evidence, from findings of the present work, that this is probably due to the limiting effect of alkali vapour saturation, and it would be interesting to investigate this further. The alkalis which are retained in the clinker are mostly absorbed in the clinker complex, e.g., as $8CaO.Na_2O.3Al_2O_3$, $K_2O.23CaO.12SiO_2$, etc. or remained as the more stable sulphates, i.e. Na_2SO_4 and K_2SO_4.

As a result of this phenomenon, an internal alkali and dust cycle is developed in which the alkali recirculation load within the kiln is considerably higher than that actually entering the system. Lehmann and Plassmann (1957) have established by radio-isotope tracing that in a wet

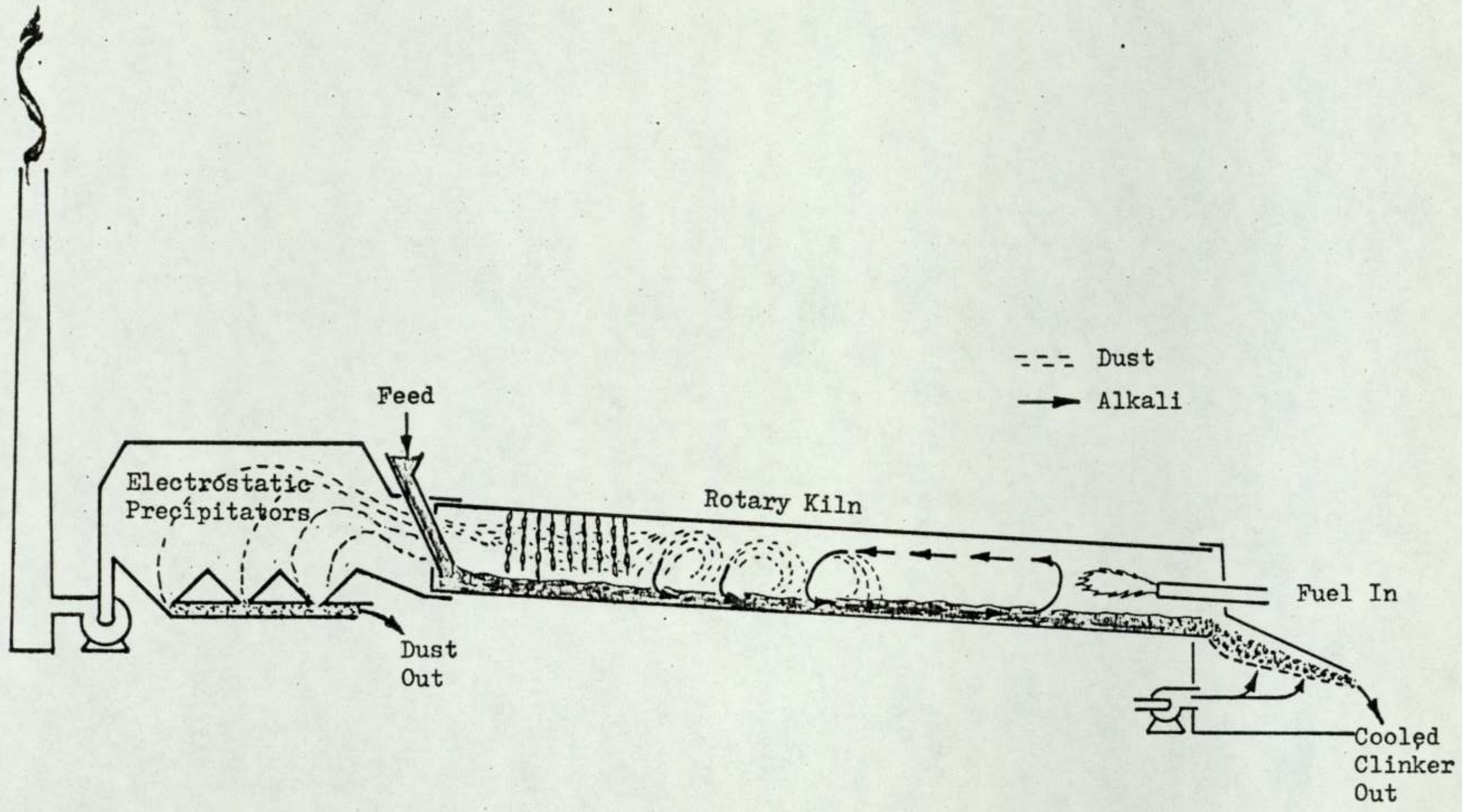


FIGURE 2.2

Alkali and Dust Cycle in a Wet Process Kiln

process kiln, each potassium atom may volatilise and condense 5 times before it leaves the kiln. According to Brown (1976), the circulating load of alkali oxides and sulphur is typically about 2½–3 times that of the input rate while for the more volatile chlorine, the recirculation load may be as much as 65 times the input rate. The relevance of this to dust recycling is discussed later.

2.3.2 Flue Dust Data of BCI Cement Works in U.K.

The dust which does not remain in the kiln is usually collected in an electrostatic precipitator or a bag filter. For the majority of kilns, the quantity of dust, which is generally referred to on the basis of clinker throughput, lies between 2 and 40%, but may be as high as 100% under unfavourable conditions (Weber, 1963).

The quantity of dust produced in 19 major cement works operated by BCI in the U.K. during 1975 is shown in Table 2.3. The works are grouped according to process type and as can be seen, the average dust production is significantly higher for the wet process plants (9.5% average) than for the dry and semi-dry process (1.2% average). Furthermore, whereas all but one semi-dry process plant completely recycled the dust produced, only 2 wet process plants managed a complete dust recycle. Consequently, the total dust dumped by the wet process works in 1975 amounted to over 350,000 t, compared to less than 6,000 t dumped by the semi-dry process works.

The gross chemical composition of the dust is intermediate between that of the raw kiln feedstock and the clinker product but with an increased concentration of alkalis and other volatiles. For the works shown in

TABLE 2.3

Quantity and Utilisation of Cement Flue Dust produced by Blue Circle Industries in U.K. (1975)

Works Location	Clinker Production (t.p.a.)	Average Dust Loss (% on clinker)	Total Dust Loss (t.p.a.)	Recycle to System	Sale as Filler	Dumping
Dry and Semi-dry Processes:-						
Cauldon (Lepol)	660,000	0.9	5,900	5,9000	-	Nil
Cookstown (Lepol)	420,000	1.4	5,900	-	-	5,900
Dunbar (Lepol)	980,000	1.4	13,500	13,500	-	Nil
Hope (S.P.)	1,315,000	(negligible)		Yes	-	Nil
Plymstock (S.P.)	252,000	6.0	15,100	15,100	-	Nil
Weardale (Lepol)	734,000	1.6	12,000	12,000	-	Nil
TOTAL	4,361,000	1.2	52,400	46,500	-	5,900
Wet Process:-						
Holborough	185,000	6.5	12,000	-	5,000	7,000
Humber	307,000	12.0	36,800	36,800	-	Nil
Kirton Lindsey	231,000	20.0	46,200	46,200	-	Nil
Magheramorne	310,000	9.0	27,000	(experimental)	-	27,000
Masons	321,000	20.0	64,200	61,900	-	2,300
Norman	113,000	25.0	28.300	17,000	-	11,300
Northfleet*	2,900,000	7.0	203,000	(experimental)	15,000	188,000
Oxford	110,000	10.0	11,000	10,400	-	600
Shoreham	338,000	12.5	42,200	4,000	-	37,000
Sundon	104,000	8.0	8,600	-	-	8,600
Swanscombe*	330,000	3.5	11,500	-	-	11,500
Westbury*	640,000	10.5	67,200	6,500	2,500	58,000
Wouldham	204,000	9.0	18,400	-	18,400	-
TOTAL	6,093,000	9.5	576,400	182,800	40,900	351,300

Data provided by the Northern and Southern Area Technical Service Department of Blue Circle Industries Ltd.

Table 2.3, the average analysis of the dusts produced in 1973, (the only complete set of figures available) are shown in Table 2.4. Since the composition of flue dust is sensitive to changes in raw material and fuel chemistry, as well as the processing conditions, many of the figures are probably out-of-date. Nevertheless it can be seen that the feasibility of dust recycle is not dependent simply on the alkali content of the dust but also on the amount of dust, i.e. the total amount of alkalis. Thus, although the alkali content of Weardale dust was considerably higher than that of either Northfleet or Westbury, all the dust produced (< 2%) was able to be recycled because of the small quantity involved. The usual methods of flue dust recycle and their limitations are reviewed below.

2.4 Conventional Methods of Flue Dust Recycle and their Limitations

2.4.1 Conventional Methods of Flue Dust Recycle

Recycling is probably the most effective and rational method of flue dust utilisation and in general, provided chemical considerations permit, flue dust may be returned to the kiln directly. There are several established methods of dust return, e.g., the dust may be returned by admixing with the kiln feed, or fed separately through special scoops inserted through the circumferential kiln shell at a point where the composition of the dust matches that of the material inside, or by insufflation - the blowing in of dust through the firing pipe or a separate pipe from the front end of the kiln.

Generally, dust recycle is more readily accomplished in a dry or semi-dry process as the dust and raw material are physically similar and the quantity of dust involved is usually fairly small. In a wet process,

TABLE 2.4

Chemical Analyses of Cement Flue Dust Produced by Blue Circle Industries in U.K.

Works Location	SiO_2	Al_2O_3	Fe_2O_3	CaO	MgO	L.O.I.*	K_2O	Na_2O	Cl	SO_3	† Trace Elements	Total
Dry Process:-												
Cauldon	13.99	4.10	2.38	38.96	0.91	23.65	4.89	0.37	N.D.	8.42	N.D.	97.67
Cookstown	15.79	3.04	1.78	45.5	1.01	12.50	3.45	0.32	0.30	15.92	0.52	100.13
Dunbar	12.81	5.37	3.77	27.18	1.94	N.D.	9.52	0.70	N.D.	28.41	N.D.	89.70
Hope	-	-	-	-	-	-	-	-	-	-	-	-
Plymstock	18.66	0.86	1.68	41.40	1.30	34.03	0.39	0.08	0.43	0.47	0.71	100.10
Weardale	13.06	5.68	2.41	28.50	1.31	11.57	13.81	1.31	2.42	20.06	N.D.	100.13
Wet Process:-												
Holborough	22.00	2.00	1.40	38.90	0.80	22.95	5.80	0.72	1.80	2.50	1.65	100.52
Humber	13.67	5.10	2.90	40.94	0.80	20.60	7.40	0.54	N.D.	7.23	N.D.	99.18
Kirton Lindsey	13.75	4.37	2.76	44.62	1.01	23.23	2.83	0.63	N.D.	6.49	N.D.	99.69
Magheramorne	16.16	1.79	3.17	43.17	0.91	21.06	6.56	1.20	2.99	2.40	1.20	101.01
Masons	15.80	5.25	2.65	42.85	0.40	21.28	5.05	1.20	N.D.	5.35	N.D.	99.83
Norman	14.77	5.15	2.02	43.20	0.63	25.48	3.88	0.64	0.60	3.68	N.D.	100.05
Northfleet	16.20	1.60	1.40	40.80	0.50	16.24	10.90	1.40	3.90	7.20	0.78	100.92
Oxford	14.50	6.37	3.64	37.22	0.95	25.42	4.05	1.17	1.18	5.10	N.D.	99.60
Shoreham	18.20	1.90	1.40	45.20	0.60	24.32	4.00	0.72	1.40	1.80	0.85	100.39
Sundon	19.26	7.34	3.02	37.90	0.83	23.20	6.32	0.72	0.85	2.47	N.D.	101.91
Swanscombe	12.62	1.55	1.27	41.75	0.94	23.08	5.92	0.68	0.99	10.94	0.48	100.27
Westbury	16.20	1.80	1.20	42.70	0.60	23.63	6.20	0.63	0.70	7.0	0.91	100.27
Wouldham	11.19	3.22	2.07	48.79	0.94	26.43	1.85	0.44	1.10	3.21	1.14	100.38

* L.O.I.: Loss-on-ignition at 950 ± 25°C (consists mainly of CO_2 and H_2O)

† Trace elements : TiO_2, P_2O_5, Mn_2O_3, S, C, F, etc.

however, adding dust to slurry tends to thicken the slurry and causes various caking and handling problems, so the insufflation or scoop system is normally used. However, high dust insufflation rates can interfere with the kiln flame while the scoop system tends to suffer from the problem of air in-leakage due to the difficulty of maintaining an adequate air seal around the scoops. Moreover, both the techniques tend to increase the internal dust cycle which can give rise to problems of build-up or 'ring formation' and can impair the performance of the electrostatic precipitator. Although the problem of the increased dust cycle can sometimes be overcome by returning flue dust as nodules, tests carried out at Northfleet Works showed that the feeding of nodules in itself presented considerable operation problems (BCI Internal Report, 1971). The main features of the various dust recycling techniques are summarised in Table 2.5, which also gives some references where more information can be obtained.

However, even when all the physical problems of dust recycle are resolved, the feasibility of dust recycle is ultimately dependent on chemical considerations discussed in the next section.

2.4.2 Effects of Excessive Alkali on Cement Manufacture

When the recirculating load of alkalis in a kiln is allowed to increase progressively by recycling alkali-rich flue dust, a point is soon reached at which serious build-up and plugging problems can result, particularly in the case of the preheater kiln system. The problem is initiated by the formation of a quaternary eutectic comprising $CaSO_4$-K_2SO_4-Na_2SO_4-KCl which has a melting temperature approaching 700°C or less and can therefore

TABLE 2.5

Conventional Methods of Direct Dust Recycle

Dust Return Options	Descriptions	Advantages	Disadvantages	References
(A) Admixed with Feed	Dust is blended directly into kiln feed and return from the back-end	· Simple · Low capital and handling cost	· Increases viscosity or caking of slurries in wet process kiln · Increases dust load in kiln	Semchenko (1969) Whitely (1973) Bethke (1975) Sell et al (1976)
(B) By Scoops	Dust is fed mid-way into kiln via curved pipes inserted around the kiln circumference and is scooped up from an air-tight box under the kiln	· Avoid problem of dust hydration for wet process kiln	· Relatively high capital cost · Problem of maintaining adequate air-seal · Increase dust load	Semchenko (1969) Bracher (1973) Bethke (1975) Sell et al (1976)
(C) Insufflation	Dust is blown with the firing end of the kiln and by compressed air through the firing pipe or a separate pipe	· Avoid problem of dust hydration for wet process kiln · Relatively low capital cost	· Increase dust load · Interfere with flame combustion	E.N.C.I. (1939) Pashcenko et al (1971) Bethke (1975) Sell et al (1976)
(D) As Nodules	Dust is formed into nodules and return with the feed via scoops, or injected from the firing end by compressed air	· Reduce dust load · Minimise dust handling problem	· Relatively high capital and handling costs · Problem of feeding	Garoutte (1956) Semchenko (1969) **BCI Internal Report (1971)** Bethke (1975)

readily coat the surrounding kiln or duct wall, thereby enabling further process material or flue dust to be absorbed and solidified to form a build-up (Ritzmann, 1971· Kozlowski, 1972; Sylla, 1978). Once this occurs, both the gas flow and kiln feed become restricted and the output is reduced, or in more severe cases, total shut down of the plant is necessary for cleaning. In addition to an excessive recirculation of alkalis and in particular chlorides, can increase the corrosion rate of the kiln shell and impair the efficiency of an installed electrostatic precipitator (Ramesohl, 1978).

As the alkali recirculating load increases, an increasing proportion of alkalis is absorbed into the clinker complex. Excessive alkalis can produce many deleterious effects on the quality of cement, most serious of which is the so-called 'alkali-aggregate' reaction. The phenomenon, which was first reported by Stanton (1940), involves the reaction of potassium and sodium ions released during cement hydration with certain reactive aggregates, such as opal, chalcedony, etc. This produces an alkali calcium silicate gel which has the ability to imbibe water and swell and eventually develop sufficient pressure to crack the concrete. A similar expansive reaction between alkali and dolomite to produce alkali carbonate and magnesium hydroxide has also been reported (Plum et al, 1958). Consequently, it is a common practice for users, particularly in certain geographical locations in the U.S.A. where reactive aggregates are commonly found, to specify low alkali cement. For instance, the optional A.S.T.M. specification of low alkali cement stipulates a maximum level of alkali equivalent to less than 0.6% Na_2O. (However, as pointed out by Mather (1975), this can sometimes be a wasteful practice, since only a small proportion of aggregates is potentially reactive, as well as creating an unnecessary dust disposal problem).

Excessive alkalis are also known to cause efflorescence in cement when the alkalis are present as sulphates; when they are unattached to sulphate, they may produce deliquescence effects and affect the storage and workability properties. For example, under mildly humid conditions, potassium sulphate can promote 'airset' through the formation of a hydrated double sulphate of potassium and calcium known as 'syngenite' ($CaSO_4 \cdot K_2OSO_4 \cdot H_2O$), Murray (1973). In addition, the alkali compounds can react with carbon dioxide in the presence of moisture and substantially shorten the setting time through the so-called "flash-setting" (Grimm, 1926).

Finally, the potential corrosive effects of chloride on reinforcing wires coupled with its ready migration, particularly in the more permeable concretes, is one of the greatest concerns and has led to a recommended level of chloride in cement not exceeding 0.02%.

It is for these reasons that the recycling of flue dusts at Northfleet and Westbury cement works is precluded (Whitely, 1973).

2.4.3 Closure

The importance of alkalis in relation to the problem of flue dust disposal was highlighted recently by Davis (1975). In a survey of 101 cement plants in the U.S., it was reported that over a quarter of the dusts collected was having to be discarded due to alkali consideration. A similar observation was made by Whitely (1973) in a paper presented to the BCI group technical conference: in a survey of BCI cement works world-wide, it was found that, in general, dust recycle was feasible only when the level of potash did not exceed 5-6%. The paper included an assessment of the effect of dust recycle at Northfleet Works and suggested that the recirculation of alkalis would reach an unacceptable level after just a few cycles.

In the following chapter, the options for utilising or processing the dusts are reviewed. As will be seen, all the processing options involve, basically, the removal and recovery of the excess alkalis in one way or another.

CHAPTER 3

LITERATURE SURVEY

Summary

A survey of published and unpublished work on means of disposing high alkali cement flue dust indicated that the dust may be utilised directly, subjected to physical treatment before recycle, or calcined separately to yield a low grade clinker and alkali product. The potential for direct utilisation is considerable, e.g., the dust may be used as potassic/lime fertiliser, binder, filler, etc. However, because of high handling and transportation costs involved, it is thought unlikely that there is any real prospect for the sale of this material in U.K.

In the second approach, there are 2 options available. The first involves leaching out the soluble alkalis, which are then recovered by fractional crystallisation, and returning the treated dust to the kiln. Tests carried out on Northfleet flue dust showed that this approach is technically feasible, enabling up to 90% of the alkalis to be removed and recovered. However, the costs involved appeared to be high and there may also be a problem in returning the dust sludge to the kiln. The second method of treatment involves separating the dust by mechanical means into a fine fraction, which is sufficiently high in alkali concentration to make it saleable as a fertiliser, and a coarse fraction, of sufficiently low alkali content to make it suitable for recycle. Although the method is simple in principle, tests carried out with Northfleet and Westbury

dusts showed that the separation obtained was unsatisfactory.

In the third approach, the dust is calcined in a separate furnace , e.g. a grate, flash calciner, rotary kiln or fluidised bed. Each option has certain advantages and disadvantages but all share a common advantage in that contrary to the method most recently described, the dust is processed independently of the kiln and therefore does not interfere with its operation. Various work carried out in BCI showed that the first two suggested furnace options were technically non-feasible and that while the rotary kiln option seemed feasible, the cost and space required for the equipment would be high, although it may be considered under certain circumstances such as those arising recently at Northfleet where a surplus kiln became available nearby. The application of a fluidised bed for calcining flue dust was considered as novel, but it had the advantage that the plant would be relatively compact and inexpensive. Small scale laboratory tests showed that significant removal of alkalis from the dusts could be achieved and that the performance was generally better than for a static bed. Limited trials carried out in a 300mm diameter fluidised bed showed also that continuous large-scale operation was technically feasible, provided that a suitable method of handling the exhaust gases was developed.

3.1 Introduction

Dust control in the cement industry is a long standing problem which has attracted innumerable publications. However, much of the literature is concerned with either techniques of reducing dust emission, e.g., Burke (1969), McCubbin (1969), Ward and Watson (1973), Ellinger (1976), Kirschbaum (1978) or methods of recycle which, as discussed previously (Section 2.3), have various limitations and are applicable primarily to low alkali dust. There are comparatively few publications which deal specifically with the problem of high alkali dust and most of these have made their general appearance only recently, e.g., Davis and Hooks (1975); Bethke (1975); Greening et al (1976); and Tettmar et al (1977).

The lack of published information can be attributed to 2 factors. Firstly, the problem of high alkali dust is a relatively recent phenomenon which has arisen primarily as a result of the tightening of dust control regulations and the need to minimise alkali levels in cement. Prior to the mid-sixties, dust emission from existing cement kilns was still not quantified (Table 3.1) and a significant proportion of the alkalis, which tend to concentrate on the finer fraction of the flue dust, was allowed to escape collection so that recycling of the remaining dust did not cause any alkali problem. The second factor is simply that much of the information known to cement manufacturers (such as BCI) has not been generally published.

In the survey to follow, both the published and unpublished literature relevant to the present work is reviewed. The areas covered are as follows:

TABLE 3.1

Dust Emission Requirements for Cement Plant

Date	Document	Maximum Kiln Chimney Emission. New Plant	Maximum Kiln Chimney Emission. Existing Plant	Maximum Emission Associated Cement Plant e.g. Coolers New Plant	Maximum Emission Associated Cement Plant Existing
1945	82nd Report Alkali & C. Works by Chief Inspectors P.16	0.4 grains/ft^3 wet gas at 60°F 30" Hg 20% CO_2 (0.9g/Nm^3)	Not specified	Not specified	Not specified
1962	99th Report as above P.11	0.2 grains/ft^3 wet gas at 60°F 30" Hg (0.46/Nm^3)	Not specified	Not specified	Not specified
1966	103rd Report as above P.51 (Appendix V)	0.2 grains/ft^3 wet gas at 60°F 30" Hg (0.46/Nm^3)	0.5 grains/ft^3 wet gas at 60°F 30" Hg (1.15g/Nm^3)	Not specified	Not specified
1967	104th Report as above P.56 (Appendix V)	Works Size (t/day clinker) 1500 1500 to 3000 3000 0.2 Sliding scale 0.1 grains/ 0.2 0.1 grains ft^3 grains/ft^3 ft^3 (0.46g/ (0.46-0.23g/ (0.23g/ Nm^3) Nm^3) Nm^3)	0.2 to 0.5 grains/ft^3 at 60°F 30" Hg (wet gas) depending on age of plant. (0.46 to 1.15g/Nm^3)	0.1 grain/ft^3 (0.23g/Nm^3)	0.2 grains/ft^3 (0.46g/Nm^3)

- Direct Utilisation of Flue Dust,
- Treatment of Flue Dust for Recycle,
- Separate Calcination of Flue Dust,
- Calcination of Northfleet and Westbury Flue Dust.

3.2 Direct Utilisation of Flue Dust

3.2.1 Historical Development

The possibility of using cement flue dust as a source of potash was first suggested in the early 1900's (Cramer and Seger, 1904; Richardson, 1904). In those days, primary potash compounds were obtainable only from Germany and when the supplies were cut off in the First World War, potash became so valuable that flue dust became a saleable commodity. The problem then was to devise an efficient method of collecting the fine dust particles as the electrostatic precipitator was only just being developed by Dr. F.G. Cottrell. In 1916, the first precipitator erected primarily for the purpose of potash recovery was installed, and by 1918 at least 19 cement plants were reported to have installed similar equipment (Wilson, 1918).

As the potash concentration present in the dust was low ($< 2-3\% K_2O$), there was an incentive to produce a more concentrated alkali product. In 1917, Huber and Reath (1917) patented a scheme involving the calcination of flue dust in a kiln followed by leaching and crystallisation treatment of the resultant dust to produce a concentrated potash. The operating experience of an experimental plant producing 1 t/d of potassium sulphate was described by Dean (1918). Today, the capital and energy requirement of such a scheme would almost certainly render it non-viable financially.

At that time, however, potash was so scarce that the price of a 50% muriate of potash reached U.S. $500 per ton (Shreve, 1967). Apparently, during the last years of the war, the principal business of cement plants was potash recovery, with cement having rather the nature of a by-product (Wilson, 1918).

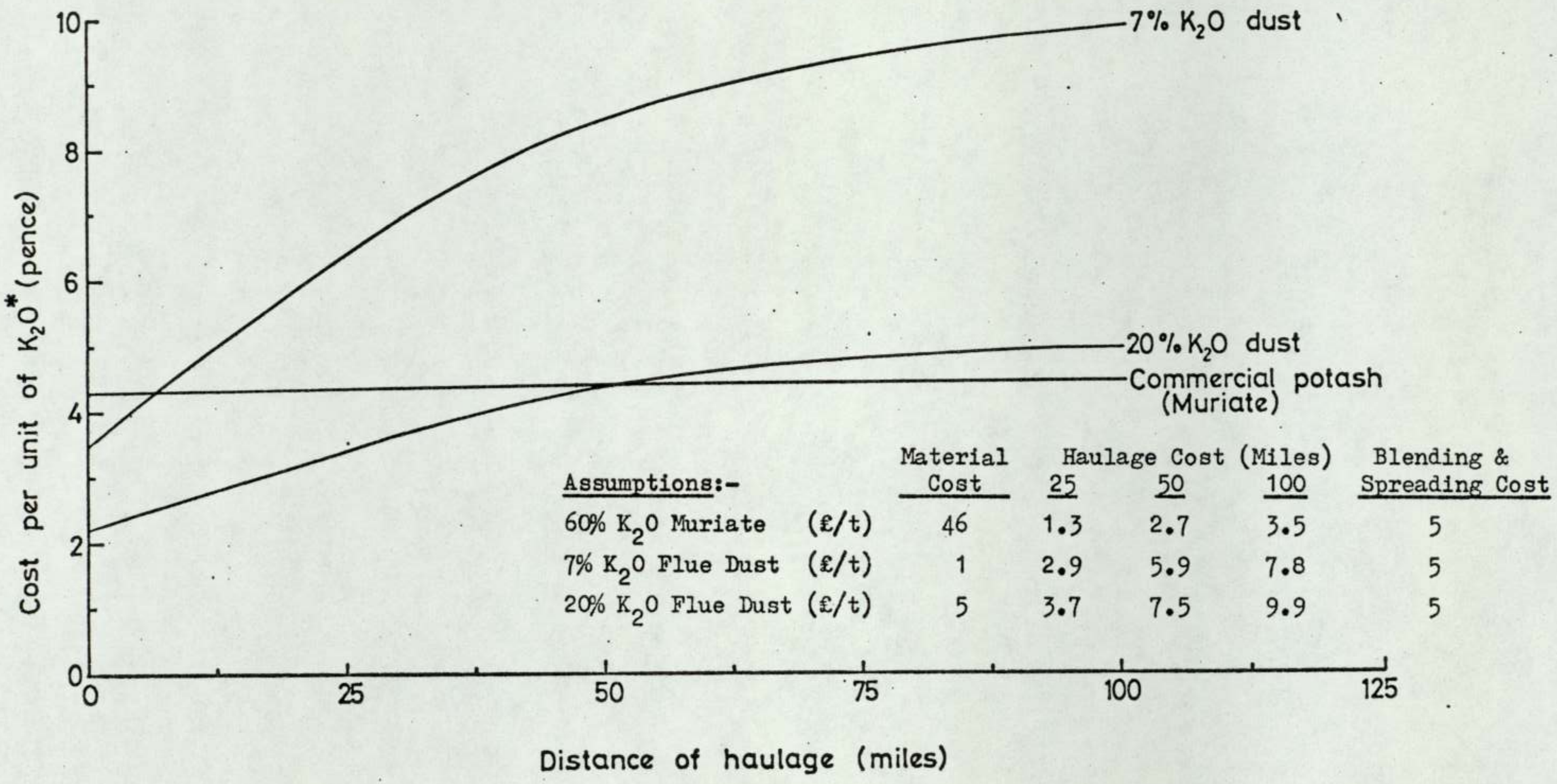
After the war, when Germany resumed its supply of potash and cheaper sources were discovered, the sale of flue dust was no longer viable. Elsewhere, however, in countries such as Belgium and Holland where there was no natural source of potash, the use of flue dust as a fertiliser continued for many years and extensive laboratory and field tests were reported (Hudig and Planje, 1939; Leouw, 1956; Demortier et al, 1956). In the U.S.S.R. (Rogalev, 1966; Tiklonov and Litvak, 1967; Magnitski et al, 1973), Czechloslovakia (Holobrady et al, 1970, Kulich, 1972) and particularly Poland (Litynski, 1955-1970), interest and research efforts continued until the present day.

The beneficial effect of flue dust as a liming agent has also been reported by Whittaker et al (1959); Carroll et al (1964); and Bambergs and Apenite (1967) and recently other potential uses have also been cited. In the following sections, the prospects for various possible uses in the U.K. are discussed.

3.2.2 Sale as Potassic/Lime Fertiliser

In the U.K., nearly a million tonnes of potash in various forms are imported each year for use in farmland (Healing, 1975) and over 2 million tonnes of lime and limestone are spread (Ashworth, 1975). Therefore, if only part of the market can be replaced with flue dust, this use alone could potentially absorb all the flue dusts that are currently being dumped in this country. This prospect was recently assessed by BCI in consultation with the Ministry of Agriculture, the Rothamsted Research Station, and various fertiliser suppliers and manufacturers (Lawton, 1975). While it was the general consensus that flue dust containing 7% K_2O, as was typical of that produced at Northfleet and Westbury Works, could in principle be effectively used as fertiliser, and that the levels of various trace elements also present, such as Pb, Cu, etc., were not considered to be excessive, there was very little commercial appeal for the material due to the low concentration of potash. However, it was suggested that a flue dust containing +20% K_2O, which was obtainable from the final chamber of the electrostatic precipitators used at Northfleet, could find a small demand of, say, up to 10,000 t.p.a.

The feasibility of using a 7% K_2O and a 20% K_2O flue dust as potential substitutes for commercial grade fertiliser such as a 60% K_2O muriate of potash has been examined by Lawton (1975). Based on the assumptions used in that report, the comparative costs of the 3 alternative sources of K_2O are shown in Figure 3.1. It is evident that a 7% K_2O dust is unlikely to have any real commercial prospect while a 20% K_2O dust may just be competitive for a haulage distance of up to 50 miles. However, when a high alkali dust extraction system was subsequently installed at Northfleet Works for the purpose of producing +20% K_2O dust, it was found that the cost involved in the extraction (~ £8/t) actually exceeded the selling price obtainable for the material (£5/t), primarily because of the low and inconsistent output caused by frequent dust blockages. After only a short operation period, the fertiliser merchant also became reluctant to purchase the material and by early 1976, production was ceased



Assumptions:-		Material Cost	Haulage Cost (Miles) 25	50	100	Blending & Spreading Cost
60% K_2O Muriate	(£/t)	46	1.3	2.7	3.5	5
7% K_2O Flue Dust	(£/t)	1	2.9	5.9	7.8	5
20% K_2O Flue Dust	(£/t)	5	3.7	7.5	9.9	5

FIGURE 3.1

Comparative Cost of Using Northfleet Flue Dust and Commercial Potash as Fertiliser (1975)

(*A unit of K_2O is the potash content of 1 cwt (~51kg) of a notional fertiliser containing 1% K_2O)

(Lawton, 1976 a).

The high cost involved in handling and transporting flue dust also ruled out the feasibility of selling the dust as an agricultural lime, which has an even lower selling price (£2-3/t) and is normally supplied by small firms operating over a limited area. The feasibility of admixing flue dust with, for example, ammonia sulphate and super phosphate, or sewage sludge in order to produce a composite fertiliser has also been considered, but due to both technical and economical considerations, the matter has not been pursued to any extent (Lawton, 1976 b).

3.2.3 Sale as Binders and Fillers

Due to its hydraulic properties and finely divided state, flue dust is potentially a useful substitute for the production of hydraulic binders and various building elements in which strength requirement is minimal. In the Soviet Union, for example, Chufistov (1959) has reported that a low grade cement was made by grinding about 60% of flue dust with ordinary cement clinker, and more recently, Ashraf'yan et al (1970), reported that a satisfactory 'plugging' cement, for productive strata of operational drillings, was produced by admixing various levels of flue dust with cement. In the U.K., the British Standard Specification B.S.12 : 1958 Pt. II prohibits the mixing of cement clinker with any material other than gypsum or its derivatives and therefore, unless the specification is altered, this approach can be ruled out.

In Poland, the 'Institute for the Industry of Binding and Building Materials' is reported to be investigating the production of a clinker-free, local hydraulic binder from mixtures of flue dust, blast furnace slag and gypsum for use as foundry cement and as a soil stabiliser or verge hardener in road construction (Bethke, 1975). Apart from a small quantity of flue dust being sold as an asphalt filler (Table 2.3), none of these uses have so far been explored in the U.K. However, the value commanded by such material is generally low (e.g. less than £1 per tonne ex works for the Northfleet dust in 1975) and the market is severely limited by the cost of handling and transportation. Nevertheless, under the prevailing trend of rapid increase in both energy and material costs, the various potential applications mentioned, plus other possibilities of using flue dust as fillers in various building elements and cellular concretes such as composite roofing, insulating board, concrete expansion strips, sound-deadening material, wall elements, floor tiles, decorative products, etc., as suggested by Davis and Hooks (1975) and Bethke (1975), may become more viable in the future.

3.2.4 Other Uses of Flue Dust

Several other uses of flue dust, based essentially on the neutralising capability of the material, have also been reported in the literature. For example, Trembley et al (1958) have reported the use of flue dust for clearing an acidic bog in America: it was claimed that the acidophilic vegetation was eliminated and that the bog has become part of a lake bottom. Farnham (1960) reported the use of flue dust for the treatment of municipal and process water supplies in the lime-alum coagulation process: the required optimum pH of 6.4 was said to be adequately controlled by the lime in the dust while the insoluble dust particles provided a large nucleation site for coagulation. Apparently, a more rapid settling and a denser floc were achieved.

In glass manufacture, flue dust has been shown to be effective as a partial substitute for soda which is normally used for reducing foam in the molten glass baths. The rate of decomposition of the sulphates, which is the main cause of foaming, was enhanced by the lowering of melting point caused by the potash in flue dust (Emer, 1969).

The possibility of applying flue dust for the treatment of acidic wastes such as pickle liquor derived from metal plating and leather tanning processes has also been suggested by Spinola (1971), and for the sorption of sulphur-bearing gas from stacks by Gorman (1972). Recently, Wheeler (1978) reported some encouraging results of using flue dust as a feed ingredient for livestock in the U.S.A. Although none of these applications has so far been explored in the U.K., the market potential is unlikely to be significant, mainly because the material value for such uses is low and the costs of handling and transporting the material would again lower the potential sales. Moreover, considerable time and effort may be required to develop the initial market.

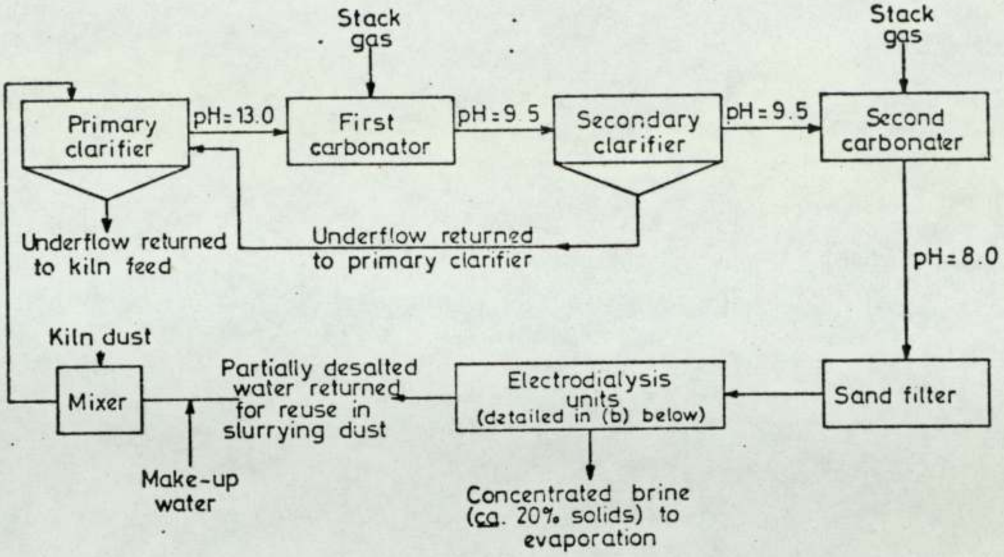
3.3 Treatment of Flue Dust for Recycle

3.3.1 Reduction and Recovery of Alkalis by Leaching and Crystallisation

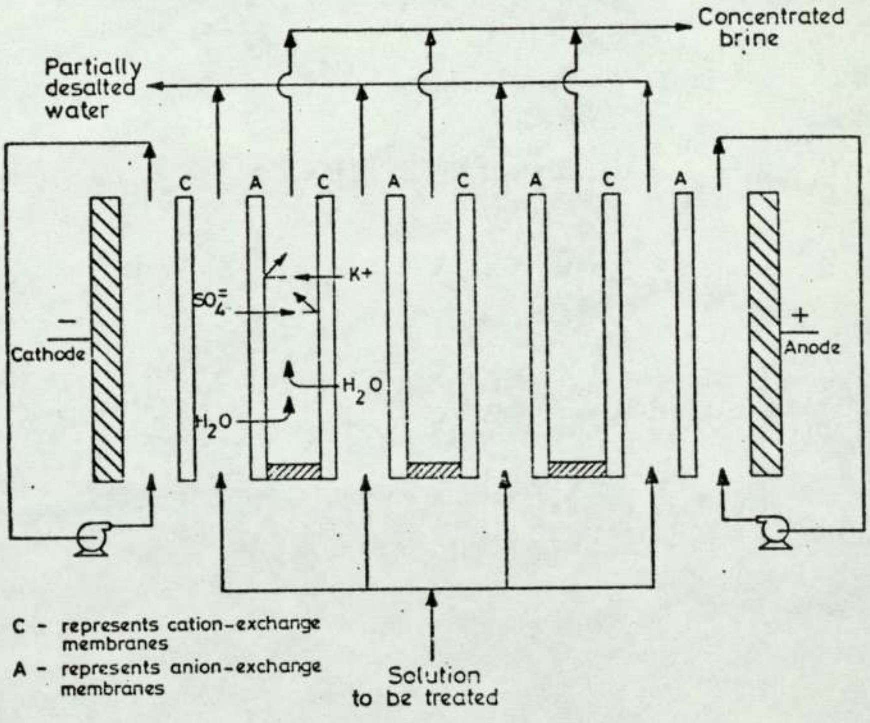
As mentioned earlier, a large proportion of the alkalis present in flue dust is water-soluble and can therefore be extracted by leaching. The method conventionally in use involves mixing flue dust with about an equal quantity of water to produce a slurry, which is then pumped to a clarifier or thickener where the solids settle to the bottom and the excess water overflows. The overflow, which contains most of the soluble alkalis, is usually discharged into rivers or ponds while the underflow, a slurry containing about 60% solids, is returned to the kiln (Goes, 1963). According to Yurganov et al (1966), it is possible to extract 45-90% of the alkalis in this way, depending on the nature of the dust.

However, the method has been found to be generally unsatisfactory in practice due to the hydraulic property of flue dust, which can cause caking of slurries, formation of mud rings in the kiln and various handling problems. In a survey of flue dust utilisation in 29 U.S. cement plants, Sell and Fischbank (1976) found that 6 were using this method for treating part of the dusts and the results obtained ranged from 'adequate' to 'barely satisfactory', while 6 other plants had tried the method but had given it up as totally unsuccessful. Moreover, the disposal of alkali leachate from the process has recently caused some concern, and effluent limitation guidelines stipulated by the U.S. Environmental Protection Agency require that this leachate is neutralised by 1977 and no discharge of pollutants is to be allowed after 1983 (Davis and Hooks, 1975). The method has never been adopted by cement manufacturers in the U.K.

A scheme for improving leaching and eliminating the discharge of pollutants has been proposed by Lacey and Loeb (1972). The dissolved lime, which is the main cause of various handling problems, is precipitated by carbonation with CO_2, e.g., from cement stack gas, and after removal of the precipitated calcium carbonate, the alkali salts remaining in solution are first concentrated by electrodialysis and then evaporated to dryness to produce a mixed salt, or fractionally crystallised to obtain separate fractions of pure salt (Figure 3.2). However, there has not been a reported case of practical application and moreover, electrodialysis membranes are usually non-durable and require



(a) Process Flowsheet



(b) Details of the Electrodialytic Concentration Stack

FIGURE 3.2

A Leaching and Crystallisation Scheme for Treating Alkali-Rich Cement Flue Dust (From Lacey and Loeb, 1972) expensive maintenance. Various alternative schemes which rely on filtration for dewatering have been proposed by Luginin et al (1973). The principle is basically the same as that developed by Woodall-Duckham and Humphreys & Glasgow working with BCI on the feasibility of leaching Northfleet dust. The details of the work, which included both small scale laboratory tests and fairly large scale pilot plant trials, are contained in various reports submitted by W-D (1972) and H & G (1972, 1973), but essentially it was shown that under laboratory conditions, virtually all the water-soluble alkalis in Northfleet dust (which represent approximately 90% of the total alkalis present) could be extracted by leaching with fresh water in a mass ratio of 2:1 (water:dust) at 80°C for about 20 minutes (Figure 3.3), although the efficiency obtained in subsequent pilot plant trial carried out by H & G was only 75%. (This lower efficiency was attributed to the limitations of experimental equipment and inadequate site facilities, and H & G suggested that with a properly designed production plant a higher efficiency should be attained). In both the laboratory and pilot plant tests, substantially pure fractions of K_2SO_4, KCl plus a mixture of KCl, K_2SO_4 and Na_2SO_4 were recovered.

The separate schemes forwarded by W-D and H & G for treating up to 300,000 t.p.a. of Northfleet flue dust are shown in Figures 3.4 and 3.5 respectively. The major difference between the 2 schemes is that in the W-D proposal, which has since been patented (Woodall-Duckham Patent, 1976), the kiln waste gas is utilised for supplying the CO_2 requirement, whereas a waste gas incinerator is used for CO_2 generation in the H & G scheme. The performance and economics of the 2 schemes originally envisaged (i.e. in 1972) are given in Tables 3.2 and 3.3. It can be seen

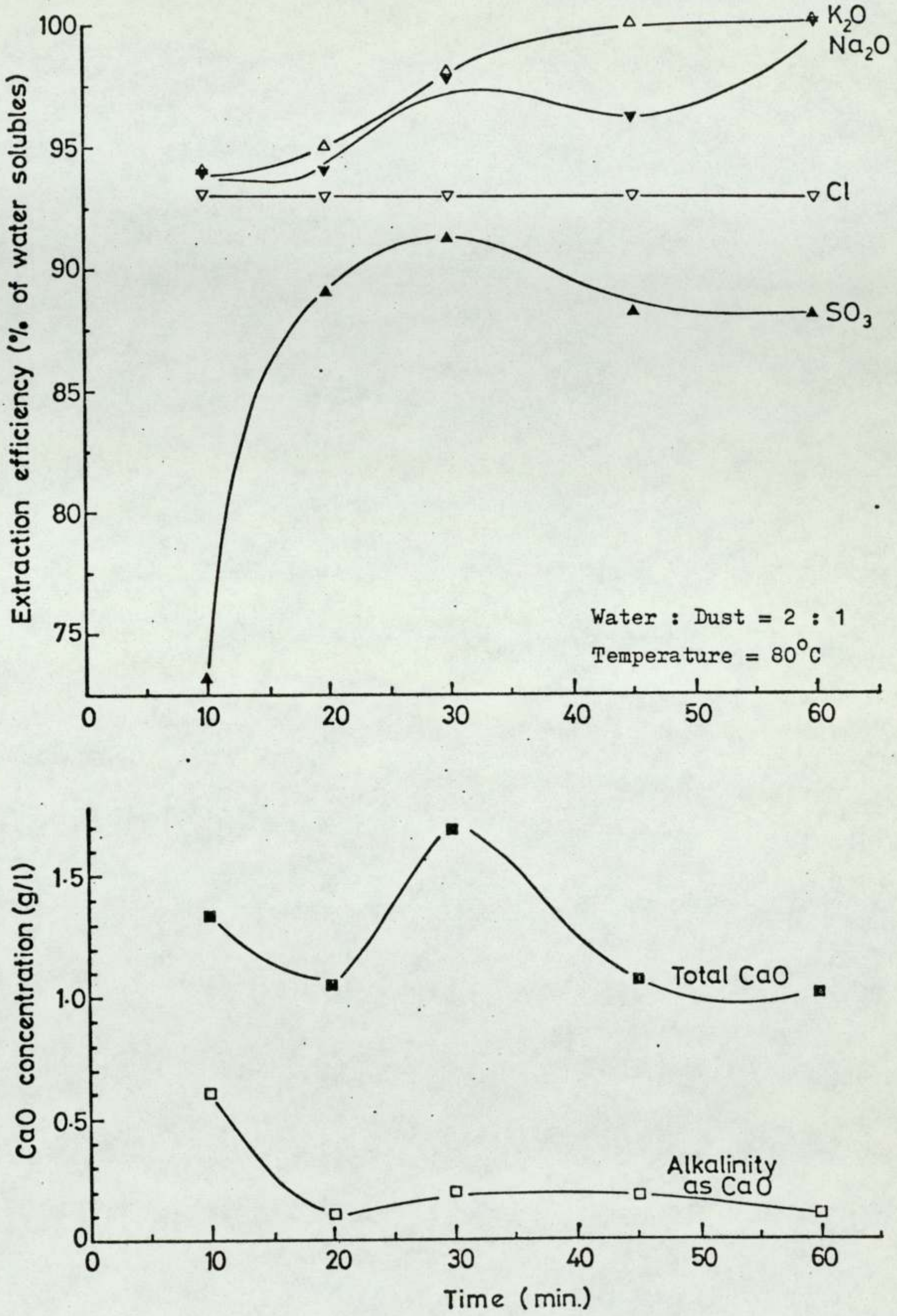


FIGURE 3.3

Leaching Characteristics of Northfleet Flue Dust

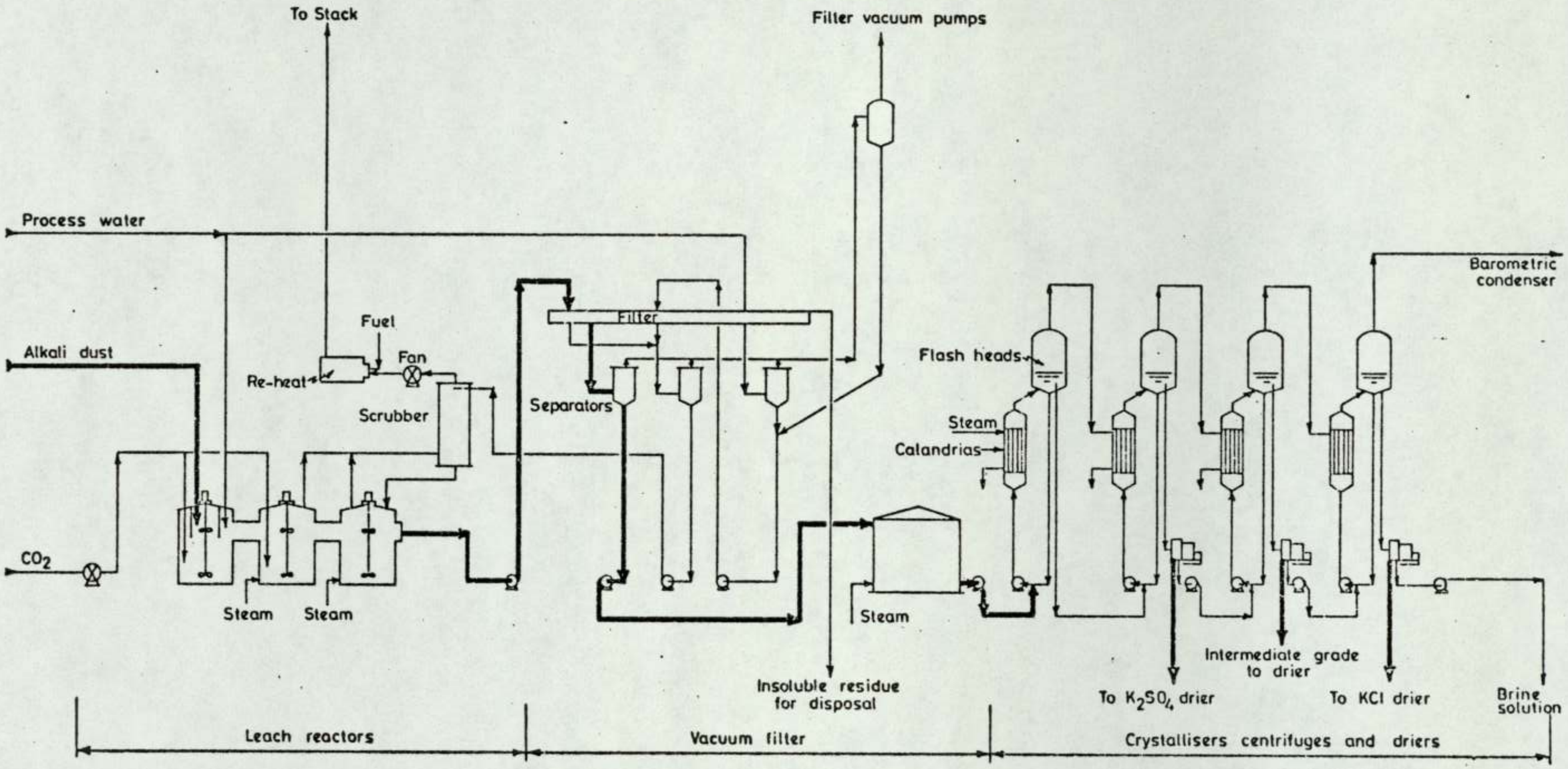


FIGURE 3.4

Woodall-Duckham's Proposed Leaching and Crystallisation Scheme for Northfleet Works

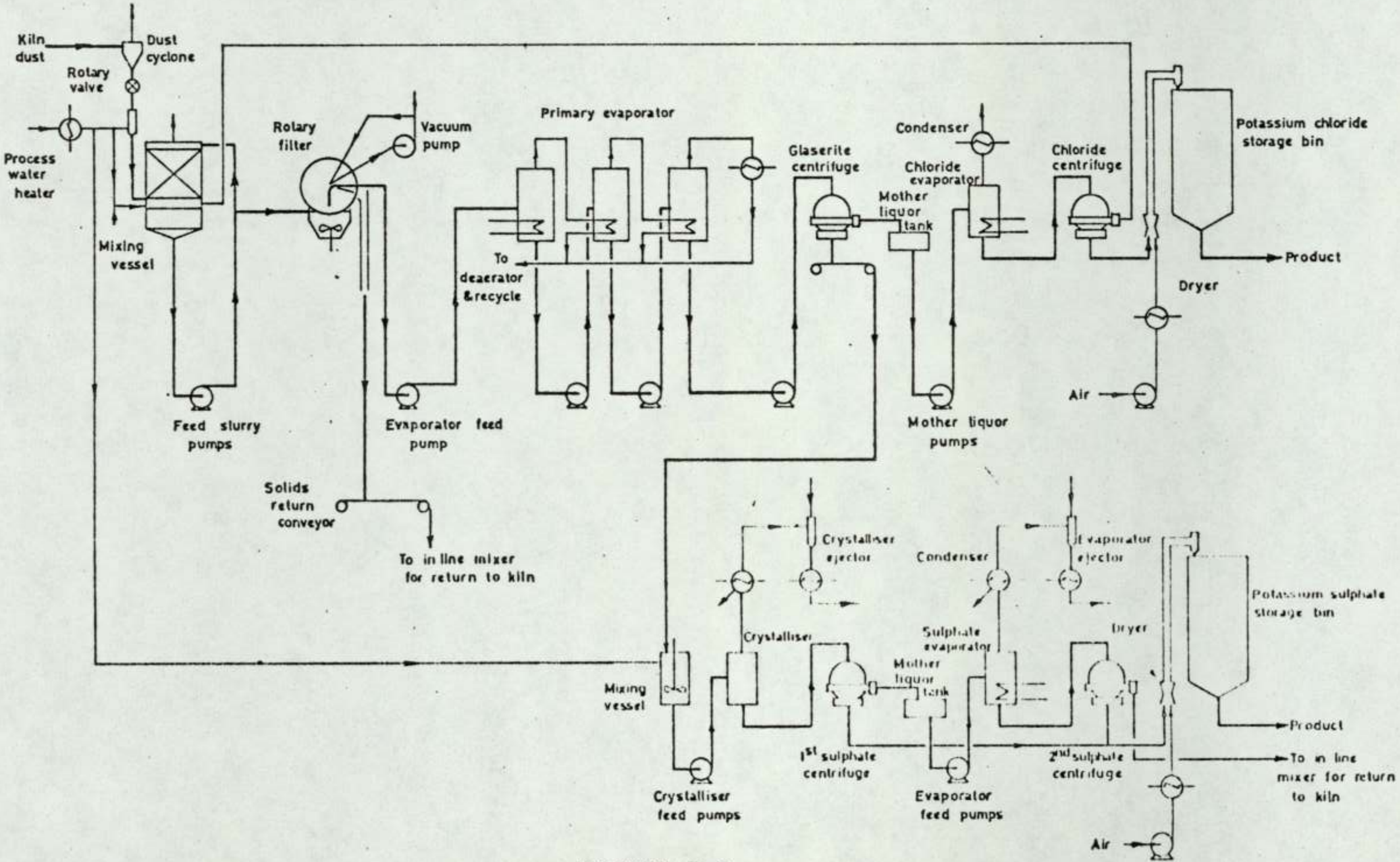


FIGURE 3.5

Humphreys & Glasgow's Proposed Leaching and Crystallisation Scheme for Northfleet Works

TABLE 3.2

Performance and Economics of the Leaching and Crystallisation Process Anticipated by Woodall-Duckham (September 1972)

Design Capacity : 200,000 t.p.a.

Nominal Throughput : 200,000 t.p.a.

Water : Dust Ratio : 2 : 1

Capital Investment : £1-1,500,000

Utilities and Labour	Requirement per ton of dust treated	Assumed unit cost	Cost/ annum
Steam	0.77t	£1.10/t	£170,000
Fuel Oil - waste gas reheating	0.025t	£8.50/t	£ 42,000
Electricity	30 kWh	0.65p/kWh	£ 39,000
Process Water	$1.36m^3$	$3.30p/m^3$	£ 9,000
Cooling Water	$28.6m^3$	0.66p/kWh	£ 38,000
Kiln Flue Gases (at 200°C)	$6800m^3$	Nil	-
Labour and Supervision @ 4 men/shift		-	£ 34,000
		Total	= £332,000

Salts Yield*	Yield per ton of dust treated	Assumed unit cost	Revenue /annum
High purity K_2SO_4	0.0775t	£23/t	£357,000
KCl (+ some K_2SO_4)	0.0815t	£20/t	£326,000
Mixed K_2SO_4/Na_2SO_4	0.026t	£16/t	£ 82,000
	0.1850t	Total	= £765,000

Gross Return : £433,000/annum or £2.17/t of dust treated

Simple Payback : 2.3-3.5 years

* Assumed dust comparison of 75.3% water insolubles and balance of water solubles comprising 4.7% CaO, 8.5% KCl, 10% K_2SO_4 and 1.5% NaCl.

TABLE 3.3

Performance and Economics of the Leaching and Crystallisation Process Anticipated by Humphreys & Glasgow (November 1972)

Design Capacity : 300,000 t.p.a.

Nominal Throughput : 193,500 t.p.a.

Water : Dust Ratio : 2.5 : 1

Capital Investment : £1,850,000

Utilities and Labour	Requirement per ton of dust treated	Assumed unit cost	Cost/annum
Steam	1.16t	(converted to fuel oil cost)	
Fuel Oil			
- steam raising	0.067t	£9/t	£116,100
- waste gas incineration	0.063t	- Not included -	
Electricity	31 kWh	0.7p/kWh	£ 42,000
Process Water	$1.60m^3$	- Not included -	
Cooling Water		- Not Specified -	
Kiln Flue Gases		- Not Required -	
Labour and Supervision		- Not Specified -	
		Total =	£158,100

Salts Yield*	Yield per ton of dust treated	Assumed unit cost	Revenue /annum
Potassium Chloride	0.0982t	£20/t	£380,000
Potassium Sulphate	0.0350t	£20/t	£135,000
	0.1332t	Total =	£515,400

Gross Return : £357,300/annum or £1.79/t of dust treated

Simple Payback : 5.2 years

* Assumed dust composition of 76.5% water insuluble, balance of water solubles comprising 5.3% CaO, 8.1% K_2O, 0.8% Na_2O, 5.5% SO_3,

that the 2 evaluations differed considerably, e.g. the W-D's case showed a pay back period of <3.5 years compared to 5.2 years in the H & G's case. The discrepancy is due partly to the difference in capital costs and partly to the inconsistent data assumed. A more realistic evaluation is presented and compared with the fluidised bed process under investigation in Chapter 7.

3.3.2 Mechanical Separation of Alkali Fines

In the horizontal gas flow type of electrostatic precipitators commonly in use in the cement industry today, there are usually at least 2 or more series-connected compartments. Due to the difference in mechanical as well as electrical properties between particles of different sizes, flue dusts collected in the precipitator tend to decrease in size from the inlet to the outlet end. Since finer dust particles tend to contain a higher alkali concentration because of the larger specific surface area, the dust collected in the final chamber of the precipitator generally contains a higher concentration of alkalis. A method of alkali separation using this principle is patented by F.L. Smidth & Co. (1969). According to the invention, the coarser flue dusts obtained from the inlet-end are returned to the kiln while the finer dusts obtained in the later sections are subjected to additional mechanical classification, for example, by cyclone separation, to produce a fine fraction of say below 5 μm, which is sufficiently high in alkali content to render it directly saleable as a potash fertiliser, and a coarse fraction relatively low in alkali concentration for recycle.

The feasibility of separating Northfleet and Westbury flue dusts into alkali-rich and alkali-poor fractions has also been investigated by BCI

(Smith, 1975): 3 samples of Northfleet flue dust representing the average dust (N1), the 2nd and 3rd chamber dust, i.e. outlet-end, (N2) and the first chamber dust, i.e. inlet-end, (N3) were split into 3 nominal cut-sizes of 10, 5 and 2 μm using a laboratory 'Alpine MZR 100' air classifier and the alkali contents were analysed. Since a proportion of the finest particles escaped collection, the alkali analyses of the undersize were corrected by calculation based on the analyses and masses of the feedstock and oversize. The results are shown in Table 3.4 and, as can be seen, the separation obtained was generally poor. In separation at 10 μm cut-size, the alkali beneficiation of the undersize was minimal and the alkali concentration of the oversize was still unacceptably high for recycle. In separation at 5 and 2 μm, some improvements were obtained but the extent of alkali reduction in the oversize (which forms the bulk of the material) was still inadequate, while the undersize (which contained slightly over 20% K_2O) may still not be readily saleable. Moreover, it is considered that a 5 μm cut-size is probably the limit at which separation on a commercial scale can presently be obtained. Similar results were obtained for the Westbury dust, as can be seen in Table 3.5. Thus, it is concluded that the separation of alkali fines by size classification for both Northfleet and Westbury flue dust is technically not feasible at present.

3.4 Separate Calcination of Flue Dust

A major advantage of calcining flue dust separately is that it does not affect the operation and performance of the cement kiln. Apart from the fluidised bed approach under investigation, which is reviewed separately in Section 3.5, there are several alternative methods of dust calcination.

TABLE 3.4

Results of mechanical separation of Northfleet Works' Precipitator Dusts

	Whole Dust	+10µm	-10µm	Calculated -10µm	+5µm	-5µm	Calculated -5µm	+2µm	-2µm	Calculated -2µm
1. Northfleet Works Precipitator Dust. N1										
% by wt.	-	40.3	54.8	59.7	55.8	35.3	44.2	81.9	8.3	18.1
% K_2O	7.8	5.9	8.0	9.1	6.4	7.8	9.6	6.5	12.3	13.7
% Na_2O	0.85	0.62	0.79	1.0	0.68	0.73	1.1	0.7	1.4	1.5
% SO_3	4.1	3.8	3.9	4.3	3.6	3.7	4.8	3.4	6.3	7.3
% Cl	3.0	2.3	3.1	3.5	2.1	3.3	4.1	2.8	4.8	3.9
% Total Volatiles	15.75	12.62		17.9	12.78		19.6	13.4		26.4
2. Northfleet Works Precipitator Dust. (2nd and 3rd Chambers only) N2										
% by wt.	-	25.4	61.1	74.6	50.5	33.0	49.5	79.0	4.1	21.0
% K_2O	19.0	11.7	20.2	21.5	11.8	23.6	26.3	17.4	28.3	25.0
% Na_2O	2.4	1.3	2.4	2.8	1.0	3.0	3.9	2.1	4.1	3.5
% SO_3	18.3	12.0	14.7	20.4	8.0	16.8	28.7	13.0	24.8	38.0
% Cl	5.3	3.7	5.8	5.8	4.6	6.0	6.0	5.3	6.0	5.3
% Total Volatiles	45.0	28.7		50.5	25.4		64.9	37.8		71.8
3. Northfleet Works Precipitator Dust. (1st Chamber only) N3										
% by wt.	-	52.3	42.1	47.7	82.7	11.0	17.3	92.6	1.2	7.4
% K_2O	6.3	4.4	6.2	8.4	4.9	8.1	13.0	5.4	12.4	17.6
% Na_2O	0.80	0.75	0.75	0.85	0.70	0.79	1.3	0.75	1.1	1.4
% SO_3	3.8	2.9	3.2	4.8	2.8	2.1	8.6	2.7	2.8	17.0
% Cl	2.6	1.6	2.9	3.7	1.9	4.2	5.9	2.3	6.9	6.4
% Total Volatiles	13.5	9.65		17.75	10.3		28.8	11.15		42.4

TABLE 3.5

Results of mechanical separation of Westbury Works' Precipitator Dusts

	Whole Dust	+10µm	-10µm	Calculated -10µm	+5µm	-5µm	Calculated -5µm	+2µm	-2µm	Calculated -2µm
1. Westbury Works Precipitator Dust. (1st Sample) W1										
% by wt.	-	39.8	50.2	60.2	52.1	36.4	47.9	76.7	11.1	23.3
% K_2O	9.5	3.6	10.0	13.4	4.2	11.5	15.3	5.4	20.9	23.0
% Na_2O	1.0	0.60	1.2	1.3	0.65	1.2	1.4	0.73	2.1	1.9
% SO_3	8.2	4.5	8.2	10.6	4.6	9.6	12.1	5.1	17.2	18.4
% Cl	1.2	0.52	1.2	1.6	0.58	1.4	1.9	0.69	2.6	2.9
% Total Volatiles	19.9	9.22		26.9	10.03		30.7	11.92		46.2
2. Westbury Works Precipitator Dust. (2nd Sample) W2										
% by wt.	-	54.4	41.1	45.6	82.2	12.5	17.8	89.1	1.8	10.9
% K_2O	6.3	3.6	9.0	9.5	4.7	12.2	13.7	5.6	12.2	12.0
% Na_2O	0.55	0.30	0.75	0.80	0.30	1.3	1.6	0.40	1.6	1.6
% SO_3	6.1	4.7	7.3	7.8	4.8	10.9	12.0	5.6	12.9	10.0
% Cl	0.8	0.6	1.0	1.0	0.7	1.3	1.3	0.7	1.2	1.6
% Total Volatiles	13.75	9.2		19.1	10.5		28.6	12.3		25.2

3.4.1 Sinter Grate Calcination

The calcination of flue dust from Hope Works was among the earliest documented work in BCI, in 1956 when Hope used a wet process plant. The dust was granulated with the addition of water and approximately 17% by weight of coke fines and calcined on a sinter grate at the Ambergate Brick Works (Barnes, 1956). The record of this work is incomplete but a proposal for a 4 t/h plant was included and is reproduced in Figure 3.6.

For reasons which are not clear no record of follow-up work was found until a similar test was carried out for Northfleet flue dust in 1971 at the Lytag Plant in Tilbury (BCI Internal Report, 1971). The dust was nodulised, but without any coke addition, and calcined on an oil-fired sinter grate. Details of the test conditions were not reported but it was stated that for the nodules on the top layer, only 50% decarbonation was achieved while at mid-depth, the decarbonation was less than 15%. The sudden exposure to the oil flame caused violent decrepitation of the nodules and the fines produced caused serious blinding of the bed. Although the extent of alkali removal was not reported, it can be surmised from the poor decarbonation obtained that this was unlikely to have been very significant.

This method of calcination has not been pursued any further.

3.4.2 Flash Calcination

The feasibility of removing alkalis from flue dust by flash calcination has also been investigated by BCI in conjunction with Air Products of Rotherham (Evans, 1974 a). A simple experiment was carried out in which typical Northfleet flue dust was fed directly into an oxy-fuel fired

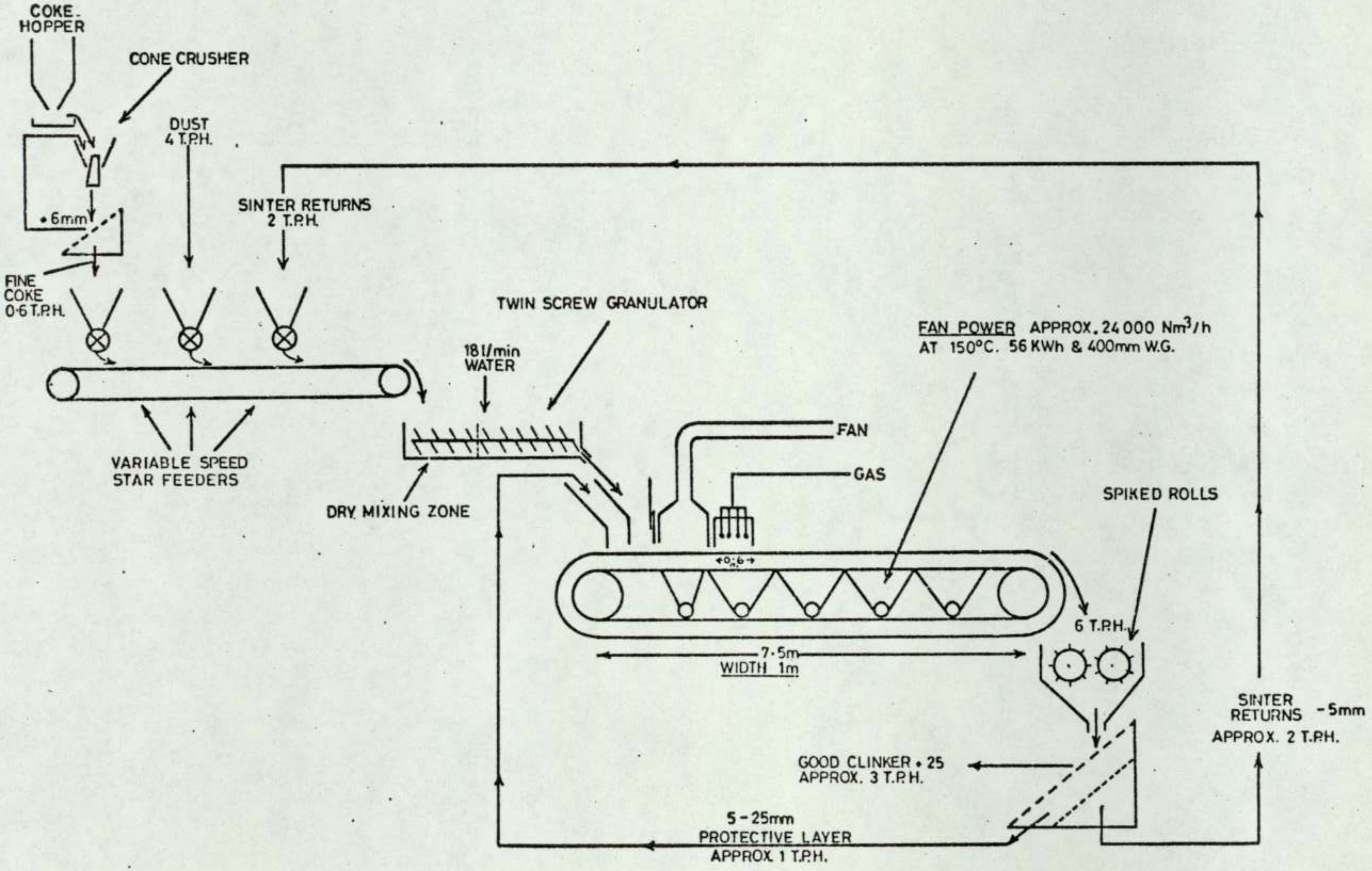


FIGURE 3.6

A Proposed Scheme for Calcining Flue Dust in a Sinter Grate Plant furnace as shown in Figure 3.7. The temperature was not determined but less than 20% alkali removal was obtained. This was attributed to the short residence time of the dust particles when dropped through the flame. Significant build-up of alkali and dust in the furnace wall and gas outlet was also observed and no further work has since been carried out.

More recently, the U.S. Environmental Protection Agency reported a similar attempt to 'flash' calcine an alkali-rich flue dust by injecting the dust with a gas fuel into a tube furnace (Greening et al, 1976). The amount of alkali removal was reported to be 'modest' and the main reason suggested for this was the re-condensation of alkali vapour on the dust particles as they traversed co-currently in the tube furnace. Various operational problems such as feed control, dust agglomeration and deposition were also reported and the problem of recovering the volatilised alkalis was unresolved.

Although none of the above investigations proved to be successful, the simplicity of flash calcination is attractive and merits further consideration. However, this is outside the scope of the present work.

3.4.3 Rotary Kiln Calcination

Although the use of a rotary kiln for dust calcination may seem an obvious consideration for cement manufacturers, kiln plant is highly capital-intensive, e.g., on the basis of current estimates for a cement plant costing, say, £70 per annual tonne, the capital investment required for processing the Northfleet dust would amount to over £10M. Moreover, the space requirement for a rotary kiln is fairly substantial and is simply not available at many works, including Northfleet. Thus, this

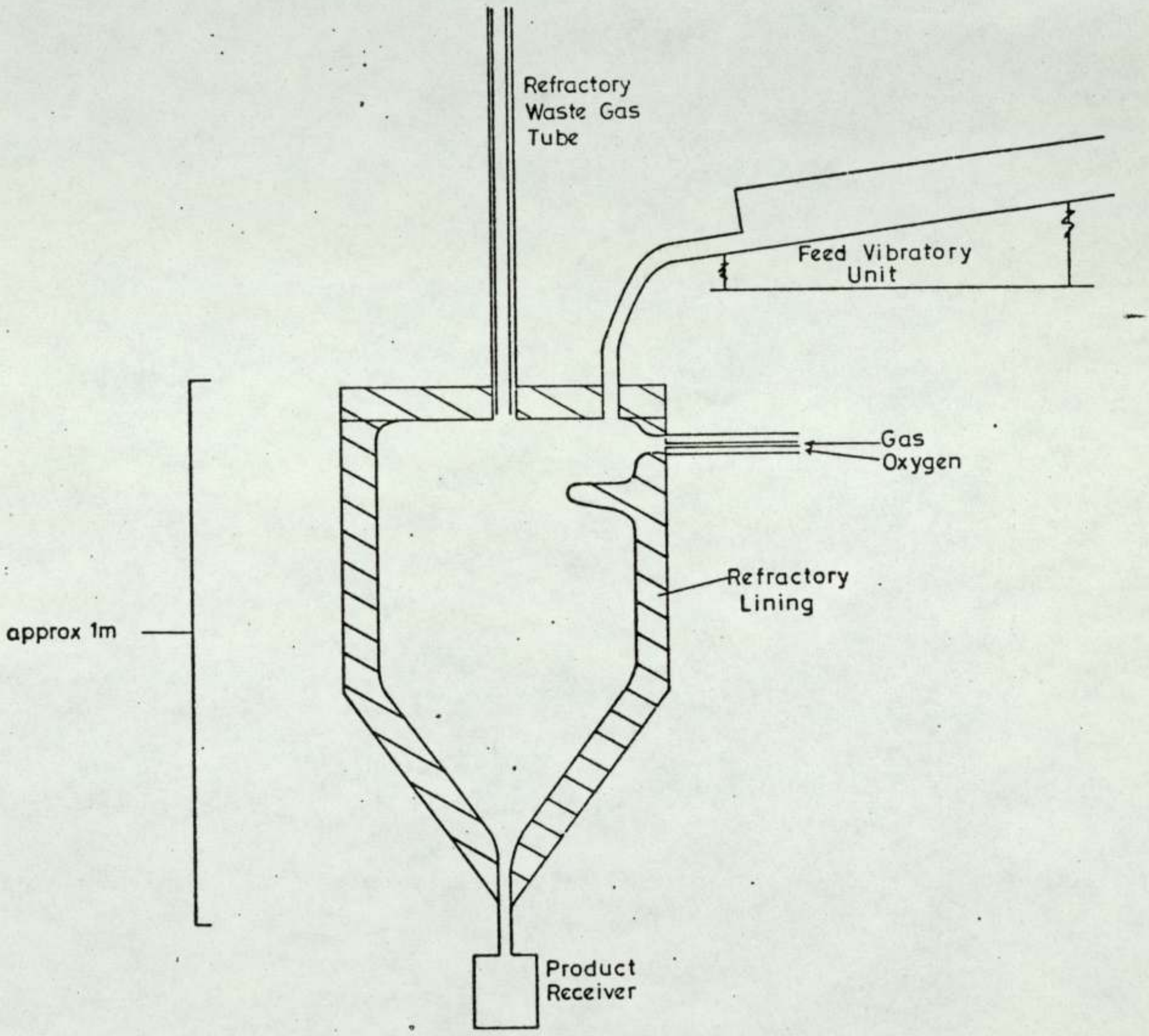


FIGURE 3.7

Oxy-Fuel Fired Furnace used in Northfleet Flue Dust Calcination Experiment at Air Products, Rotherham option has not been investigated to any extent until recent years: since 1973, demand of cement in the U.K. has been falling and the industry is faced with surplus production capacity. Consequently, some of the older, less efficient plants have been closed as convenient reserves of raw materials became exhausted, including Wouldham Works, near to Northfleet. This gave rise to the suggestion that the feasibility of converting this works' kilns to process Northfleet dust should be examined.

In 1976, a preliminary trial to calcine Northfleet flue dust was initiated by Evans et al (1976) in which the dust was calcined, either pelletised or non-pelletised, in a rotary kiln of 0.6m diameter x 13m long (Figure 3.8). Similar tests were subsequently conducted by Onions (1976 a & b) using Northfleet flue dust and Evans (1978) using a Westbury flue dust. In the later tests, various additives such as coal (which was initially thought to enhance alkali volatilisation by inducing a local reducing condition), calcium chloride, hydralime and calcium sulphate anhydrite were added to the dust in order to simulate different calcining conditions and feed characteristics.

The details of the 4 trials can be found in the reports cited and the main findings are summarised in Tables 3.6-3.9, but basically, for Northfleet dust, it is concluded that a clinker can be formed with relatively low alkali and free lime contents at a material temperature above 1300°C. This clinker should be acceptable for admixing with normal works production to produce a cement of satisfactory quality. For the Westbury dust, however, owing to the limited test carried out and the relatively unstable burning conditions and feed compositions encountered, the results were inconclusive. The addition of up to 20% of coal in either Northfleet

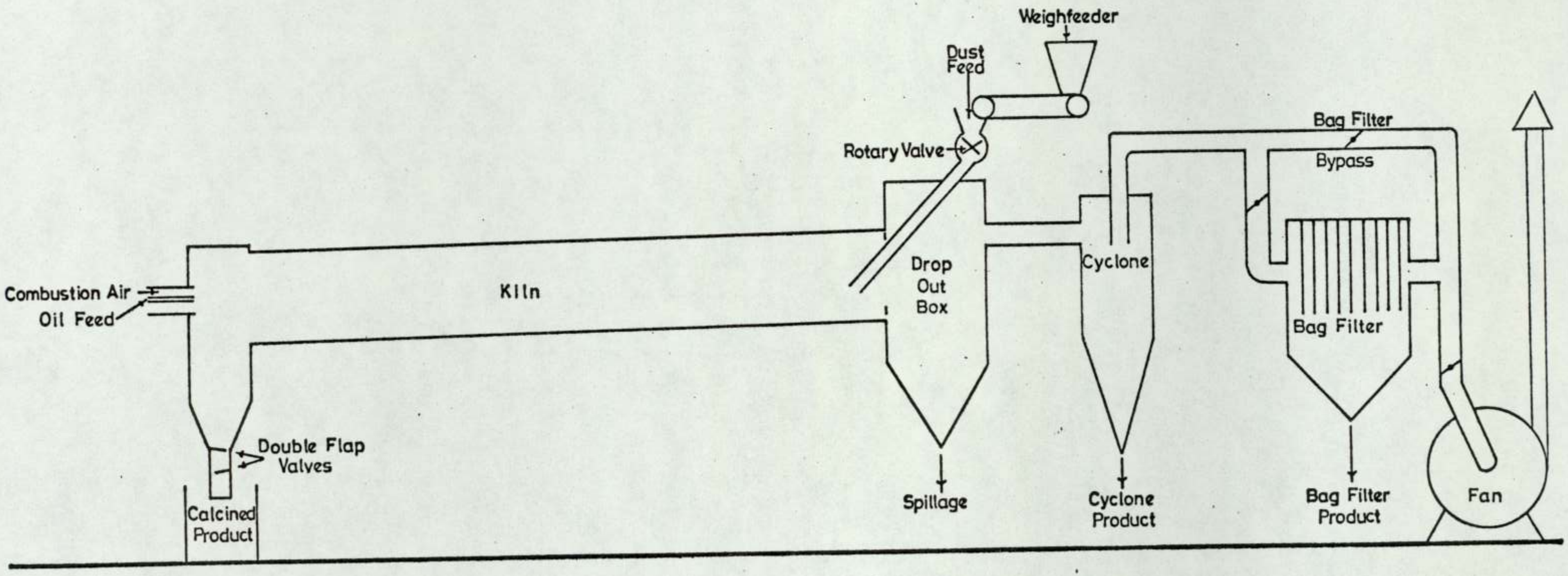


FIGURE 3.8

Rotary Kiln Plant used in Northfleet and Westbury Flue Dusts Calcination Trials at Barnstone

TABLE 3.6

Alkali and Lime Analyses of the Northfleet Flue Dust Feed and Calcined Products from the 1st Kiln Trial

Wt. %	Dust	Calcined Product		Pellet	Calcined Product			
	Feed	@ 1150°C	@ 1230°C	Feed	@ 1250°C	@ 1300°C	@ 1350°C	>1350°C
K_2O	5.80	5.70	4.50	5.40	4.0	4.20	3.10	1.44
Na_2O	0.84	1.10	1.05	0.80	1.0	0.93	0.92	0.68
Cl	2.68	1.32	0.08	2.58	0.04	0.02	0.025	0.09
SO_3	3.50	6.32	7.32	4.80	8.24	6.86	3.70	2.32
Total Volatiles	12.82%	14.44%	12.95%	13.58%	13.28%	12.01%	7.75%	5.24%
CaO	42.70	56.70	54.04	35.56	57.82	57.54	52.50	55.30
Free Lime	(3.26)	11.98	7.04	(1.72)	0.48	0.27	0.17	0.25

TABLE 3.7

Alkali and Lime Analyses of the Northfleet Flue Dust (+ Additives) Feed and Calcined Products from the 2nd Kiln Trial

Weight %	CALCINED AS PELLETS						CALCINED AS DUST		
	Average Feed	1250°C			1300°C		Average Feed	1300°C	
		½% Coal (τ= 2h)	2% Coal (τ= 2h)	5% Coal (τ= 2h)	No Additive (τ= 2h)	No Additive (τ= 2h)		No Additive (τ= 2h)	2% Coal (τ= 2h)
K_2O	7.1	7.0	4.8	3.2	7.6	6.0	7.25	3.0	3.4
Na_2O	1.1	1.2	0.9	0.9	1.0	0.8	0.85	0.6	0.7
Cl	2.8	0.5	0.1	0.06	1.8	0.8	3.39	0.02	0.03
SO_3	5.6	10.7	7.8	4.3	7.5	9.1	3.68	5.5	6.3
Total Volatiles	16.6	19.4	13.6	8.46	17.9	16.7	15.17	9.12	10.43
CaO	36.8	53.8	55.5	58.2	52.5	55.2	41.1	60.1	58.9
Free Lime	-	1.0	0.6	8.6	8.5	9.6	-	0.2	0.2

τ = Total residence time in the kiln

TABLE 3.8

Alkali and Lime Analyses of the Northfleet Flue Dust (+ Additives)

Feed and Calcined Products from the 3rd Kiln Trial

Weight %	Flue Dust Feed (Range)	1250°C				1350°C				
		No Additive	10% Coal	20% Coal	10% $CaCl_2$	No Additives		10% Coal		20% Coal
		(τ= 2h)	(τ= 2h)	(τ= 2h)	(τ= 2h)	(τ= 2h)	(τ= 4h)	(τ= 2h)	(τ= 4h)	(τ= 2h)
K_2O	4.6 - 6.5	3.2	2.9	3.5	0.2	1.9	0.6	0.4	3.9	0.3
Na_2O	0.8 - 1.0	0.5	0.5	0.7	0.5	0.5	0.2	0.2	0.6	0.7
Cl	1.8 - 4.5	0.04	0.03	0.01	0.5	0.04	0.02	0.01	0	0.01
SO_3	4.7 - 7.5	9.1	6.2	5.7	5.3	4.3	2.5	1.5	8.1	0.9
Total Volatiles	11.9 - 19.5	12.84	9.63	9.98	6.5	6.74	3.32	2.1	12.6	1.9
CaO	28.7 - 35.1	58.2	62.3	59.1	65.7	63.1	64.7	65.1	57.7	64.7
Free Lime	-	0.6	0.8	0.5	3.2	1.7	1.2	1.0	0.3	0.8

TABLE 3.9

Alkali and Lime Analyses and L.S.F. of the Westbury Dust (+ Additives)

Feed and Calcined Products from the 4th Kiln Trial

	Without Coal Addition						With 10% Coal Addition					
	'As Received'		+ 14% Hydralime		+ 35% Anhydrite & 1.5% Shale		'As Received'		+ 14% Hydralime		+ 35% Anhydrite & 1.5% Shale	
	Raw	Calcined	Raw	Calcin d	Raw	Calcined	Raw	Calcined	Raw	Calcined	Raw	Calcined
K_2O	6.3	2.5–3.3	5.6–9.7	2.2–9.3	4.7–7.1	1.4–9.1	6.1	2.3–3.4	6.4–7.6	1.1–6.0	5.85	0.2–7.3
Na_2O	0.9	0.9–0.95	1.9–1.3	0.6–1.6	0.8–1.0	0.3–1.7	0.88	0.9–1.1	0.8–1.0	0.9–1.4	0.82	0.1–1.4
Cl	2.15	0.3–0.9	1.3–1.6	0–1.3	1.1–1.2	0.02–1.4	2.03	0.1–0.2	1.3–1.9	0.07–1.1	0.84	0.2–1.7
SO_3	5.5	2.2–3.3	5.8–8.7	2.1–11.1	1.45–18.3	3.2–16.2	5.4	3.3–3.9	5.4–7.3	3.7–9.4	21.5	2.6–14.0
Total Volatiles	14.85	5.9–8.5	13.6–21.3	4.9–23.3	21.1–27.6	4.9–28.4	14.4	6.6–8.6	13.9–17.8	5.7–17.9	29.01	3.1–24.4
CaO	32.75	56–59	32–37	51–40	31–36	55–N.D.	31.71	55–57	33.3	56–66	32.2	58–N.D.
Free Lime	-	N.D.	-	1.2	-	2.5	-	N.D.	-	N.D.	-	10–13
L.S.F.	86.3	76–82	103	83–111	122	97–135	102	67–75	107	100–122	137	131–186
BZT(°C)	-	~ 1280	-	1300–1240	-	1350–1240	-	1280–1240	-	1330–1280	-	1370–1290

or Westbury flue dust did not enhance the volatilisation of alkalis, as was suggested by Onions (1976, 1977), when the results are more closely scrutinised (Tables 3.7, 3.8). However, the addition of $CaCl_2$ to enhance volatilisation and the use of hydralime or calcium sulphate to increase the L.S.F. (lime saturation factor) were effective. Generally, the degree of alkali volatilisation increases with temperature as would be expected. Above 1350°C, however, severe material fluxing, particularly with the Westbury dust, was observed, although the extent of melt formation appeared to decrease under reducing burning conditions, say with 1-2% CO at the kiln exit. The alkali product obtained was of fairly high purity, typically with a K_2O content above 45%, and the dust carry-over, which was pre-separated in the cyclone, typically amounted to about 10% of the feed.

A discussion of the technical and economic aspects of using a rotary kiln for flue dust processing, based on the feasibility study carried out for converting the redundant Wouldham Works to process Northfleet flue dust, is presented in Chapter 7.

3.4.4 Pyzel Fluidised Bed Process

During the course of the present investigation, an alternative fluidised bed process, known as the Pyzel process, came to light. The process was developed for cement making and was originally intended to compete with the conventional rotary kiln processes by virtue of lower capital cost and an ability to make a low alkali clinker. However, due to the rapid improvements made in the rotary kiln process over the development period, the process did not reach commercialisation (Pyzel, 1949-1962).

The operating principle and features of the Pyzel process have been described by Schroth (1971) and Margiloff and Cascone (1976). Basically, it involves feeding finely ground cement raw meal into a deep fluidised bed of clinker seed maintained at the incipient fusion temperature of the feed (about 1315°C). At this temperature, the fine feed particles accrete on the surface of the clinker seed where chemical reactions occur and convert the feed to clinker. A continuous discharge of clinker and recycling of clinker seed ensure the continuity of the process (Figure 3.9). In the paper by Schroth (1971), the author mentions, in passing, the possibility of using alkali-rich cement flue dust as a feedstock.

In 1975, BCI approached Fuller Company (a U.S. based organisation which held licence control of the process) for further details on the possibility of processing flue dust. According to Warshawsky (1975), Research Director of Fullers, although alkali-rich flue dust had been successfully calcined in a 450mm diameter fluidised bed, because of the different nature of flue dust, further development work was required before the process could be properly evaluated. Fullers were willing to carry out joint development work with BCI but indicated that they would prefer the rotary kiln approach, probably for commercial reason. In 1976, in concurrence with the present investigation, BCI carried out a trial using Fullers' 450mm diameter Pyzel fluidised bed to calcine Westbury flue dust. The results obtained are compared with the present work in Chapter 6 and a techno-economic assessment of the process is given in Chapter 7.

In addition to the discussion with Fullers, BCI also established close co-operation with Scientific Design Corporation, another U.S. company

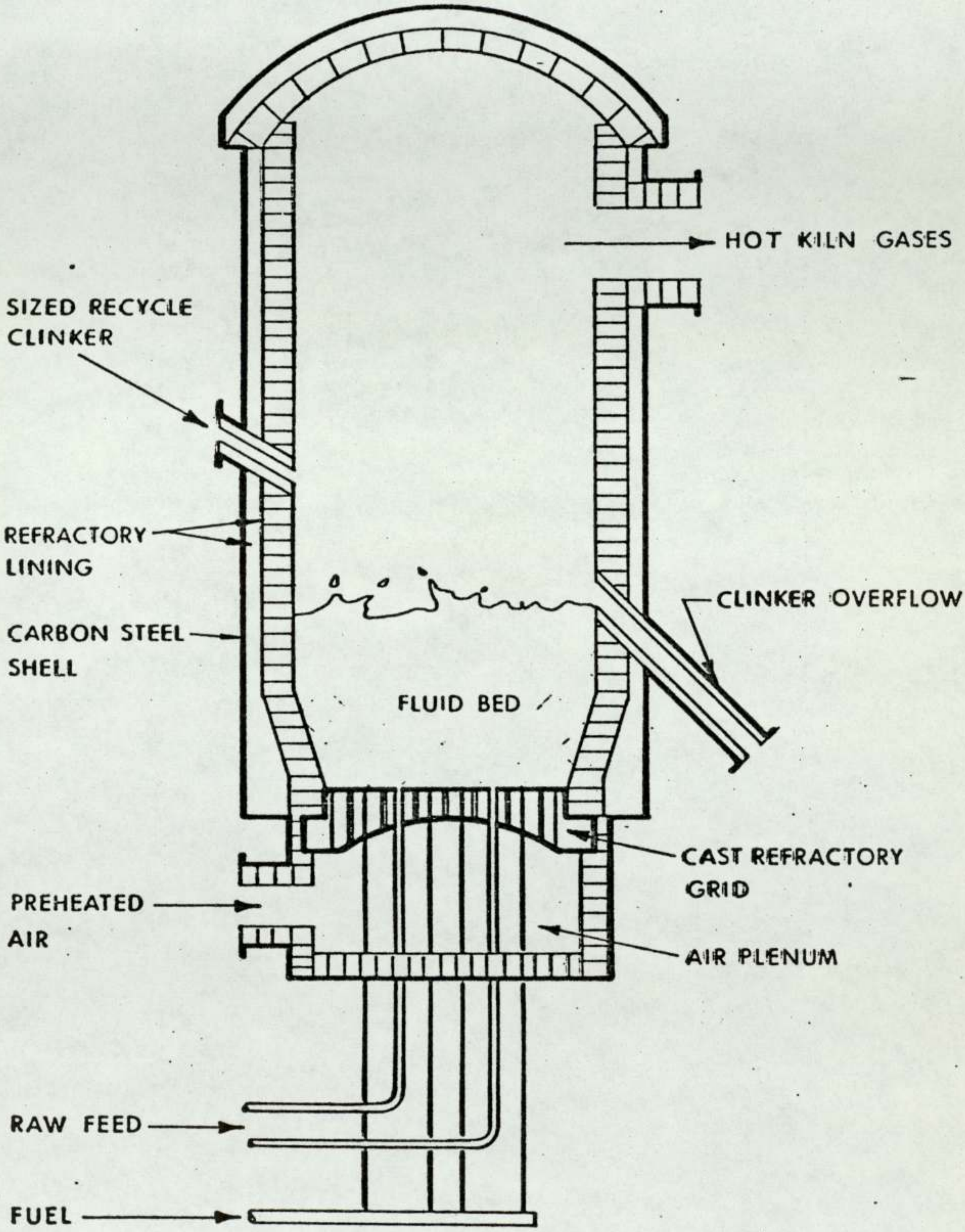


FIGURE 3.9

The 'Pyzel' Fluidised Bed

holding licence control of the Pyzel process, with the objective of developing the process to a commercial stage. However, for reasons outside the scope of the present discussion, this objective was not met.

3.5 Calcination Characteristics of Northfleet and Westbury Flue Dusts

3.5.1 Introduction

Work on the development of a fluidised bed process for calcining Northfleet and Westbury flue dusts was initiated in BCI in late 1973. The preliminary calcination tests were conducted initially at Warren Spring Laboratory in Stevenage (Evans, 1974 b) and subsequently in a 300mm diameter fluidised bed pilot plant operated by West's (Australasia) in Artarmon, Australia (Bowden, 1974 a & b). In the Artarmon trials, which were conducted jointly between BCI and West's (Manchester) - a specialist in fluidised bed equipment invited to forward proposals for a fluidised bed calcining scheme - methods of producing pellets suitable for treatment in a fluidised bed were also investigated.

In the following sections, the results of this work are reviewed. Additionally, laboratory tests carried out at the start of the present work, including the investigation of the effects on quality of admixing calcined dust with normal cement clinker are also presented. The related investigation of feed preparation, which was carried out concurrently with the present work and involved the present author to some extent, is presented in Appendix B.

3.5.2 Alkali Retention Characteristics in Static Bed

The main objective of flue dust calcination was to reduce the concentration of alkalis. Therefore, in all previous work, the results were reported in terms of the proportion of the original alkalis retained in the material after calcining, or, in short, the degree of alkali retention (see Appendix A for the definition). However, as will be shown later, this simple interpretation of results is inadequate to characterise the calcining performance.

The apparatus used in the Warren Spring Laboratory investigations is shown in Figure 3.10. The 30mm diameter x 100mm long tube furnace was electrically heated and swept with an artificial gas stream of N_2, CO_2 and H_2O in order to simulate the condition of normal combustion products. In the first series of tests, granulated Northfleet flue dust of 300-600 μm in size was heated at 800°C for 5, 10, 15 and 20 minutes. The degrees of K_2O, Na_2O, Cl and SO_3 retention obtained are shown in Table 3.10, which also includes the results of similar tests subsequently carried out by the Fuller Company on Northfleet and Westbury flue dusts at higher temperatures and longer residence time. As can be seen, the effect of residence time was, in general, fairly negligible and suggests that alkali diffusion from the material was probably not the controlling factor: this is considered in detail in the next chapter and verified later.

In the second series of tests, the granulated dust was calcined at various temperatures between 800°C and 1200°C for 10 minutes. Additionally, in a separate series of tests, the effect of a $CaCl_2$ addition, long known to cement manufacturers for enhancing the removal of potash and soda (Woods, 1942; Holden, 1950), was also investigated by incorporating 10% $CaCl_2$ in the granulated dust. The results of the tests are shown in Figures 3.11 and 3.12. As can be seen, the degree of alkali retention declined sharply

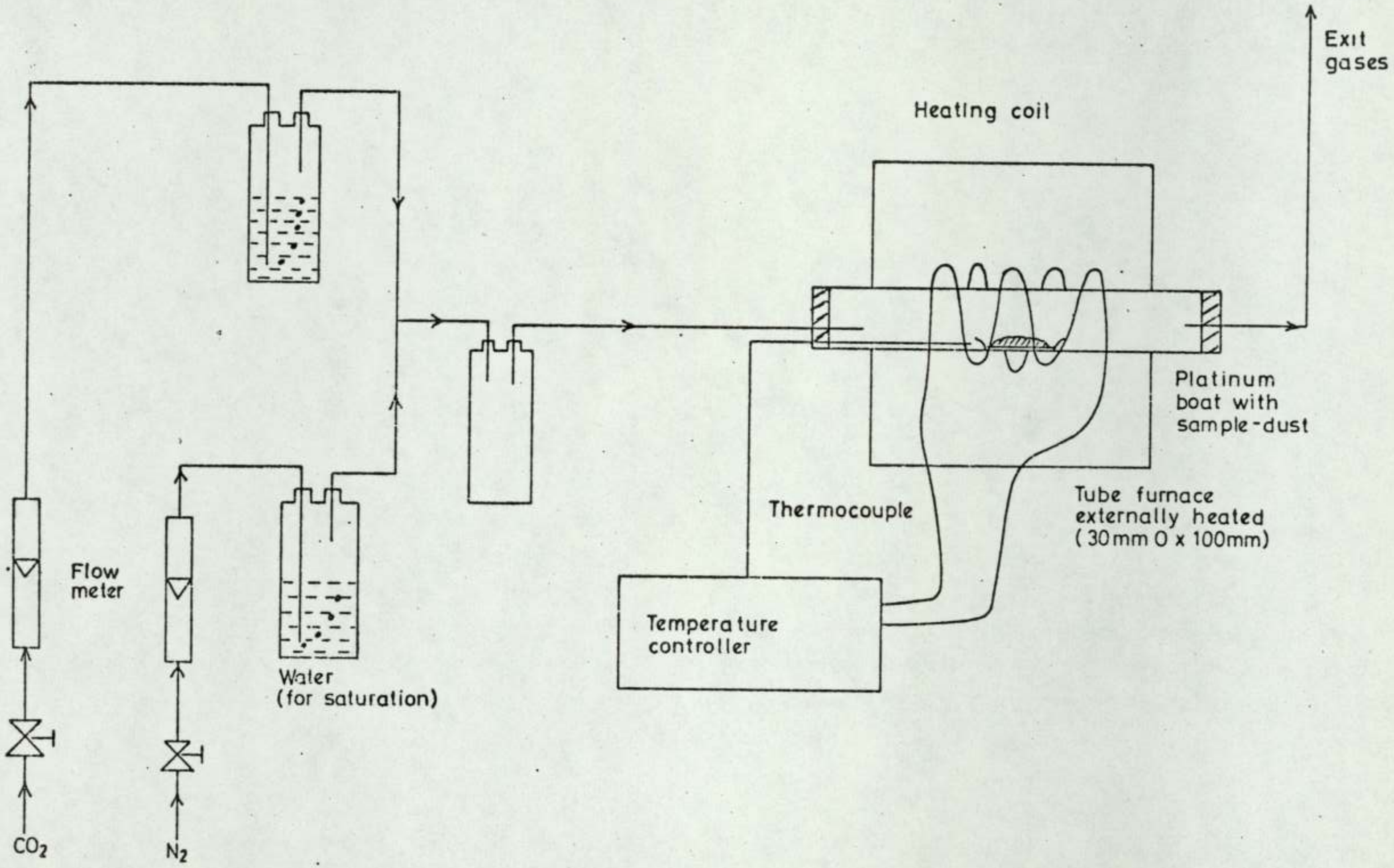


FIGURE 3.10

Static Bed Apparatus used in Preliminary Northfleet Flue Dust Calcination Experiments at Warren Spring Laboratory

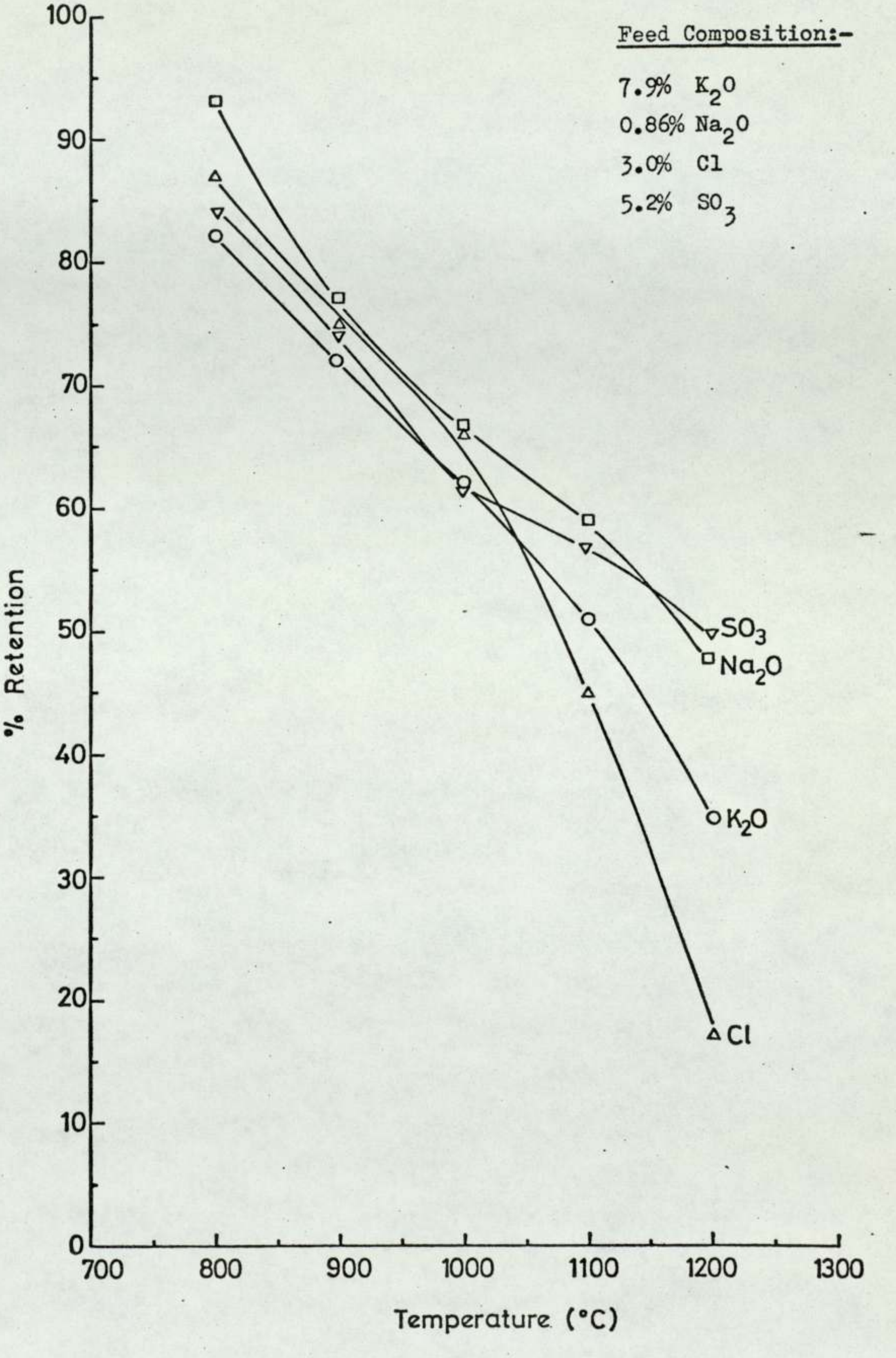


FIGURE 3.11

Effects of Temperature on Alkali Retention Characteristics of Northfleet Flue Dust Calcined in a Gas-Swept Furnace for 10 min

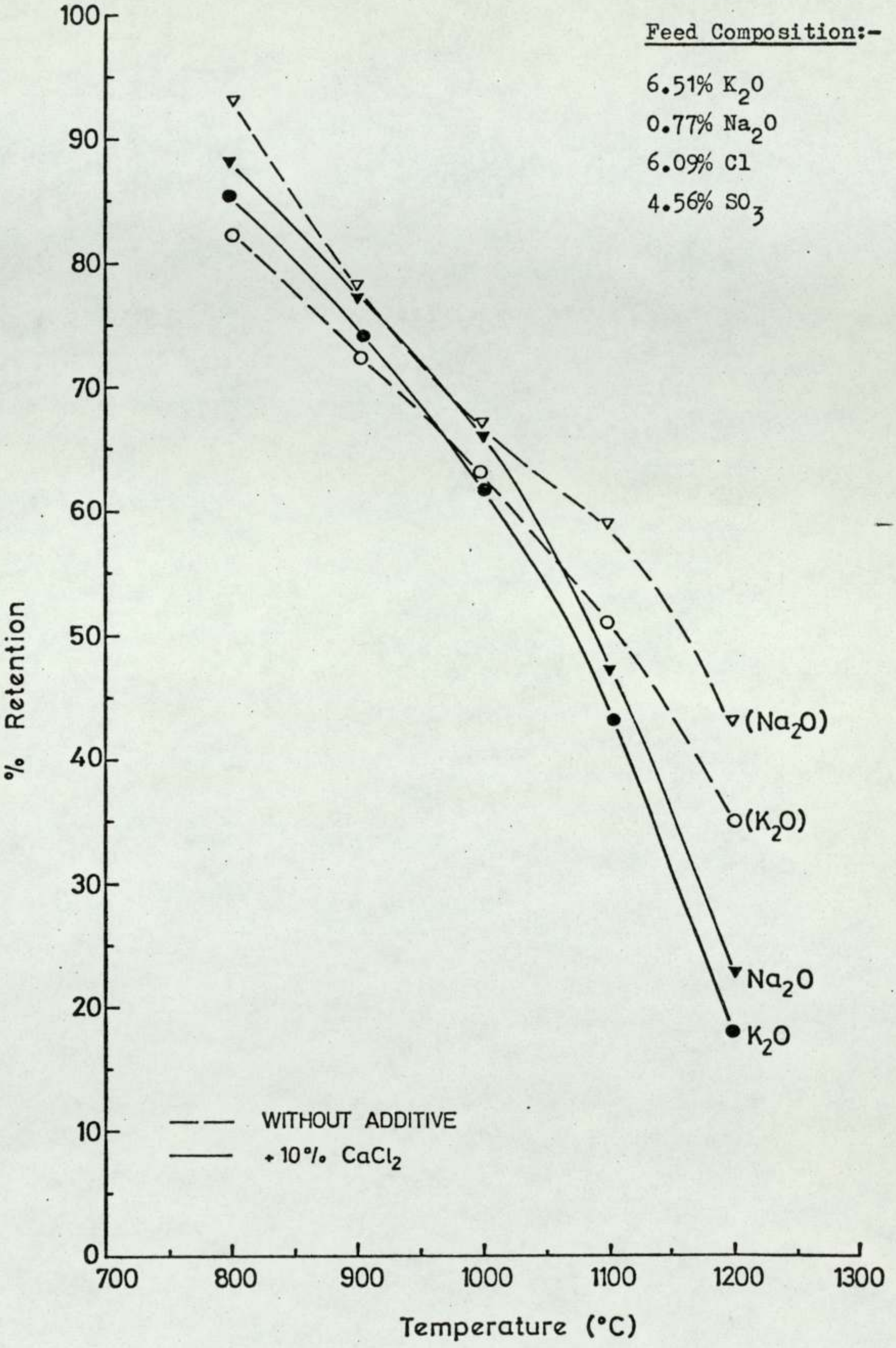


FIGURE 3.12

Effects of $CaCl_2$ Addition on Alkali Retention Characteristics of Northfleet Flue Dust Calcined in a Gas-Swept Furnace for 10 min

TABLE 3.10

Effects of Residence Time on Alkali Retention Characteristics of Northfleet and Westbury Flue Dust in a Gas-swept Laboratory Furnace

Temperature	Residence Time	Northfleet Flue Dust				Westbury Flue Dust			
(°C)	(min)	% K_2O	% Na_2O	% Cl	% SO_3	% K_2O	% Na_2O	% Cl	% SO_3
(Feed Composition)*		(7.9)	(0.86)	(3.0)	(5.2)				
800	5	86	94	91	91				
	10	82	93	87	84				
	15	83	91	89	85				
	20	81	87	84	84				
(Feed Composition)⊗		(7.30)	(0.80)	(3.12)	(5.49)	(11.80)	(0.82)	(2.14)	(10.42)
1090	20	60	65	N.D.	99	81	100	N.D.	87
	40	53	63	N.D.	86	70	98	N.D.	90
	60	47	59	N.D.	88	67	93	N.D.	97
1200	20	44	62	N.D.	96	66	93	N.D.	92
	40	41	58	N.D.	98	64	88	N.D.	94
	60	38	54	N.D.	96	62	83	N.D.	93
1320**	20	41	52	N.D.	92	56	79	N.D.	72
	40	42	53	N.D.	87	52	78	N.D.	87
	60	42	53	N.D.	94	48	72	N.D.	83

* Tests conducted at Warren Spring Laboratory (Evans, 1974 a)
⊗ Tests conducted at Fuller Company U.S.A. (Warshawsky, 1975 b)
** Sample partially melted
N.D. Not Determined

with rising temperature and at 1200°C, less than 15% Cl, 35% K_2O and 50% Na_2O and SO_3 were retained in the case of calcining without $CaCl_2$ additive (Figure 3.11). The decreasing order of retention is consistent with the phase composition and thermodynamics of the alkalis involved, as will be shown in Chapter 4. In the case of $CaCl_2$ addition, the retention of both K_2O and Na_2O was considerably lowered, as would be expected (Figure 3.12). However, the additive was only effective at temperatures above 1000°C. According to McCord et al (1977), this is because the reaction

$$CaCl_2 + K_2O \longrightarrow CaO + 2KCl \qquad .....(3.1)$$

only occurs at material temperature in excess of 980°C.

The effects of adding $CaCl_2$ were not studied in the present work primarily because it was found to be unnecessary for the Northfleet dust. However, in the case of Westbury dust, this is a necessary practical consideration and will be discussed later.

3.5.3 Alkali Retention Characteristics in Fluidised Bed

The fluidised bed experiments carried out at Warren Spring Laboratory involved essentially the same experimental technique described previously, except that the horizontal tube furnace was replaced by a 50mm diameter silica tube equipped with a gas distributor, as shown in Figure 3.13. A small amount of alumina chips was provided in order to enhance the heat capacity of the bed and hence the temperature stability. The size of the granulated Northfleet dust was in the range of 212-300 μm.

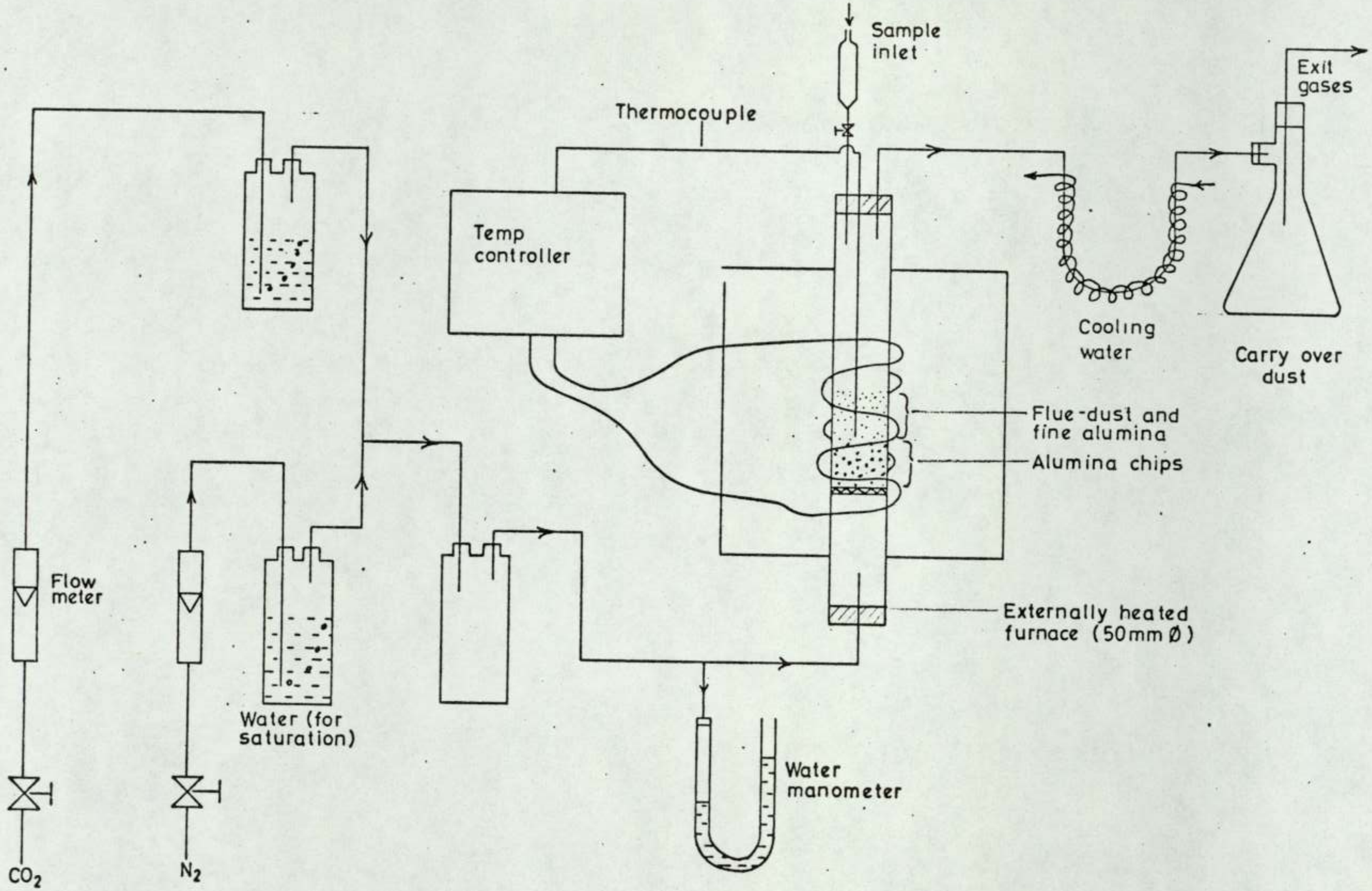


FIGURE 3.13

Fluidised Bed Apparatus used in Preliminary Northfleet Flue Dust Calcination Experiments at Warren Spring Laboratory

The degree of alkali retention obtained after calcining for 10 minutes at various temperatures between 800°C and 1100°C (the maximum temperature limit of the silica tube) is shown in Figure 3.14. Although the same order of alkali retention as that found in the static bed was obtained, the degree of retention of all the alkali components was significantly lower and, indeed, the performance at 1100°C in the fluidised bed was considerably better than that at 1200°C in the static bed. Apart from better heat and mass transfer characteristics, the main reason for the better performance in the fluidised bed can be attributed to a higher gas:solid throughput, although this information was not given in the report. As will be shown later, the amount of alkalis removed is proportional to the gas:solid ratio when the volatilisation of the alkali is controlled by the partial pressure.

The 300mm diameter fluidised bed pilot plant in the Artarmon trials is shown schematically in Figure 3.15. The trials were carried out in 2 phases, the first being a general feasibility study in which Northfleet flue dust was pelletised in a peg pelletiser and then dried and calcined batch-wise and in separate stages in the 300mm bed shown. It was found that the dust could be pelletised, albeit at low throughput (see Appendix B), dried and calcined without significant problems. However, it was found that between 600°C and 800°C, the pellets tended to soften and produced an excessive dust carry-over. At higher temperatures say, above 900°C, the pellets hardened and at still higher temperatures, up to about 1100°C (the limit of the equipment) they showed some sticking tendencies and required vigorous fluidisation in order to prevent agglomeration. The loss of strength at the temperature range indicated suggests that decarbonation was probably the main reason for dusting while the hardening

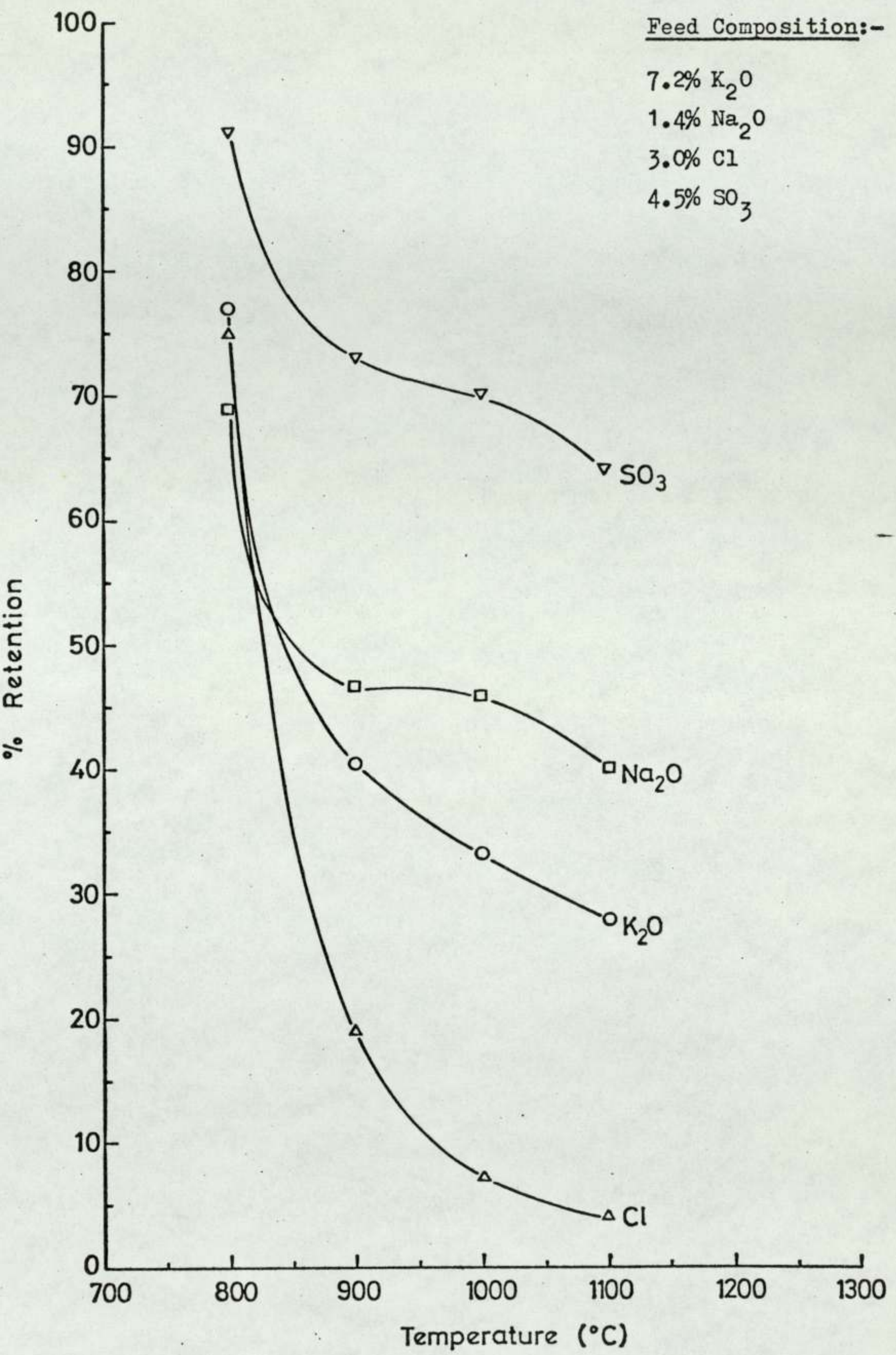


FIGURE 3.14

Effects of Temperature on Alkali Retention Characteristics of Northfleet Flue Dust Calcined in a Fluidised Bed for 10 min

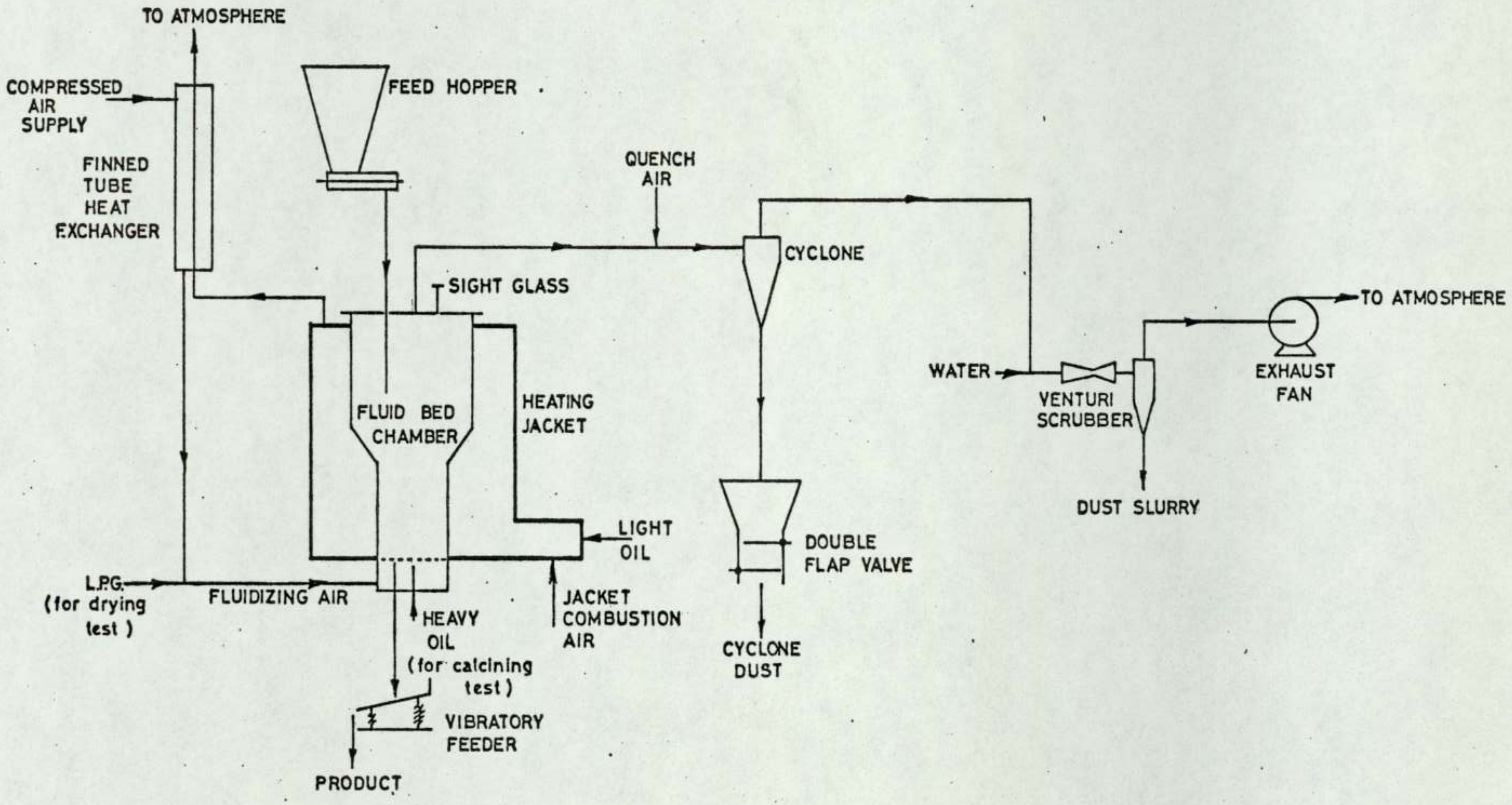


FIGURE 3.15

The 300mm Diameter Fluidised Bed Pilot Plant used in Northfleet Flue Dust Calcination Trials at Artarmon (Australia) and sticking behaviour at higher temperatures was probably a result of the formation of a liquid melt. At 1100°C the retention of K_2O and Na_2O was in the order of 50% for 30 minutes residence time, which is similar to that of the static bed, but significantly higher than that of the fluidised bed reported in the Warren Spring experiments.

The main objective of the second phase of the trial was to obtain additional information on the operating characteristics and performance of the fluidised bed under continuous operation. However, because of extreme dust build-up in the off-gas duct-work and the subsequent operating difficulties which continually interrupted the experiment, this objective was not met and no meaningful conclusions could be drawn. However, it did provide some insight to the problem which could arise.

3.5.4 Lime Combination Characteristics of the Materials

After removal of alkalis, the next objective of flue dust calcination was to ensure that the lime, silica, alumina and iron oxide present were fairly well combined so that when the calcined dust was admixed with the normal works clinker, the resultant material would not be significantly diluted by a poorly combined material. The extent of lime combination is reflected in the L.S.F. of the material (see Appendix A) but also, and more conveniently for the present purpose, in the amount of residual free lime, i.e. the amount of unreacted lime. For a normal O.P.C., the amount of residual free lime is typically below 2% (Lea, 1971).

In the Warren Spring experiments, the residual free lime of the calcined materials was not determined, but in the Artarmon trials the residual free lime of the calcined material was typically in the order of about 10%.

The relationship between free lime and calcining temperature for typical Northfleet and Westbury dusts were determined at the start of the present work using an oil fired laboratory furnace (Smith and Stephenson, 1975). The dusts were made into 'standard' cubes of 20 x 20 x 25mm in size and calcined for 20 minutes at various temperatures between 1050°C and 1300°C. The effects of adding 1% and 2% CaF_2, a fluxing agent known to enhance combination, were also investigated. As can be seen in Figures 3.16 and 3.17, the free lime was high, especially for Northfleet dust, when no additive was used. With CaF_2 addition, the combination was enhanced significantly. However, as will be explained in Chapter 4, the tolerable limit of free lime in either Northfleet or Westbury calcined dust is not critical for admixing with the works clinker. Therefore, the use of CaF_2 would only be an additional unnecessary expenditure at these works.

3.5.5 Quality Aspects of Intergrinding Calcined Flue Dust with Clinker

The effects on quality of intergrinding calcined Northfleet and Westbury flue dusts with the respective works clinker were determined at the beginning of the present work and reported by Smith and Stephenson (1975). The calcined dusts used were produced either from the Artarmon trials (for Northfleet dust only) or in a laboratory oil-fired furnace. A 10% dust addition (i.e. 1 part of calcined dust : 9 parts of clinker and gypsum), which was approximately the level of addition anticipated for both Northfleet and Westbury Works (see Section 4.2.3), was used and the amount of gypsum addition was adjusted so that the dust-incorporated and normal cement had a consistent SO_3 content of 2.2-2.3%. The mixes were all ground to a typical nominal specific surface area of 330 $m^2\ kg^{-1}$ and tested for various properties as shown in Table 3.11.

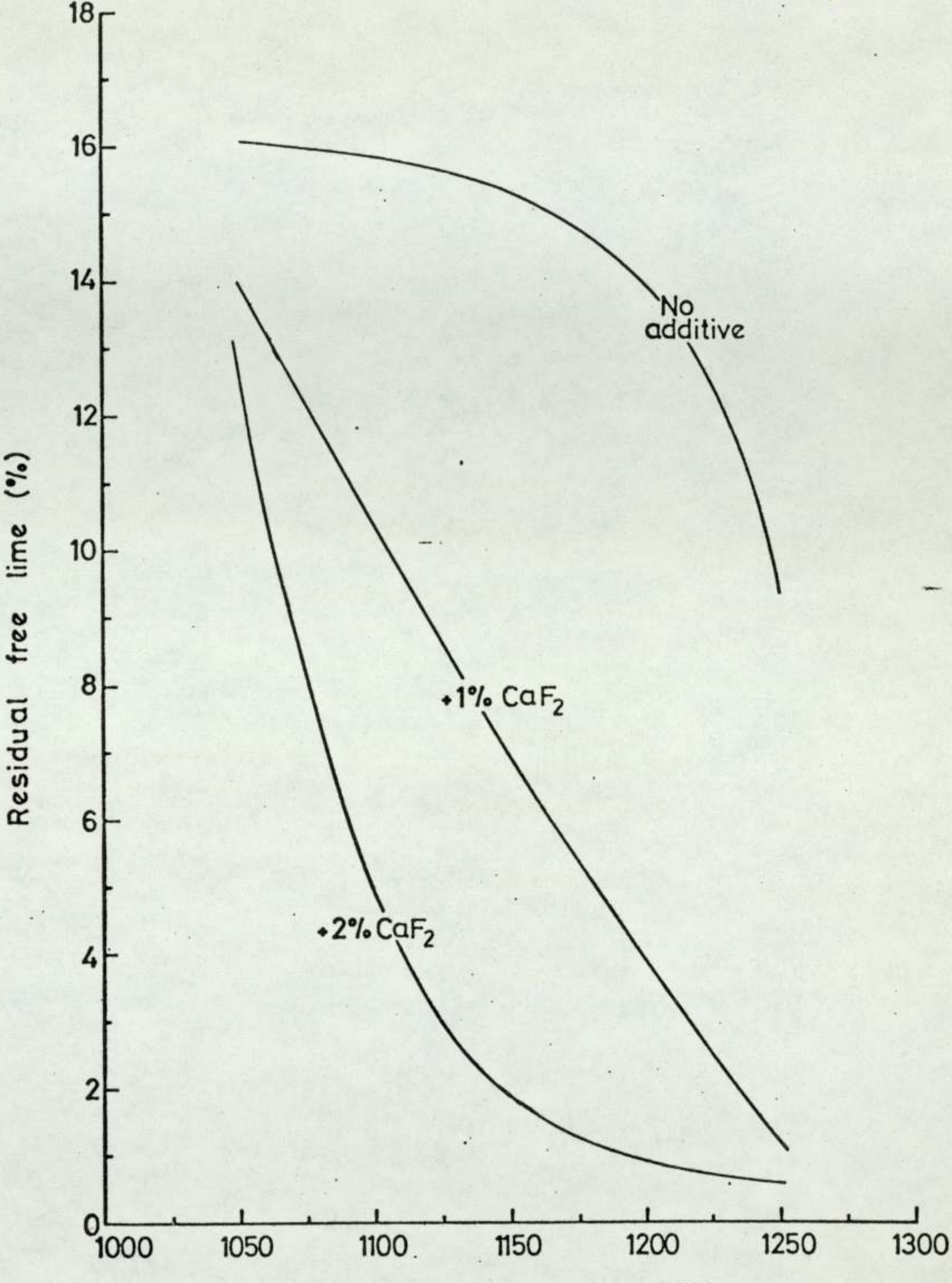


FIGURE 3.16

Effects of Temperature and CaF_2 Addition on Lime Combination Characteristics of Northfleet Flue Dust Calcined in an Oil-Fired Furnace for 20 min

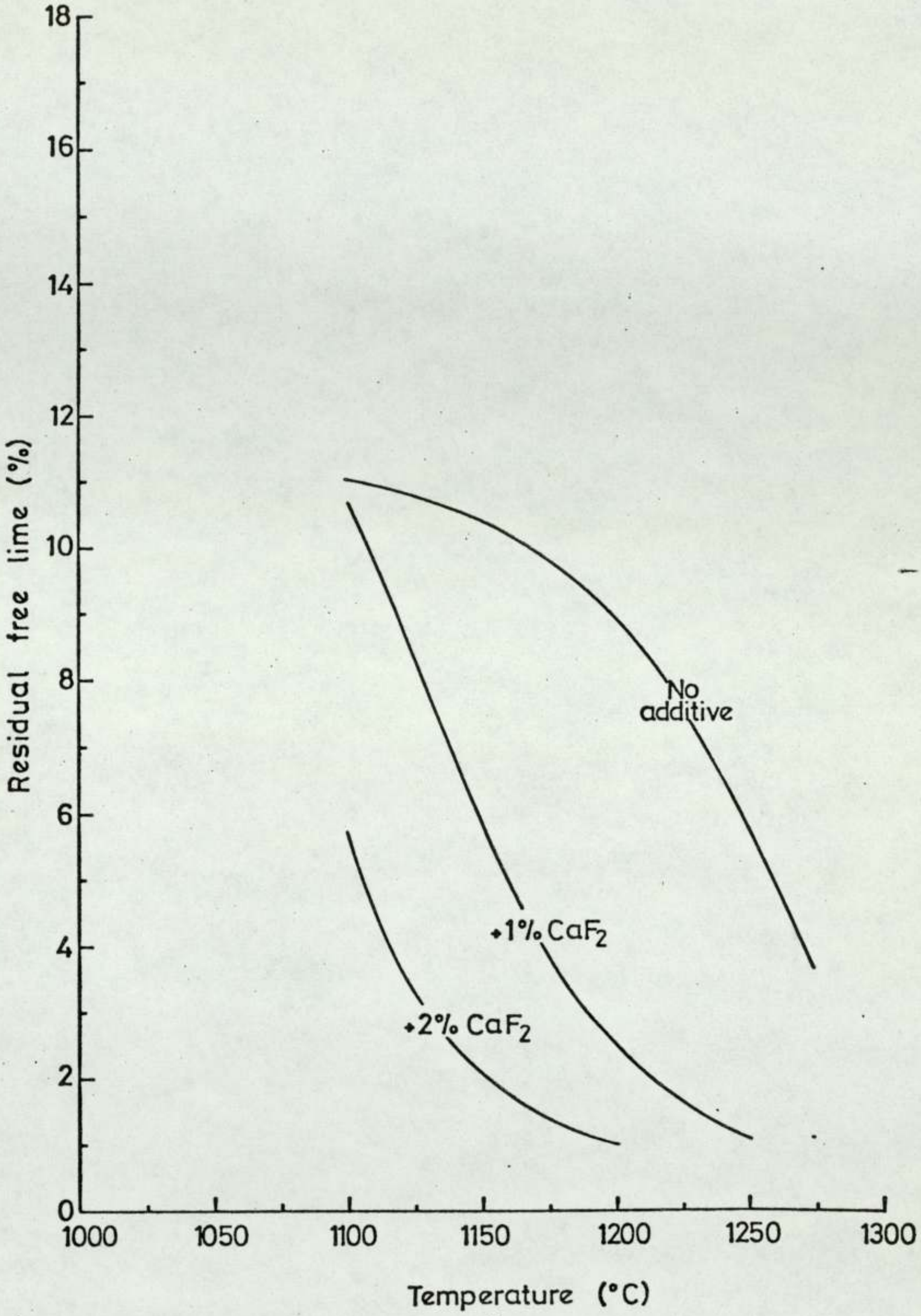


FIGURE 3.17

Effects of Temperature and CaF_2 Addition on Lime Combination Characteristics of Westbury Flue Dust Calcined in an Oil-Fired Furnace for 20 min

TABLE 3.11

Effects on Cement Quality of Intergrinding Northfleet and Westbury Calcined Dusts with the Works Clinker

Grinding Conditions:-	Northfleet				Westbury						
Temperature = 120-130°C	Control Cement	10% Dust Incorporated Cement			Control Cement	10% Dust Incorporated Cement					
Time = 25-30 min		No Additive	6% $CaCl_2$	5% CaCl + 2% CaF_2		No Additive		5% $CaCl_2$		5% $CaCl_2$ & 1% CaF_2	
Specific Surface Area = 330-340 m^2/kg						Oxidising	Reducing	Oxidising	Reducing	Oxidising	Reducing
	(A)	(B)	(C)	(D)	(E)	(F)	(G)	(H)	(I)	(J)	(K)
Alkali/Lime Analysis*:- K_2O (%)	0.59	1.03	0.52	0.62	0.31	0.84	0.61	0.46	0.30	0.44	0.26
- Na_2O	0.28	0.32	0.23	0.24	0.19	0.25	0.24	0.23	0.18	0.19	0.16
- Free CaO	0.6	2.1	1.4	0.7	0.8	0.6	0.7	1.1	0.7	0.8	0.6
Water Demand (%)	23.8	24.8	24.0	24.5	25.8	25.5	25.3	25.0	26.8	25.3	24.5
Setting Time:- Initial (min)	240	60	170	305	170	160	155	155	175	180	175
- Final	285	70	185	350	215	200	230	185	235	220	225
Strength Development:- 3 day (N/mm^2)	16.4	15.4	17.7	21.8	19.8	19.8	19.3	18.2	17.8	17.9	19.7
- 7 day	30.2	24.3	27.8	32.8	33.2	28.7	28.6	29.5	29.4	28.1	30.2
- 28 day	47.8	39.4	43.8	45.4	46.4	40.9	41.6	43.1	42.6	41.3	44.6
Workability Characteristics:- (mm)** - Brief mixing	11	13	8	17	10	24	22	22	17	27	10
- Extended mixing	22	27	15	27	22	28	28	28	26	28	22

Without going into too much detail, it was found that in general, the effect of the dust addition on water demand and workability of the cement was fairly negligible. However, the setting time was substantially reduced when the residual alkali contents were high (sample B) and increased when excessive CaF_2, which was added to promote combination (Sample D), was used. There was little change in the 3-day strengths but the 28-day strengths were generally depressed, by as much as 20% when both the residual alkali and free lime contents of the calcined dusts were high (Sample B). The effect of calcined dust free lime was fairly minimal, although the strength development seemed to be affected when it exceeded 2% in the mix, probably as a result of 'dilution' effect.

In practice, the loss of the 28-day strength could probably be restored by finer grinding and the only major effect to be expected was air-setting, due to the presence of excessive K_2SO_4 which could accentuate the formation of syngenite, i.e. $K_2SO_4 \cdot CaSO_4 \cdot H_2O$ (Stephenson, 1977 a & b). To avoid this problem, it was suggested that the K_2O content in the mixed concrete should be kept below about 0.9% when the works clinker contains a typical free lime level of 1.5% and about 0.7% when the clinker free lime, which inhibits the formation of syngenite, was lower, say, to 0.5%. The effect of Cl, which is potentially the most harmful because of its corrosive effect on reinforced and pre-stressed wires used in concrete structure, was not specifically determined but the general recommended limit of <0.02% in cement must be strictly adhered.

The calcining requirements for Northfleet and Westbury flue dusts is specified in Section 4.2.3.

3.6 Closure

The various methods of flue dust utilisation reviewed in this chapter are summarised in Table 3.12. The comments are addressed primarily to the cases of Northfleet and Westbury flue dusts, although they probably apply equally to other problems of a similar nature. It can be seen that, of the alternatives considered, only 3 options are potentially feasible, viz, the leaching and crystallisation option, the rotary kiln option and the fluidised bed option. The techno-economic features of these options are further considered and compared in Chapter 7.

As far as the calcination of Northfleet and Westbury flue dusts is concerned, it is seen that the scope and findings of the previous work are relatively limited and also, as mentioned, the available correlation of alkali retention with temperature is inadequate. Above all, the calcination requirements with respect to alkali retention and lime combination for the materials have not been defined. In the next chapter, the requirements and fundamental constraints of the process are considered.

TABLE 3.12

Summary of the Alternative Methods of Flue Dust Utilisation, Treatment, and Calcination

Methods	Options	Advantages/Disadvantages	Remarks
Direct Utilisation	As fertilisers, binders, fillers, etc.	Low capital investment but market uncertain	U.K. market either non-existent or limited
Treatment for Recycle	(i) Leaching and Crystallisation	Mainly proven technology and possible to recover high value alkali salts, but capital investment is high and recycle of dust sludge may present further problem	See Chapter 7 for further details
	(ii) Mechanical Separation	Simple and low cost	Not technically feasible for either Northfleet or Westbury dust
Separate Calcination	(i) Sinter Grate	Dust can be processed independently of cement kiln operation	Not feasible
	(ii) Flash Calciner	As (i) above + simplicity and low capital cost	Not feasible so far
	(iii) Rotary Kiln	As (i) above + familiar technology but kiln plant expensive	See Chapter 7 for further details
	(iv) Fluidised Bed	As (i) above + relatively inexpensive plant but unfamiliar technology	Present work

CHAPTER 4

THEORETICAL TREATMENT

Summary

The calcination requirements of Northfleet and Westbury flue dusts for intergrinding with normal works clinker are specified from consideration of the dust and clinker properties and the quantities of dust involved. At an estimated calcined dust:clinker ratio of 7:100, the calcined Northfleet and Westbury flue dusts are required to satisfy the following quality criteria:-

Calcined Dust Composition		Northfleet Works	Westbury Works
K_2O	(%)	<4%	<4%
Cl	(%)	<0.3%	<0.3%
Free Lime	(%)	<16%	<9%

Consideration of the operating principle and constraints of the fluidised bed process for the present application indicates that the fluidisation velocity required is likely to be within the range of 2-5 m s^{-1} and that the maximum operating temperature of the bed may be limited to about 1260°C.

It is suggested that the general calcination and lime reaction mechanisms are basically similar to those of cement burning, except that the

volatilisation of KCl and K_2SO_4 now assume the dominant role. The theoretical heat of reaction, which is mainly accounted for by the dissociation of $CaCO_3$, is estimated to be in the region of 230 kcal/kg dust or 350 kcal/kg calcined product. The mean residence time needed to calcine the dust particles, which is governed principally by the external heat transfer problem (i.e. the heat capacity of the gas), varied from 10-60 min. depending on the temperature difference between the gas and solid.

From consideration of the vapour saturation characteristics of KCl and K_2SO_4, it is postulated that for conditions likely to be met in practice, the volatilisation of KCl will occur freely but that of K_2SO_4 will be limited by vapour saturation of the fluidising gas. The extent to which K_2SO_4 will volatilise is shown to be dependent on the gas:solid throughput, initial K_2SO_4 concentration in the feed, and the saturation vapour pressure (and therefore the temperature).

The scale and scope of the experiment to be carried out, including a proposal for a systematic approach to developing a suitable method of handling the fluidised bed exit gases, are outlined.

4.1 Introduction

It must be stressed that the fluidised bed process under investigation is not intended for producing a cement from flue dust to a standard specification. Instead, the basic objective is to convert the dust into a calcined material which can be incorporated into a cement with the normal works clinker without adversely affecting quality.

The effect on quality of intergrinding normal cement clinker with calcined dust has already been studied previously (Section 3.5.5). In this chapter, the calcination requirements of Northfleet and Westbury flue dusts, taking into consideration the potential availability of the calcined dust and the property of the clinker involved, are defined. The principles and constraints of fluidised bed operation for the present application are briefly considered, followed by a postulation of the mechanism involved in dust calcination and of the probability of limitation of alkali sulphate volatilisation as a result of vapour saturation. The chapter ends with the consideration of a plan of experiments.

4.2 Properties of Northfleet and Westbury Flue Dusts and the Calcination Requirements

4.2.1 Physico-chemical Characteristics of the Dusts

The dusts as obtained from the electrostatic precipitator consist of fine cohesive powders, greyish-white in colour. The particle size distribution is generally finer than that of the cement raw meal, ranging from approximately 0-150 μm in size, Figure 4.1. For the dusts shown, the surface mean diameter is only of the order of 3 μm. Hence, pelletisation

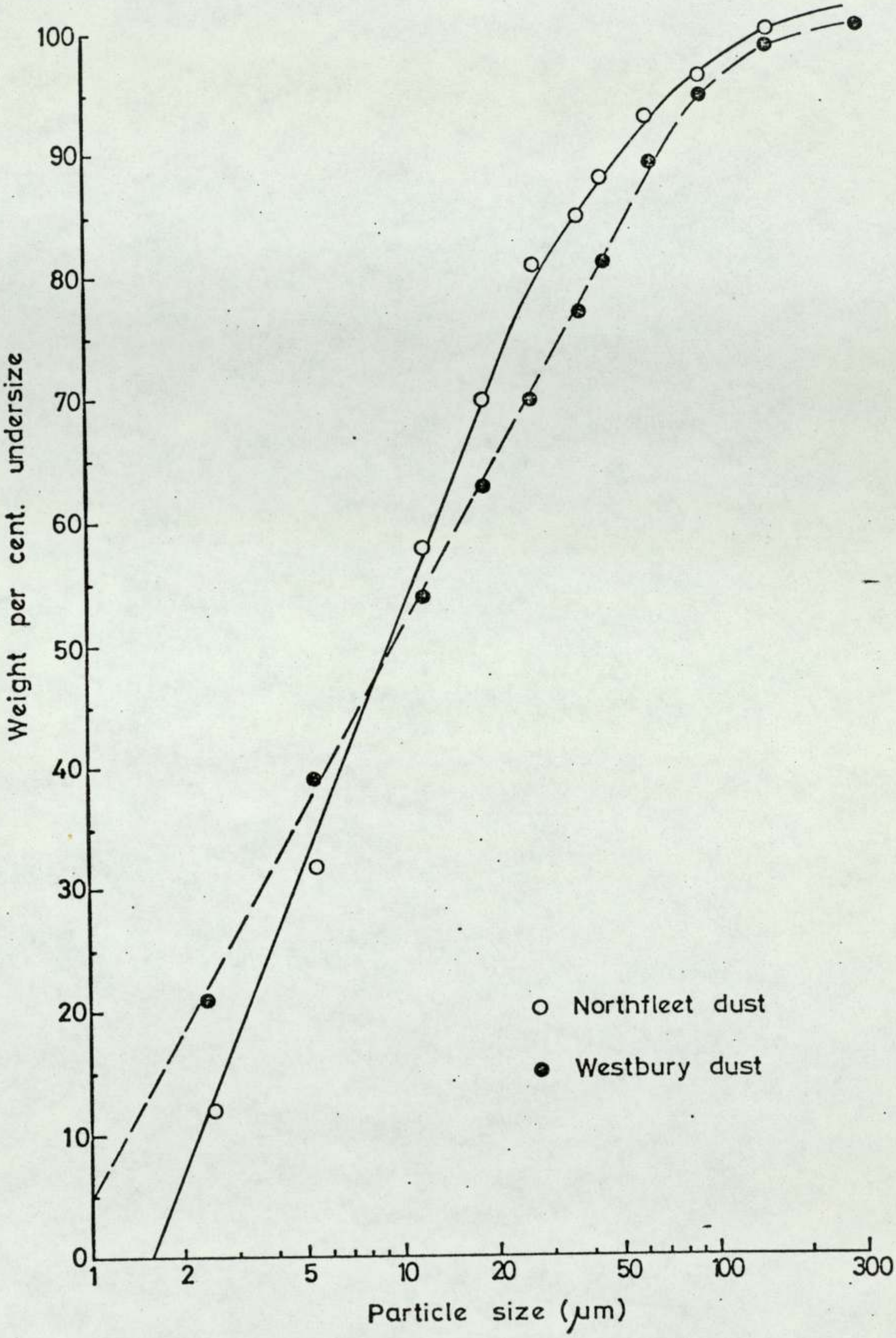


FIGURE 4.1

Particle Size Distribution of Typical Northfleet and Westbury Flue Dusts of the dust was considered necessary to ensure that the particles could be calcined at a practical fluidisation velocity. The density of the dusts, as calculated from the material composition, is typically about 2800 kg m^{-3}, but the bulk density was found to be typically in the range of 500-600 kg m^{-3}, or less as the alkali content increased, e.g., the bulk density of a Northfleet dust containing 30% k_2O was only 300 kg m^{-3}.

The chemical composition of the dusts can vary within quite large limits, mainly as a result of the variability of the kiln firing conditions and of the raw material and fuel composition. Additionally, in the case of Northfleet Works where the horizontal gas flow type precipitators are in use, the dust obtained from the different precipitator chambers tends also to vary significantly, particularly with respect to the alkali composition. The typical compositions of Northfleet and Westbury flue dusts are shown in Table 4.1, alongside a typical O.P.C. raw meal. In order to ensure that the compositions were indeed 'typical', the alkali analyses of the dusts were checked and found to be consistent with the overall alkali balance of the works.

As can be seen, the two dusts are practically identical except for the amounts of Cl and SO_3 present, which indicates the different alkali phases present (as will be shown later). When compared with the O.P.C. raw meal, the most striking difference is the alkali concentrations which totalled nearly 18% for both the dusts but the lime saturation factor and silica ratios of the dusts are also lower than those of the O.P.C. raw meal. If coal is used for calcining the dusts, the ash contribution may lower the L.S.F. still further, and unless some form of lime blending is carried out (which is outside the scope of the present investigation), the potential

TABLE 4.1

Typical Composition of Northfleet and Westbury Cement Works Flue Dust and Comparison with an O.P.C. Raw Meal

Analysis (%)	Northfleet	Westbury	O.P.C. Raw Meal
SiO_2	13.3	13.2	13.2
Al_2O_3	4.3	4.5	3.5
Fe_2O_3	1.9	1.8	1.2
CaO	40.0	39.8	44.1
MgO	0.7	0.5	0.6
K_2O	7.9	7.6	0.3
Na_2O	1.0	0.9	0.2
Cl	3.4	0.8	-
SO_3	5.3	8.4	0.1
CO_2	21.0	21.0	35.0
H_2O*	2.0	2.0	2.0
Total	100.8	100.5	100.2
L.S.F.⊗	91	91	105
S/A + F	2.2	2.1	2.8
S/F	2.3	2.5	2.9

* Combined water

⊗ Assume 2% SO_3 is combined with CaO

quality of the calcined dusts will be fairly low, even if all the alkalis are volatilised.

The dusts are moderately soluble in water, the extent of solubility varying according to the alkali contents. Typically, almost 100% of Cl, 85% of SO_3, 70-80% of K_2O and Na_2O and 15% of CaO were found to be soluble. For the dusts shown, the water soluble content totalled about 15%.

4.2.2 Phase Compositions and Alkali Distribution of the Dusts

The phase composition of a typical Northfleet dust was determined by XRD (X-ray diffraction) analysis and the following phases were identified:-

Calcite (the main phase)
KCl
Quartz
$(K,Na_2)SO_4$
Glassy phase

This is consistent with the XRD analyses of a large variety of flue dusts published by Sprung (1966). Although the phase determination of Westbury dust was not carried out, there is no reason to suspect that the composition was any different apart from a much lower KCl and higher K_2SO_4 concentration. Ignoring, for simplicity, the fact that a small proportion of the alkalis may be present in their natural forms, e.g. $KAlSi_3O_8$, or absorbed in the clinker complex, e.g., $(K_2O$ or $Na_2O).8CaO.33Al_2O_3$, the approximate phase compositions of flue dusts can be calculated from simple stoichiometry, and for the dusts of Table 4.1 the phase compositions are presented in Table 4.2 (see Appendix C for the calculation). It can be seen that while the K_2O content of Northfleet dust is present in about equal proportions as KCl and K_2SO_4, most of the K_2O content of Westbury dust is present as K_2SO_4. This difference is of the utmost importance, as will become evident later.

Most of the alkalis were present not as discrete particles but as thin granular coatings about 1 μm or less in thickness adhering to the dust surfaces, as can be seen in the micrographs from a Scanning electron microscope (S.E.M.), Figures 4.2-4.4. The S.E.M., which was on hire from the SIRA Institute (Chislehurst, Kent), incorporated an 'ORTEC' solid state X-ray detector which allowed a limited and semi-quantitative analysis of the particles to be determined. The coatings were found to consist largely of potassium sulphate and chloride. Some coal ash particles rich in potassium aluminium sulphate were also present in the dusts as is shown in Figure 4.5.

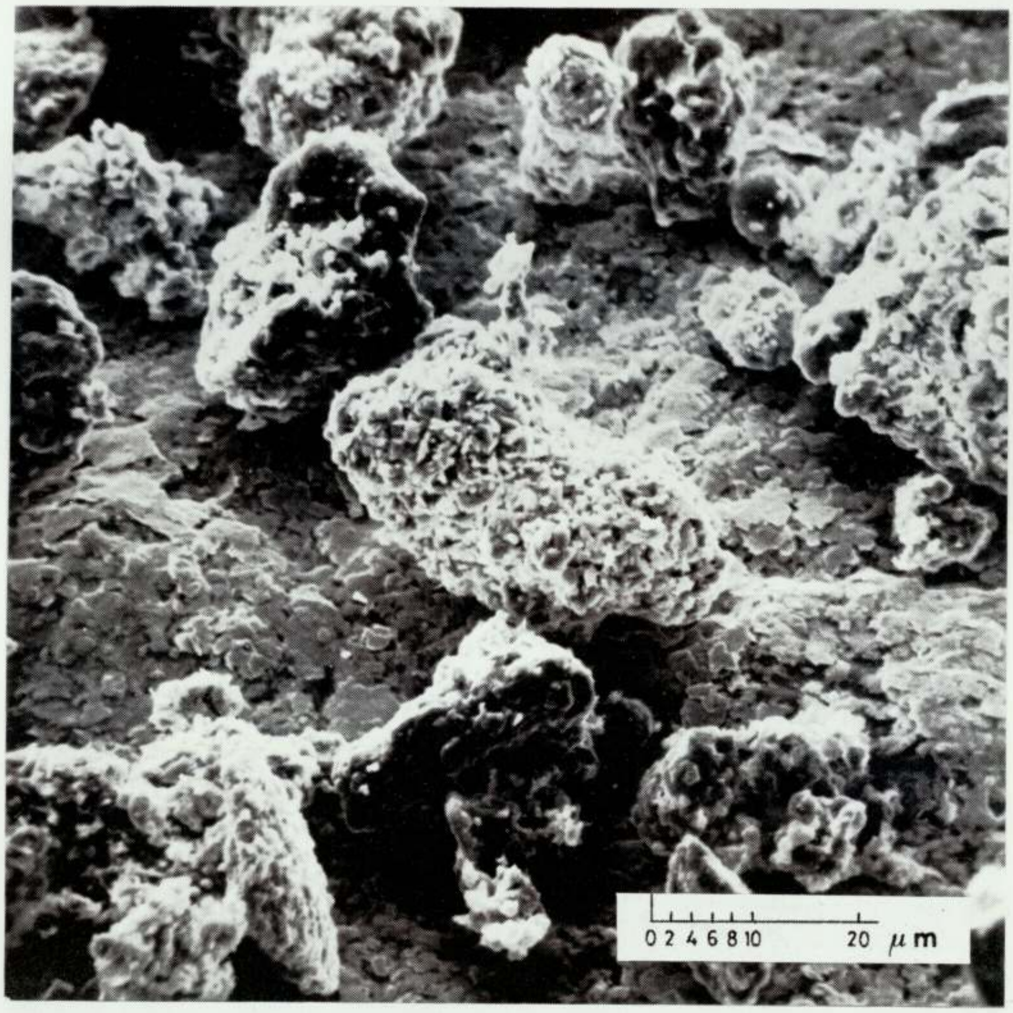
4.2.3 Anticipated Levels of Calcined Dust Addition and the Calcining Requirement

The amount of flue dust produced in Northfleet and Westbury cement works averaged about 7% and 10.5% (of clinker output) respectively in 1975 (refer Table 2.3). More recent figures (1976/77) show a slight increase in the Northfleet dust level to 8%, and a slight drop at Westbury, to 10%. Assuming that all CO_2 and H_2O is evolved after calcination and taking the latter figures of dust production, the amounts of calcined dust potentially available for addition to clinker at Northfleet and Westbury Works are 4.8-6.2t and 5.9-7.7t respectively per 100t of clinker, depending on whether the alkalis are all removed or retained. In

TABLE 4.2

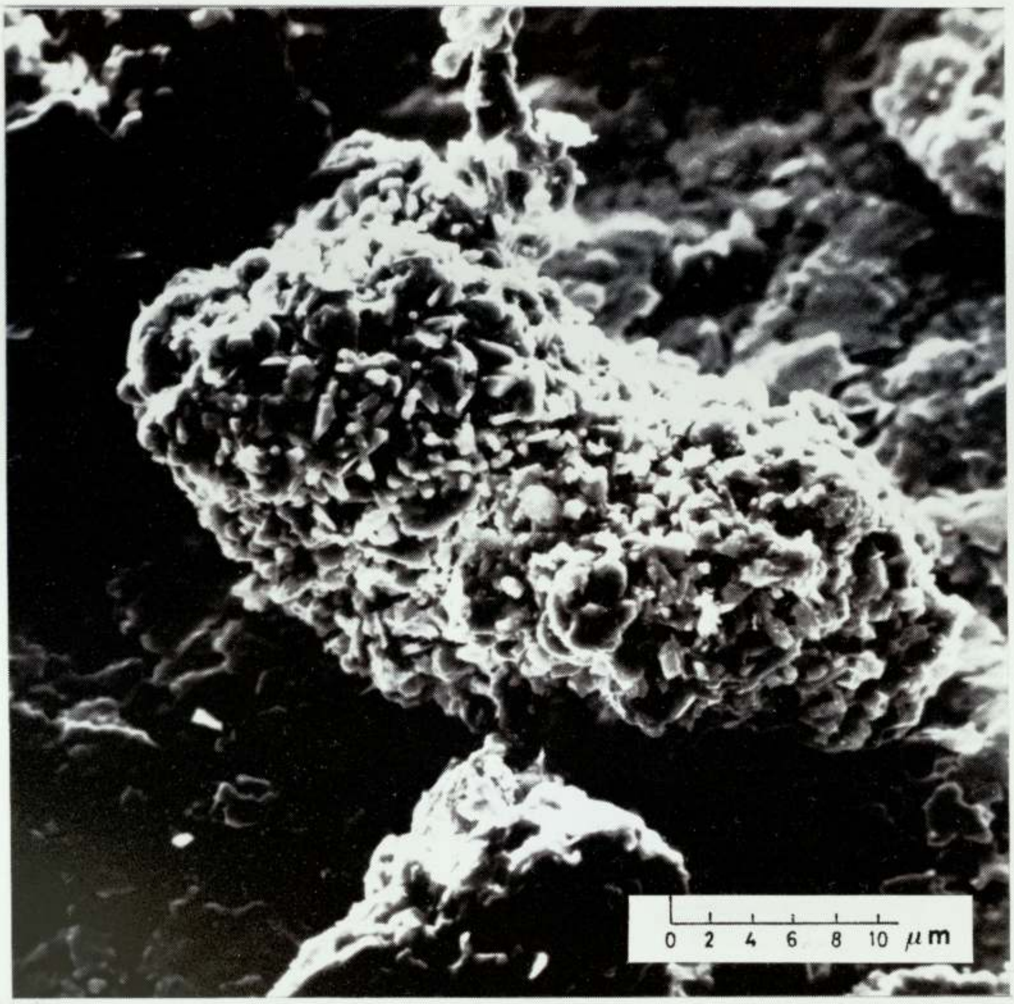
Calculated Phase Compositions of Typical Northfleet and Westbury Flue Dusts

Compositions (%)	Northfleet	Westbury
KCl	7.2	1.7
K_2SO_4	6.3	12.1
Na_2SO_4	2.5	2.3
$CaSO_4$	1.9	2.9
$MgCO_3$	1.5	1.1
Calcite	46	47
Clay, Clinker, Free Lime, etc.	35	33
TOTAL	100.4	102.1



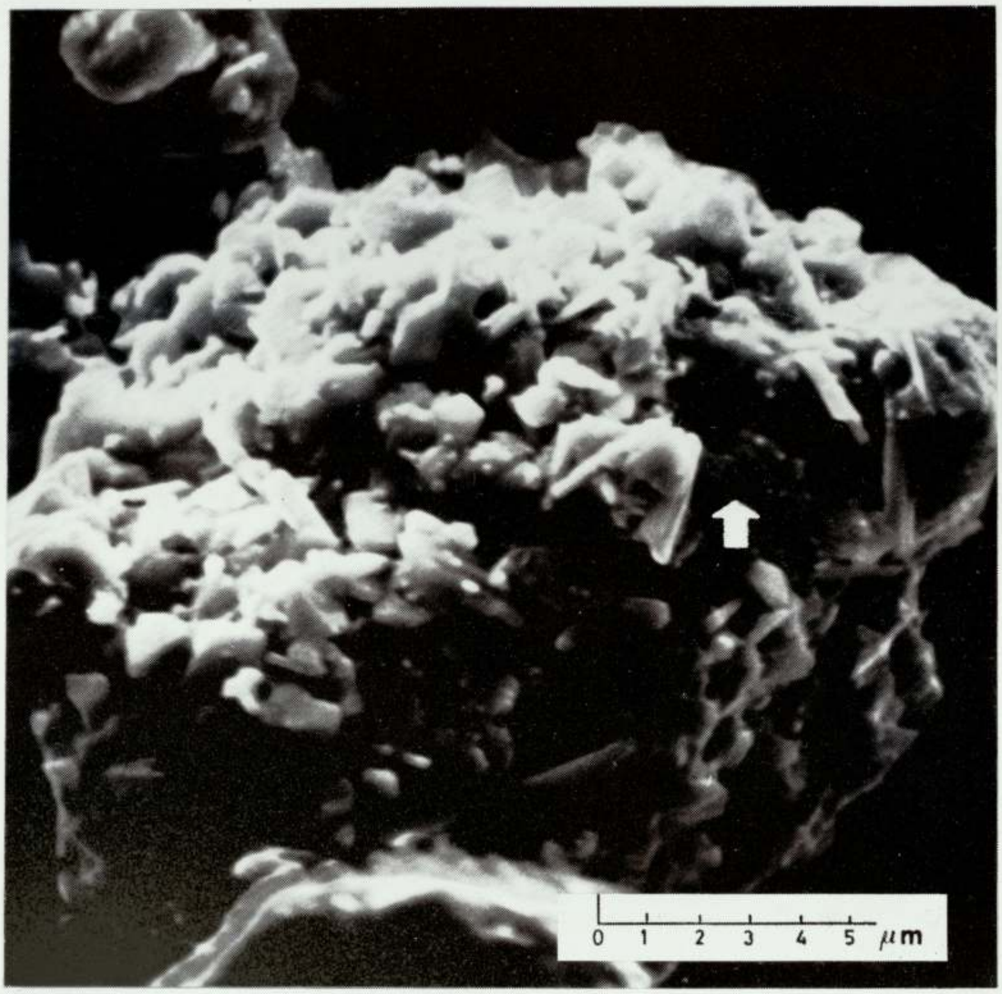
x1350

FIGURE 4.2 General particles of dust mounted on conducting silver 'dag' paste, the flakey material on which the dust grains are sitting. A scan for potassium over this whole field indicated that the surface of all these particles were rich in this element.



x2700

FIGURE 4.3 Detail of Figure 2.3 showing surface coating of alkali salts.



x6500

<u>FIGURE 4.6</u> Alkali salts adhering to dust grain. "Ortec" analysis of most of the surface indicated it to be rich in alkali sulphate and chloride. The region arrowed where the coating appeared to be absent was analysed as rich in Ca indicating probable calcite raw feed particle underlying the alkali salt coating.

x7000

FIGURE 4.5 PFA sphere in precipitator dust. "Ortec" analysis on clear region of sphere, arrowed 1, indicates material rich in K, Al and Si i.e. Alkaline Aluminium Silicate while surface deposit arrowed 2 is rich in K, S and Cl i.e. Potassium sulphate and chloride.

practice, the figures achieved will be somewhere between the two extremities. At Northfleet, about a quarter of the clinker is normally exported, so that the amount of potential calcined dust may be as much as 6.4-8.3t per 100t of clinker for the home market. Taking the typical Northfleet and Westbury Works clinker compositions of respectively, 0.55% and 0.6% K_2O; 1.5% and 1% free lime and zero Cl in both cases, the maximum acceptable limits of K_2O, Cl, and free lime for different calcined dust:clinker addition ratios in order to conform with the quality requirements stipulated in Section 3.5.5, are depicted in Figures 4.6-4.8. For an average addition ratio of 7:100, the limits of K_2O, Cl and free lime in the calcined dusts are shown below:-

Maximum Acceptable Limits of:-	Northfleet Calcined Dust	Westbury Calcined Dust
K_2O - Upper (%)	<6	<5
- Lower (%)	<3	<2
Cl (%)	<0.3	<0.3
Free Lime (%)	<16	<9

The lower limit on K_2O, as explained in Section 3.5.5, is only needed when the works clinker free lime is reduced to an abnormally low level of 0.5%. Since a low free lime clinker normally indicates harder burning, the K_2O of the clinker will be concomittantly decreased so that the acceptable limit of K_2O in the calcined dust can be increased. Therefore, the upper limit should probably suffice for all conditions normally encountered, although to allow for some 'safety margin', it was considered prudent to specify for a maximum of 4% K_2O in both cases.

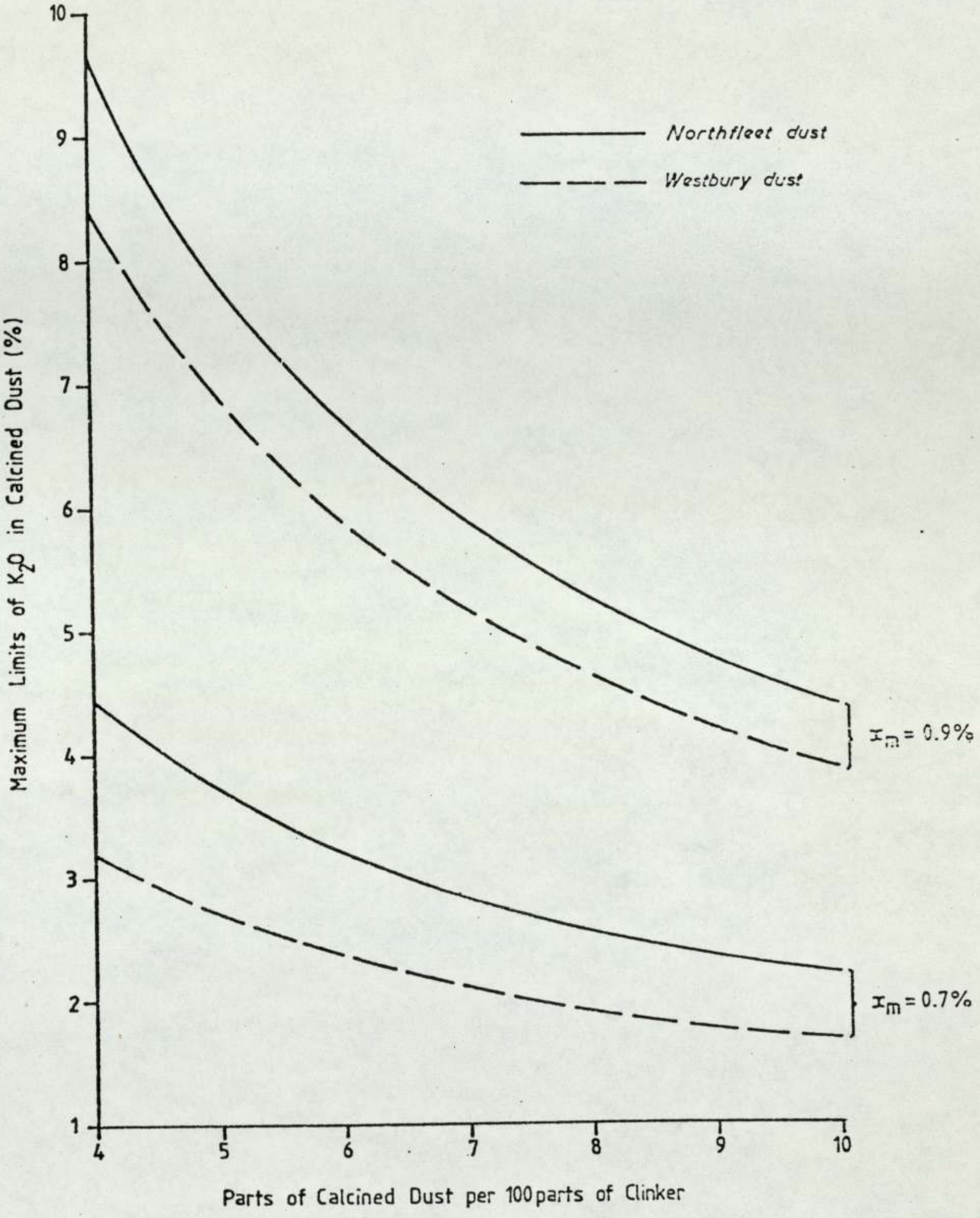


FIGURE 4.6

Calculated Maximum Permissible Limits of K_2O in Calcined Northfleet and Westbury Flue Dusts at Various Levels of Dust Addition to Clinker

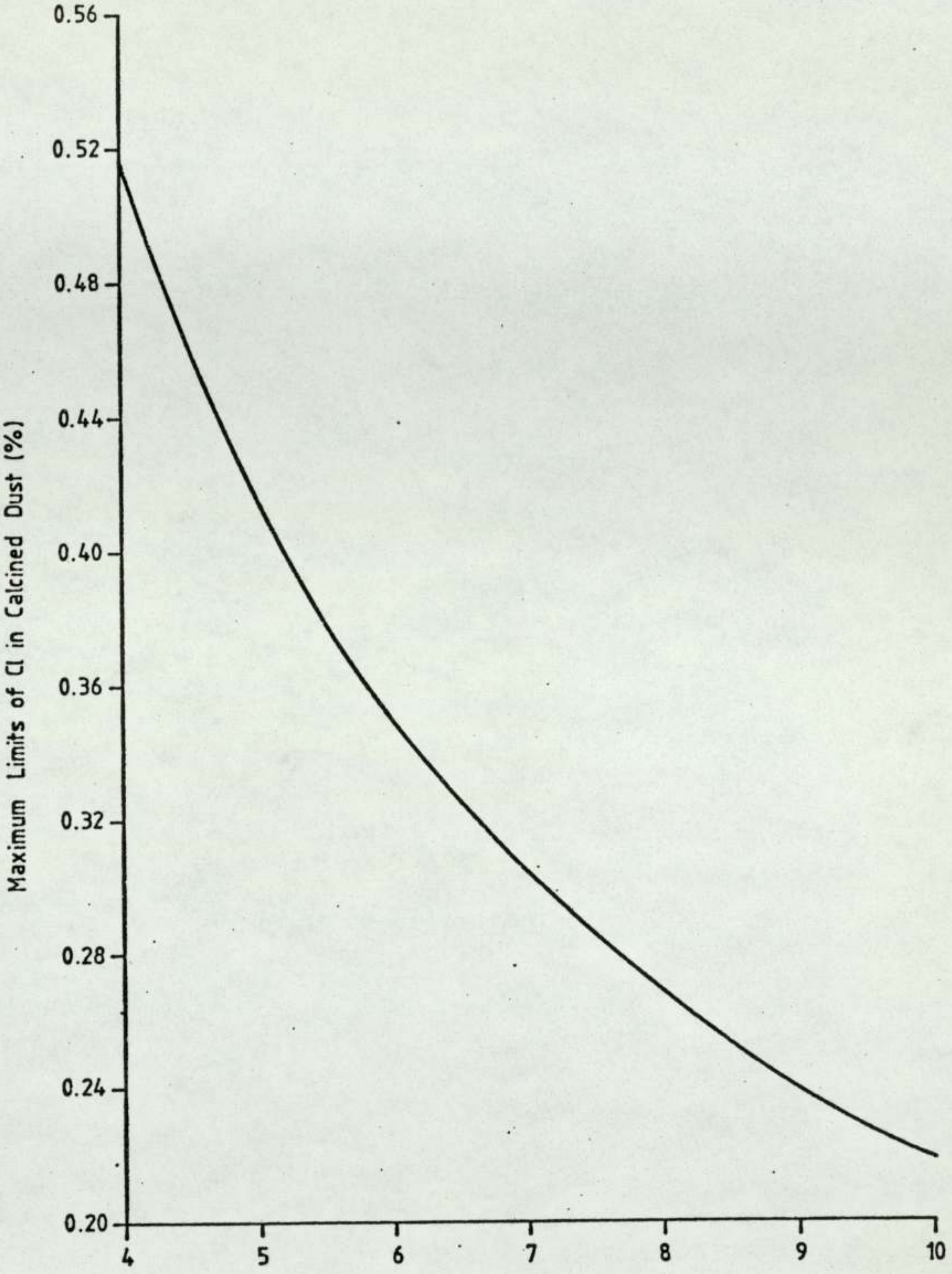


FIGURE 4.7

Calculated Maximum Permissible Limits of Cl in Calcined Northfleet and Westbury Flue Dusts at Various Levels of Dust Addition to Clinker

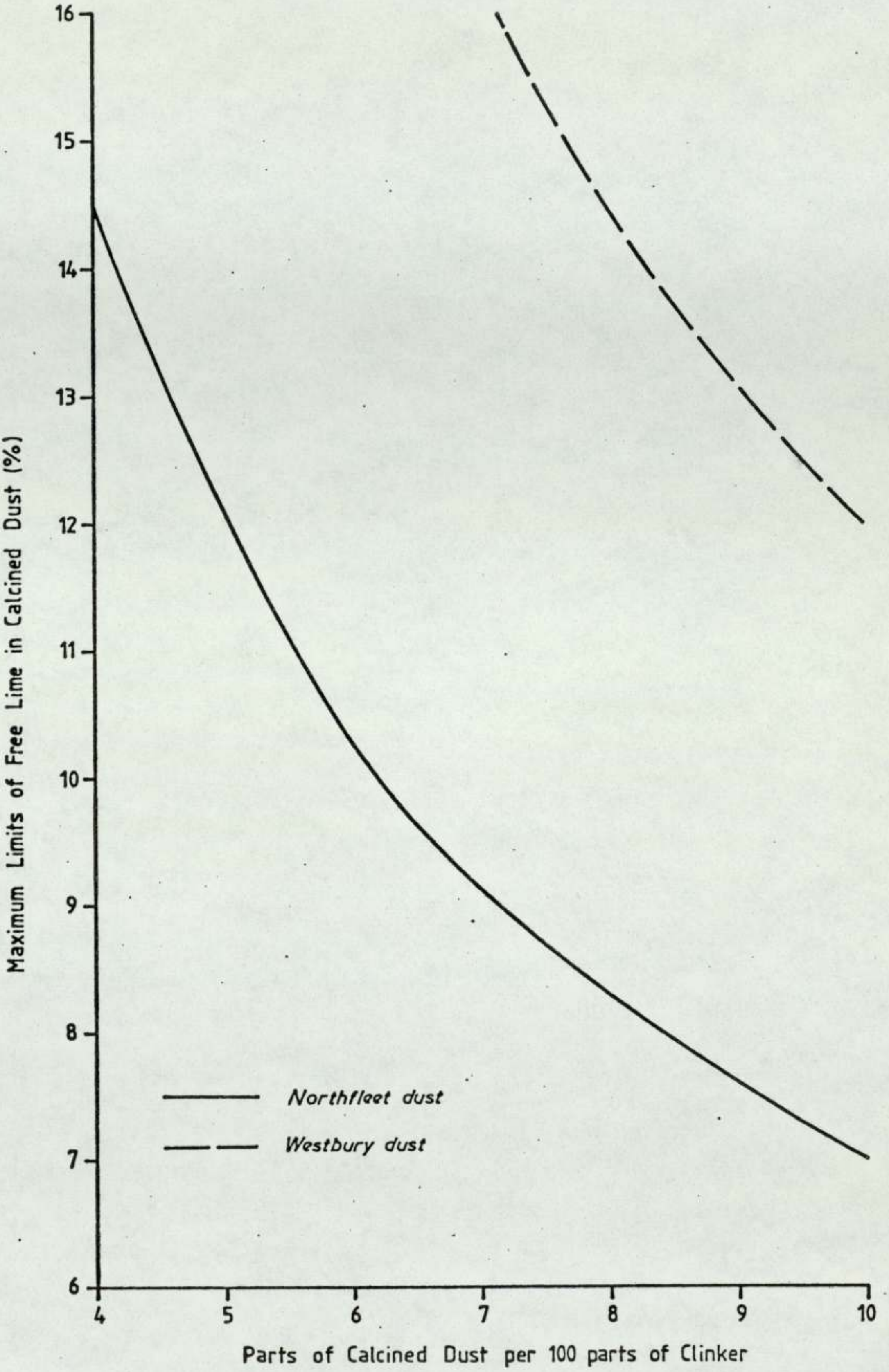


FIGURE 4.8

Calculated Maximum Permissible Limits of Free Lime in Calcined Northfleet and Westbury Flue Dusts at Various Levels of Dust Addition to Clinker

In the above consideration, no allowance is made to the possibility of any long term variability of raw material and fuel compositions.

4.3 Principle and Constraints of Fluidised Bed Operation

4.3.1 Principle of Gas-Solid Fluidisation

There is an abundance of literature dealing with various aspects of fluidisation, e.g. Kunii and Levenspiel (1969), Davidson and Harrison (1971), etc. In the following sections, only the general operating principle and constraints are reviewed; the factors of particular relevance to flue dust calcination are considered in Section 4.4

When a gas is passeds upward through a bed of particles at a steadily increasing velocity, the pressure drop across the bed increases as the flow is increased until a point is reached when the particles are all just suspended in the gas stream. At this point, the pressure drop through the bed equals the weight of the bed and the bed is said to be just fluidised. The superficial gas velocity at which this occurs is called the minimum or incipient fluidisation velocity (U_{mf}).

When the flow rate of the gas is increased further, the pressure drop through the bed remains constant and the additional gas flow passes through it as bubbles. This is accomplished by an increased movement of particles in the bed. At a higher gas velocity, say about 3 to 5 times greater than U_{mf}, agitation becomes more violent and a very rapid mixing of the particles is obtained. Because of this, a near-isothermal condition exists throughout the bed and the heat and mass transfer rates between the gas and particles are high, mainly due to the large surface area and excellent contact between the gas and particles, rather than the coefficients of transfer which are relatively low. However, the rapid mixing of particles also leads to non-uniform residence time of solids in a continuous operating bed and therefore gives a product of non-uniform thermal history.

The upper limit of the gas velocity corresponds to the terminal velocity of the particle (U_t): at this velocity, all the particles will be blown out of the bed. However, since the bed usually contains a distribution of particle sizes rather than a single size, the operating velocity (U_o) is normally kept well below the velocity at which significant loss of fines, or 'elutriation', can result. In addition, particles can also be carried out of the bed by another mechanism, called 'entrainment'. As the bubbles reach the surface of the bed and burst, particles of all sizes are ejected into the free space above the bed, termed the 'freeboard'. Those particles whose terminal velocity is greater than the gas velocity in the freeboard, will rise to a certain distance, called the 'transport disengagement height' (TDH), before the drag forces cause them to fall back to the bed. However, if the height of the freeboard is less than the TDH of all the particles, then some of the particles may be entrained in the exit gas and still be carried away.

4.3.2 Range of Fluidising Gas Velocity

One of the first considerations in fluidised bed application is the selection of a suitable fluidisation velocity. It is normally best to determine this practically, but for a given feed the approximate range of fluidisation velocity can be readily calculated.

The usual method of calculating U_{mf} is by equating the weight per unit area of the bed to the pressure drop of the bed. For large particles, Ergun's equation is more applicable and the expression derived is as follows (Kunii and Levenspiel, 1969):-

$$\frac{d_p{}^3 . \rho_g (\rho_s - \rho_g) g}{\mu^2} = 150 \frac{(1 - \epsilon_{mf})}{\phi_s{}^2 \epsilon_{mf}{}^3} \frac{U_{mf} . d_p . \rho_g}{\mu} + \frac{1.75}{\phi_s \epsilon_{mf}{}^3} \left(\frac{U_{mf} . d_p . \rho_g}{\mu} \right) \qquad .....(4.1)$$

where the meanings of the symbols are given in the nomenclature. As ϕ_s and ϵ_{mf} are unknown, the following values suggested by Wen and Yu (1966) can be substituted -

$$\frac{1}{\phi_s . \epsilon_{mf}} \simeq 14 \quad \text{and} \quad \frac{(1 - \epsilon_{mf})}{\phi_s{}^2 \epsilon_{mf}{}^3} \simeq 11 \qquad .....(4.2)$$

by defining the groups

$$Ga = \frac{d_p{}^3 . \rho_g (\rho_s - \rho_g) g}{\mu^2} \quad \text{and} \quad Re_{mf} = \frac{d_p . U_{mf} . \rho_g}{\mu} \qquad .....(4.3)$$

equation (4.1) can be simplified, to the following quadratic equation:-

$$Re_{mf} = [(33.7)^2 + 0.0408 \, Ga]^{\frac{1}{2}} - 33.7 \qquad .....(4.4)$$

which is used to calculate the minimum fluidisation velocity.

The terminal velocity U_t can also be calculated from analytical expressions derived from fluid mechanics but it is more convenient to use the experimental correlation of Re_p vs $C_d . Re_p{}^2$ presented in Kunii and

Levenspiel (1969), where the velocity independent group

$$C_d . Re_p^2 \quad = \quad \frac{4_g . d_p^3 . \rho_g (\rho_s - \rho_g)}{3\mu^2} \qquad .....(4.5)$$

can be calculated and provided the shape factor ϕ_s of the particles is known, Re_p can be obtained, from which U_t is calculated:-

$$Re_p \quad = \quad \frac{d_p . \rho_g . U_t}{\mu} \qquad .....(4.6)$$

Assuming that the calcined flue dust particles have a density of 2000 kg m^{-3} and shape factor of 0.9, the U_{mf} and U_t of particles of 0.1-5mm diameter fluidised by air at 0°C and 1200°C are shown in Figure 4.9. For pellets with a mean diameter of, say, 2mm calcined at 1200°C, the minimum fluidisation velocity is 0.8 m s^{-1}. In practice, it is usually necessary to have a fluidisation velocity several times greater than the minimum velocity in order to ensure proper mixing of the solid particles. This is particularly important in the present application since at the calcining temperature envisaged (>1100°C), the dust particles are liable to fuse, as is discussed in the next section. The maximum fluidisation velocity, assuming that the amount of fines below, say, 1mm is insignificant, may be as high as 5-6 m s^{-1}.

The optimum fluidisation velocity however, can only be reliably established by practical means since a substantial quantity of fines can be produced as a result of particle decrepitation or attrition. Apart from the loss of material, an excessive amount of dust carry-over, in the present application, can aggravate the problem of alkali blockage in the gas handling plant as will be seen later.

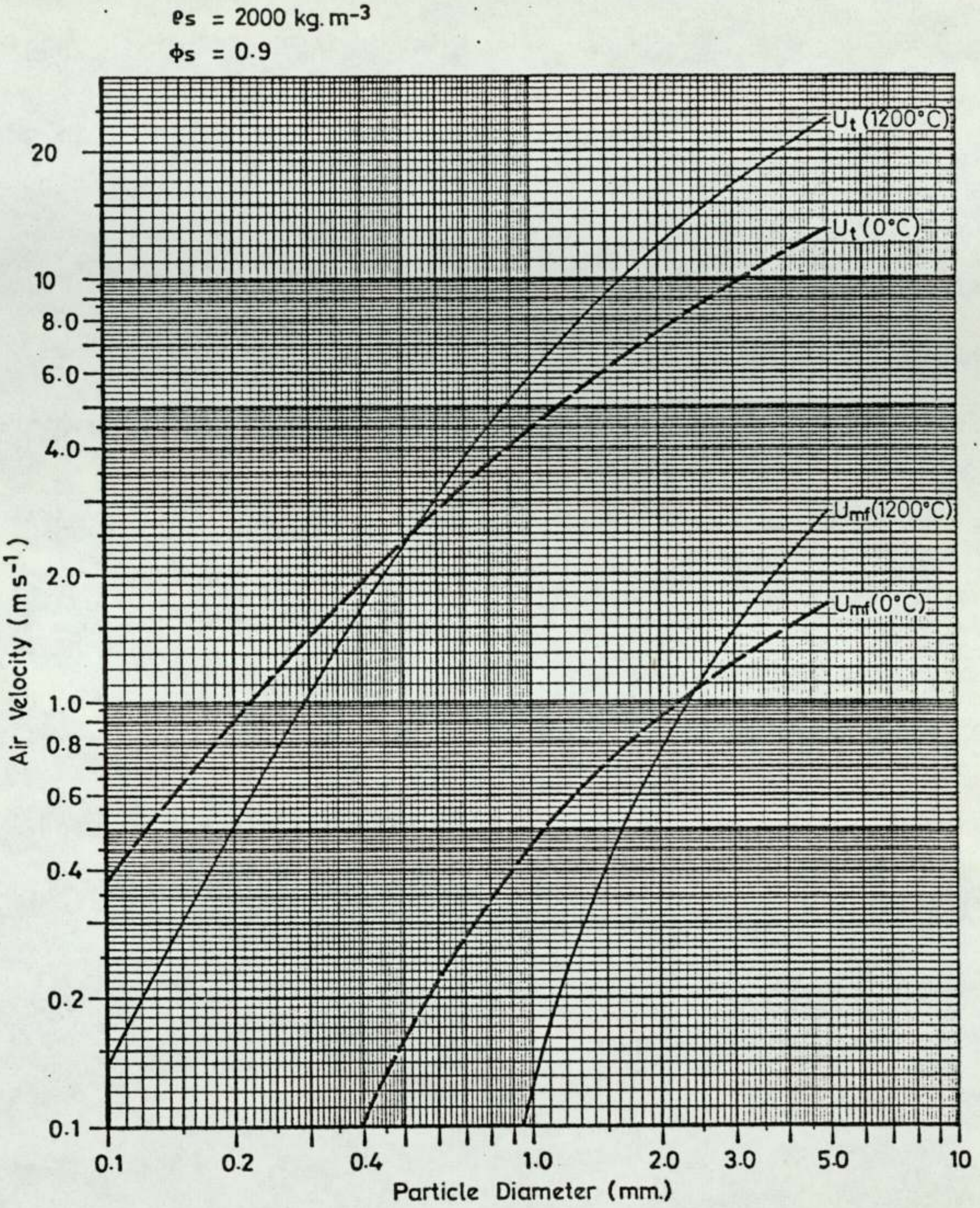


FIGURE 4.9

Calculated Minimum Fluidisation and Terminal Velocities of Particles of 0.1–5mm Diameter at $0^{o}C$ and $1200^{o}C$ in Air

4.3.3 Limiting Temperature of the Fluidised Bed

The maximum operating temperature of the fluidised bed is limited by the propensity of the bed particles to fuse and defluidise when there is an excessive amount of liquid melt present. In cement burning, the amount of liquid melt formed does not normally become significant until the material temperature exceeds about 1260°C (Lea, 1971). With flue dust, however, the amount of liquid melt formed may be augmented by the presence of excess Fe_2O_3, MgO and alkalis and additionally, the alkalis will also contribute directly to the liquid melt as a result of the formation of an eutectic between $CaSO_4$, K_2SO_4 and Na_2SO_4. The fusion temperature of this eutectic can be <800°C and in the presence of KCl, as low as <700°C (Figure 4.10).

In the first Artarmon trial (refer Section 3.5.3), it was reported that fusion was observed at a bed temperature of 900°C when the fluidisation velocity was maintained at about 1.5 $m\ s^{-1}$, but when the velocity was increased to 2 $m\ s^{-1}$, the bed operated satisfactorily at 1100°C, the maximum limit of the equipment. Therefore, it appears that provided the particles are kept rigorously fluidised, the sticking tendency due to the eutectic melt should not be a serious concern. This is a particular advantage in the fluidisation of large particles since the high particle momentum and reduction in particle-particle contacts tend to minimise agglomeration (Geldart, 1973).

At higher temperature of, say, above 1260°C, the increasing liquid melt formation will still pose a problem. However this limit will have to be determined practically.

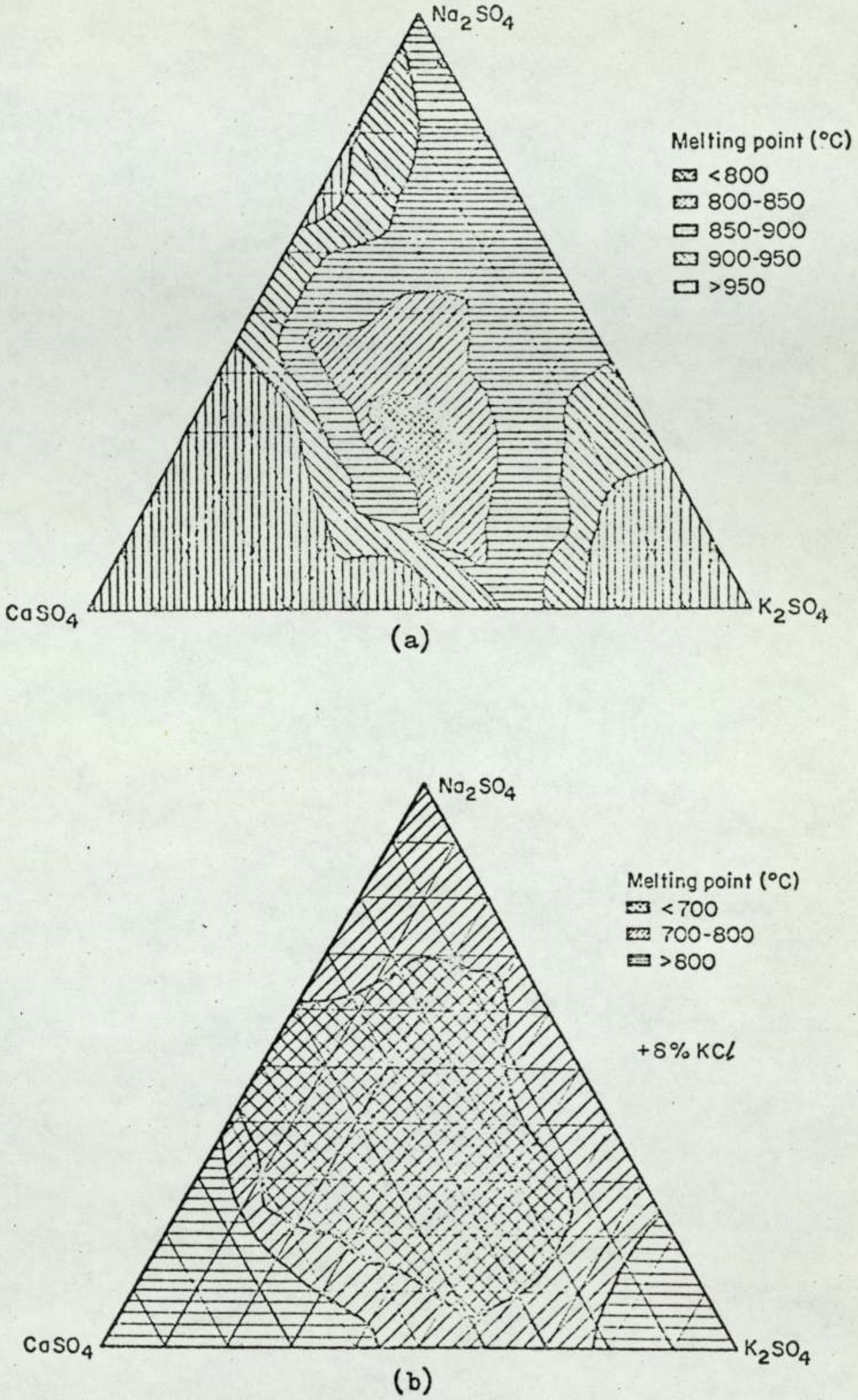


FIGURE 4.10

Melting Range of (a) the $CaSO_4$-K_2SO_4-Na_2SO_4 System and (b) the Effect of 8% KCl

(Source: Ritzmann, 1971)

4.4 Thermochemical Aspects of Flue Dust Calcination

4.4.1 Postulation of the Reaction Mechanism

Flue dust may be regarded as essentially a cement raw meal that has been partially decarbonated and enriched with alkalis. The thermochemistry of cement burning has been studied extensively, e.g., Lea (1971), Locher (1975), the alkali volatilisation characteristics of cement raw meal, too, have been investigated (Goes and Keil, 1960; Pyacher and Plyacheva, 1965). However, while it is considered that the lime dissociation and combination characteristics are probably similar in flue dust and cement raw meal, except for the fluxing effect of the alkalis, the alkali volatilisation characteristics are unlikely to bear much resemblance since the forms of alkalis present in the two materials are almost totally different. In cement raw meal, the alkali oxides are mainly in combination with the silica and alumina whereas in flue dust, they are present predominantly as the alkali salts. In the following postulation, the lime reactions and alkali volatilisation mechanism are treated independently.

When flue dust pellets are fed into a fluidised bed operating at an elevated temperature, the material is heated up rapidly and any residual moisture is quickly evaporated. At higher temperatures of, say, above 500°C, the combined water present is released and at about 550°C, dissociation of calcium carbonate commences. The lime produced then reacts immediately with the surrounding silica, alumina and ferric oxide to form various intermediate complex compounds and these reactions proceed simultaneously with the decarbonation reaction until the solid reaches a temperature above 900°C when the dissociation pressure is sufficiently high for the gas to be liberated faster than the intermediate lime combination reaction. At this point, the free lime content of the material reaches a maximum.

Above 900°C, formation of cement constituents begins, starting with tricalcium aluminate, tetracalcium alumino ferrite and dicalcium silicate or belite. Most of these reactions are completed at about 1200°C and the content of belite reaches a maximum. The formation of tricalcium silicate or alite does not normally occur to any significant extent in cement burning until liquid formation appears at about 1260°C. With flue dust, however, the finer particle size coupled with a higher concentration of alkalis, alumina and ferric oxide, which are generally regarded as fluxing agents (Murray, 1973), may enhance the formation of alite as a result of greater intimacy and liquid formation.

The volatilisation of alkalis starts at about 800°C with KCl which vaporises directly to the gaseous monomers as follows (JANAF, 1964):-

$$KCl_{(s\ or\ l)} \rightleftharpoons KCl_{(g)} \qquad .....(4.7)$$

The volatilisation of alkali sulphates, on the other hand, can occur by the vaporisation to gaseous molecules as well as decomposition (Figalora et al, 1968):-

$$\begin{aligned} (K\ or\ Na)_2\ SO_{4(s\ or\ l)} &\rightleftharpoons (K\ or\ Na)_2\ SO_4 && .....(4.8) \\ &\rightleftharpoons 2(K\ or\ Na)_{(g)} + SO_2 + O_2 && .....(4.9) \\ &\rightleftharpoons (K\ or\ Na)_2\ O_{(g)} + SO_2 + \tfrac{1}{2}O_2 && .....(4.10) \end{aligned}$$

- etc. -

In normal atmospheres and at temperatures up to about 1300°C, equation (4.8) predominates for K_2SO_4 (Halstead, 1970) while both equations (4.8) and (4.9) are of about the same order of importance for Na_2SO_4 (Cubicciotti and Keneshea, 1972). Reaction (4.10) does not normally occur to any significant extent and is normally disregarded. In addition to the above, the following reactions may occur under reducing conditions which may arise from combustion:-

$$K_2SO_4 + CO \rightleftharpoons 2K_{(g)} + CO_2 + SO_2 + \tfrac{1}{2}O_2 \qquad .....(4.11)$$

$$K_2SO_4 + CO_2 \rightleftharpoons K_2CO_{3(g)} + SO_2 + \tfrac{1}{2}O_2 \qquad .....(4.12)$$

$$K_2SO_4 + H_2O \rightleftharpoons 2KOH + SO_2 + \tfrac{1}{2}O_2 \qquad .....(4.13)$$

However, according to Halstead (1976), the thermodynamics of the reactions are not favourable for the calcining condition and temperature range of interests.

Apart from the major reactions considered, there may be other reactions involving the alkalis including, e.g., the metathesis of K_2O and Na_2O in silicates or aluminosilicates to the sulphates or halides (Greening et al, 1976) and the decomposition of $CaSO_4$. However, the amount of alkalis involved in these reactions is relatively small and their effects are unlikely to be very significant.

A list of the major reactions postulated, including the heat of reaction involved, is contained in Table 4.3 and additional thermodynamic data concerning alkali volatilisation is given in Table 4.4.

TABLE 4.3

Postulated Flue Dust Calcination Mechanism and the Heat of Reaction

	Principle Reactions	Heat of Reaction/kg Reactant (kcal/kg)	Reference
Lime Combination	Illite Kaolinite $\rightarrow$ α- alumina, β- quartz, H_2O	+41.7 +141.0	(Boynton, 1966) BCI Report, 1964
	$Fe(OH)_3 \rightarrow \frac{1}{2}Fe_2O_3 + \frac{3}{2}H_2O$	-26.0	
	$Ca(OH)_2 \rightarrow CaO + H_2O$	+206.8	
	$CaCO_3 \rightarrow CaO + CO_2$	+422.0	
	$MgCO_3 \rightarrow MgO + CO_2$	+310.0	
	$3CaO + Al_2O_3 \rightarrow C_3A$	-3.7	
	$4CaO + Al_2O_3 + Fe_2O_3 \rightarrow C_4AF$	-20.1	
	$2CaO + SiO_2 \rightarrow C_2S$	-171.0	
	$3CaO + SiO_2 \rightarrow C_3S$	-126.2	
Alkali Volatilisation	$KCl_{(s\ or\ l)} \rightarrow KCl_{(g)}$	+670	See Table 4.4
	$K_2SO_{4(s\ or\ l)} \rightarrow K_2SO_{4(g)}$	+563 (+1805)*	
	$Na_2SO_{4(s\ or\ l)} \rightarrow Na_2SO_{4(g)}$	+733	
	$\rightarrow 2Na + SO_2 + \frac{1}{2}O_2$	(+20.96)*	

* for decomposition

TABLE 4.4

Thermodynamic Data of KCl, K_2SO_4, and Na_2SO_4

[Data obtained or derived from JANAF (1960); Janz (1969); Hart and Laxton (1969); Cubiciotti and Keneshea (1972)]

		KCl (M = 74.6)	K_2SO_4 (M = 174.3)	Na_2SO_4 (M = 142.1)
Melting Point	(^oC)	772	1069	884
Boiling Point	(^oC)	1407	2100 (Theoretical)	-
Mean Specific Heat	(kcal K^{-1} $mole^{-1}$)	9×10^{-3}	32×10^{-3}	22×10^{-3}
Latent Heat				
Fusion	(kcal/$mole^{-1}$)	6.3	9.1	5.7
Evaporation @ 298^{o}K	(kcal/$mole^{-1}$)	43.7	89.0	98.4
Sublimation @ 298^{o}K	(kcal/$mole^{-1}$)	50.0	98.1	104.1
Decomposition	(kcal/$mole^{-1}$)	-	314.6	297.8

4.4.2 Theoretical Heat of Reaction

The theoretical heat of reaction required for flue dust calcination can be estimated from the change in phase composition between the feed and calcined product. For the typical Northfleet and Westbury flue dusts shown in Table 4.1, it is reasonable to assume that, after calcining, all CO_2 and H_2O, and a significant proportion of the alkalis are evolved to leave, for 1 kg of dust calcined, 0.65 kg of calcined product containing 4% K_2O, 0.3% Cl (to meet the quality requirement), approximately half the original Na_2O and an amount of SO_3 corresponding to the stoichiometric proportion in K_2SO_4 and Na_2SO_4. The resultant analyses and phase composition of the 2 calcined dusts are presented in Appendix C (Tables C.1 and C.2).

Neglecting the small amount of clinker phase which is already present in the dust feed, and assuming that the material contains 5% residual free lime, the heats of reaction required to transform the dusts into the calcined product are listed in Table 4.5. Depending on whether the alkali-sulphates are assumed to be vaporised or decomposed, the heats of reaction are as follows:-

	Northfleet Dust	Westbury Dust
Heat of Reaction, $\Delta H_r'$ (kcal/kg dust)	214-256	198-313
$\Delta H_r''$ (kcal/kg product)	329-294	305-481

As discussed earlier, under normal operation and at the temperature range of interest, most of the K_2SO_4 is expected to vaporise rather than decompose. Although Na_2SO_4 can decompose to a significant extent, the

TABLE 4.5

Theoretical Heat of Reaction of Calcining Northfleet and Westbury Flue Dusts

(**Basis**:- 1 kg dust → 0.65 kg product)

Reactions:-	Heats of Reaction kcal/kg reactant	Northfleet		Westbury	
		x 10^{-2} kg reactant/kg dust	kcal/kg dust	x 10^{-2} kg reactant/kg dust	kcal/kg dust
Dehydration of combined water	+100	2.0	+2.0	2.0	+2.0
Dissociation of $MgCO_3$	+310	1.5	+4.7	1.1	+3.4
Dissociation of $CaCO_3$.	+422	46.1	+194.5	46.5	+196.2
Decomposition of $CaSO_4$	+675	1.9	+12.8	0.1	+0.7
Vaporisation of KCl	+670	6.8	+45.6	1.3	+8.7
Vaporisation/Decomposition of K_2SO_4	+563/+1805	2.0	+11.3/+36.1	7.8	+43.9/+140.8
Vaporisation/Decomposition of Na_2SO_4	+733/+2096	1.3	+9.5/+27.3	1.3	+9.5/+27.3
Formation of C_3A	-3.7	5.7	-0.2	5.5	-0.2
Formation of C_4AF	-20.0	8.2	-1.6	8.8	-1.8
Formation of C_2S } Assume 5% free lime	-171.0	25.5	-43.6	25.9	-44.3
Formation of C_3S }	-126.2	16.8	-21.2	15.7	-19.9
Theoretical Heat of Reaction (kcal/kg dust) :-			214/256		198/313
(kcal/kg calcined product):-			329/394		305/481

effect on the heat of reaction is small due to the low proportion involved. For heat balance purpose, the theoretical heat of reaction required for calcining Northfleet and Westbury dust may be taken as 230 kcal/kg dust or 350 kcal/kg clinker product.

4.4.3 Kinetics and Heat Transfer Considerations

Because of the large area of contact between gas and solid in a fluidised bed, the rates of heat and mass transfer obtained are high and in general, thermal equilibrium between a fluidised bed gas and solid is reached in no more than 20 or 30mm above the gas distributor plate (Kunii and Levenspiel, 1969). For this reason, heat transfer (and mass transfer) coefficients are difficult to measure in fluidised beds and the values reported by different observers can differ by several order of magnitude. As far as the present problem is concerned, the rapid attainment of equilibrium means that the overall calcination of the dust particles is determined by the heat capacity of the fluidised bed gases and not the kinetics of the process. This can be readily verified by the criteria suggested by Gelperin and Einstein (in Davidson and Harrison, 1971), and the calculation is shown in Appendix D.

Consider the steady-state calcination of a continuous stream of cold dust particles by hot gas in a single fluidised bed as shown in Figure 4.11. Neglecting heat losses to the surroundings, an overall heat balance over the whole bed gives,

$$\begin{pmatrix} \text{Heat gained} \\ \text{by solids} \end{pmatrix} = \begin{pmatrix} \text{Heat lost} \\ \text{by gas} \end{pmatrix}$$

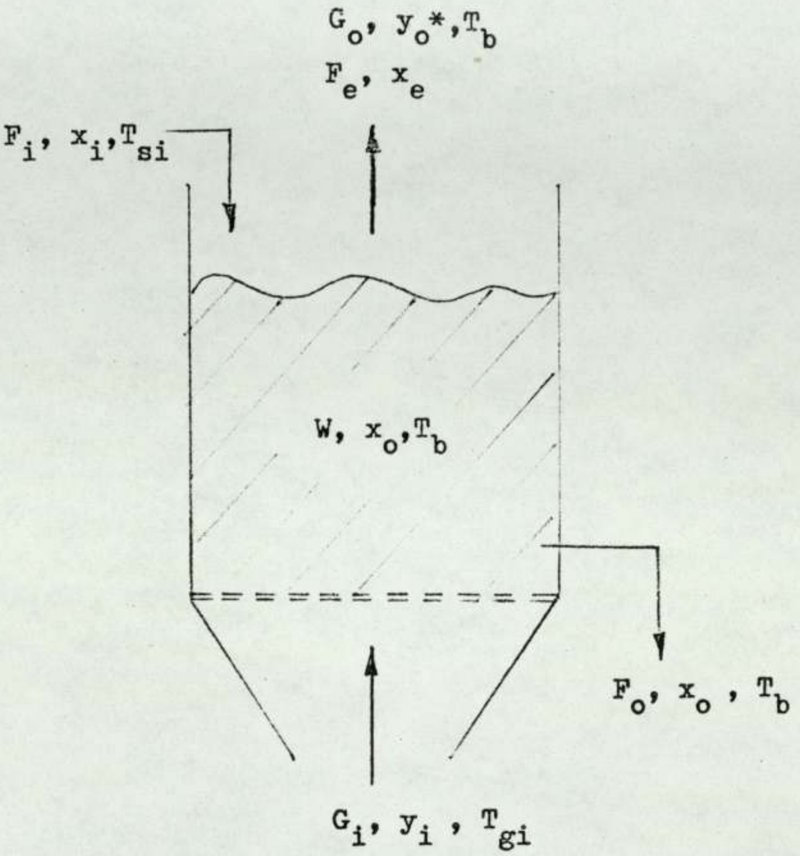


FIGURE 4.11

Model for the Continuous Volatilisation of Alkalis from Flue Dust in a Fluidised Bed

At equilibrium, the bed solids, and existing solids and gas are all at the same temperature. Assume, for simplicity, that the dust carry-over is negligible, so that the above heat balance becomes, in symbols,

$$F_o(C_{ps} \cdot T_b + \Delta H_r') - F_i \cdot C_{ps} \cdot T_{si} = A_t \cdot \rho_g U_o \cdot C_{pg} \, (T_{gi} - T_b) \qquad \text{.....(4.14)}$$

Assume that the entering feed is at a datum of 0°C and introducing the bed weight, so that,

$$W = A_t \cdot L_m \, (1 - \epsilon_m) \, \rho_s \qquad \text{.....(4.15)}$$

Equation (4.14) can be rearranged to yield the following expression:-

$$\frac{W}{F_o} = \tau_s = \frac{\left[C_{pg} \cdot T_b + \Delta H_r''\right] \left[L_m \, (1 - \epsilon_m) \, \rho_s\right]}{\rho_g \cdot U_o \cdot C_{ps} \, (T_{gi} - T_b)} \qquad \text{.....(4.16)}$$

where τ_s represents the mean residence time of the solid required to satisfy the R.H.S. conditions.

As an example, take the following conditions:-

T_b = 1200°C; U_o = 3 ms^{-1}; L_m = 0.2 m; ϵ_m = 0.5; $\Delta H_r''$ = 350 kcal kg^{-1} calcined dust; ρ_s = 2000 kg m^{-3}; ρ_g = 0.24 kg m^{-3}; C_{ps} = 0.25 kcal °C^{-1}; and C_{pg} = 0.27 kcal kg^{-1} °C^{-1}; the mean residence time of the solid needed to balance the equation at various gas inlet temperatures is shown in Figure 4.12. As can be seen, the residence time needed is sensitive to the gas inlet temperature and is fairly long, ranging from 10-60 min. for a gas inlet temperature of 1400-2200°C. The effect of varying the bed height or fluidisation velocity can be seen from

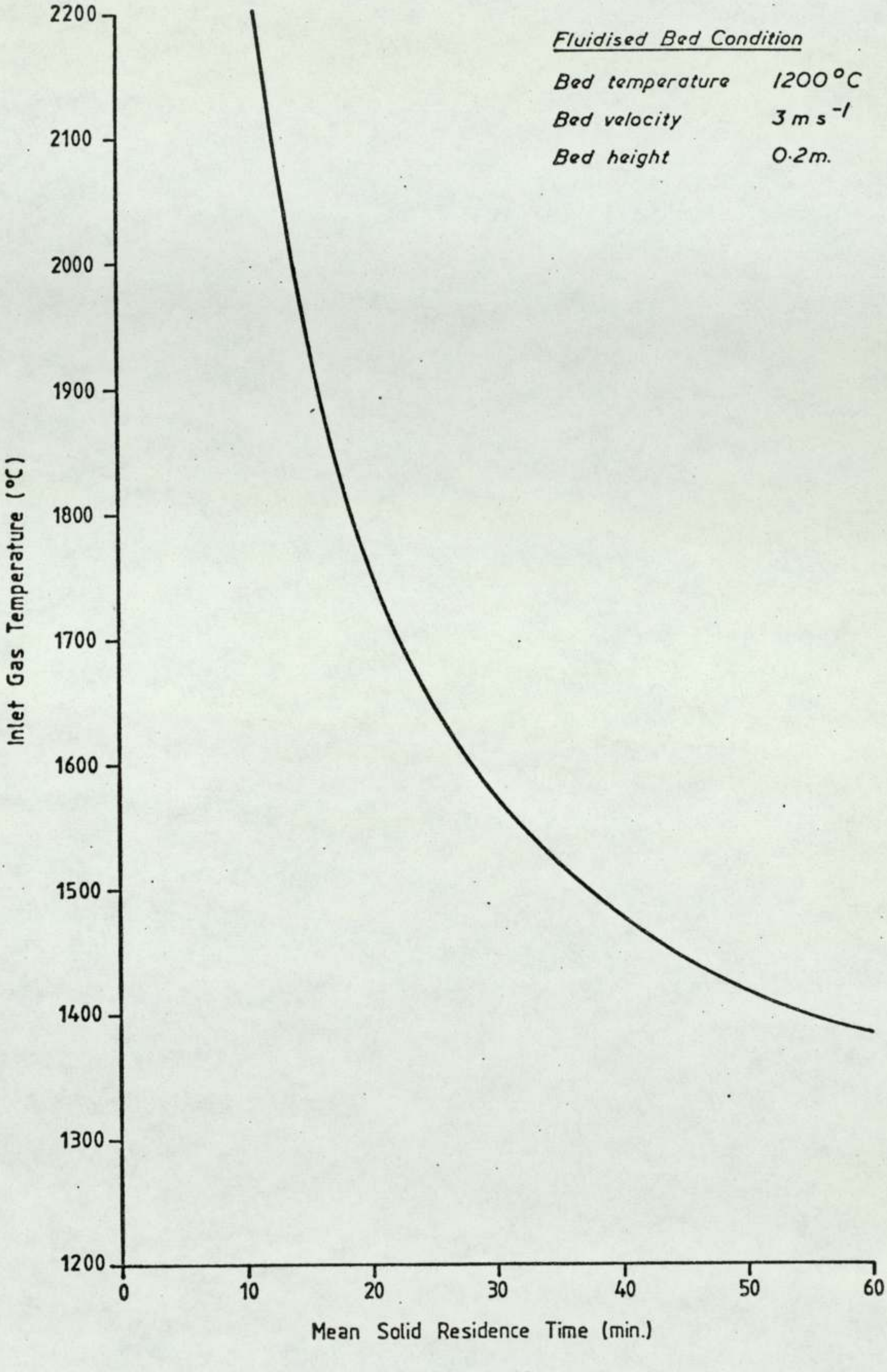


FIGURE 4.12

Relationship Between Fluidised Bed Inlet Gas Temperature and Mean Solid Residence Time Required for Flue Dust Calcination equation (4.16).

In the present application, the situation is slightly more complicated since part of the fuel was intended to be injected directly into the bed.

However, provided most of the fuel is burned within the bed and there is not an abnormally high level of excess air, the rate of heat release from an 'in-situ' combustion should be better than that considered above, and therefore a lower residence time may be possible.

Another factor of interest is the residence time distribution E(t) of the solid particles which, for a perfectly mixed bed, is given by,

$$E(t) = \frac{1}{\tau_s} \exp\left(-\frac{t}{\tau_s}\right) \qquad \ldots\ldots(4.17)$$

where E(t) represents the fraction of particles with a residence time between t and t + dt, and τ_s = mean residence time (= $\frac{W}{F_o}$). The fraction of particles with a residence time less than t is called the 'hold-back' and is given by,

$$F(t) = \int_0^t E(t)\,dt = 1 - \exp\left(-\frac{t}{\tau_s}\right) \qquad \ldots\ldots(4.18)$$

It can be calculated from the above expression that for a single perfectly mixed bed, approximately 40% of the particles stay in the bed for less than half the mean residence time and 10% for less than one-tenth. Therefore, unless the mean residence time is extremely long or special baffle-inserts are used, there will always be some under-calcined material produced.

4.4.4 Alkali Volatilisation and Vapour Saturation Consideration

Provided the fluidised bed is not too shallow, say with $L_m/d_p > 100\text{-}200$, the bed solids and the leaving gas can be assumed to be at equilibrium Kunii and Levenspiel (1969). The amount of alkalis volatilised is determined from an overall alkali balance for the system. Referring to Figure 4.11, the alkali balance, assuming that a proportion of alkali is contained in the dust carry-over, is as follows:-

$$\begin{bmatrix}\text{Mass of Alkalis}\\ \text{Volatilised from Dust}\end{bmatrix} = \begin{bmatrix}\text{Mass of Alkali}\\ \text{Vapour in Gas}\end{bmatrix}$$

i.e. $$F_i x_i - F_o x_o - \Sigma F_e x_e = G_o y_o{}^* - G_i y_i \qquad \text{.....(4.18)}$$

where F & G = mass throughput of solid and gas,

x & y = mass fraction of alkalis in solid and gas,

$\Sigma F_e x_e$ = sum of alkalis in dust carry-over,

Subscripts i and o denote the inlet and outlet condition,

and * denotes the equilibrium state.

The equilibrium alkali concentration $y_o{}^*$ in the exit gas can also be expressed in terms of the equilibrium vapour pressure p^*,

$$y_o{}^* = \left(\frac{p^*}{P - p^*}\right) \frac{M_v}{M_g} \qquad \text{.....(4.20)}$$

where P = Total pressure

and M_v, M_g = Molecular weight of alkali vapour and fluidising gas.

Assume that the fluidised bed gas inlet is alkali-free, i.e. $y_i = o$, equation (4.18) is reduced to,

$$F_i x_i - F_o x_o - \Sigma F_e x_e = G_o \left(\frac{p^*}{P - p^*} \right) \frac{M_v}{M_g} \qquad .....(4.21)$$

The equation may be simplified further by expressing it in terms of the degree of alkali volatilisation, ψ, as defined below:-

$$\psi = \frac{\Sigma \text{ Alkali Input} - \Sigma \text{ Alkali Output}}{\Sigma \text{ Alkali Input}} \times 100\%$$

$$= \frac{F_i x_i - F_o x_o - \Sigma F_e x_e}{F_i x_i} \times 100\% \qquad .....(4.22)$$

Substituting equation (4.22) in (4.21),

$$\psi = \frac{G_o}{F_i x_i} \left(\frac{p^*}{P - p^*} \right) \frac{M_v}{M_g} \times 100\% \qquad .....(4.23)$$

In the pure state, the equilibrium vapour pressure of alkalis is the same as the saturation vapour pressure. In flue dust, however, due to possible interactions among the alkalis and between the alkalis and other constituents present, and possibly also due to the effect of capillary retention, the equilibrium pressure can be substantially depressed. Nevertheless, if p* in the R.H.S. of equation (4.21) is replaced by the saturation vapour pressure p_s of the component, the potential maximum vapour carrying capacity of a gas at different temperature can be evaluated when p_s is known.

The saturation vapour pressure of KCl, K_2SO_4 and Na_2SO_4 are quite well studied and a list of references and the vapour-pressure/temperature relationships are given in Table 4.6. Values of p_s between 1050°C and 1300°C are calculated from the equations and shown in Figures 4.13-4.15. As can be seen, the saturation vapour pressure of KCl is easily the highest, being at least two orders of magnitude higher than that of K_2SO_4 and three orders higher than that of Na_2SO_4. The mass of KCl and K_2SO_4 vapour that could potentially be carried in air ($M_g = 29$) at temperatures of 1100-1300°C are shown in Figure 4.16. If it is assumed that 2kg of gas is produced for every 1kg of dust calcined, it can be seen that the potential maximum carrying capacity for KCl in air at, say, 1200°C is 1.2kg, whilst that of K_2SO_4 is just over 8g when decomposition is not suppressed and less than 7g when decomposition is suppressed. For the typical Northfleet and Westbury dusts shown in Table 4.1, the amount of KCl falls well below the potential vapour carrying capacity, whilst the converse applies to K_2SO_4. Therefore, unless the equilibrium vapour pressure deviates significantly from the saturation vapour pressure, it is postulated that under the expected conditions the volatilisation of KCl will occur freely whilst that of K_2SO_4 will be limited by the partial pressure in the exit gas.

A factor which has so far not been considered is the effect of gas by-pass, which is a function of the bubbling characteristics of the bed (Davidson and Harrison, 1971). Bubble behaviour in a fluidised bed is still a subject of much controversy and according to a recent paper by Grace and Clift (1974), the 'classical' two-phase theory (Davidson and Harrison, 1971), tends to over-estimate the amount of gas by-passing. However, returning to the present problem, provided the gas within the bed is saturated, the volatilisation rate of K_2SO_4 will still be governed by equation (4.21) but with G replaced by G', which may be expressed in terms

TABLE 4.6

Saturated Vapour Pressure of KCl, K_2SO_4 and Na_2SO_4

	Equation	Temperature Range (^oK)	Reference
KCl	$\mathrm{Log}_{10}\ (p_s/\mathrm{mm\ Hg}) = -\frac{11023}{T} - 3.526 \log T + 20.798$	-	Janz, 1969 (cf. Perry and Chilton, 1973; Halstead, 1970)
K_2SO_4	$\mathrm{Log}_{10}\ (p_s/\mathrm{atm}) = -\frac{14700 \pm 900}{T} + (6.84 \pm 0.69)$	1180 - 1342	Hart and Laxton, 1967; Halstead, 1970 (cf. Kosugi, 1967; Dubois et al, 1968)
	Decomposition Suppressed		
	$\mathrm{Log}_{10}\ (p_s/\mathrm{atm}) = -\frac{12700 \pm 900}{T} + (53.7 \pm 0.69)$	1342 - 1668	
	Decomposition Unsuppressed		
	$\mathrm{Log}_{10}\ (p_s/\mathrm{atm}) = -\frac{13800}{T} + 6.23$	1342 - 1668	
Na_2SO_4	Decomposition Suppressed		Cubicciotti and Keneshea, 1972
	$\mathrm{Log}_{10}\ (p_s/\mathrm{atm}) = -\frac{15540 \pm 380}{T} + (5.858 \pm 0.15)$	1400 - 1625	
	Decomposition Unsuppressed		
	$\mathrm{Log}_{10}\ (p_s/\mathrm{atm}) = -\frac{16190}{T} + 7.081$	1400 - 1625	

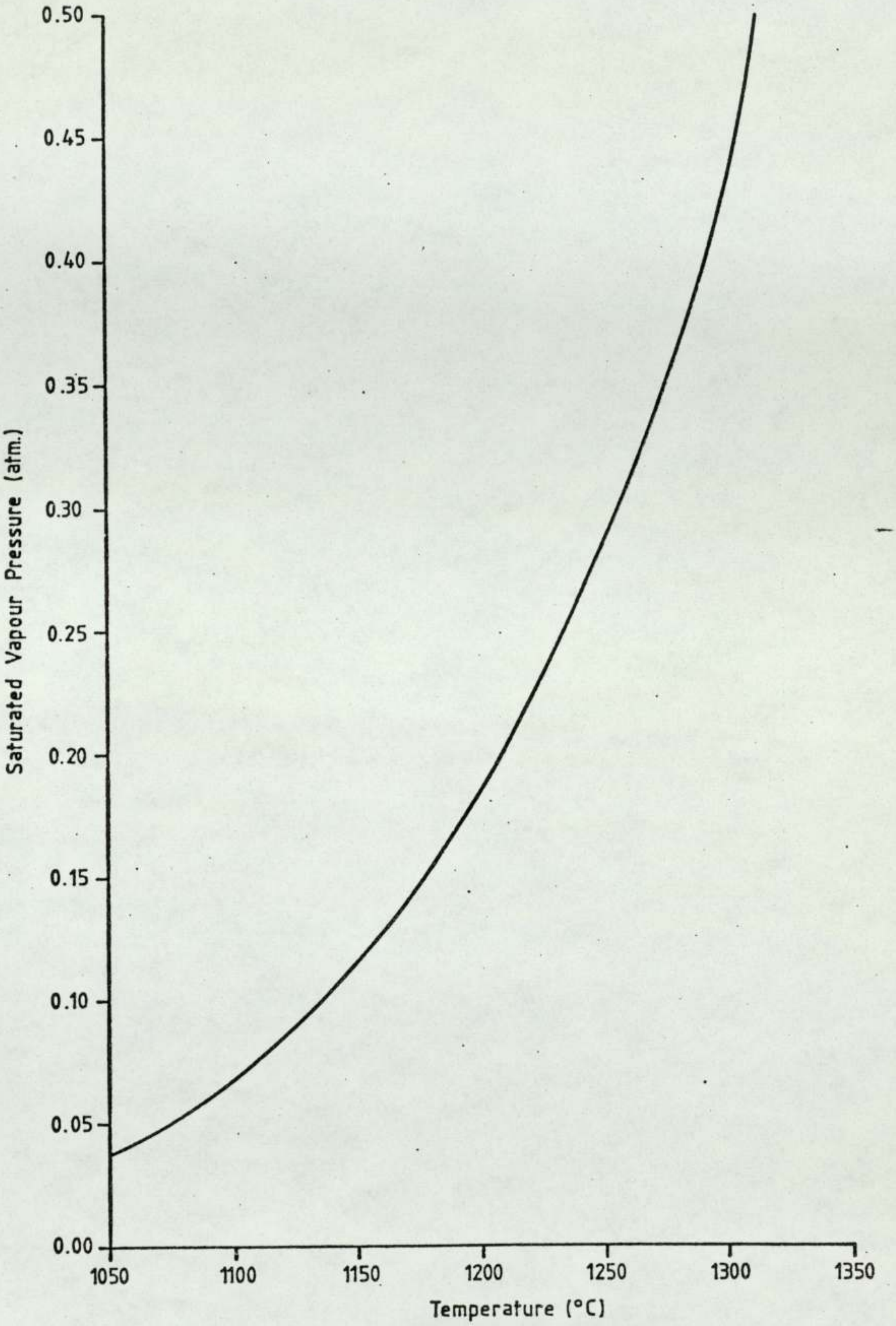


FIGURE 4.13

Saturated Vapour Pressure of KCl
(Source: JANAF, 1960 or Janz, 1969)

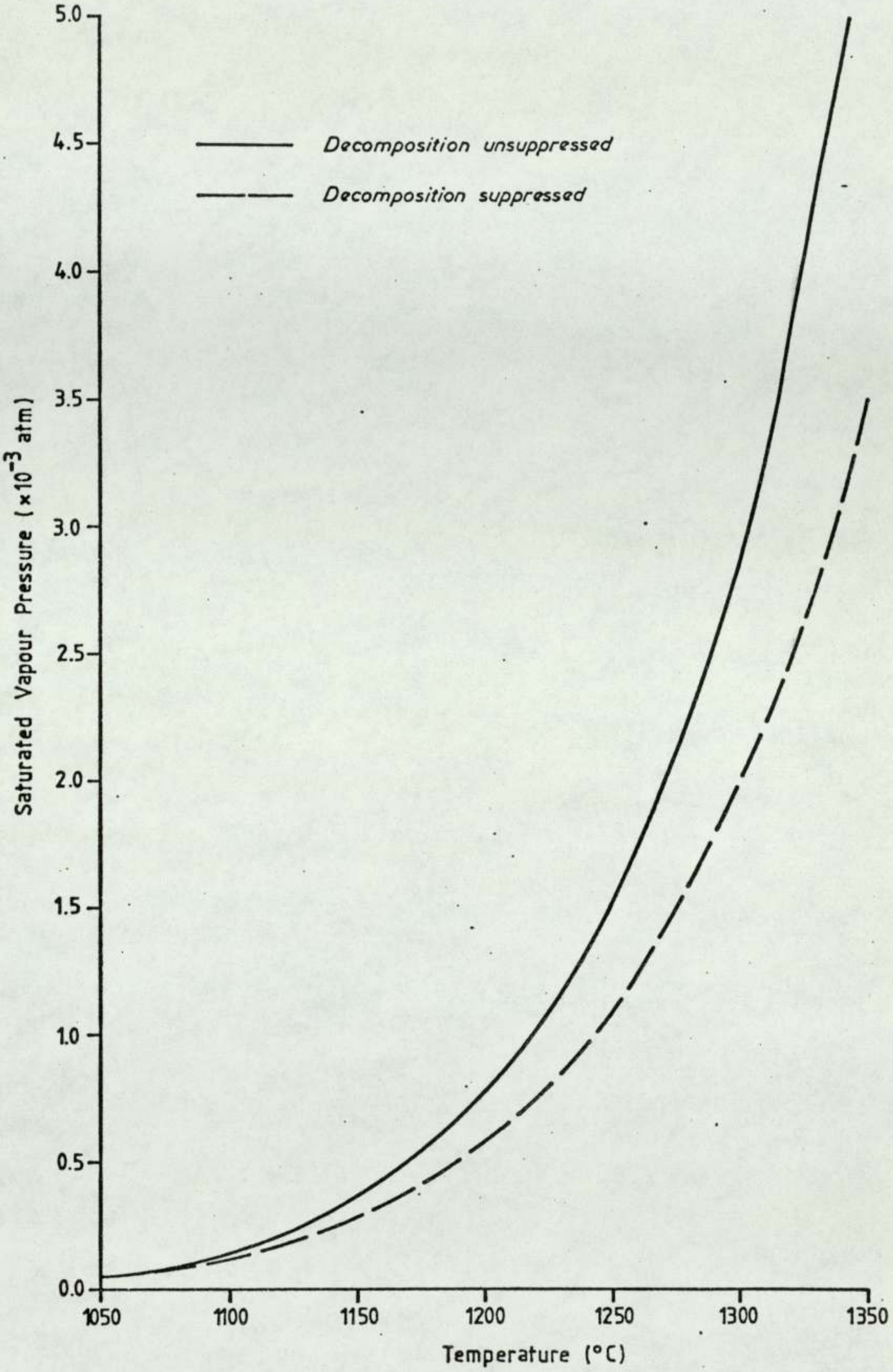


FIGURE 4.14

Saturated Vapour and Decomposition Pressures of K_2SO_4
(Source: Hart and Laxton, 1967; Halstead, 1970)

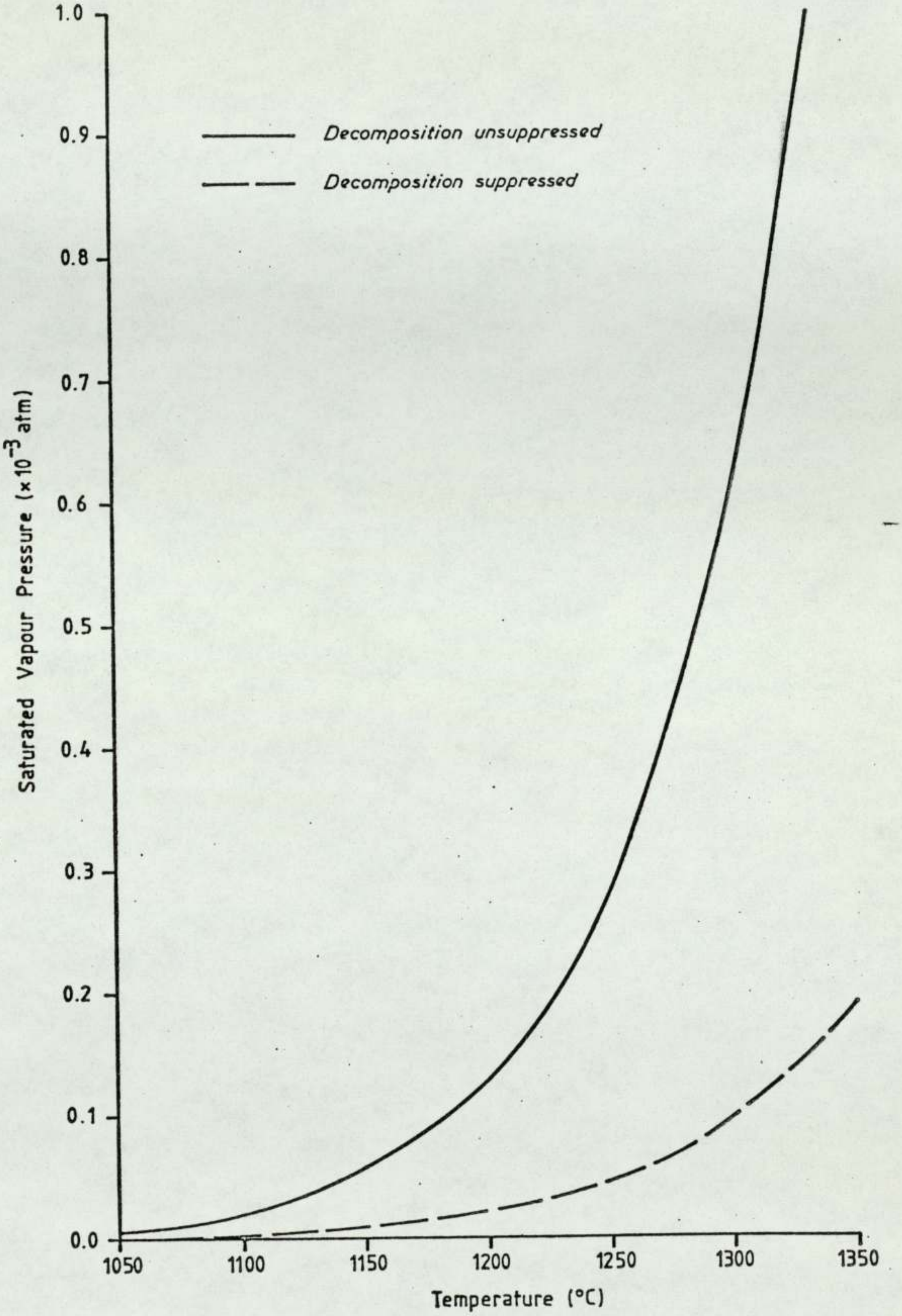


FIGURE 4.15

Saturated Vapour and Decomposition Pressures of Na_2SO_4
(Source: Cubicciotti and Keneshea, 1972)

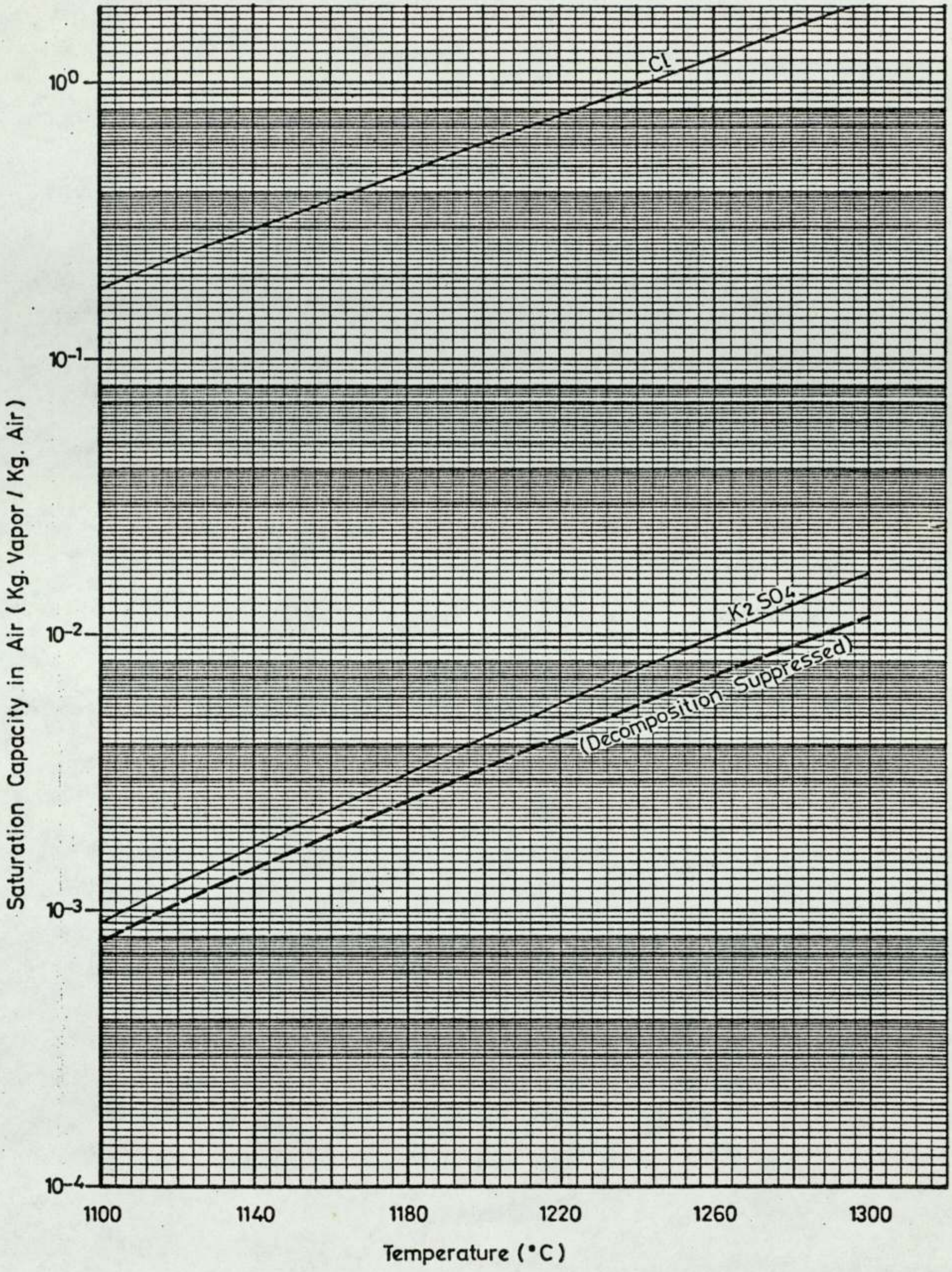


FIGURE 4.16

Saturation Capacity of KCl and K_2SO_4 Vapour in Air from 1100–1300°C of G as follows,

$$G' = (1 - \varphi) G \qquad .....(4.24)$$

where φ is the fraction of total gas flow passing through the bed as bubbles. Under these conditions, increasing the gas flow rate at constant temperature will not increase the rate of volatilisation since the excess gas merely increases φ. However, an absorption/desorption experiment conducted by Richardson and Backhtier (1958), it was reported that the amount of gas by-pass was only about 5%. For large particle systems, the effect is probably lower (Geldart and Cranfield, 1972).

The volatilisation of Na_2SO_4 will also be limited similarly to that of K_2SO_4 but, as already stated, this is of no consequence.

4.5 Plan of Experiment

4.5.1 General Considerations

One of the first considerations in experimental design is the scale of operation. Normally, in fluidised bed modelling, the experimental unit is regarded as a column of the full-scale plant so that the heights of the beds are the same and only the areas are different. But slugging must be avoided as far as possible. According to the investigations of Werther (1974), for typical laboratory units smaller than 200mm, the fluidisation characteristics can be significantly affected by the bed diameter. Generally, the effect decreases as the bed diameter increases. Therefore, it follows that if the experimental results are to be applied directly to scaling-up, a fluidised bed diameter of 200mm or more should be used.

However, prior to the start of the present investigation, a 100mm diameter fluidised bed had already been designed and fabricated, although the bed was subsequently enlarged to 150mm diameter and separate larger scale trials involving 300mm and 450mm diameter fluidised beds were carried out.

4.5.2 Programme of Investigation

The dust feed to be used was obtained from the pelletisation and drying experiments carried out in parallel with the present work. Initially, the experiments were planned mainly to calcine Northfleet flue dust as the problem there was considered to be more critical than that at Westbury because of the quantity of dust involved. However, it was discovered later that the alkali volatilisation characteristics of the two dusts were quite different and subsequently, the experiments were extended to cover the Westbury dust.

Most of the early work was geared towards the development of the exhaust gas handling system, which is considered in the following section. Additionally, the suitable range of operating conditions for the fluidised bed, such as velocity and temperature were also determined in the early period of the investigation. The principal aim of the later experiments, particularly those carried out in the 150mm bed, was to determine the effect of feed characteristics on the alkali volatilisation performance and also to check for reproducibility of results.

4.5.3 Method of Handling the Fluidised Bed Exhaust Gases

The exhaust gases leaving the fluidised bed will be laden with carry-over dust and volatilised alkalis. As mentioned earlier, the melting range of alkali and calcium sulphate eutectic, particularly in the presence of KCl can be as low as 700°C or less (see Figure 4.10). Therefore, unless the gas is quenched rapidly, the molten alkalis may deposit on the duct walls and cause serious problems of build-up as was reported in the Artarmon trials. Prior to the start of this work, a vortex mixing vessel, similar in design to that of the 'Humboldt' alkali by-pass system used in cement plants and a 100mm diameter cyclone intended for collecting the condensed alkalis had already been procured and the initial experiments were based on the equipment available.

However, the particle size range of alkali fume reported in the literature is only of the order of 0.1-5 μm (Perry and Chilton, 1973), and is therefore beyond the collection capability of even the most efficient present-day cyclone, unless the alkalis condensed substantially on the entrained dust paricles. Therefore, provisions were made for alternative methods of collecting the alkali fume and several possibilities were considered, as indicated in Table 4.7. Initially, the experiment followed the approaches marked 1 and where necessary or if time permitted, approaches marked 2 would be investigated.

TABLE 4.7

Alternative Approaches of Alkali Fume Collection

<table>
<tr><th></th><th colspan="6">ALTERNATIVE APPROACHES</th></tr>
<tr><td>Type of dust feed</td><td colspan="3">[1] Northfleet</td><td colspan="3">Westbury</td></tr>
<tr><td>Quench mixing technique</td><td colspan="2">[1] Vortex mixer (e.g. Humboldt type)</td><td colspan="2">Jet entrainment mixer</td><td colspan="2">Tangential mixer (e.g. Polysius type)</td></tr>
<tr><td>Quench media</td><td colspan="2">[1] Cold air</td><td colspan="2">Water evaporation</td><td colspan="2">Cold processed dust</td></tr>
<tr><td>Position of quench admission</td><td colspan="2">[1] Before entrained solid removal</td><td colspan="2">After entrained solid removal</td><td colspan="2">Within solid removal vessel</td></tr>
<tr><td>Particle growth residence time</td><td colspan="2">[1] Short</td><td colspan="2">Medium</td><td colspan="2">Long</td></tr>
<tr><td>Solid seeding material</td><td>[1] None</td><td colspan="2">K_2SO_4</td><td colspan="2">KCl</td><td>Cold processed dust</td></tr>
<tr><td>Entrained solid removal</td><td colspan="2">[1] None</td><td colspan="2">[2] Cold cyclone</td><td colspan="2">Hot cyclone</td></tr>
<tr><td>Condensed alkali salts collection</td><td>[1] High efficiency cyclone</td><td colspan="2">[2] Glass bag filter</td><td colspan="2">[2] Packed or electrostatic precipitator</td><td>Wet scrubber or pebbled bed</td></tr>
</table>

CHAPTER 5

APPARATUS AND TEST PROCEDURE

Summary

The apparatus used in the experiment initially consisted of a 100mm (D) x 305mm (H) fluidised bed with an enlarged freeboard of 200mm (D) x 420mm (H), a quench vessel for cooling the fluidised bed exit gas, and a 100mm cyclone intended for collecting the alkali fume. Later, a twin-compartment glass bag filter and a single-electrode tubular electrostatic precipitator were installed to improve the alkali collection efficiency and the bed was enlarged to 150mm (D) to gain flexibility and scale advantage.

The heat requirement for calcining was supplied partially by preheating the oxygen-enriched air with a propane gas burner in a 'hot-box' and partially by injecting diesel oil directly into the bed using a positive displacement pump. Oxygen was needed to compensate for the high heat losses in order to maintain the desired fluidisation velocity.

The pellets were fed into the bed through a 38mm 'Inconel' pipe using a 'Magco' variable-speed vibratory feeder. The bed product was discharged through the centre of a perforated distributor plate via a similar pipe and feeder device. The distributor plate was designed to give a pressure drop of 350mm W.G. and was constructed of a 6mm thick stainless steel plate drilled with approximately 150 holes of 1.5mm diameter.

The test procedure involved first the warming up of the fluidised bed using only the propane gas burner for 2 hours until the temperature reached about 600°C. The oil was then injected and the quench air and exhauster fans switched on. The bed was gradually brought to the working temperature of around 1200°C over a further 2 hours. The fuel and gas inputs were then adjusted to give the required fluidising and temperature conditions and the suction of the exhauster fan was regulated to give a neutral pressure in the freeboard. Once the conditions were stabilised, the feed was trickled into the bed at a steady rate and great care was taken to ensure that the bed temperature was maintained as constant as possible. Usually, about ½-1 hour was required to obtain a bed 300-350mm deep. When this state was reached, the material was removed. By regulating the input and output rate of material, a constant temperature and approximately constant bed height could be maintained.

The rig was extensively instrumented to give direct readings of the fuel and gas flows and the temperature and pressure at various points. For each test, the feed and various products obtained were weighed and representative samples were sent for chemical and physical analyses.

5.1 Introduction

The apparatus and instrumentation used for the experiment are described in detail in this chapter. As mentioned earlier, the fluidised bed unit, quench vessel and cyclone were already designed and in the process of fabrication when the present study was initiated. Nevertheless, a considerable amount of time was spent in casting the fluidised bed, assembling the various components and installing and calibrating various instruments required. In addition, significant modifications, including the enlargement of the fluidised bed diameter and installing the bag filter and electrostatic precipitator were carried out. Much of the ancillary equipment such as the quench air and exhauster fans, fuel-oil injection pump and the transformer-rectifier set for the electrostatic precipitator were redundant equipment available on site and were considerably over-sized. However, they did not pose any undue problem of operation.

The initial commissioning of the rig and the experimental procedure followed are also reported.

5.2 Construction and Modification of the Apparatus

5.2.1 Description of the Fluidised Bed and Ancillary Equipment

A schematic of the experimental rig is shown in Figure 5.1. Note that in the first half of the experiments, the fluidised bed diameter was 100mm and not 150mm as is shown and that the bag filter and electrostatic precipitator were only installed after several tests.

The fluidised bed unit was constructed by first lining the mild steel

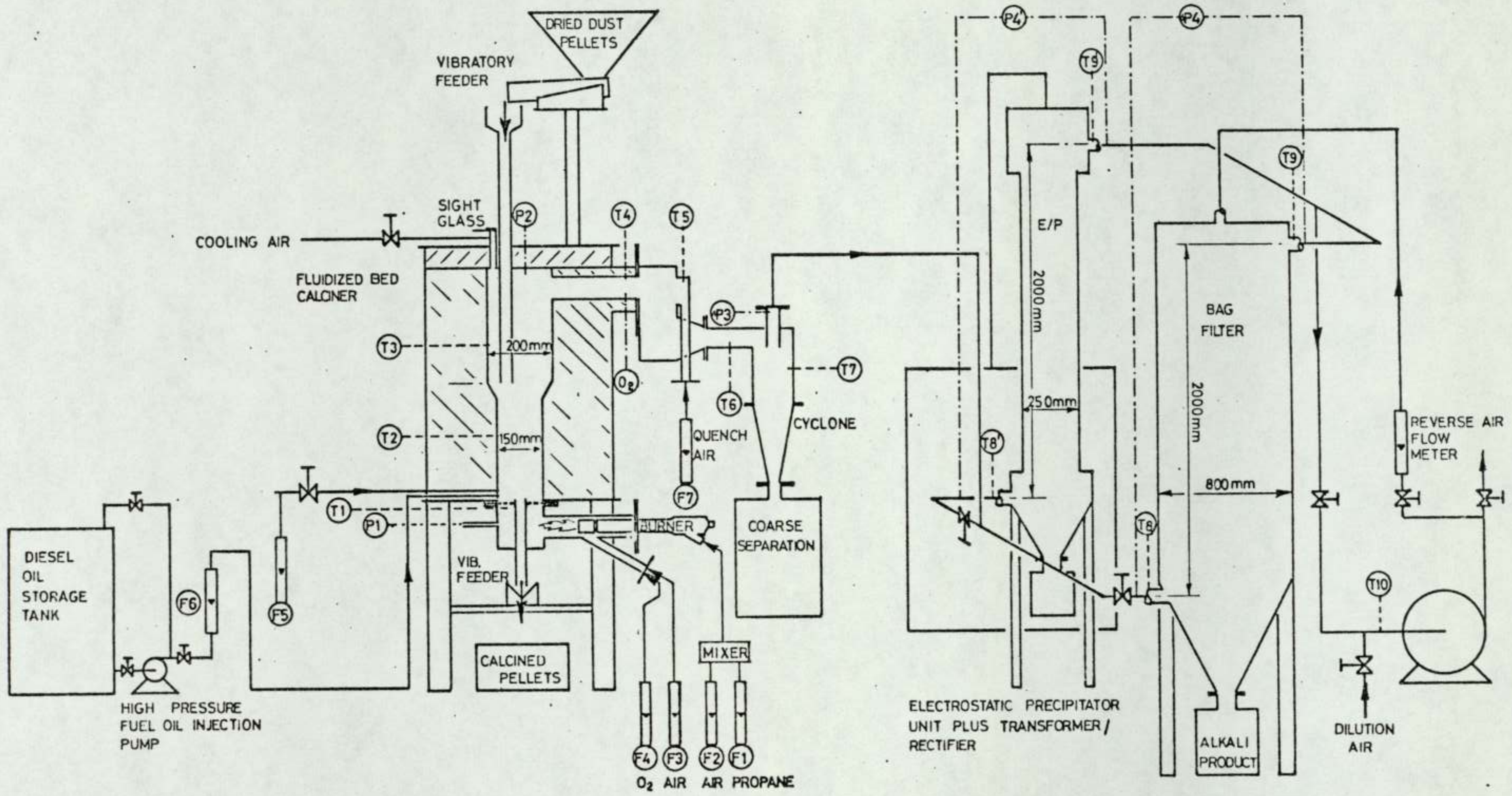


FIGURE 5.1

Schematic of the Fluidised Bed Rig

cylindrical casing (610mm (D) x 840mm (H)) with a layer of insulating refractory brick and then moulded into shape with castable refractory with the aid of a wood-former, Figure 5.2. The freeboard was enlarged in order to reduce the dust carry-over as the height of freeboard allowed in the original design was considered to be inadequate*. The gas distributor was made of a 6mm thick 'Inconel' steel plate perforated with 1.5mm holes to give a free area of about 2.5% and a design pressure drop of not less than 350mm W.G. (~ 3.5 kN m^{-2}), as recommended by Agarwal et al (1962). However, as will be seen later, the design was probably on the generous side for the material treated, which appeared to fluidise readily. A 'hot-box' housing a propane gas burner with a rated duty of 60 Mcal h^{-1} for preheating the incoming oxygen and air was bolted beneath the distributor plate. Oxygen was needed to compensate for the high heat losses of the small unit so that the fluidisation velocity could be kept to an acceptable level. In the last 4 experiments contained in this thesis, an electric furnace was used for preheating the fluidising air in order to simulate the plant conditions more realistically. These experiments were initially intended to be an extension of the present work but for reasons outside the scope of the present discussion, the programme was abandoned.

More than half of the heat requirement was supplied by injecting diesel oil directly into the bed during calcination. A positive displacement

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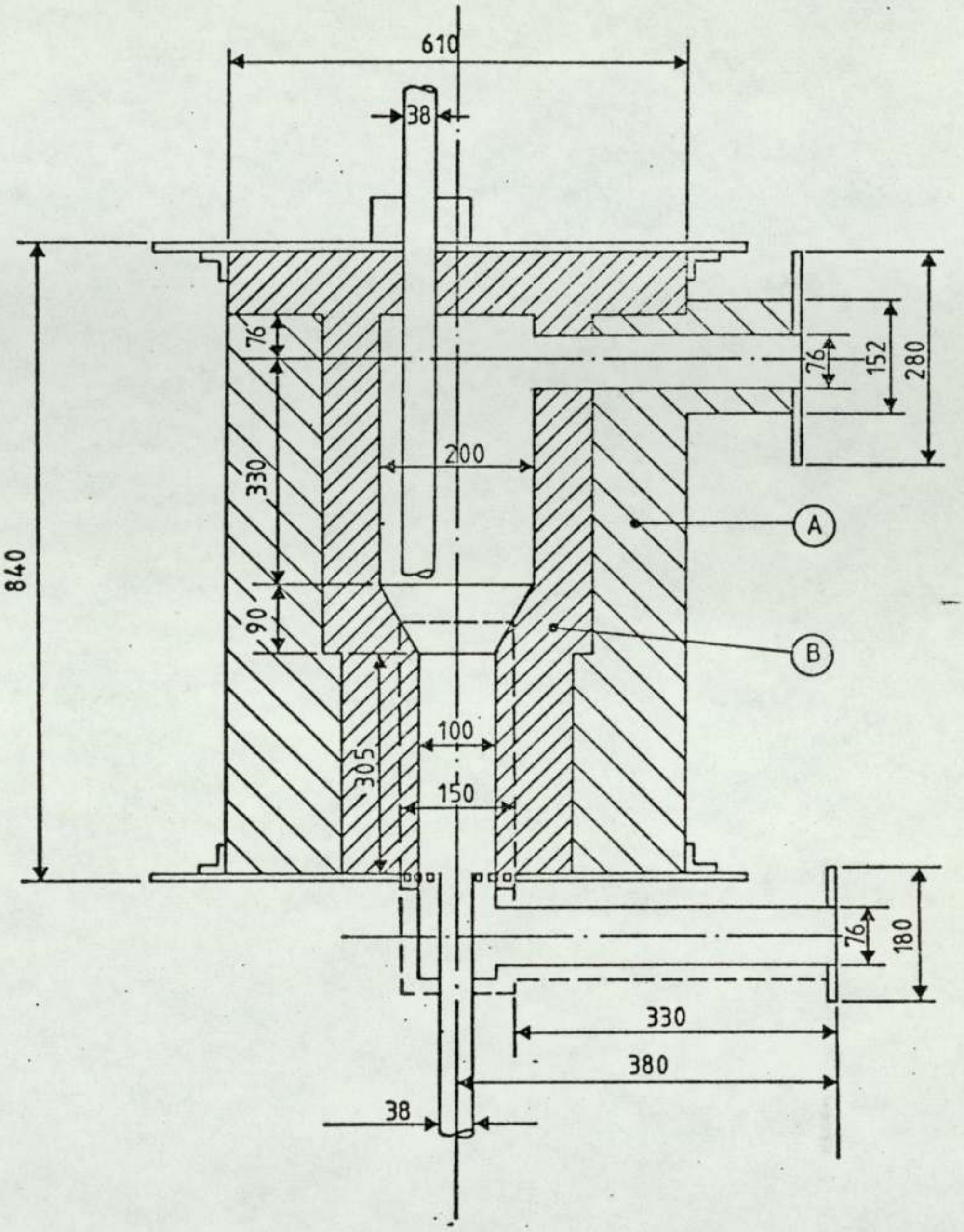
* Freeboard is governed by the transport disengagement height or TDH of the bed particles. At present, there is no reliable method of predicting TDH, although an 'order-of-magnitude' type estimate can be obtained from the semi-empirical equations of Zenz and Weil (1958) or Do et al (1972). According to Vanecek et al (1965, 1970), a height of at least 1-2m should normally be allowed in practice.



KEY

Ⓐ Brick refractory
Ⓑ Cast refractory

ALL DIMENSIONS IN mm.

FIGURE 5.2

Details of the 100/150mm Fluidised Bed

pump operating at a pressure of up to 1 MN m^{-2} was used to deliver the oil from a 205 l (i.e. 45 gallon) storage drum via a 10mm bore pipe and a 2mm bore stainless steel tubing pinched at the tip serving as an atomiser. The stainless tubing was located approximately 5mm above the distributor plate, flush with the refractory face, and inserted co-axially within another 10mm bore tube which enabled a small volume of cooling air to be passed. (It was found initially that without the co-axial cooling air, the tip of the stainless steel tubing tended to be damaged by heat after shut-down).

The dust pellets to be processed were gravity fed into the bed using a 'Magco' variable-speed vibratory feeder via a 38mm bore 'Inconel' pipe. The inlet was not mechanically sealed but relied simply on a neutral pressure in the freeboard, which was achieved by controlling the suction of the exhauster fan to minimise air leakages. The bed product was discharged through the centre of the distributor plate via another 38mm bore 'Inconel' pipe and the rate was also controlled by a 'Magco' variable speed vibratory feeder.

The flue gas was exhausted via a 76mm (D) horizontal exit directly into the quench vessel without going through any bend or additonal ducting. A sight glass (which could be air cooled if needed) was located on top of the bed to give a clear view of the fluidised bed in operation.

5.2.2 Description of the Exhaust Gas Handling Systems

The design of the quench vessel used for cooling the fluidised bed exit gas was based on that of the swirl mixing vessel used in the 'Humboldt' alkali by-pass system installed in certain cement plants. The vessel, which resembled in some respect the top part of a cyclone lying on its side, was constructed of stainless steel and consisted of a mixing chamber of approximately 1300 ml in volume. The positions and dimensions of the hot gas inlet, cooling air inlet and quenched gas outlet are shown in Figure 5.3. A centrifugal fan with a rated capacity of 178 Nm^3 h^{-1} at 400mm W.G. was used to supply the quench air.

The cyclone was designed according to the standard practice shown in Perry and Chilton (1973). Stainless steel was used in the fabrication of the 100mm cyclone (for the 100mm bed), while ordinary mild steel was used in the 200mm cyclone (for the 150mm bed). A small sampling drum was bolted onto the bottom outlet of the cyclone to collect the material separated.

From the cyclone, the gas could be passed into either the bag filter or the electrostatic precipitator. The bag filter was fabricated of mild steel and consisted of twin compartments, each of which contained four glass fibre bags suspended vertically as shown in Figure 5.4. The bags were obtained from 2 different manufacturers, viz, Western Precipitator and Tilghman Wheelabrator. The bags had a recommended operating temperature of 200°C normal and 290°C maximum. The effective collecting area of the 'Western' bags was $0.71m^2$ per bag while the Tilghman bags had an area of $0.66m^2$ per bag, otherwise they were both fairly similar.

The electrostatic precipitator was designed and manufactured by Sturtevant Gas Cleaning and consisted of a 2000mm long hexaganol tube measuring 250mm across the flats with a 3mm discharge electrode suspended centrally from an insulator above, Figure 5.5. The tube had a cross-sectional area of

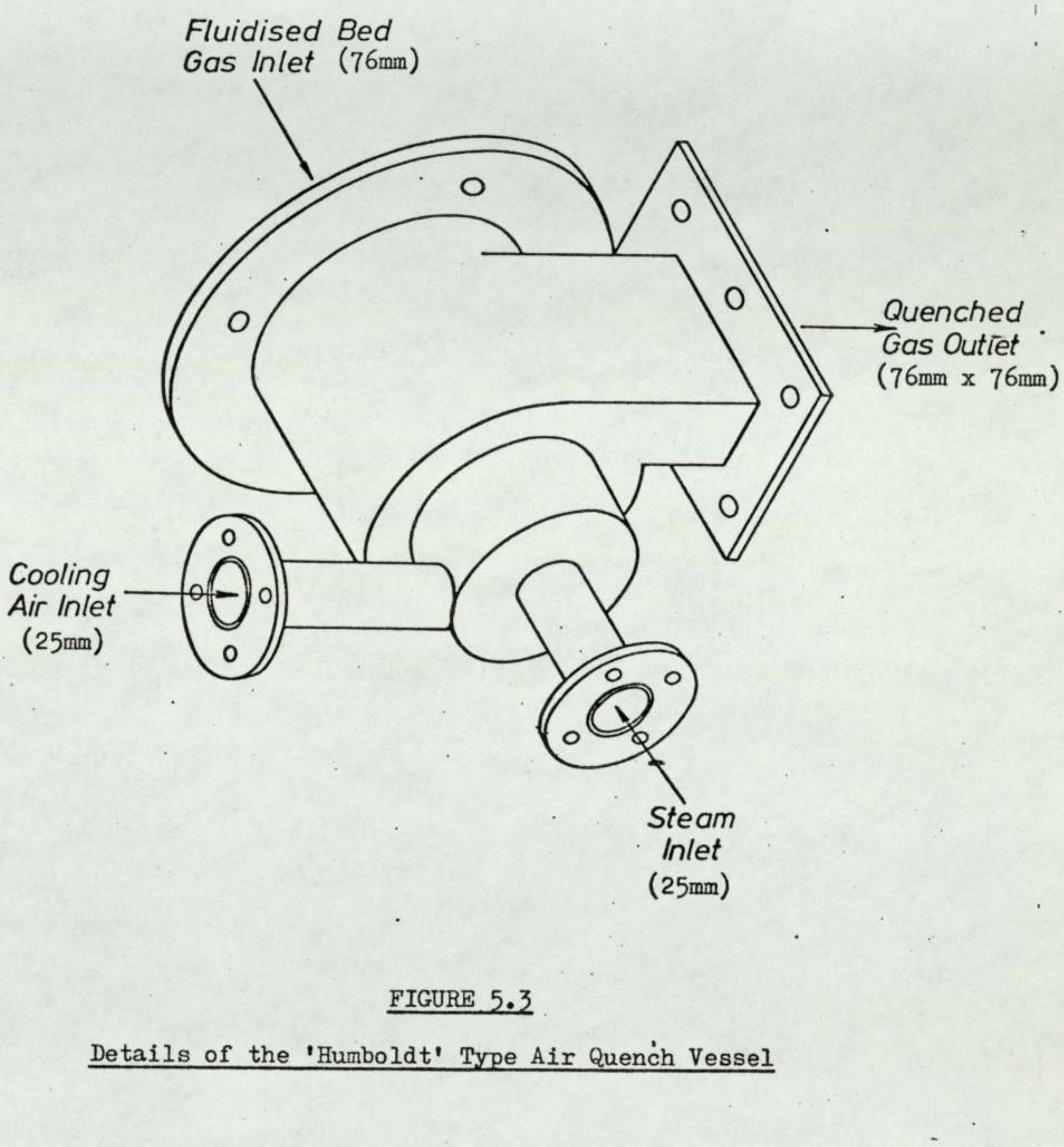


FIGURE 5.3

Details of the 'Humboldt' Type Air Quench Vessel

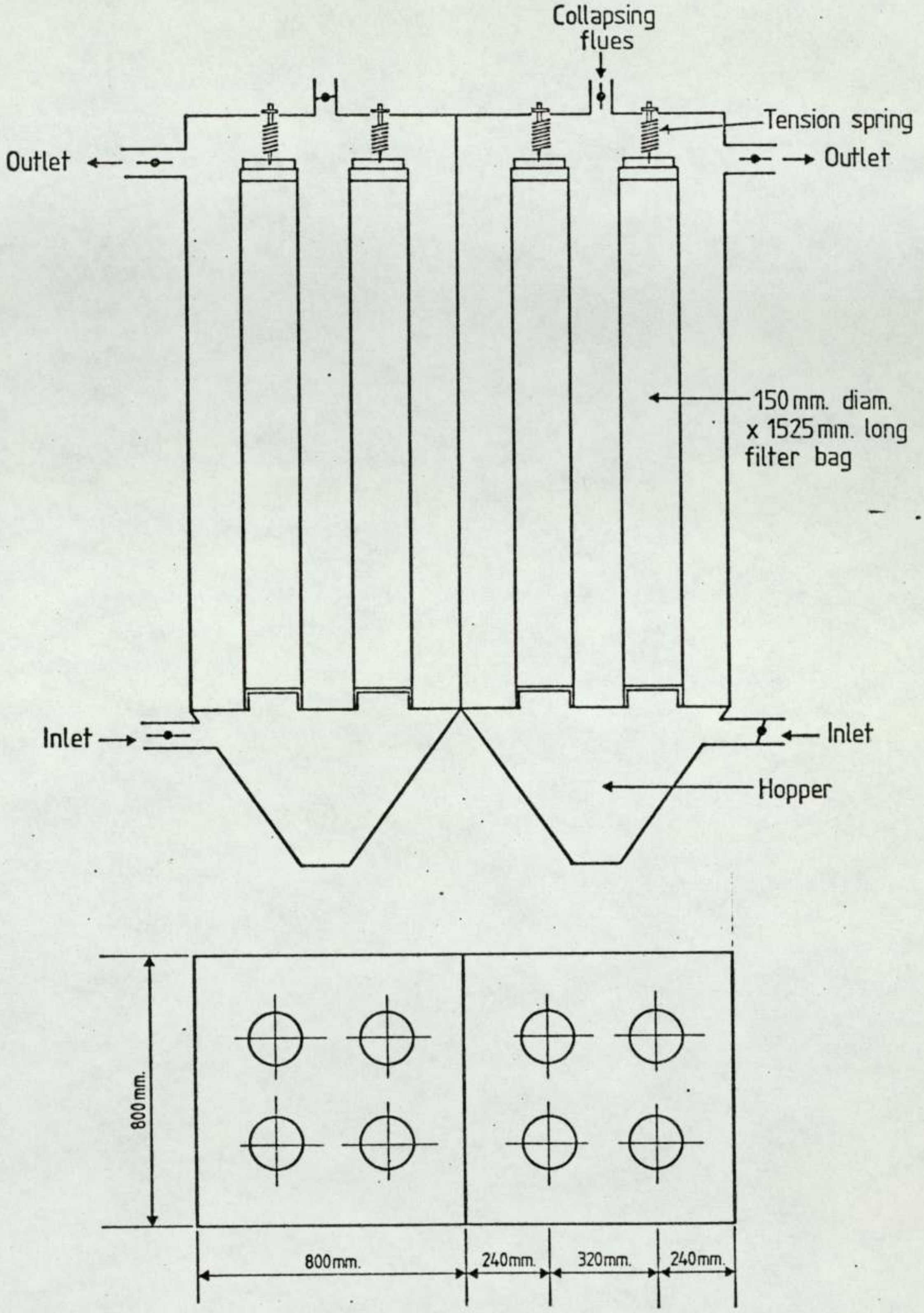


FIGURE 5.4

Details of the Twin Compartment Bag Filter

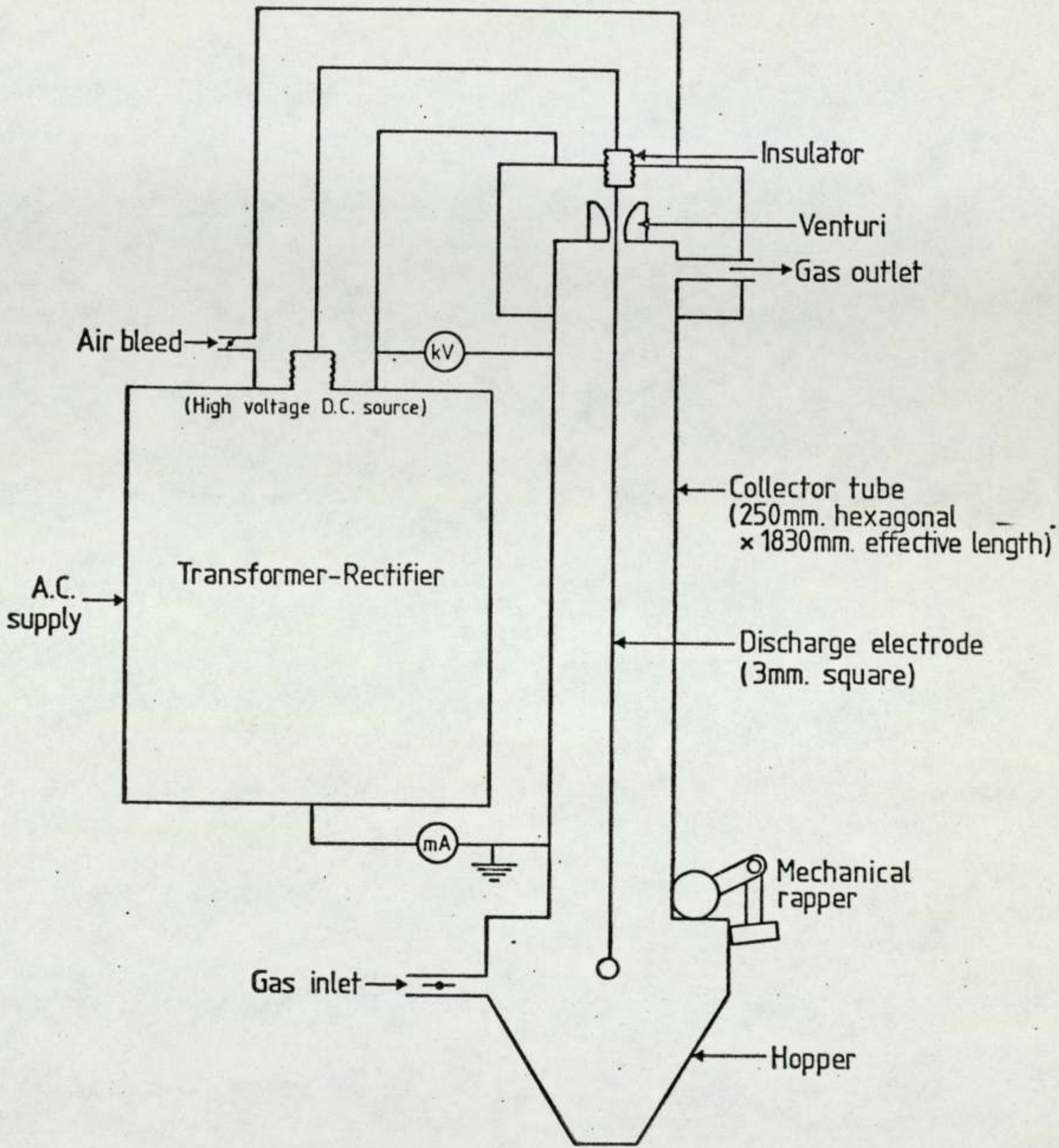


FIGURE 5.5

Details of the Single Tube Electrostatic Precipitator

$0.0558m^2$ and an effective collecting surface of $1.61m^2$ and was designed to operate at 250°C and 350°C maximum. A transformer-rectifier unit, which was acquired from a redundant cement works and was capable of delivering up to 60 mA at 60 kV, was used to supply the current and high voltage needed (~ 2 mA and 40-50 kV). A mechanised rapping hammer situated at the base of the collector tube was provided for dislodging material from the collecting surface. Because of the high heat losses, the unit was extensively insulated with mineral wool and also trace-heated electrically. In spite of this, there was still a significant temperature gradient across the precipitator tube, as will be seen later.

A number of photographs illustrating the various features of the apparatus are shown in Figures 5.6-5.10.

5.3 Instrumentation of the Rig

The rig was extensively instrumented to give various flow, temperature and pressure readings, as is shown in Figure 5.1. A list of the instruments involved is given in Table 5.1 and some additional comments on the range and accuracy are given below.

5.3.1 Flow Measurement

The flow rate of fuel oil and various gases involved were measured with 'Rotameters' (a variable area flow meter) of the appropriate size range. These instruments were pre-calibrated at 15°C and 760mm Hg, and any deviation of the working temperature and pressure could be readily corrected. The accuracy, according to the manufacturers, was ±2½%. However this necessarily assumed a steady flow condition which was observed in all but the compressed air supply. For the compressed air,

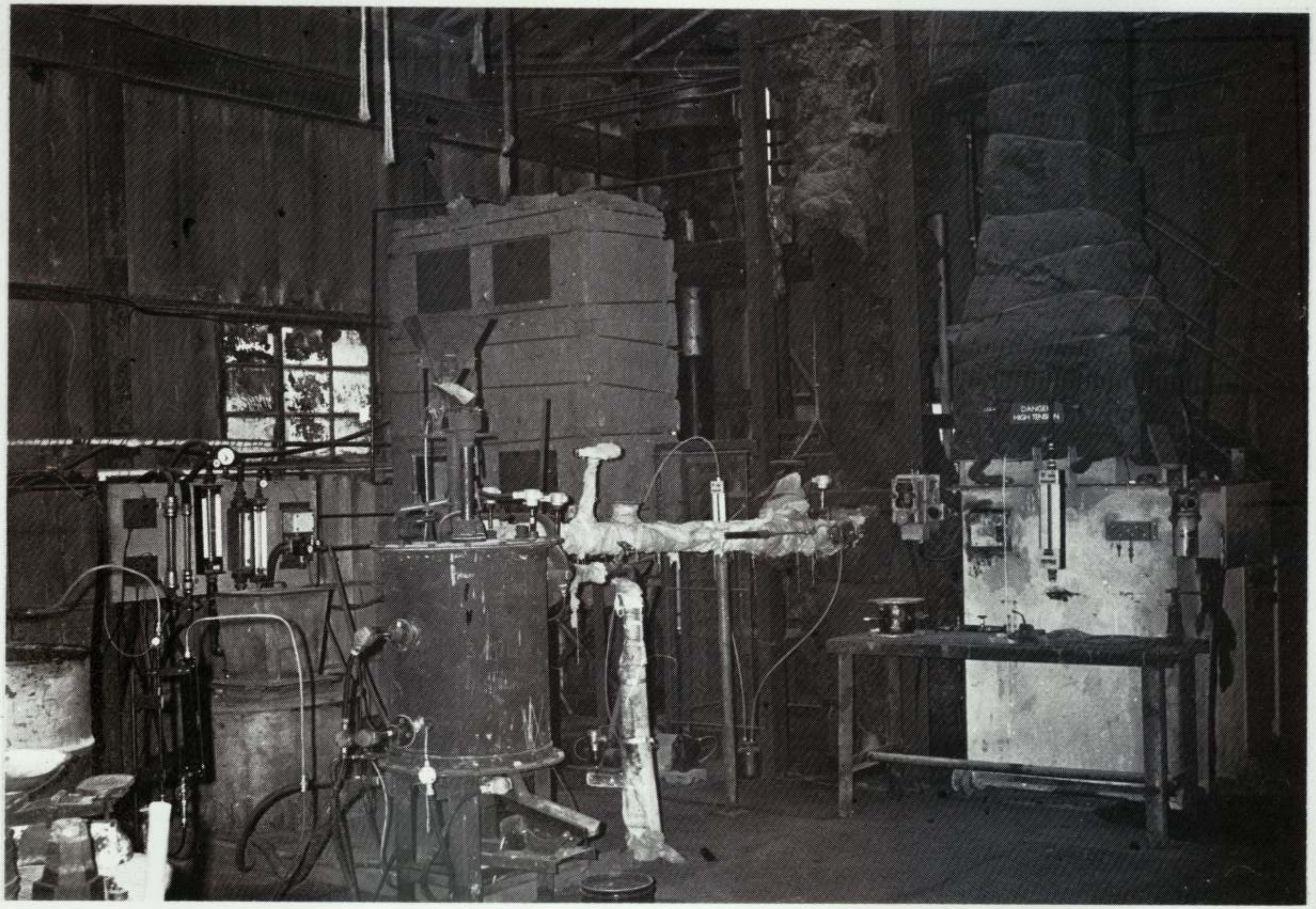


FIGURE 5.6 : An overall view of the apparatus

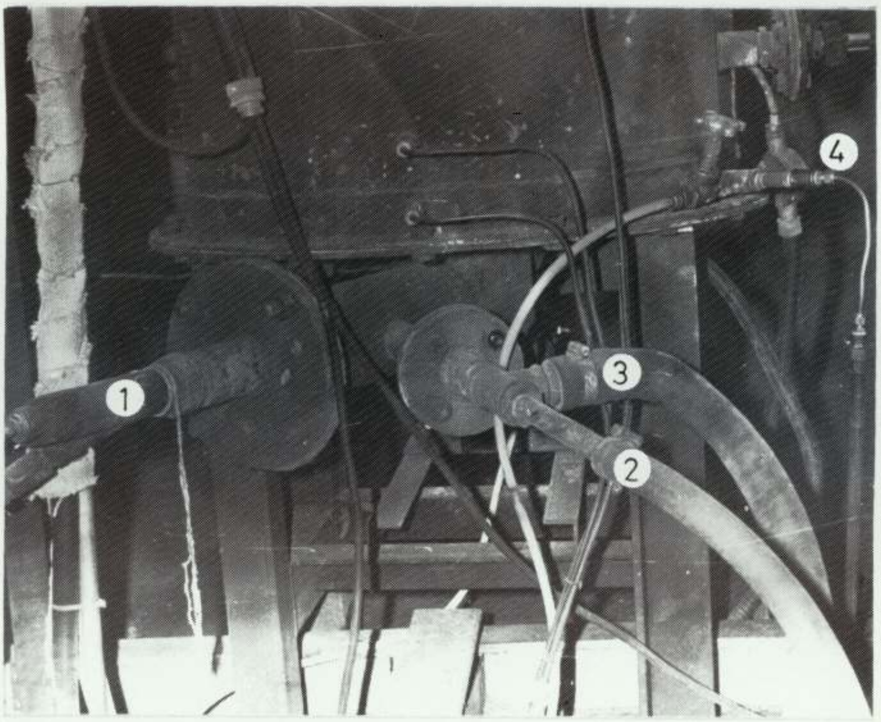


FIGURE 5.7 : A close-up of the Hot Box showing: (1) the pilot propane burner; (2) the fluidisation-combustion oxygen inlet; (3) the fluidisation-combustion air inlet; and (4) the concentric air cooled fuel oil injector.

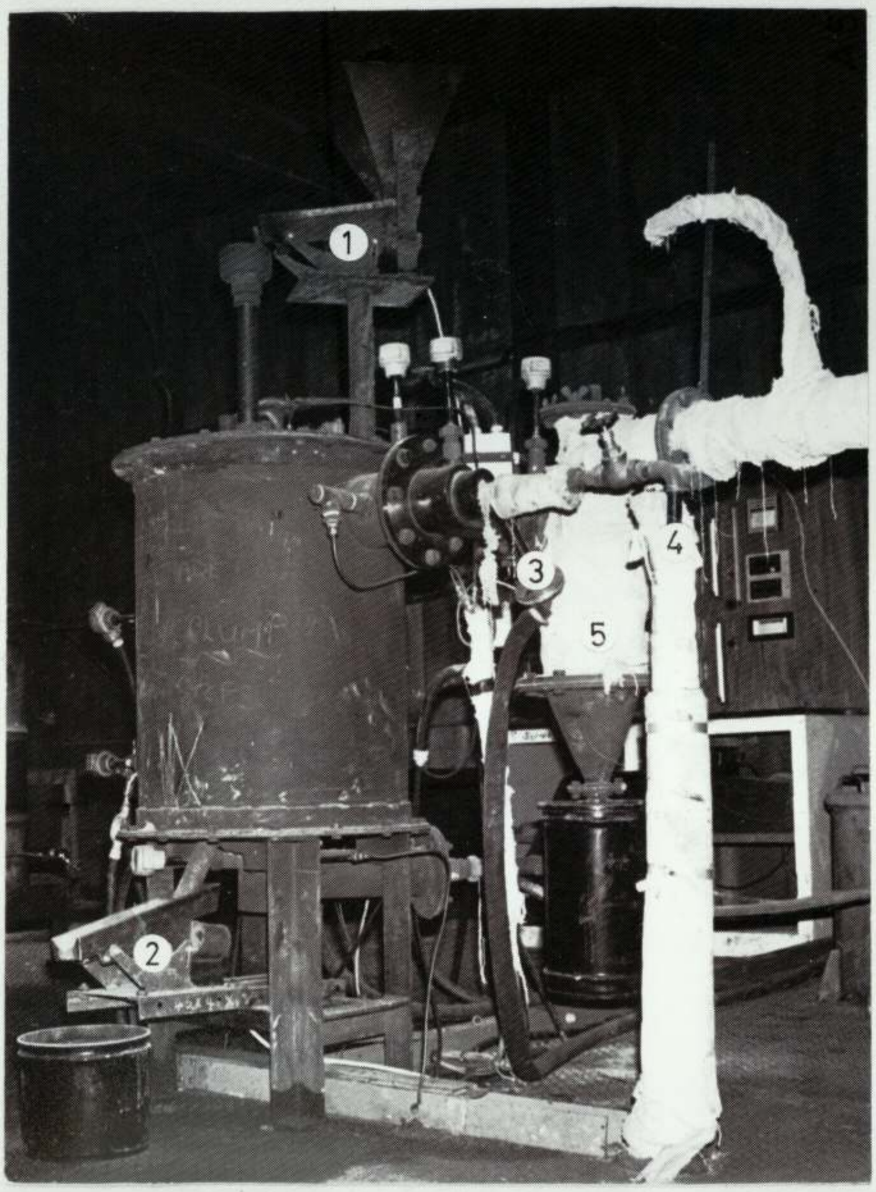


FIGURE 5.8 : Detail of the Fluidised Bed indicating the inlet (1) and outlet (2) vibratory feeders; (3) the tangential air inlet and the steam pipe (4) to the quench vessel; and the 200mm diameter cyclone (5).

FIGURE 5.9 : The twin-compartment Bag Filter. The reverse air cleaning arrangement is out of view but the pulse air cleaning mechanism can be seen(1).

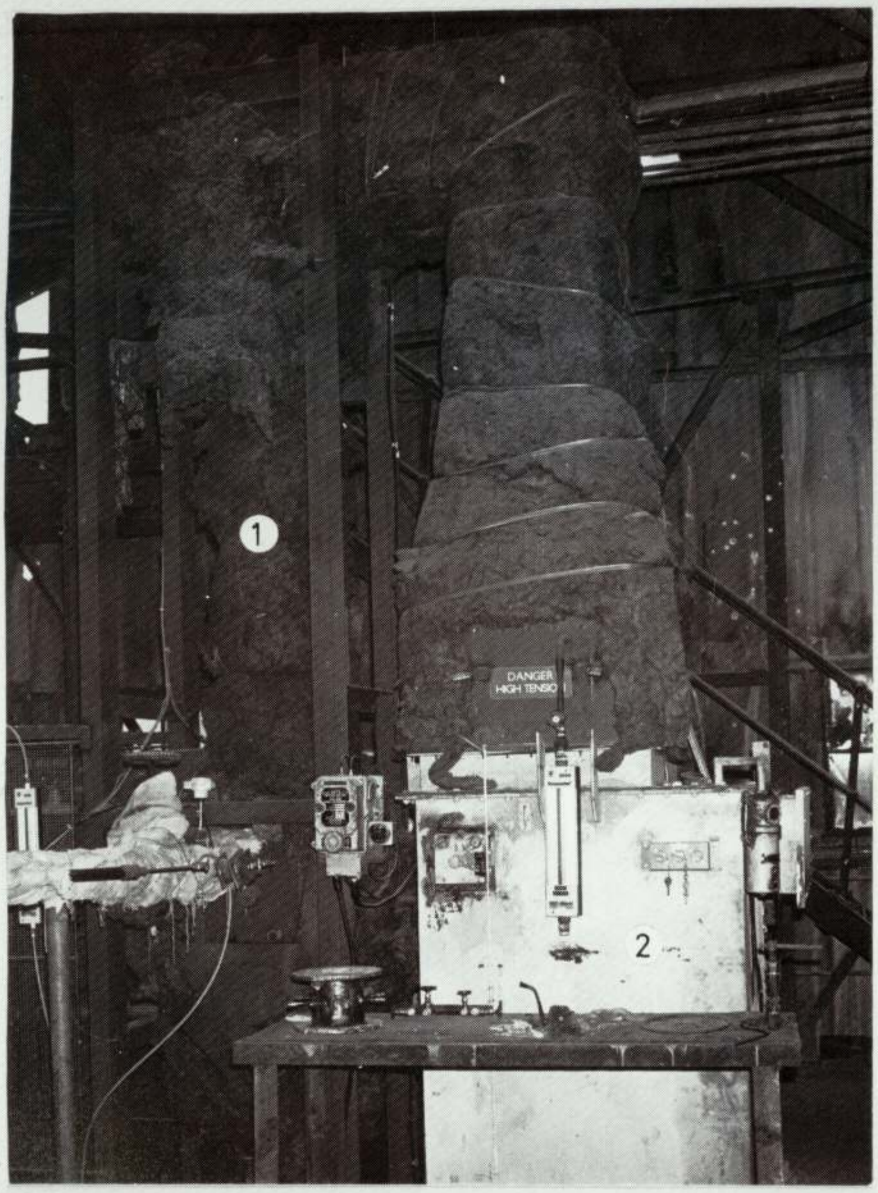


FIGURE 5.10 : The Electrostatic Precipitator showing the collector tube (1) and the transformer-rectifier unit (2). The rotameter seen in the picture metered the quantity of air required to maintain the Venturi inlet for the discharge electrode free of the alkali fume.

TABLE 5.1

Instrumentation Details of the Fluidised Bed

(refer Figure 5.1)

Notation	Description	Instrument Type	Range
(A) FLOW RATE		(Variable Area Flow Meter)	
F1	Pilot Burner Air	'Rotameter' (35A)	0 – 500 l min^{-1}
F2	Pilot Burner Propane	'Rotameter' (14A)	0 – 50 l min^{-1}
F3	Fluidisation – Combustion Air	'Rotameter' (65A)	0 – 1000 l min^{-1}
F4	Supplementary Oxygen	'Rotameter' (24A)	0 – 200 l min^{-1}
F5	Oil Injector Cooling Air	'Rotameter' (18A)	0 – 100 l min^{-1}
F6	Fuel Oil	'Rotameter' (special)	0 – 150 l min^{-1}
F7	Quench Air	'Rotameter' (35K)	0 – 1000 l min^{-1}
(B) TEMPERATURE		(Thermocouple)	
T1	Hot Box (Preheated Air)	Chromel-alumel (sheathed)	0 – 1200°C
T2	Fluidised Bed	Pt/Pt 13Rh (sheathed)	0 – 1400°C
T3	Freeboard	Pt/Pt 13Rh (sheathed)	0 – 1400°C
T4	Fluidised Bed Exit	Pt/Pt 13Rh (sheathed)	0 – 1400°C
T5	Quench Vessel	Chromel-alumel (bare-ended)	0 – 1200°C
T6	Cyclone Inlet	Chromel-alumel (bare-ended)	0 – 1200°C
T7	Cyclone Vessel	Chromel-alumel (bare-ended)	0 – 1200°C
T8	B. Filter/E. Precipitator Inlet	Chromel-alumel (bare-ended)	0 – 1200°C
T9	B. Filter/E. Precipitator Outlet	Chromel-alumel (bare-ended)	0 – 1200°C
T10	Fan Inlet	Chromel-alumel (bare-ended)	0 – 1200°C
(C) PRESSURE			
P1	Hot Box (Distributor + Bed)	Draught Gauge	0 – 1000mm W.G.
P2	Freeboard	Inclined Tube	-5 – +5mm W.G.
P3	Cyclone Differential	Vertical Manometer	0 – 200mm W.G.
P4	B. Filter/E. Precipitator Differential	Vertical Manometer	0 – 200mm W.G.
(D) GAS COMPOSITION			
O_2	Fluidised Bed Exit	'Kent' Paramagnetic	0 – 20%

the 'Rotameter' tended to fluctuate about the set-point and might be subjected to additional inaccuracy.

5.3.2 Temperature Measurement

Two types of thermocouples were used: in the high temperature locations, i.e. the fluidised bed, freeboard and bed exit, mullite-sheathed Pt/Pt-13 Rh 'Type R' thermocouples were used, while ordinary industrial chromel-alumel 'Type K' thermocouples were used in the remaining locations. These thermocouples were left bare-ended except for the one in the hot-box where the thermocouple was clad in a stainless steel sheath. The readings from the 'Type R' thermocouples were monitored on a 'Chessel' 3-point variable speed chart recorder while those of the 'Type K' on a 'West' 12-point digital display unit. Although the errors normally associated with thermocouple and recorder inaccuracy are less than ±1-2%, because of variability of the temperatures being measured, the actual errors could be considerably higher.

5.3.3 Pressure Measurement

A draught gauge with a range of 0-1000mm W.G. was used to measure the pressure drop across the distributor plate and fluidised bed. The pressure drop of the fluidised bed material was deduced by subtracting the pressure reading of the distributor (i.e. before feeding commenced) from the pressure reading at steady fluidisation. Attempts to measure the bed pressure drop directly by inserting a tapping point just above the distributor plate was unsuccessful due to frequent blockages.

The pressure above the freeboard was indicated on an inclined tube water manometer with a range of ±5mm W.G., and the pressure drops across the cyclone, bag filter and electrostatic precipitator were measured on separate vertical tube manometers (0-200mm W.G.).

5.3.4 On-Line Oxygen Analysis

A 'Kent' paramagnetic on-line oxygen analyser was used to monitor the oxygen content of the fluidised bed exhaust gas at the bed exit. However, the readings obtained were generally higher than those calculated from the gas and fuel input and the problem appeared to be caused by the ingress of air from the swirl vessel as well as possibly from the feed inlet pipe. Furthermore, the sampling point was also subjected to frequent blockages. As the precise oxygen level was not considered to be crucial, no serious attempt was made to improve the function of the analyser, which was used simply as an indicator of any relative change that might occur.

5.4 Commissioning of the Rig

5.4.1 Curing of the Fluidised Bed Refractory Lining

Before the fluidised bed was ready for use, it was necessary to properly cure the refractory lining. For the castable refractories in use, the curing process recommended by the manufacturers (G.R.-Stein Refractories) was followed. After completion of the casting, all the exposed surfaces were kept damp by covering with a wet cloth ('wet-curing'). After 2 hours of wet-curing, the refractory was allowed to be air dried for a further 48 hours. On completion of this period, the lining was heated slowly to 110°C using the propane gas burner at a low gas rate and with a large amount of dilution air. After a further 12 hours, the temperature was raised to 150°C and held for about 5 hours more, based on the recommended period of 1 hour per 25mm thickness. The temperature was then raised at

25°C h^{-1} to 650°C and held at this temperature for 5 hours (1 hour per 25mm thickness of castable). Finally, the temperature was raised at 50°C h^{-1} until the working temperature was reached, in this case up to 1300°C. The whole process took about a week to complete.

For normal operation, the refractory was recommended to be heated at a rate not exceeding about 300°C h^{-1}. The time required to achieve steady state, as indicated by the equilibrium temperature of the refractory material, was found to be in excess of 12 hours. This was regarded as impractical to operate and was ignored in the experiments described here.

5.4.2 Determination of the Minimum Fluidisation Velocity Needed

The minimum velocity needed to fluidise the dust pellets was crudely determined following the usual procedure of taking pressure drop measurements across the bed over a range of gas flow rates until it was fully fluidised (Davidson and Harrison, 1971). The pressure drop across the bed was obtained by subtracting the pressure drop across the distributor, which was first determined, from the overall pressure drop readings. The results obtained, together with the properties of the air and solid used, are shown in Figure 5.11. Various heights of bed material were investigated, but for clarity only the 75mm and 225mm bed heights are shown. The minimum fluidisation velocity was found to be 1.5 m s^{-1} for the 75mm bed and 1.7 m s^{-1} for the 225mm bed. The slight increase in the apparent minimum fluidisation velocity for a deeper bed has also been noted by other observers (Geldart and Cranfield, 1972) and is probably due to the wall effect or other imperfections (Davidson and Harrison, 1971). Compared with the calculated U_{mf} of 1.2 ms^{-1}, the agreement is considered to be fair. The effect of temperature was not determined but as can be

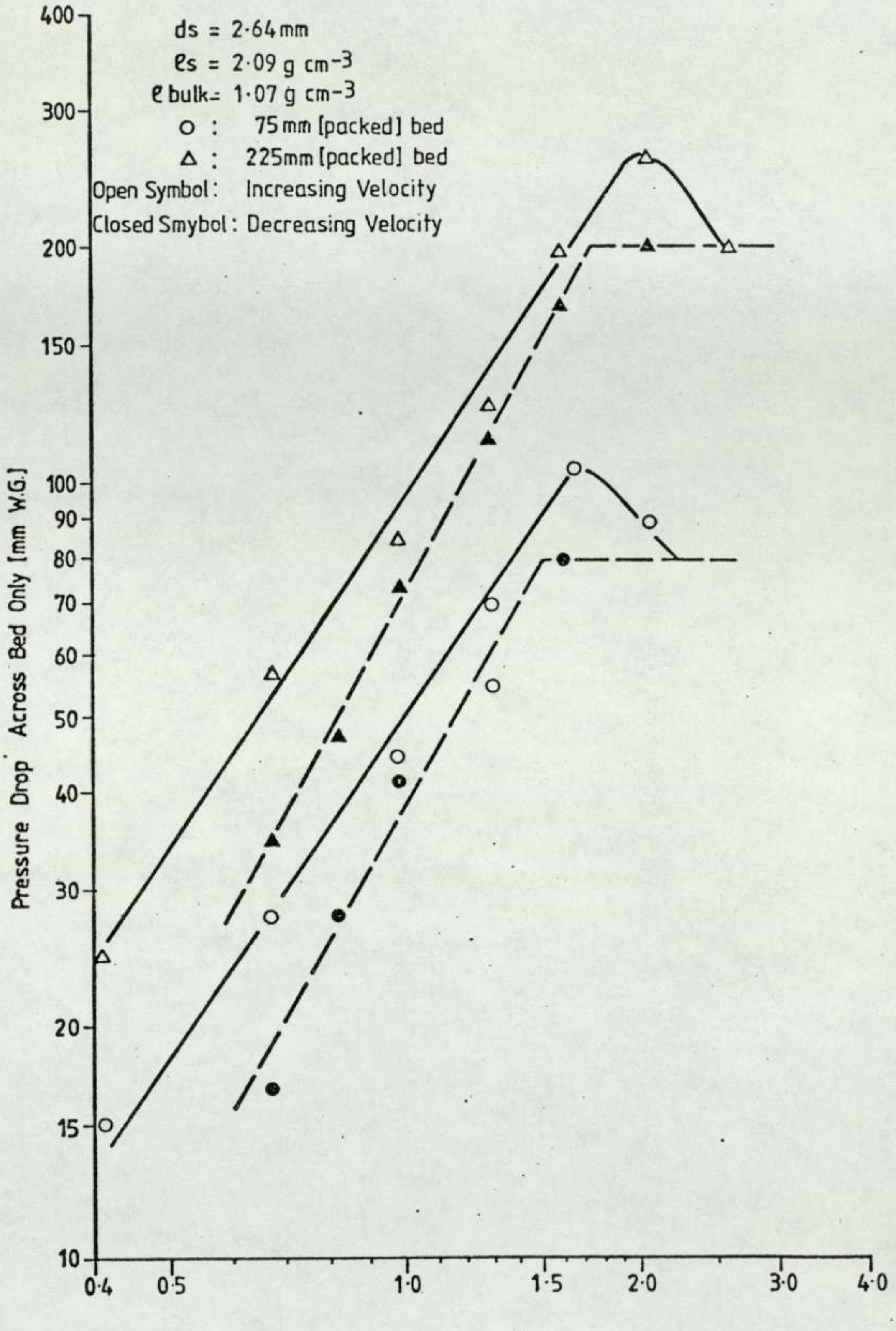


FIGURE 5.11

Pressure Drop Measurements Over Fixed and Fluidised Beds seen in Figure 4.9, U_{mf} can be increased or decreased at elevated temperature depending on the particle size (see also Teoman and Botterill, 1978; Doheim and Collinge, 1978).

5.5 Test Procedure

5.5.1 Preliminary Preparation

For most of the tests, the feed used was obtained from the feed preparation experiments conducted concurrently with the present work but in a small number of tests, a 560mm diameter dish noduliser and a 150mm diameter fluidised bed drier were used to produce the feed material as required. Prior to starting up the fluidised bed, the feed hopper was filled with a known quantity of feed pellets to be tested and the product discharge pipe was sealed with a small known weight of pre-calcined pellets. Depending on the filter system to be used, the electric heaters were switched on to warm up the equipment. The compressor was then turned on, taking a few minutes to reach normal operation. A small volume of cooling air was admitted in the double-concentric oil injection tube and the instrument panel was switched on and checked. The fluidised bed was then ready for start-up.

5.5.2 Start-Up and Shut-Down Procedure

The procedure adopted for start-up was as follows. First, the propane-air burner was ignited with approximately 10 $l\ min^{-1}$ of propane and 250 $l\ min^{-1}$ of air and simultaneously, about 400 $l\ min^{-1}$ of fluidising air was admitted to keep the temperature of the hot-box to below about 750°C in order to reduce the thermal stresses on the distributor plate and bed refractory. The fluidised bed was left to be heated at a gradual rate of about 300°C h^{-1}, as recommended for the refractory lining in use, for approximately 2 hours until the temperature of the empty bed reached above 600°C. The oil injector pump was then switched on and a small quantity of fuel oil (about 10-20 l min^{-1}) was injected into the bed. If the oil failed to ignite, it meant the bed was insufficiently warm.

Once combustion was initiated, the air quench and exhaust fans were switched on. The suction of the exhaust fan was adjusted to give a pressure of ±0.2mm W.G. in the freeboard. This ensured that any air leakages via the feed pipe was kept to a minimum. The bed temperature was raised graduallyby increasing the rate of oil injection over a further 2 hours. When the bed reached the working temperature ($\sim$1200°C), the air was replaced either fully (in the case of the 100mm bed) or partially (in the case of the 150mm bed) with oxygen gas. The various gas and oil flow rates were calculated beforehand to give the desired fluidisation velocity and combustion conditions. Once the required conditions were estabilised, the bed was ready for feeding.

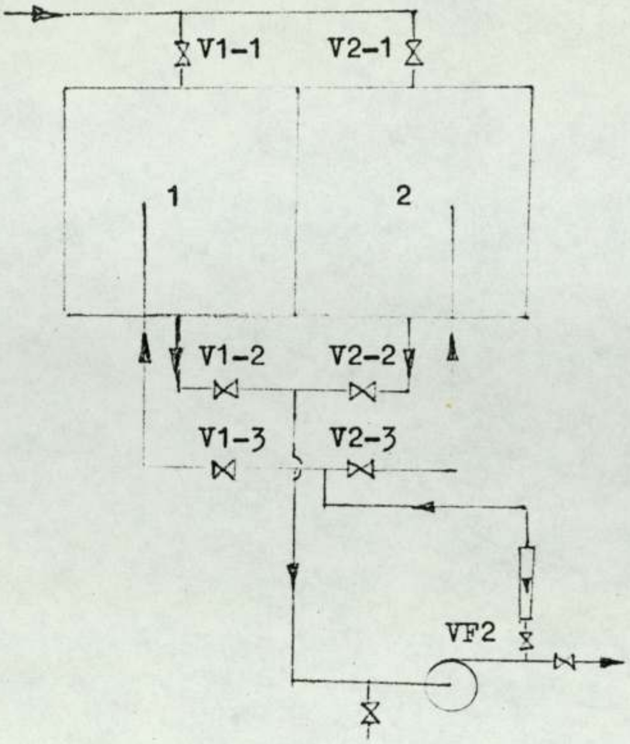
The shut-down procedure, after the removal of the bed material, was basically the reversal of the above sequence, i.e. turned off the oil, then oxygen, air, and finally the exhauster fan.

5.5.3 Establishment of a Stable Fluidised Bed

At the intended working temperature, the dust pellets to be calcined were slowly trickled into the bed. It was important to ensure that initially, the feed was kept at a fairly low and steady rate. Otherwise, the bed temperature might rise or fall rapidly, leading to either bed fusion or unsatisfactory combustion. It was found that the best way to control the bed temperature at this stage was to vary the feed input rate rather than the oil input rate, as soon as the temperature showed any sign of variation. Usually, about an hour was required to obtain a stable fluidising bed of 300-350mm in height. In some of the earliest tests, this period was reduced considerably by using pre-calcined pellets to build up a stable bed, however this technique tended to complicate the evaluation of results and was not followed in the subsequent tests. Once a stable bed had been established, the discharge vibratory feeder was started and the pre-calcined pellets used to seal the bed were first emptied out separately. This was possible because the initial bed product usually required 'rodding out'. The bed temperature was maintained constant by regulating either the rate of feed input or, where necessary, the fuel oil input. The height of the fluidised bed normally remained relatively constant.

5.5.4 Treatment of the Fluidised Bed Exhaust Gas

The fluidised bed exhaust gas was quenched to the required temperature by controlling the quantity of cooling air added and passed first into the cyclone and then either the bag filter or the electrostatic precipitator. When using the bag filter, the gas was initially allowed to enter one of the two filter compartments until the pressure differential had increased by about 100mm W.G., indicating that cleaning of the bags was necessary. The cleaning was effected by isolating the compartment involved and reversing the flow of part of the flue gas in order to collapse the bags, following the sequence shown in Figure 5.12. However, because of fairly unsatisfactory cleaning achieved, additional pulses of compressed air directed at the bags were also used to help dislodge the alkali material collected.



OPERATION	FILTER UNIT 1	FILTER UNIT 2
NORMAL RUNNING	V2-2, VF-2 CLOSED	V1-2, VF-2 CLOSED
CLEANING	OPEN V2-2 CLOSE V1-2 CLOSE V2-3 OPEN V1-3 OPEN VF-2 for 10 secs. then reverse procedure.	OPEN V1-2 CLOSE V2-2 CLOSE V1-3 OPEN V2-3 OPEN VF-2 for 10 secs. then reverse procedure.
	Repeat cleaning sequence as required	

FIGURE 5.12

Procedure for Reverse Air Cleaning

When using the electrostatic precipitator, the 'Castel' inter-lock system provided for safety reasons was first released with a master key and the high tension supply switched on. The voltage was gradually increased by turning up the voltage regulator until sparkings in the precipitator tube became audible. Sparking is essentially an advanced stage of corona, i.e. a local discharge which fails to propagate itself, in which complete breakdown of the gas occurs along a given path (Dorman, 1974). In theory, precipitators should be operated at the highest voltage possible without sparking. However, since this is difficult to ascertain, it is normal practice, according to the manufacturer, to operate with some sparking, the optimum rate was said to be about 100 min^{-1} (Puttick, 1975).

The electrodes were cleaned at periodic intervals by switching on the rapping hammer. As will be seen later, the efficiency of the precipitator was fairly poor and in several tests, water vapour, which is a well known gas conditioning agent for enhancing the performance of precipitators (Klipstein, 1975), was added to the exhaust gases in the form of steam through an injection point at the air quench vessel as shown in Figures 5.2 and 5.8.

5.5.5 Data Logging and Material Quantifying and Sampling

With the exception of the fluidised bed, freeboard and exit temperatures which were on continuous records, the operating conditions of the test were logged at half hourly intervals. The quantity of dust processed, and any material deposits obtained after shut-down were separately weighed and after thorough mixing in a small drum, approximately 500 g samples of each material were sent to the laboratory for chemical and physical analyses. The essential chemical analyses were the alkali and lime components which involved flame photometry for K_2O and Na_2O, 'Volhard' back titration for Cl, and spectro-photometry for SO_3. Combined and uncombined (free) CaO were determined by, respectively, E.D.T.A. (Ethylenediaminetetra-acetic acid) and KCl titration. The physical analysis involved basically the determination of particle size distribution and densities of selected samples in certain tests.

CHAPTER 6

RESULTS AND DISCUSSION

Summary

Northfleet and Westbury flue dust pellets and some Northfleet flue dust flakes of 1-5mm in size were calcined in the 100mm and 150mm diameter fluidised beds. The feed used included normal as well as high alkali dusts and the range of alkali compositions covered was as follows: 4.4-13.5% K_2O, 0.6-1.3% Na_2O, 0.7-6.3% Cl and 2.0-12.2% SO_3. The quantity of dust calcined varied from 2-30 kg and the duration of calcining ranged from 1-6 h. Because of the need to minimise the amount of dust carry-over and to avoid bed fusion, most of the tests were conducted at a fluidisation velocity of between 3 and 4 m s^{-1} and an average bed temperature of up to 1260°C.

It was established that a relatively low alkali, clinker-like material could be produced. The residual Cl and free lime contents were generally satisfactory and appeared to be virtually independent of the bed temperature and affected mainly by the variability of the material residence time for the conditions investigated. The amount of K_2O volatilised was strictly determined by the partial pressure which varied exponentially with the bed temperature, i.e. $p = a \exp(bT_b)$. The constant and exponent derived for Northfleet and Westbury dusts were, respectively, [$a = 1.95 \times 10^{-13}$; $b = 0.018$] and [$a = 1.26 \times 10^{-11}$; $b = 0.015$]. The coefficients of determination for the correlations were

0.97 and 0.96 respectively.

Applying the above equations to the case of typical Northfleet and Westbury flue dusts, it is shown that the requirement of less than 4% K_2O in the calcined product should be attained for the Northfleet dust calcined under normal condition at a temperature of below 1280°C. However, for Westbury dust, the gas:solid ratio needed is considerably beyond the normal range of calcination conditions. The possibility of enhancing K_2O volatilisation is discussed and the related results obtained from an oil-fired laboratory furnace are included. The characteristics of Na_2O and SO_3 volatilisation, which are of little relevance to the present work, are considered briefly.

Several methods of treating the fluidised bed exhaust gases to separate the alkali product had been investigated. It was found that the cyclone was incapable of collecting the very fine alkali fume, which has a size range predominantly between 0.8 μm and 5 μm. The bag filter and electrostatic precipitator were more successful but because of various operating problems, the efficiency obtained was low and a considerable amount of alkali product was not accounted for. Nevertheless, from the characteristics of the material determined, which included measurements of the electrical resistivity of the alkali fume under laboratory and in-situ conditions, the correct design of a more efficient plant should not present any major problem.

6.1 Introduction

A total of 50-60 separate tests were carried out from early 1975 to mid-1977, between modifications to the exhaust gas systems and various other changes. However, mainly because of early problems with the fluidisation velocity and material build-ups in the exhaust gas system, not all the tests were successful. In addition, because of excessive variability of the fluidised bed temperature and the possible problem of bed fusion, some of the tests were aborted. The operating characteristics and constraints of the experiment will be described but for the purpose of evaluating the calcination characteristics of the dusts, only the data from 36 relatively stable runs are presented.

In addition to the present investigation, 2 series of larger scale trials involving the calcination of Northfleet flue dust pellets in a 300mm diameter fluidised bed (Figure 6.1) at Buxton, U.K., and Westbury flue dust in a 450mm diameter Pyzel fluidised bed (Figure 6.2) at Catasauqua, U.S.A., were carried out separately. Both the pilot plant facilities were on hire, and the objective was to demonstrate the feasibility of the fluidised bed processing options on a larger scale. Details of the trials are contained in various BCI internal reports (Evans, 1976 c & d; Evans and Haspel, 1976) but where relevant, the results will be compared with the present findings.

6.2 Experimental Conditions and Constraints

6.2.1 Operating Conditions of the 100/150mm Fluidised Beds

The input variables and operating conditions of the 36 tests are presented in Tables E.1-E.4 in Appendix E. They comprise equal numbers of tests

FIGURE 6.1

The 300mm Fluidised Bed Rig Used in the Northfleet Flue Dust Calcination Trials at Buxton, England

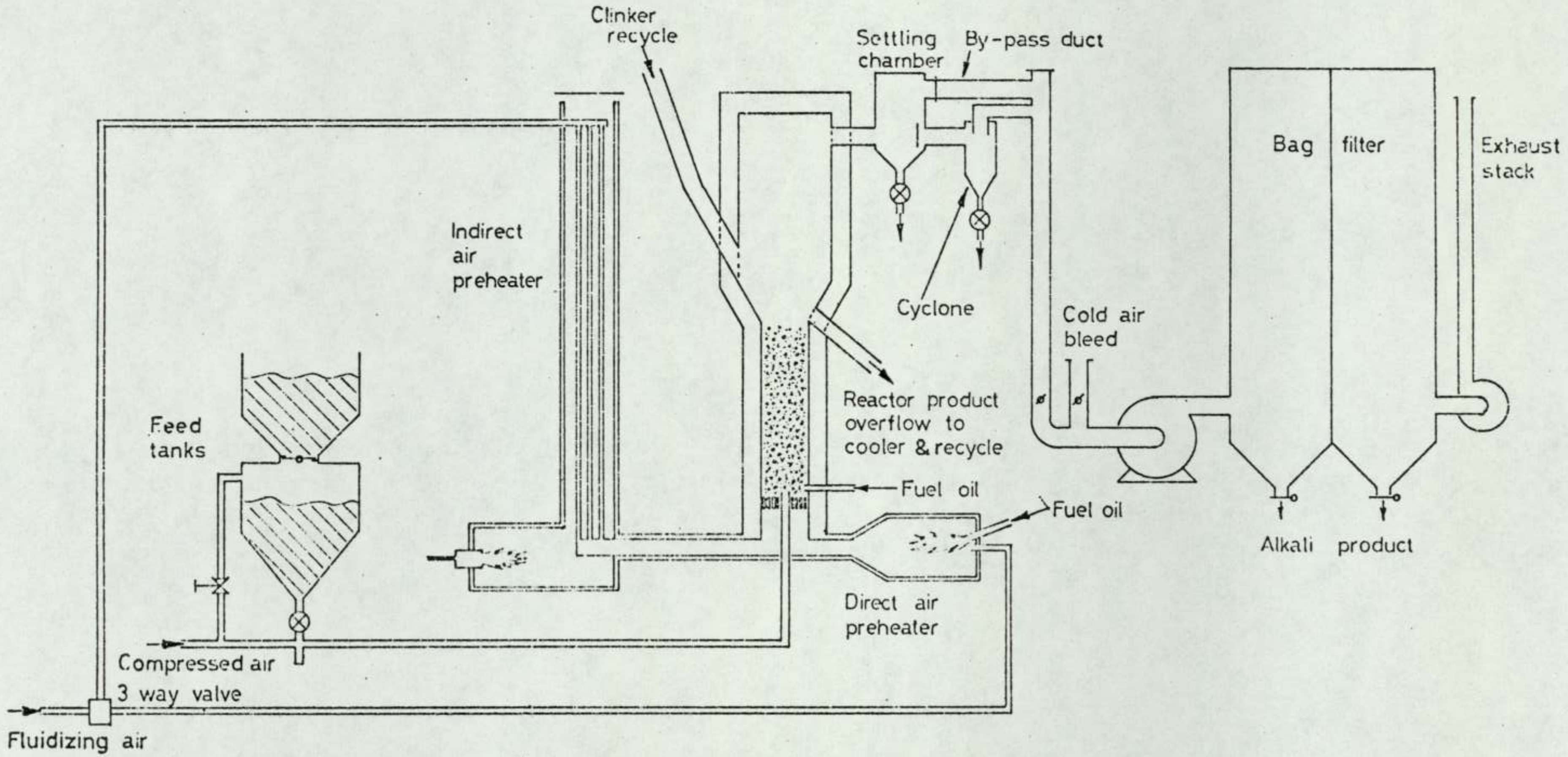


FIGURE 6.2

The 450mm 'Pyzel' Fluidised Bed Plant used in the Westbury Flue Dust Calcination Trial at Catasauqua, U.S.A.

conducted in the 100mm (Tests 1-18) and 150mm (Tests 19-36) diameter beds. All the tests were performed on a normal working day basis and because of the long period needed to bring a bed to the working condition, the actual dust processing time was relatively short, ranging from 1-6 h, and the amount of dust processed in any given test varied from 2-30 kg.

With the exceptions of Tests 11, 12, 16-18 and 23, where flakes of Northfleet flue dust were calcined, pre-dried pellets of Northfleet or Westbury flue dust were used in the remaining tests. Both the feed materials fluidised readily and provided the bed height was not less than about 200mm and the pressure drop of the bed was adequate, say, above 200mm W.G., the in-situ combustion of the fuel oil seemed also to be satisfactory. The combustion was confined mainly within the fluidised bed and the bed flowed incandescently without any visible flame. Typically, less than 0.5% CO was detected in the freeboard.

For various reasons to be discussed in the following section, most of the tests were performed at a fluidisation velocity of 3-4 m s^{-1} and a bed temperature of 1200-1260°C. The range of dust throughput varied from 3-10 kg h^{-1} and the mean residence time varied from 14-59 min. An excess of oxygen for combustion was normally maintained. A summary of the key operating factors is given in Table 6.1. Note that the fluidisation velocity shown does not include the CO_2 and H_2O evolved from the dust feed. If included, the velocity is increased by between 0.1 and 0.4 m s^{-1} depending on the feed rate and dust composition. Note also that the exit gas $[O_2]$ shown is based on the calculated rather than the measured value, as the reading of the on-line oxygen analyser was often not available because of blockage of the sampling point or was higher than would be

TABLE 6.1

Operating Conditions of the 100mm (Tests 1-18) and 150mm (Tests 19-36) Fluidised Bed Experiments

Test Number	Feed Throughput F_i (kg/h)	Bed Temperature T_b (°C)	Fluidisation Velocity U_o (m/s)	Pressure Drop ΔP_3 (mm W.G.)	Bed Inventory W (kg)	Solid Residence Time τ_s (min)	Exit Gas $[O_2]$ (%)
1	4.8	1120	9.1	360	1.1	20	1
2	8.4	1260	4.7	410	2.2	25	9
3	6.9	1220	4.5	450	2.0	24	10
4	7.3	1260	4.3	400	2.0	23	6
5	6.6	1260	4.5	350	2.0	28	18
6	7.2	1240	3.9	240	1.4	20	14
7	7.6	1160	3.2	750	1.6	21	19
8	4.4	1180	4.1	550	1.2	28	15
9	4.5	1180	3.7	950	1.6	38	10
10	7.7	1240	3.8	650	1.6	21	12
11	1.9	1200	3.7	180	0.6	38	8
12	3.4	1200	3.3	220	1.1	30	6
13	5.4	1240	3.7	250	1.4	26	7
14	5.1	1200	3.3	200	1.3	25	2
15	4.2	1240	3.1	530	1.4	31	3
16	3.8	1220	3.2	360	1.4	33	1
17	3.2	1220	3.3	300	1.1	29	1
18	3.4	1220	3.3	220	0.9	21	1
19	5.9	1220	3.8	150	1.8	27	-1
20	5.8	1200	3.8	300	1.8	31	0
21	5.5	1200	3.7	300	1.8	35	1
22	9.7	1220	4.0	340	2.1	23	1
23	4.4	1200	3.2	240	0.7	14	0
24	7.2	1240	3.2	350	1.8	25	0
25	6.8	1240	3.2	350	1.8	29	-3
26	4.2	1220	2.9	260	1.8	46	2
27	4.1	1200	3.6	150	1.6	42	4
28	5.1	1180	3.7	170	2.2	40	0
29	3.6	1240	3.7	320	2.2	53	1
30	3.3	1220	3.9	180	1.8	57	0
31	5.5	1240	4.2	240	2.3	42	4
32	5.0	1200	3.8	210	2.3	43	6
33	4.1	1220	3.0	490	2.5	59	3
34	4.4	1180	2.8	450	2.5	52	3
35	4.5	1160	2.8	430	2.7	53	10
36	6.3	1120	2.7	420	2.8	37	3

expected, probably as a result of air inleak into the sampling line.

6.2.2 Operating Characteristics and Constraints of the Fluidised Beds

The operation of the fluidised beds was subject to a number of constraints, not least of which was the fluidisation velocity. In the initial experiments when oxygen was not introduced, the gas velocity required to sustain the rate of heat input was in the order of 9 m s^{-1}. This caused substantial oil combustion to occur outside the bed as well as an excessive amount of dust carry-over - as much as 50% of the feed. The resulting combination of high exit gas temperature and dust loading led to severe build-up of material in the quench and cyclone system and caused many of the early experiments to be aborted after only a short period. These results of tests are excluded from this presentation, except Test 1, which is included for the purpose of illustration.

The optimum fluidisation velocity appeared to be in the order of 3-4 m s^{-1}. It was undesirable to operate at levels significantly below 3 m s^{-1} because of the poor mixing which followed. In several instances, the combination of low fluidisation velocity and high operating bed temperature (~1250°C) gave rise to bed fusion. The primary cause was not clearly ascertained, but in most cases it seemed to arise when there was a sudden fall in the fluidisation velocity (as a result of variation in the compressed air supply) which caused the bed to defluidise and fuse. Microscopic examination of a typical fused sample, Figure 6.3, showed that the particles were bound by silica melts, such as are normally formed at temperatures in excess of 1250°C. In the core of the sample, lath-shaped crystals of alite were present, suggesting that the central material must have experienced a temperature in excess of 1600°C (Morton, 1975),

FIGURE 6.3

Typical Sample of Fused Material

Following Bed Defluidisation

probably after the bed had collapsed.

The maximum safe working temperature was not ascertained but tests were successfully conducted at temperatures of up to about 1320°C over short periods. However, because of the sensitivity of the small bed to any change in the feed and fuel input conditions, most of the tests were performed well below 1300°C. The Westbury dust was found, in general, to be more susceptible to the risk of fusion, probably because of the presence of a higher concentration of alkali sulphate which tended to remain on the surface of the particles and can form a low temperature eutectic melt with calcium sulphate and promote adhesion, as will be shown later.

Preheating of the combustion gases was found to be necessary to support the combustion of fuel oil in the bed. The combined heat input of the propane gas and fuel oil, without allowing for the heat losses of the hot box, was typically equivalent to 4 MW m^{-2} in the 100mm bed and 3 MW m^{-2} in the 150mm bed. Both these values are considerably above the 2.56 MW m^{-2} reported by Sanari and Kadowaki (1970) for calcining cement in an oil-fired fluidised bed and the 2.52 MW m^{-2} cited by Skinner (1971) as being typical of a fluidised bed coal combustor. This is mainly due to the practice of oxygen enrichment, which also accounts for the higher heat release obtained in the 100mm bed.

There was no significant build-up of material in the fluidised bed and in general, provided the bed temperature was kept below 1280°C and the fluidisation velocity between 3 m s^{-1} and 4 m s^{-1}, the operation of the fluidised bed did not present any major problem.

6.2.3 Quenching of the Fluidised Bed Gases and the Problem of Build-up

Due to high heat losses and the entering cold feed, the gases leaving the fluidised bed cooled rapidly and the temperature usually dropped to about 1000°C in the freeboard. In the early experiments where the dust carry-over was high and there was considerable combustion taking place outside the bed, a wide-spread of material build-up ranging from 'thin' to several mm thick was found in the quench vessel, cyclone and the inter-connecting duct.

Microscopic and XRD determination showed this build-up to consist mainly of inter-locking crystals of $CaSO_4 \cdot K_2SO_4 \cdot H_2O$ (or Syngenite), KCl, $(Na, K)_2SO_4$ and traces of K_2SO_4 and calcite. The syngenite was thought to have formed after deposition and probably after removal of the sample, as a result of hydration of $CaSO_4$ and K_2SO_4 or the double sulphate $2CaSO_4 \cdot K_2SO_4$ (Morton, 1975). Similar build-up was reported in the Buxton and Catasauqua trials when the gas was inadequately quenched, i.e. above about 700°C. For the present experiments, when the gas temperature was quenched to below 600°C and the problem of excessive dust carry-over was avoided, the problem of build-up was also eliminated.

Another form of build-up was a soft white deposit of virtually pure alkali chlorides and sulphates; this was found only in some of the 100mm bed experiments, the Buxton and Catasauqua trials and not in the 150mm bed experiments. This tended to occur in the cyclone outlet and inlet (around the thermocouple) and to become more severe when the cyclone was lagged in Tests 2-5, as well as when the alkali chloride level in the feed was high (Tests 11 and 12), suggesting that high turbulence and alkali loading may have been the main causes. When a larger cyclone (200mm) was installed for the 150mm bed, and the dust pellet size was increased from about 50 to 100mm the problem was overcome.

Apart from these early problems, there was no other major difficulty in the quenching of the fluidised bed gases. A summary of the mean operating conditions of the quench and cyclone system is given in Table E.3 (Appendix E).

6.2.4 Alkali Fume Collection

The use of a cyclone for collecting the condensed alkali product in the initial tests proved totally unsuccessful. As will be seen shortly,–the material collected was comprised largely of carry-over from decrepitated dust pellets with negligible alkali beneficiation (Tests 1-5). An attempt was made to pre-separate the coarser carry-over material (Tests 6-9) by providing a large drop-out chamber made from a disused 45 gallon oil drum ($\sim 0.2\ m^3$). It was also hoped that with the longer retention time provided, there was greater opportunity for the alkali fume to increase to a larger size via further agglomeration. Although some beneficiation of alkali was achieved, most of the alkali product still escaped collection.

The installation of a bag filter and electrostatic precipitator in the remaining tests achieved only partial success. The alkali fume was recovered but the collection efficiency was unsatisfactory, ranging from about 30-80% in the bag filter and 5-70% in the electrostatic precipitator.

The problem seemed to arise mainly from the high heat losses suffered in both the units, in spite of extensive insulation and trace heating. As can be seen from Table E.4, a large temperature gradient existed between the gas inlet and outlet, which is particularly detrimental to the operation of the electrostatic precipitator.

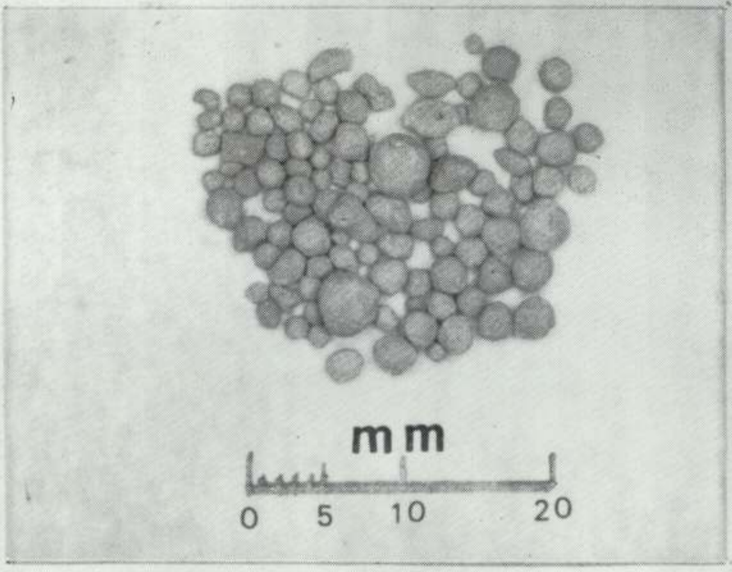
Some improvement in the precipitator performance was obtained in Tests 27-32 when a small amount of steam was injected into the quench vessel to condition the gas.

In the case of the bag filter, a condensation problem was suspected and the reverse air fabric cleaning was found to be inadequate, leaving a considerable quantity of material adhering to the bags. However, because of competing interests and requirements, no serious attempts were made to improve the performance of these collectors, although in retrospect, this should have been one of the major priorities, will become evident later. The main operating conditions of the bag filter and electrostatic precipitator are shown in Table E.4.

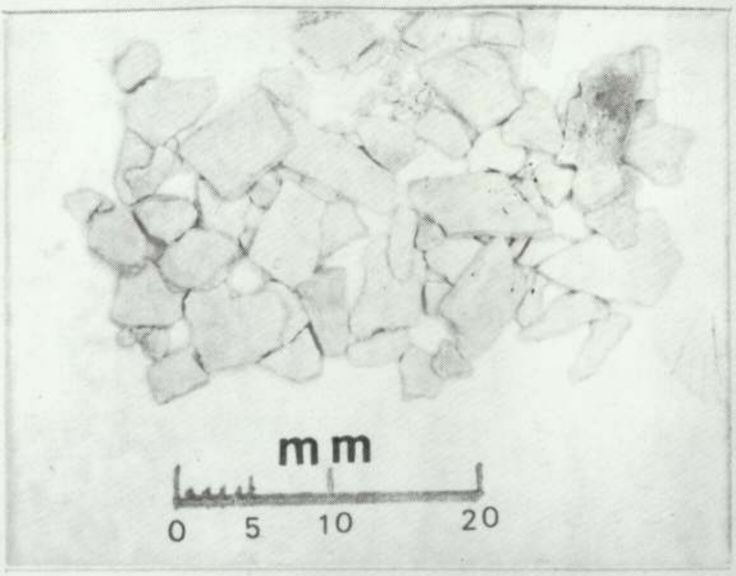
6.3 Analytical Data and Material Balance

6.3.1 Physical Characteristics of the Feed and Products

The 2 types of feed used in the experiments are shown in Figure 6.4. Both the agglomerates had a size range of 0.5-5mm and despite their major difference in shape, there was little noticeable difference in the fluidisation behaviour. After calcining, the agglomerates decreased in size, partly due to densification resulting from decarbonation and clinkering and partly to fragmentation, which arose from the shrinkage cracking and 'onion shelling', as illustrated in Figure 6.5. The particle size distribution of typical feed and calcined pellets is shown in



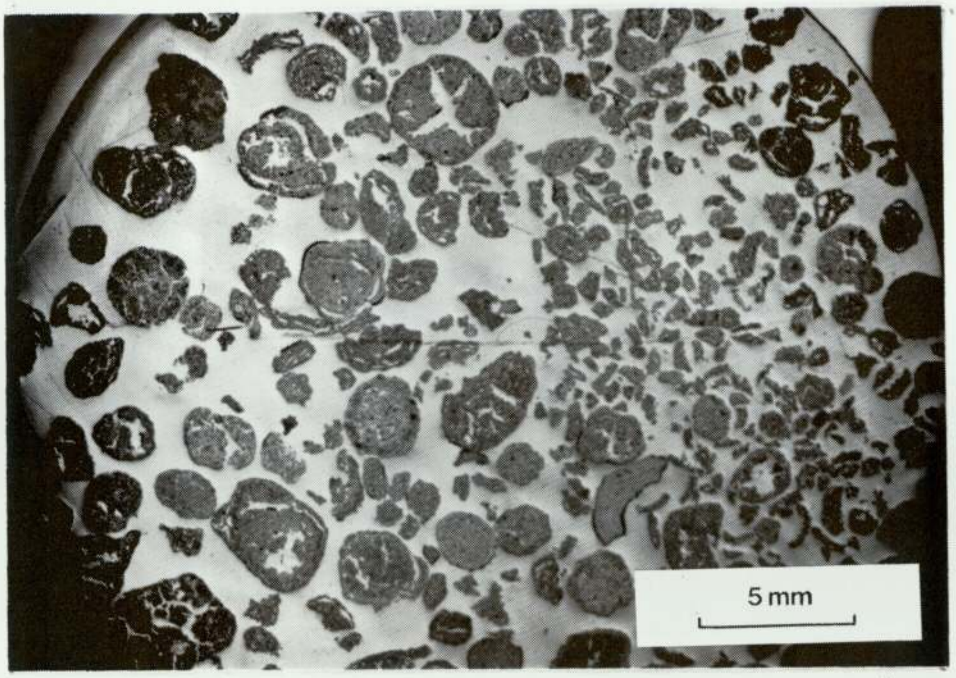
(a)



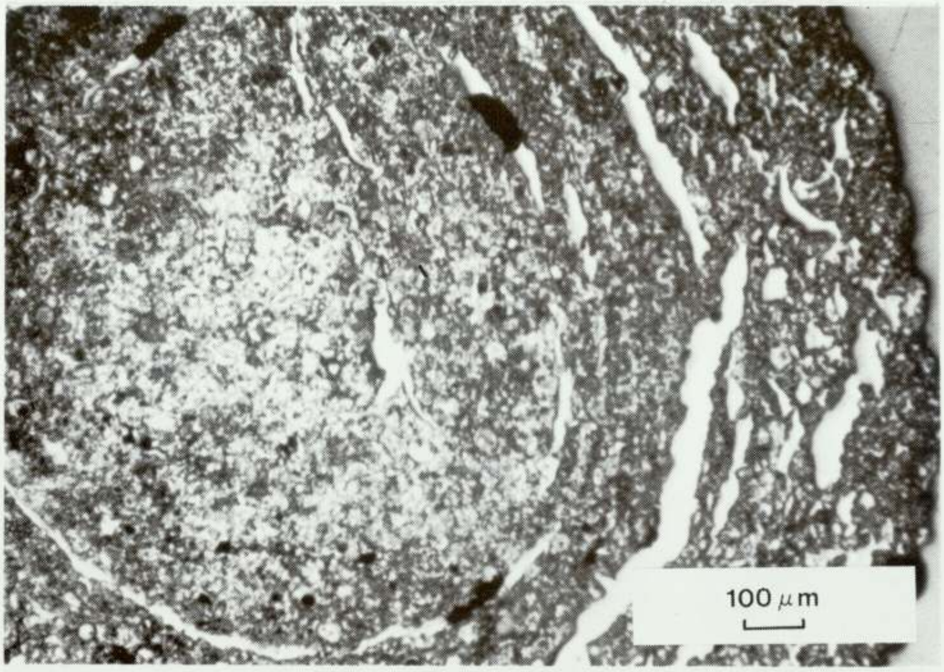
(b)

FIGURE 6.4

Typical Samples of (a) Flue Dust Pellets
and (b) Northfleet Dust Flakes
Used in the Experiment



(a) x4



(b) x 80

FIGURE 6.5

Calcining the pellets has produced both shrinkage cracking and "onion shelling" resulting in a high proportion of broken material as shown in (a). The "onion shelling" and shrinkage cracking can be more clearly seen at a higher magnification in (b). Note also the high overall porosity

Figure 6.6. The two materials had a surface mean diameter of 2mm and 1.3mm respectively, which is equivalent to a 35% reduction in the mean diameter.

The particle densities of the feed and calcined pellets were typically about 1400 kg m^{-3} and 1800 kg m^{-3}, respectively. Compared with the corresponding material densities of 2800 kg m^{-3} and 3200 kg m^{-3} calculated from the compositions, it is evident that both the feed and calcined pellets were highly porous and should be readily susceptible to loss of alkalis. The physical presence of alkalis in the feed was not readily detectable except in about 10% of the feed where an alkali-rich skin of approximately 10 μm in thickness was observed. In a separate investigation to determine the feasibility of removing the alkalis from dust pellets via physical attrition, the alkali-rich skin was found to consist mainly of KCl which was thought to have formed as a result of recrystallisation during the pelletisation and drying stage (Khor and Tettmar, 1976). A summary of the physical properties of the feed and calcined pellets is presented in Table 6.2.

The particle size distribution of the carry-over material tended to be more variable, partly because of the differences in the experimental conditions and also because of the variability of the feed quality. Figure 6.7 shows the particle size distribution of the cyclone material collected in the 100mm and 200mm cyclones under various conditions. It can be seen that the particle size distribution of the material collected in the 100mm cyclone was marginally finer than that in the 200mm cyclone, as would be expected from the higher pressure drop. However, there was little significant effect of cyclone efficiency on quality of the alkali product, as is shown later.

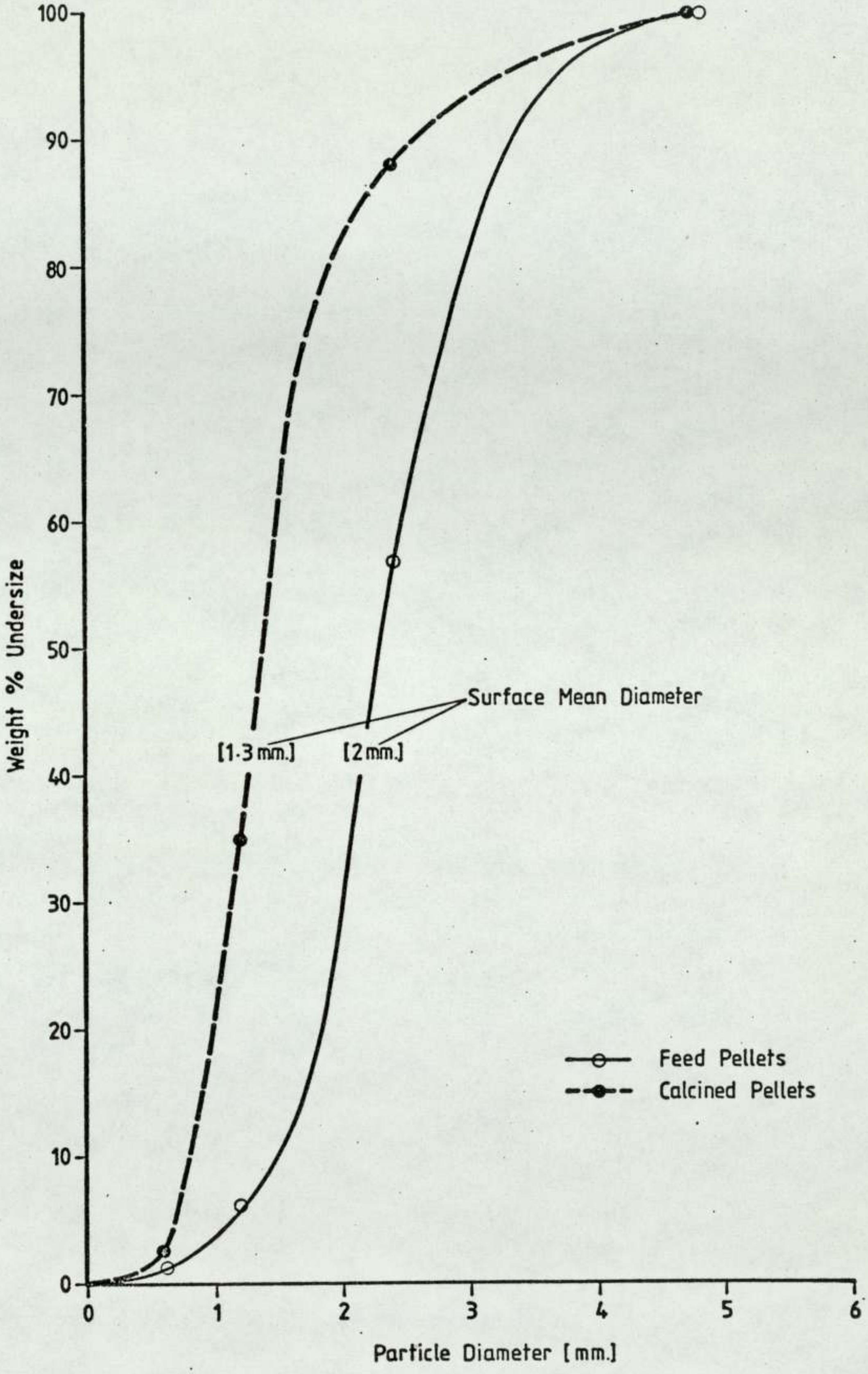


FIGURE 6.6

Particle Size Distribution of Typical Feed and Calcined Pellets

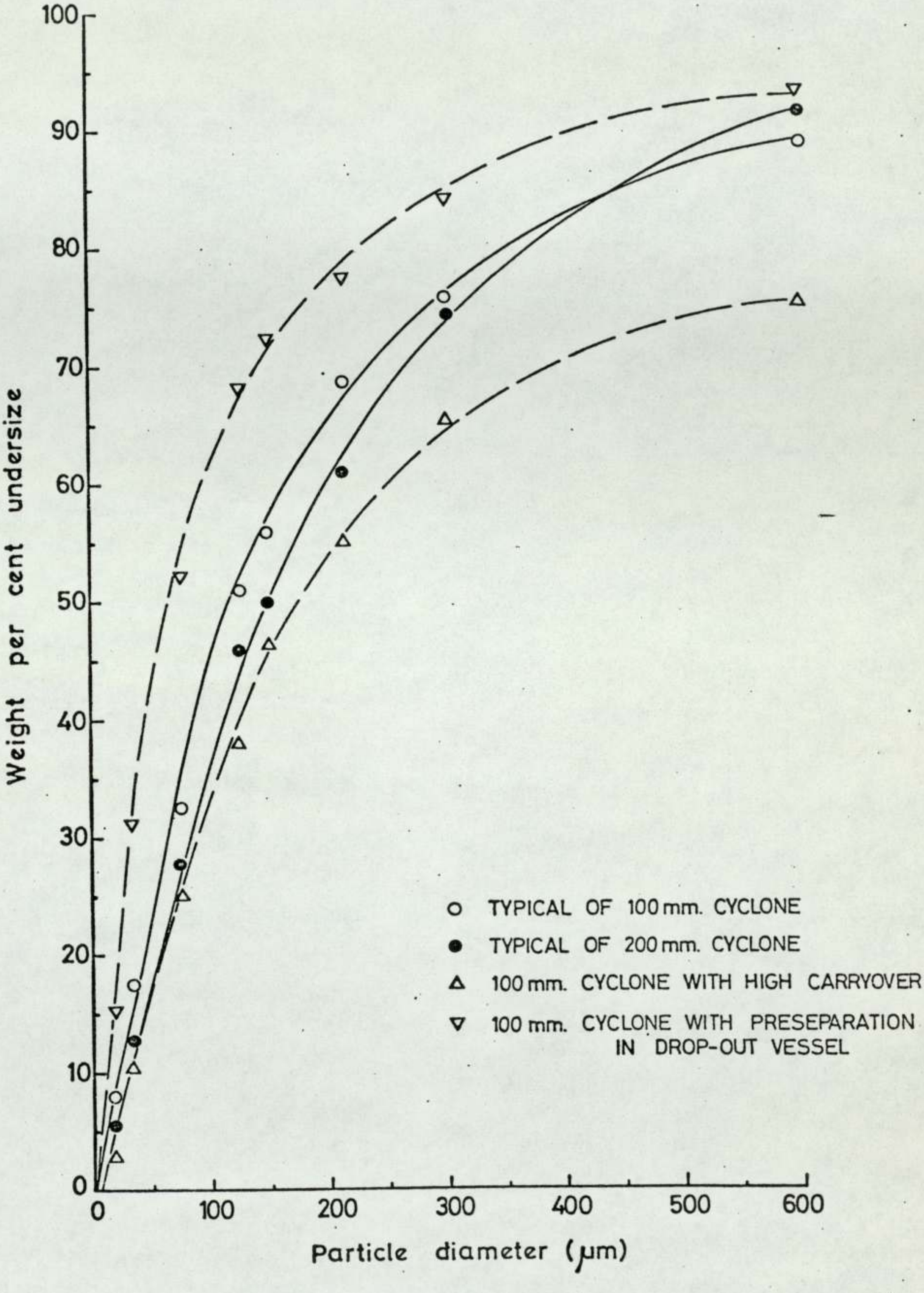


FIGURE 6.7

Particle Size Distribution of Cyclone Materials Collected Under Various Conditions

TABLE 6.2

Physical Properties of the Feed and Calcined Pellets

	Dried Feed		Calcined Product	
	Typical	(Range)	Typical	(Range)
Pellet Size Range (mm)	0-5		0-5	
Mean Pellet Diameter (mm)	2.0		1.3	
Dust Density$^{(a)}$ (kg/m^3)	2800		3200	
Pellet Density (kg/m^3)	1400	(1100-1700)	1800	(1300-2100)
Bulk Density (kg/m^3)	800	(600-1100)	1100	(1000-1300)
Pellet Porosity$^{(b)}$ (%)	50	(40-60)	45	(35-60)

Note:- (a) Calculated from the compositions

(b) Pellet Porosity $= \left(\frac{\text{Dust Density} - \text{Pellet Density}}{\text{Dust Density}} \right) \times 100\%$

The alkali product collected in the bag filter or electrostatic precipitator consisted of a cohesive, fine white powder with a particle size distribution predominantly finer than 5 μm but larger than 0.8 μm, Figure 6.8.

The electrical resistivity of the material, knowledge of which is required for the design of an electrostatic precipitator, has also been determined both in laboratory and in-situ. For the laboratory determination, samples of the typical alkali product collected in the bag filter were sent to two separate electrostatic precipitator manufacturers, viz, Lurgi (Germany) and Head Wrightson (U.K.), where the resistivity was measured under different gas temperature and dew-point conditions. The in-situ measurements were carried out in conjunction with Head Wrightson using a portable 'High Voltage Insulation Tester' shown in Figure 6.9. Different conditions of gas velocity, temperature and humidity were simulated by varying the rates of cooling air and steam addition to the quench vessel.

The results of the laboratory and in-situ determinations are presented in Figure 6.10 and Table 6.3 respectively. In the case of the laboratory determination, the family of curves produced under different temperature and dew-point conditions are consistent with the normal characteristics of fine particles. The resistivity varied from 10^8-10^{14} ohm-cm and depending on the dew-point of the gas, the temperature yielding the peak resistivity varied from 80-150°C. Above 200°C, the dew-point had little effect on resistivity. Comparing the laboratory and in-situ measurements, the resistivity value obtained by the latter method was consistently higher than that of the former. In the in-situ measurement, the gas conditions were fairly unsteady and there was also a problem with sealing the

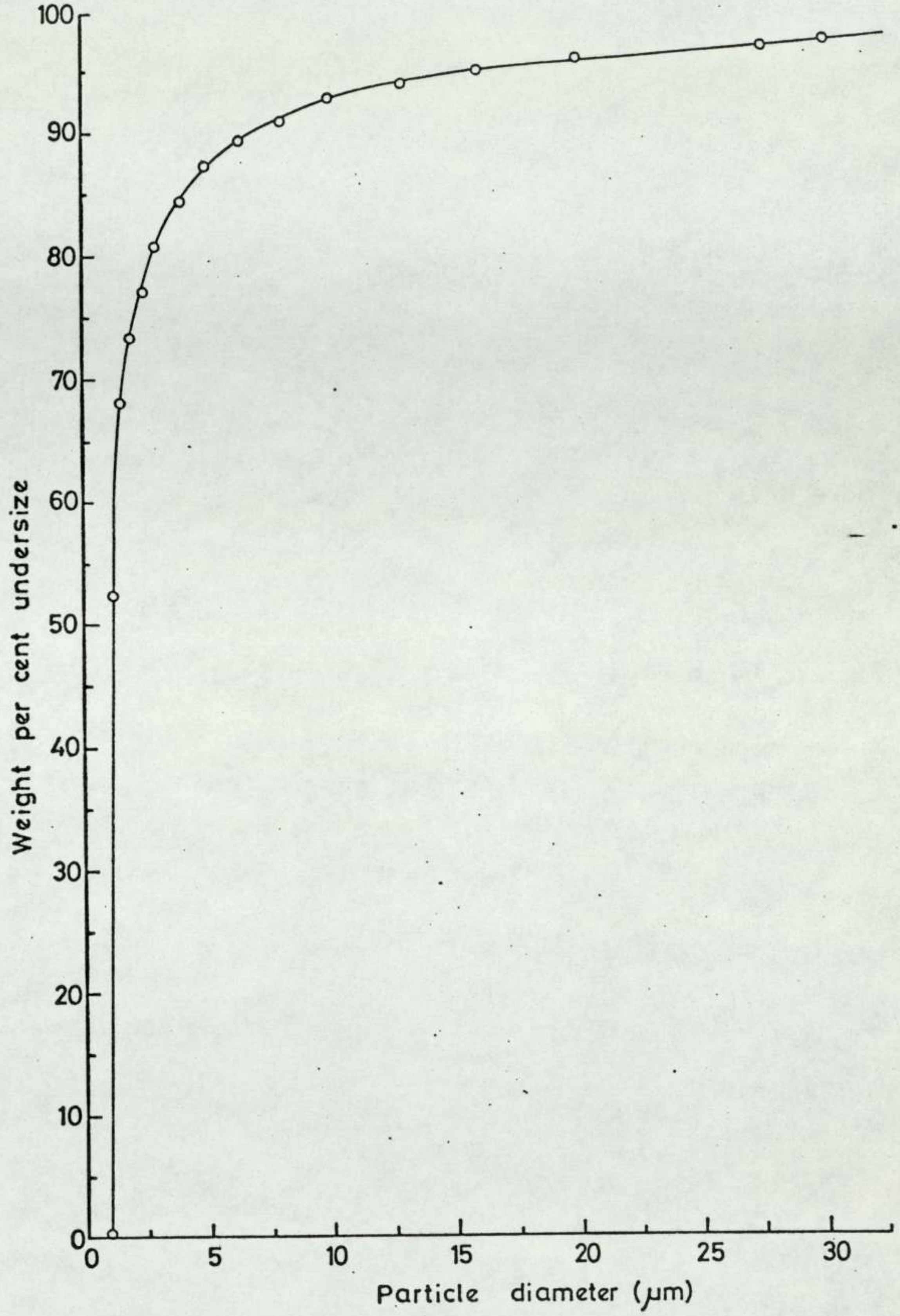
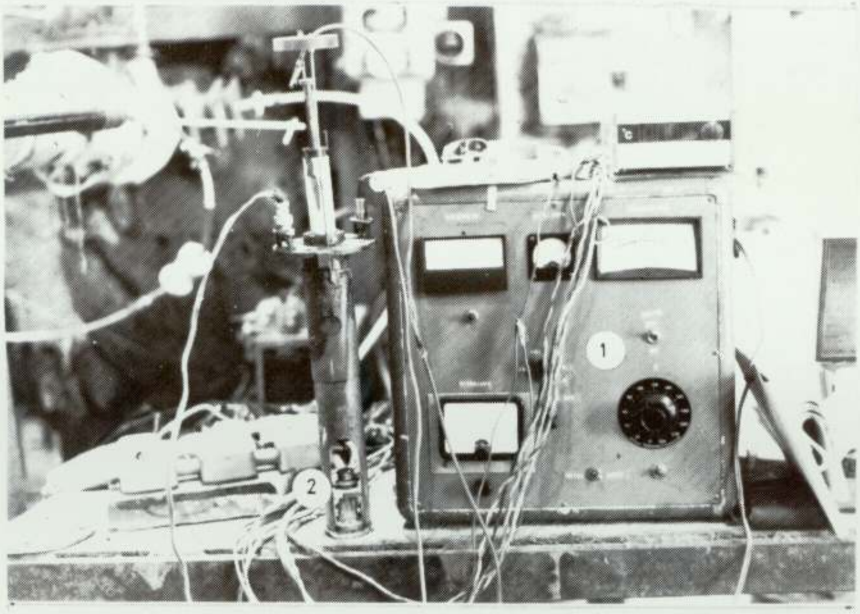
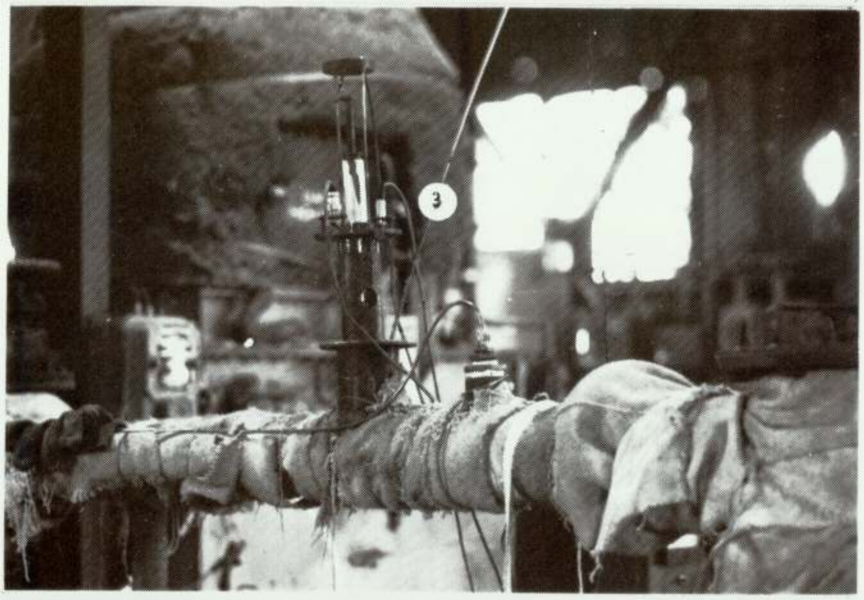


FIGURE 6.8

Particle Size Distribution of Typical Alkali Fume Product



(a)



(b)

FIGURE 6.9

The portable 'High Voltage Insulation Tester' used for in-situ determination of electrical resistivity of the alkali fume (a). The high voltage was supplied from the control unit marked (1) and the alkali fume was collected in the small electrostatic point-plane cell marked (2) situated at the end of the probe. The probe is shown together with the thermocouple (3) located in the gas stream during a test (b)

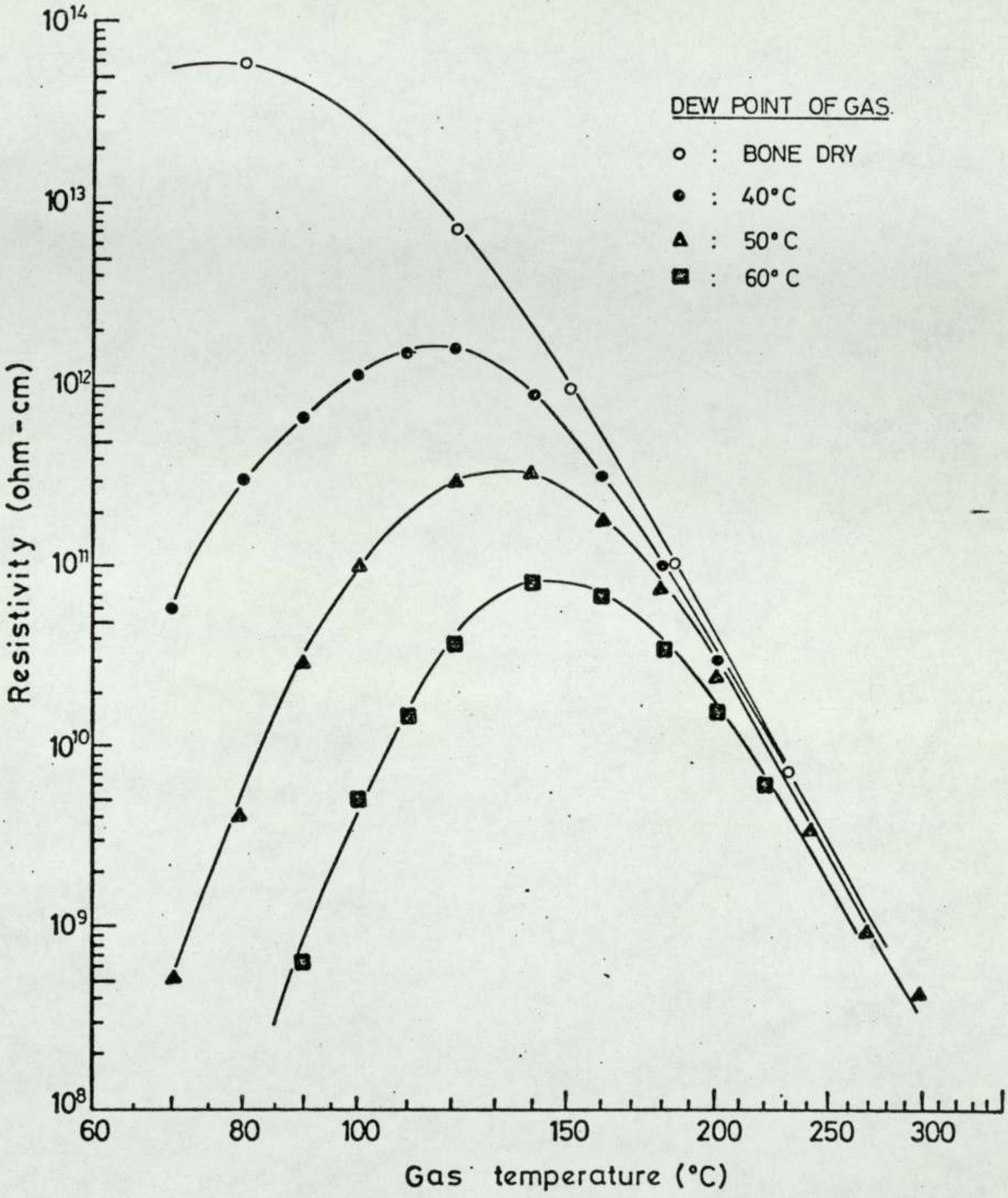


FIGURE 6.10

Electrical Resistivity of Alkali Fume at Various Gas Temperatures and Dew Points Determined Under Laboratory Conditions (Source: Lurgi, Germany and Head Wrightson, U.K.)

TABLE 6.3

Electrical Resistivity of the Alkali-Fume Determined Under In-Situ Conditions

Gas Velocity in Duct (ms^{-1})	Temperature (^oC)	Humidity (% v/v)	Alkali Resistivity (ohm-cm)
2.9	300	16.9	2.34×10^{10}
	310	8.9	1.95×10^{10}
	335	11.9	1.18×10^{9}
3.7	350	7.1	1.12×10^{10}
	370	7.0	2.86×10^{10}
4.2	385	6.7	9.54×10^{12}
	335	6.7	1.35×10^{12}

point-plane cell in the sampling port. Therefore, the latter values should be regarded with caution. Nevertheless, it is generally accepted that provided the resistivity of the material falls within 10^4-10^{11} ohm-cm, which is the case for this material at a gas temperature of above 200°C, efficient precipitation should be achieveable by correctly designed plant (Dorman, 1974).

6.3.2 Chemical Analyses of the Feed and Products

The alkali and lime analyses of the feed and various products derived from the tests are given in Tables E.5-E.9 (Appendix E). In the case of the feed, the CO_2 and H_2O which are required for the material balance, are also shown. As can be seen from Table E.5, the composition of the feed varied considerably, from a total alkali content of just under 10% to more than 27% and with the range of alkali concentration varying as follows: 4.4-13.5% K_2O, 0.6-1.3% Na_2O, 0.7-6.3% Cl and 2.0-12.3% SO_3. For the convenience of subsequent reference, the dusts with K_2O within the range of 5-9% will be referred to as the 'normal' dust and those in the 12 or 13% region will be referred to as the 'high alkali' dust. The difference between Northfleet and Westbury dusts is readily distinguished by the concentration of Cl present: in the former, the Cl level was generally above 2% while for the latter, it was generally 2% or less (except in the 'high alkali' dust, which contained about 2%).

The CaO and CO_2 contents of the dust feed were also variable, but for most of the normal dusts, they were about 40% and 22% respectively. The H_2O content was usually less than 5% in the pellets and 2% in the flakes. For the purpose of comparison, the L.O.I. (loss-on-ignition) at 950°C, which is normally used instead of CO_2 and H_2O determination in the cement industry, is also shown. As can be seen, the 2 sets of figures differed typically by about 5% but could be as much as 11-12% apart in the high alkali Northfleet dust (Tests 11 & 12). This difference is due mainly to the loss of alkalis, particularly KCl, at the temperature used for determining L.O.I. (refer Figure 3.11).

The calcined product (Table E.6) showed a significant reduction in alkalis and in most of the tests less than 30% of the original alkalis was retained. The free lime was typically below 6%. Compared with the requirements on K_2O, Cl and free lime stipulated in Section 4.2.3, the criteria of $<4\%$ K_2O, $<0.3\%$ Cl and $<16\%$ (for Northfleet dust) or $<9\%$ (for Westbury dust) free lime was readily met by all the normal dusts tested except in Tests 7 and 8 where the Cl limit was exceeded. In the case of the high alkali dusts, all but 2 of the tests (Tests 30 and 33) failed the requirements, primarily as a result of an excessive K_2O concentration. The alkali retention and lime combination characteristics will be discussed in detail in Section 6.4.

The composition of the carry-over material (Table E.7) varied with the fluidisation condition and feed properties. In Tests 1-5, where pre-calcined pellets were used to establish the initial bed, the compositions of the carry-over material lay somewhere between those of the pre-calcined and raw pellets. In Tests 6-9, where a drop-out vessel was installed and no pre-calcined pellets were used initially, the alkali content of the carry-over material was substantially increased. Apart from the apparent increase due to the loss of CO_2 and H_2O, the alkali content of the material appeared also to have been partially beneficiated by condensation of alkalis on the surface of the dust particles, as is evident from the material analysis. For most of the tests, however, there was no evidence of any significant beneficiation of alkalis due to condensation.

A small amount of material deposition was found in the quench vessel and cyclone in many of the 100mm fluidised bed tests and the analyses are given in Table E.8. As can be seen, they tended to be slightly richer in alkalis than those of the cyclone or drop-out material. However, the amount of material involved was generally small and, because of the problem of dismantling, no attempt was made to recover any deposition in the 150mm fluidised bed rig.

The alkali product obtained in the bag filter and electrostatic precipitator (Table E.9) generally contained an excess of 90% alkalis, about 5% 'contaminants' comprising silica and lime and a small amount of water, which was probably absorbed after the sample was collected. The K_2O and Na_2O contents were mainly in the range of 45-50% and 3-4% respectively but the Cl and SO_3 contents tended to vary with the type of feed and the calcining conditions. In most of the tests, the range of Cl and SO_3 concentrations obtained were respectively 20-30% and 15-25% for the normal Northfleet dust and 10-20% and 20-30% for the normal Westbury dust. The lime contents were typically less than 2% and the amount of free lime (which was considered by some fertiliser manufacturers to be undesirable due to its alkalinity) below 0.2%. A number of trace elements of interest to fertiliser manufacturers were analysed and the concentrations were found to be typically as follows: Pb = 2000 ppm, Zn = 1500 ppm, Cu = 270 ppm, F = 100 ppm, Se = 15 ppm and As = 1 ppm. According to several manufacturers, the alkali product should be acceptable for processing into a normal fertiliser.

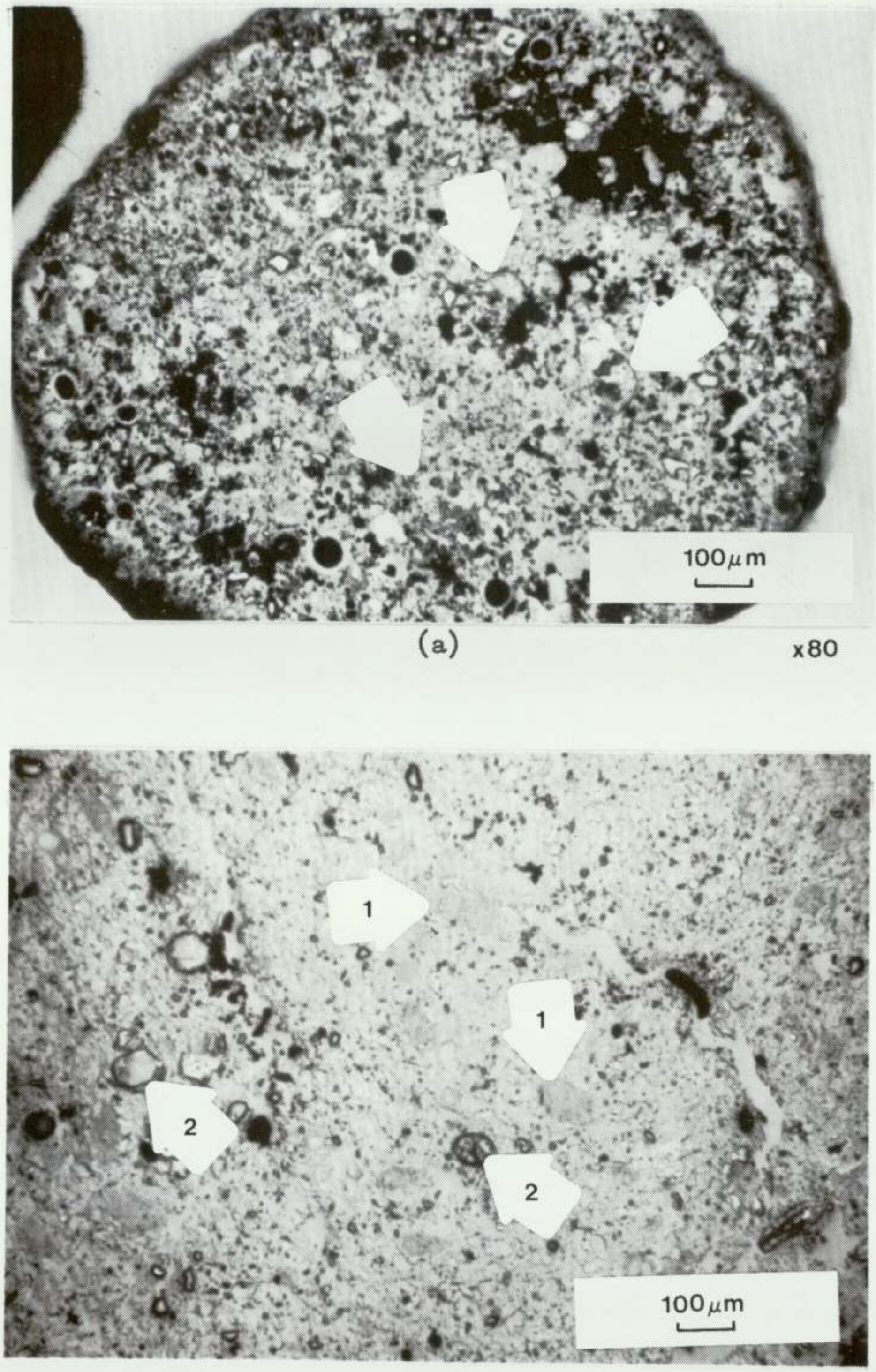
6.3.3 Material Balance

The material balance of the tests based on the weights of various materials shown in Tables E.1-E.4 and the CO_2 and H_2O analyses of the feed given in Table E.5 is presented in Table E.10. With the exception of Test 17 where there was an apparent material gain of 4%, varying amounts of material loss were recorded ranging from 1-21%, and typically about 10% of the feed input. Apart from random and systematic errors involved in quantifying the materials as well as in the analysis of the feed CO_2 and H_2O, the main cause of the inbalance was undoubtedly due to the low efficiency of the bag filter and the electrostatic precipitator. It can be seen from the alkali component mass balance in Tables E.11-E.14 that, in general, between 30% and 50% of the alkali input, or equivalent to typically 5-10% of the feed, was unaccounted for. In addition, the decomposition of $CaSO_4$ and other volatile compounds present might also account for a small proportion of the losses.

6.4 Calcination Performance and Characteristics

6.4.1 Microscopic Examination of the Calcined Product

Microscopic examination of the calcined product obtained from a number of tests was carried out with the assistance of the BCI Research Division (Morton, 1977). In general, the calcined product was found to be very variably burnt ot calcined, ranging from virtually undecarbonated material, i.e. <800°C, to clinker where the normal clinker liquid phase was just occurring, i.e. with an estimated temperature of approximately 1325°C, Figures 6.11-6.12. The apparent burning variation in burning



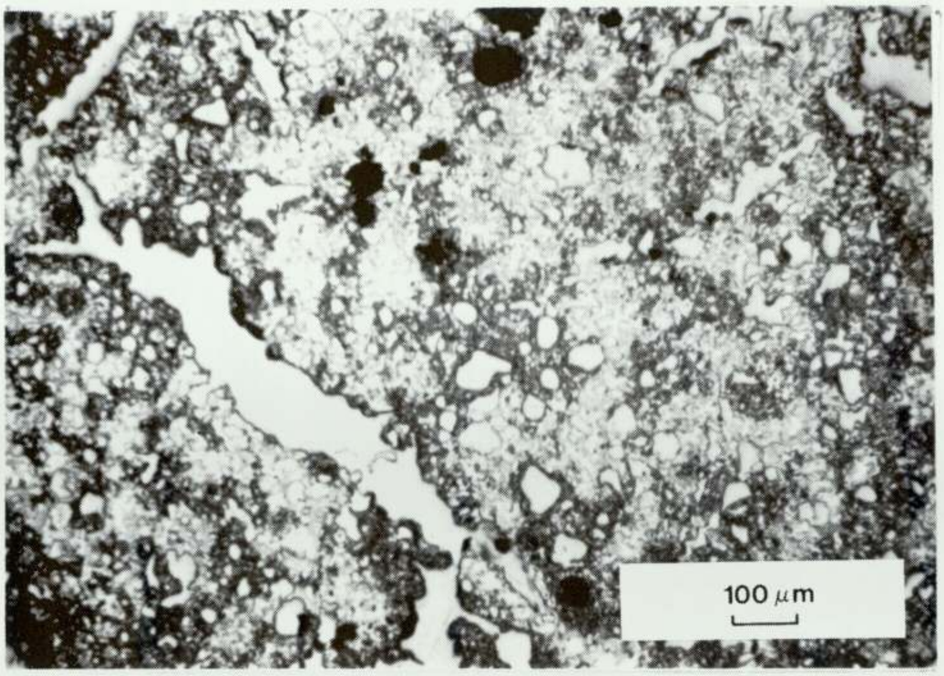
(a) x80

(b) x80

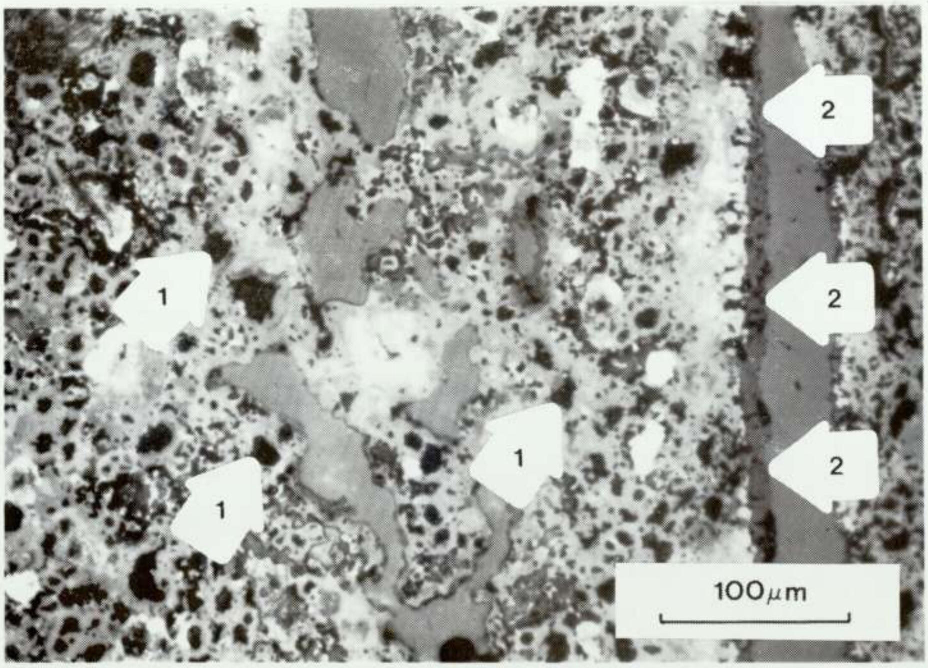
FIGURE 6.11

(a) Calcined product sample showing an undecarbonated pellet with clinker fragments (arrowed) which were present in the dust feed prior to calcination.

(b) This shows a pellet which has barely decarbonated and consists mainly of free lime (arrowed 1) and clinker fragments (arrowed 2) originate from the feed material.



(a) x80



(b) x250

FIGURE 6.12

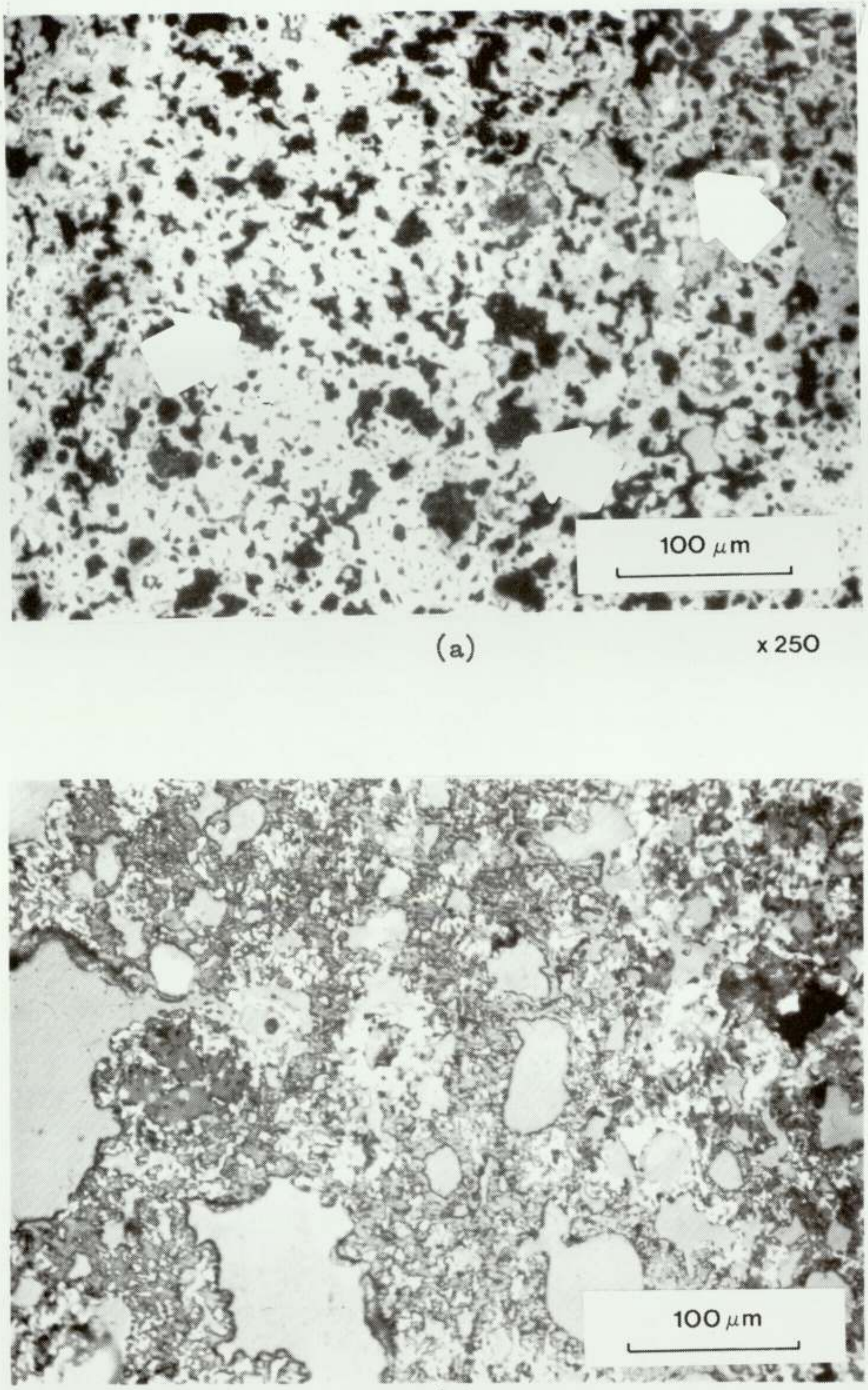
(a) Harder burning has promoted the formation of alite but has not led to the formation of normal clinker liquid phase. Note the high porosity and shrinkage cracking.

(b) Normal clinker liquid phase has formed and some densification of the pellet has occurred in this pellet. Alkali sulphate (arrowed 1) is present in the pores and along the edge of the pellet, partially hydrated free lime layers (arrowed 2) can be seen.

conditions clearly reflects the variable residence time of the material in the fluidised bed and also shows that individual particles were liable to experience temperatures considerably in excess of the mean bed temperature, possibly as a result of poorly-atomised fuel oil coating the particles and burning.

In the soft burnt material, a high concentration of free lime was noted (<20%) and in the core of some of this material, traces of KCl were also found. It was largely because of the presence of such soft burnt material that the overall free lime and Cl contents present in some of the calcined product were high. The alkali sulphate was variably distributed in-the calcined material as shown in Figure 6.13. For most of the tests, about 50% of the calcined pellets were found to contain a discontinuous peripheral densified layer rich in free lime and alkali sulphate, Figure 6.14. This was thought to be due to calcium and alkali sulphates migrating to the surface of the pellet and forming a low melting-point eutectic which would promote densification; subsequent desulphation of the calcium sulphate would leave the pellet skin rich in free lime. The presence of this eutectic is also thought to have been the principal cause of particle agglomeration, as indicated in Figure 6.15.

In the hard burnt material, some ill-shaped alite crystals typically of about 15 μm in size were present. The overall alite content was, however, low (typically <10%) and the major constituent present was belite. Consequently, the quality of the calcined product as a cement, if ground on its own, would be low, particularly at early stages of strength growth. However, if added in small quantities to normal works clinker, the overall increase in alkali sulphate level could counteract the fall in alite

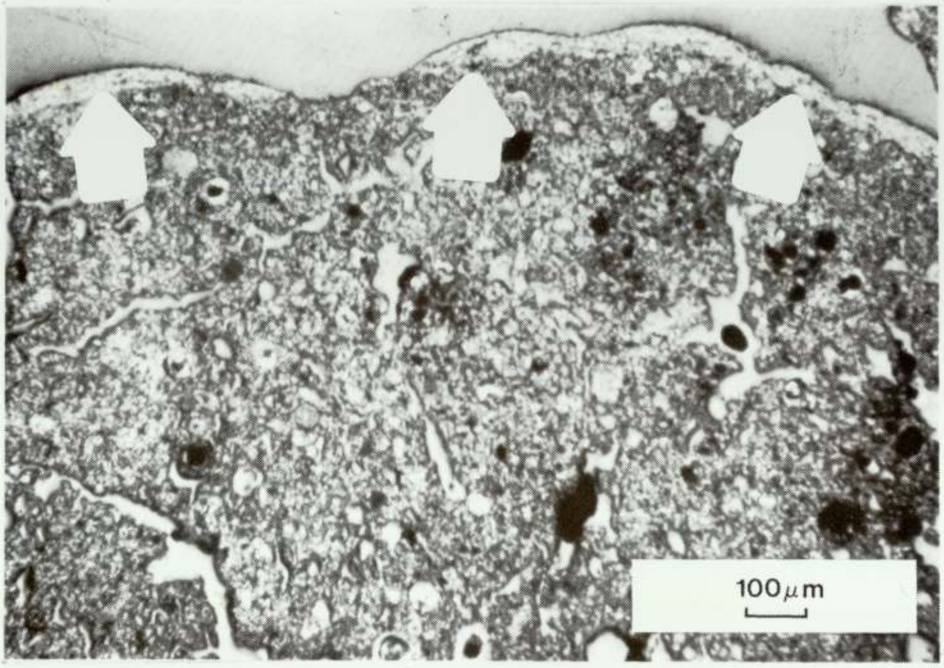


(a) x 250

(b) x 250

FIGURE 6.13

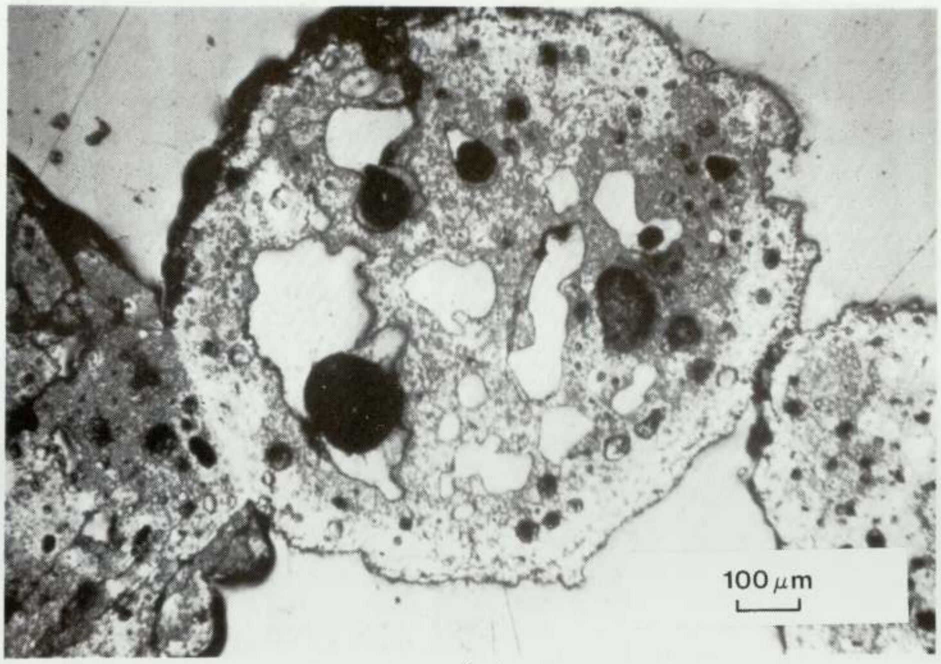
Contrast between 2 pellets from same calcined product sample showing (a) a pellet innundated with alkali sulphate and (b) a pellet virtually denuded of alkali sulphate. Some alite has formed but no clinker liquid phase is present.



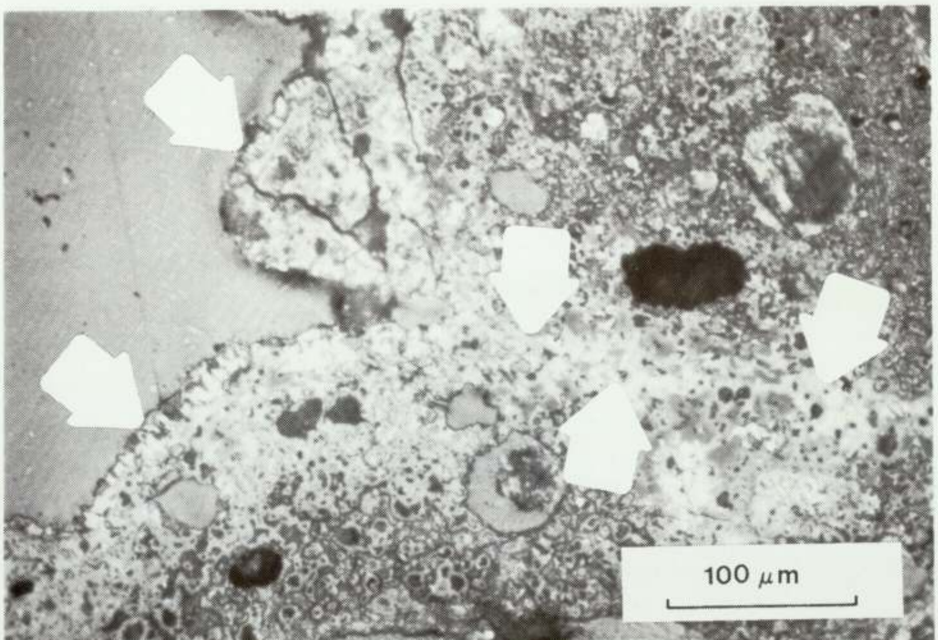
x 80

FIGURE 6.14

A small proportion of the pellets had a dense peripheral layer rich in free lime (arrowed) thought to have formed through migration of calcium sulphate to the pellet surface. Subsequent desulphation has left the lime-rich layer.



(a) x80



(b) x250

FIGURE 6.15

(a) An illustration of the adhesion that occurred between pellets in a small proportion of the calcined product. A region rich in free lime occurred at the junction of the pellets.

(b) At higher magnification the band rich in free lime (arrowed) can be clearly identified. The cause of the adhesion was thought to have been initiated by the presence of calcium sulphate/alkali sulphate eutectic melt at the peripheries of the pellets.

content so that cement quality at early stages should not be seriously affected. The factors affecting the alkali retention and lime combination characteristics are considered in the following sections.

6.4.2 Initial Correlation of the Alkali Retention and Volatilisation Characteristics

The amount of alkali retained in the calcined product was initially expressed in terms of the degree of alkali retention (see Appendix A) and plotted as a function of the fluidised bed temperature, following the method of correlation adopted in previous work. As can be seen from Figures 6.16-6.19, although the expected trend of decreasing alkali retention with increasing temperature is discernable, it was not possible to derive any meaningful correlation because of the scatter of the data, which cannot be attributed to either the bed sizes or the dust types. Initially, it was thought that the scatter of the data was due to the variable residence time of the material. However, the plots of alkali retention against residence time at various temperatures produced an almost random scatter of the data and suggest that the degree of alkali retention was virtually independent of the material residence time in the range investigated, i.e. 14-59 min.

A major limitation of the alkali retention correlation is that the effect of carry-over of dust containing essentially unvolatilised alkali was not considered. An alternative method of correlation based on the amount of alkali volatilised was attempted. By assuming that the carry-over material contained a negligible amount of re-condensed alkalis, the degree of alkali volatilisation was determined from the alkali component mass balance (Tables E.11-E.14) and plotted as a function of the bed

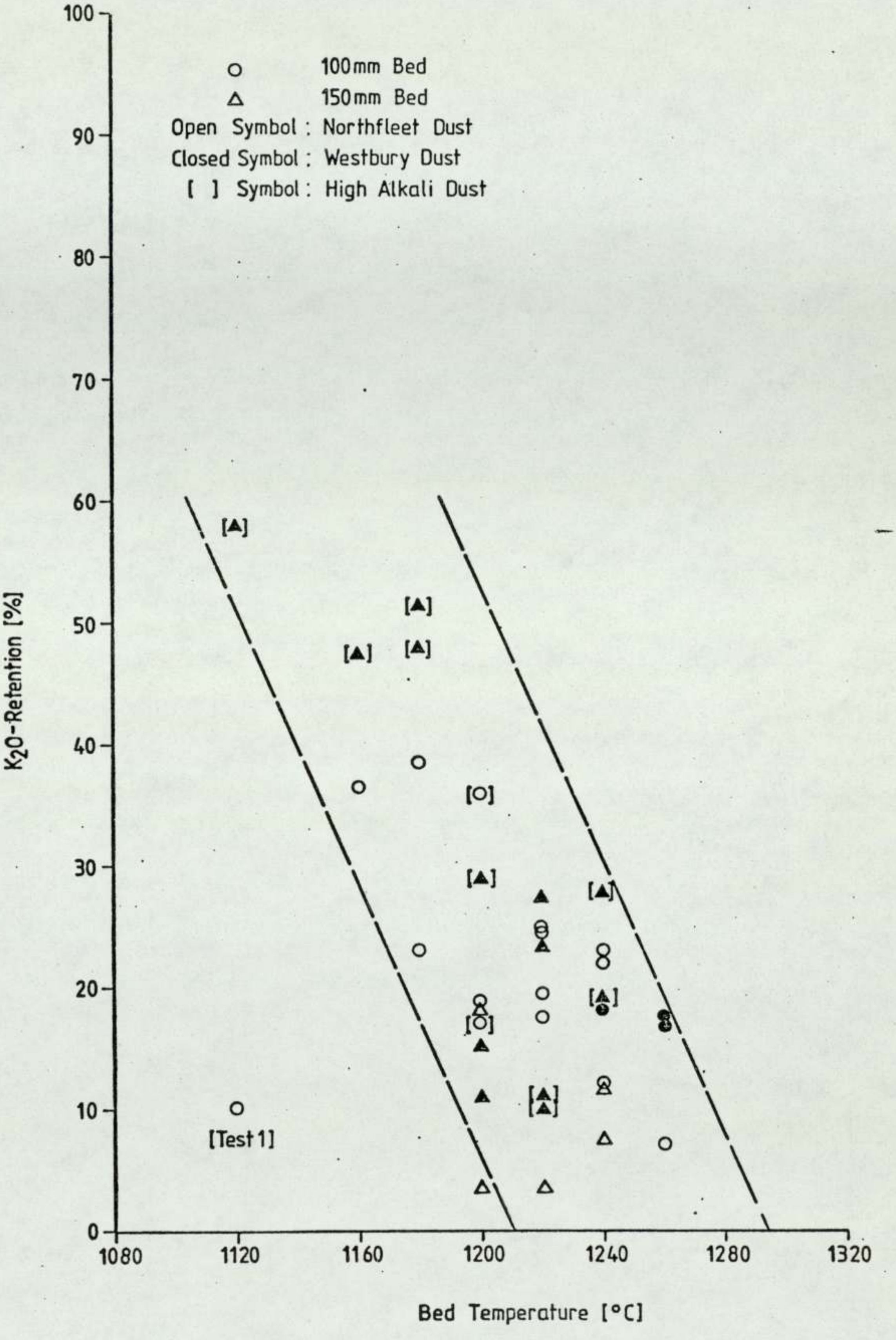


FIGURE 6.16

Effects of Calcining Temperature on the Degree of K_2O Retention

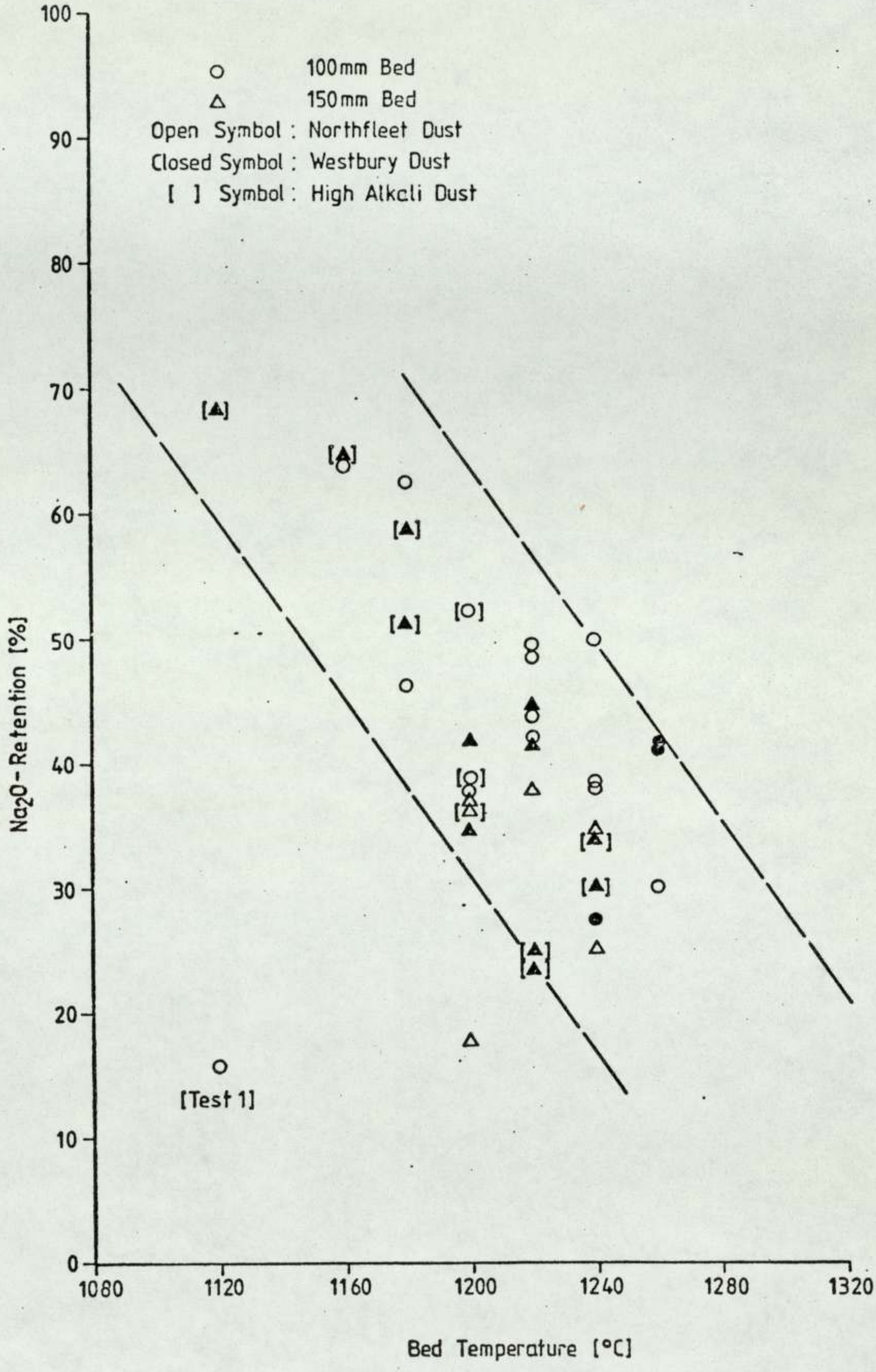


FIGURE 6.17

Effects of Calcining Temperature on the Degree of Na_2O Retention

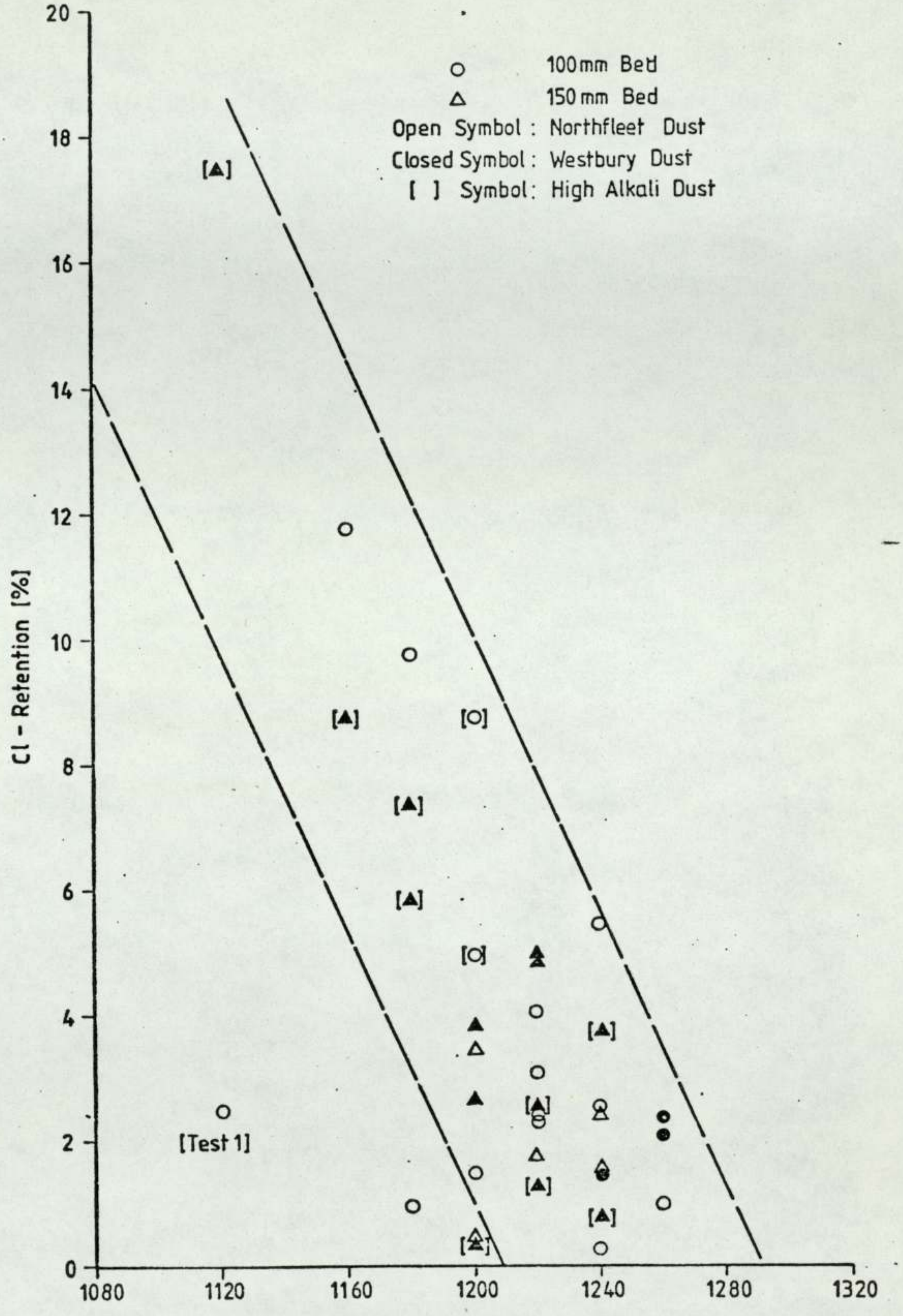


FIGURE 6.18

Effects of Calcining Temperature on the Degree of Cl Retention

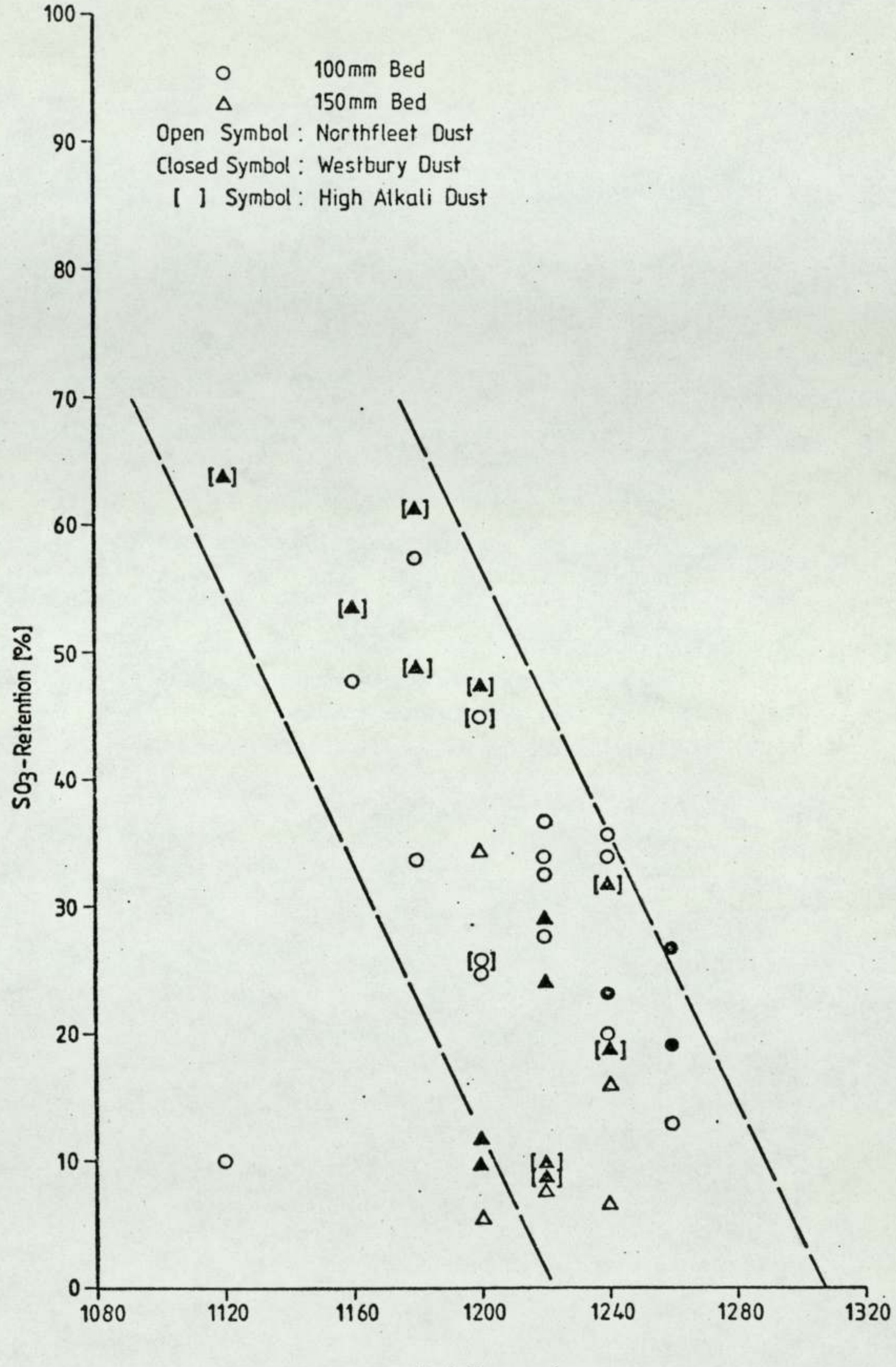


FIGURE 6.19

Effects of Calcining Temperature on the Degree of SO_3 Retention temperature. For K_2O Na_2O, Figures 6.20 and 6.21, fairly good correlations are obtained for the Westbury data, as can be seen from the coefficient of determination shown. The correlations for the Northfleet data are, however, marred by the effects of Cl and the exceptionally high gas:solid throughput of Tests 1 and 23-27, as will become evident later.

In the case of Cl, Figure 6.22, the scatter of the data suggests that the volatilisation level was virtually independent of the bed temperature, as was suggested in Section 4.4.4. In general, the degree of volatilisation obtained exceeded 85% and the lower degrees of volatilisation found in several tests were mainly associated with high dust carry-over or low residence time which increased the amount of soft burnt material. Finally, in the case of SO_3, Figure 6.23, the correlations for both Northfleet and Westbury dusts are fairly reasonable and there was little significant difference between the two materials.

In the remaining sections, the volatilisation characteristics of K_2O and Na_2O are considered in more detail. The volatilisation of Cl is directly linked to K_2O (as KCl) while that of SO_3 is of little interest in the present work and will, therefore, not be considered any further.

6.4.3 Correlation of the 'Nett-K_2O' Partial Pressure

It was suggested in Section 4.4.4 that the volatilisation of K_2O, exclusive of that which is present as KCl, is primarily controlled by the equilibrium partial pressure of K_2SO_4. Assuming that Cl is volatilised exclusively as KCl, the amount of remaining K_2O volatilised, which will be referred to as the 'Nett-K_2O' for convenience, can be derived from the K_2O mass balance (Table E.11), assuming that,

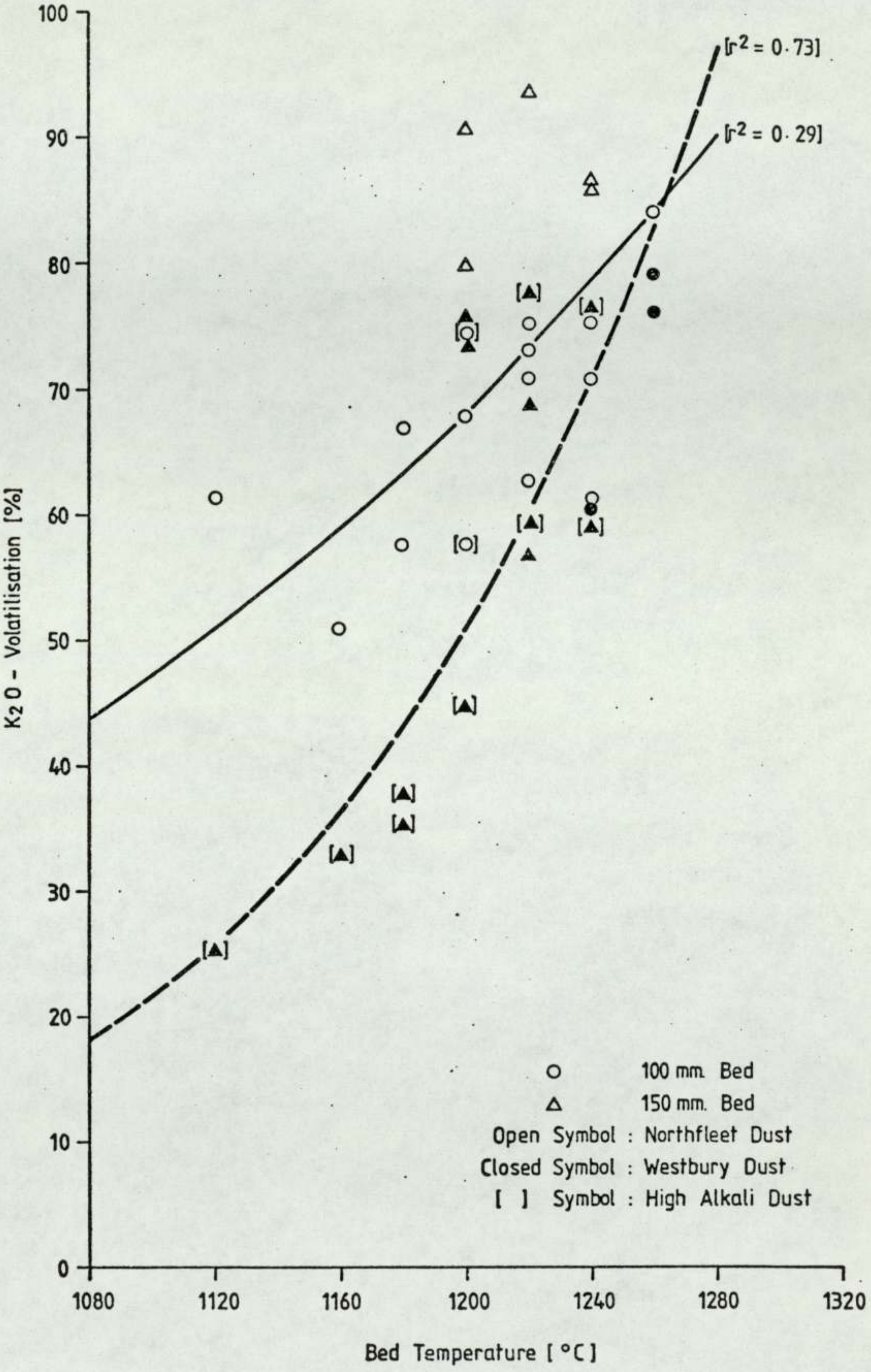


FIGURE 6.20

Effects of Calcining Temperature on the Degree of K_2O Volatilisation

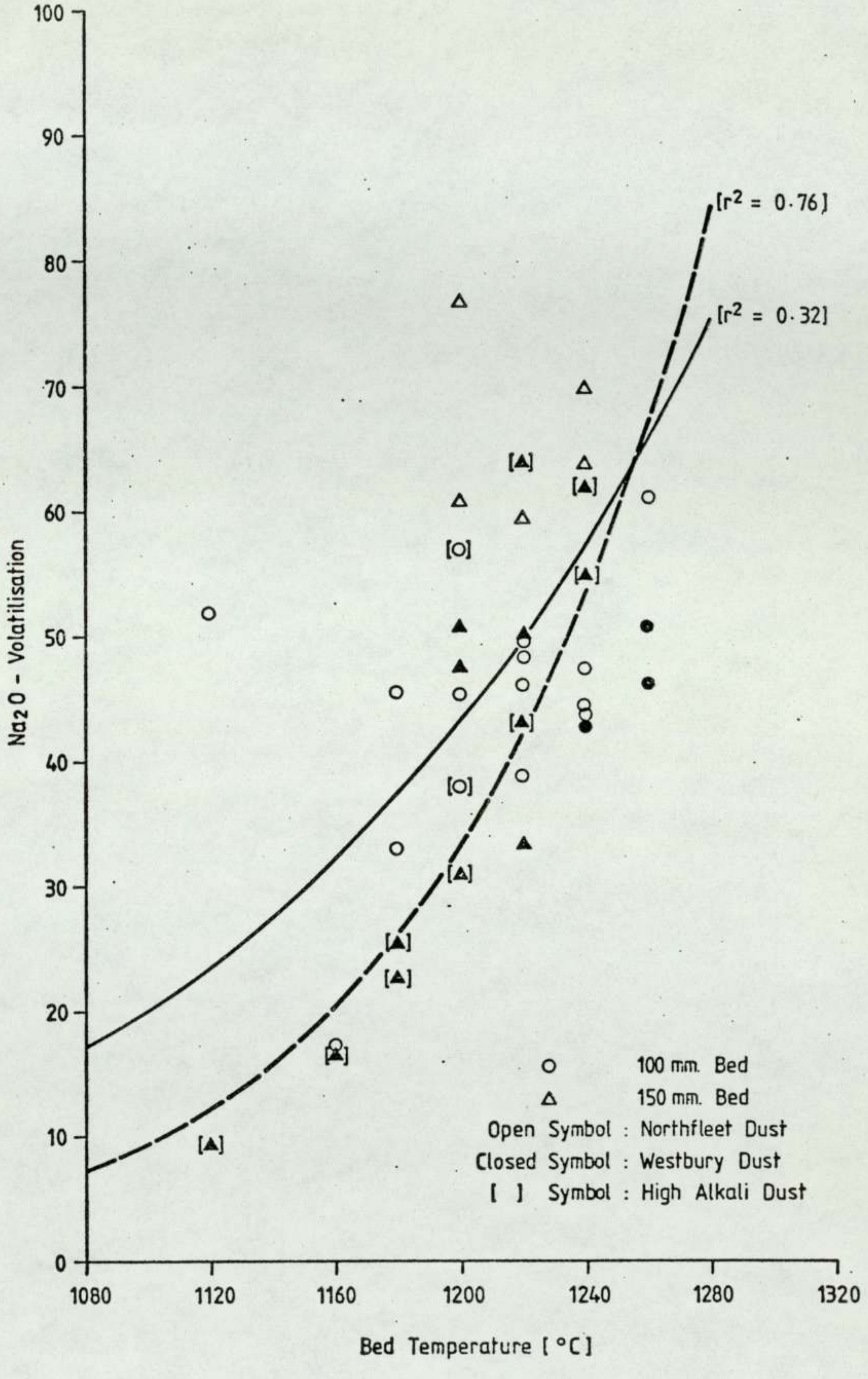


FIGURE 6.21

Effects of Calcining Temperature on the Degree of Na_2O Volatilisation

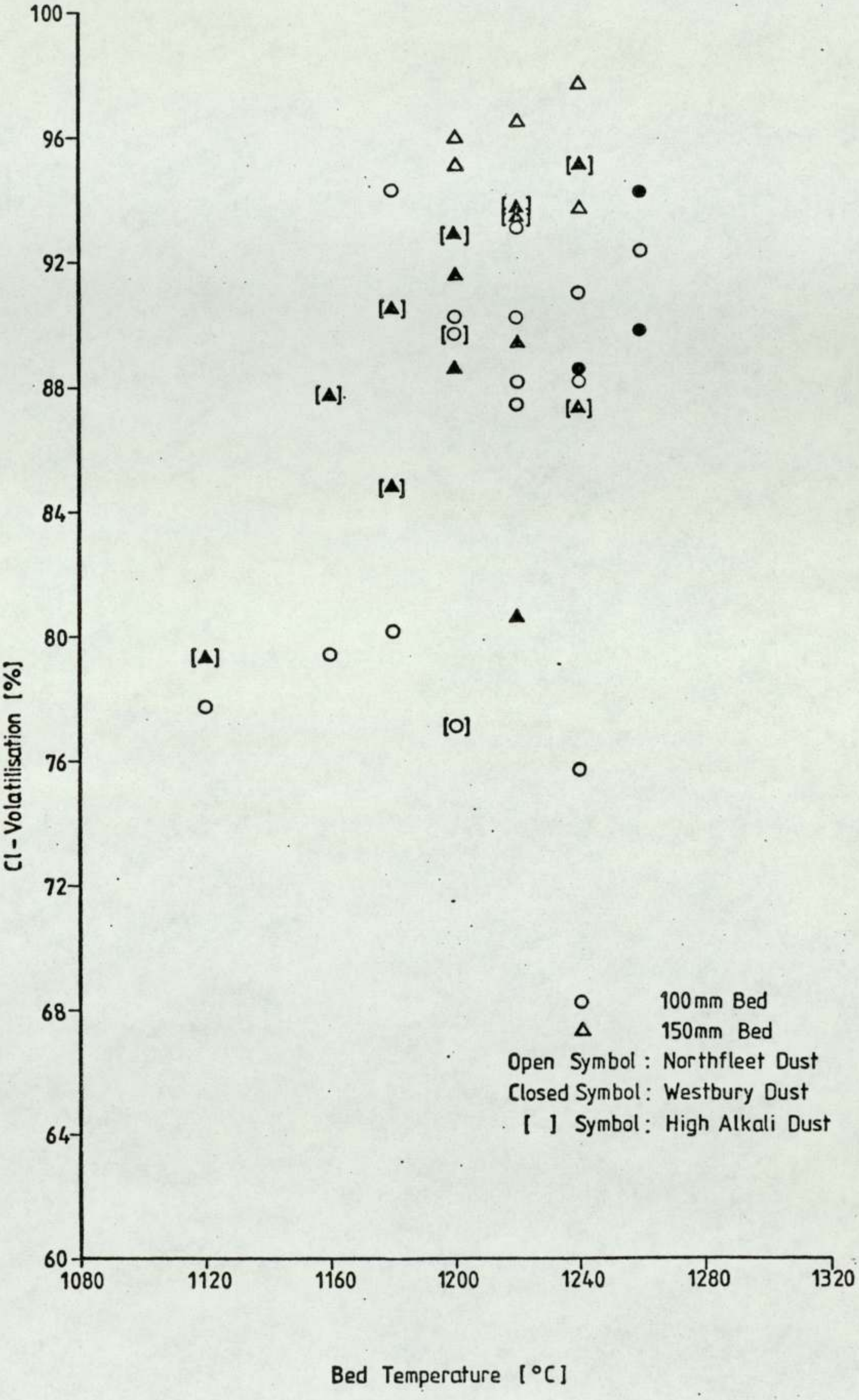


FIGURE 6.22

Effects of Calcining Temperature on the Degree of Cl Volatilisation

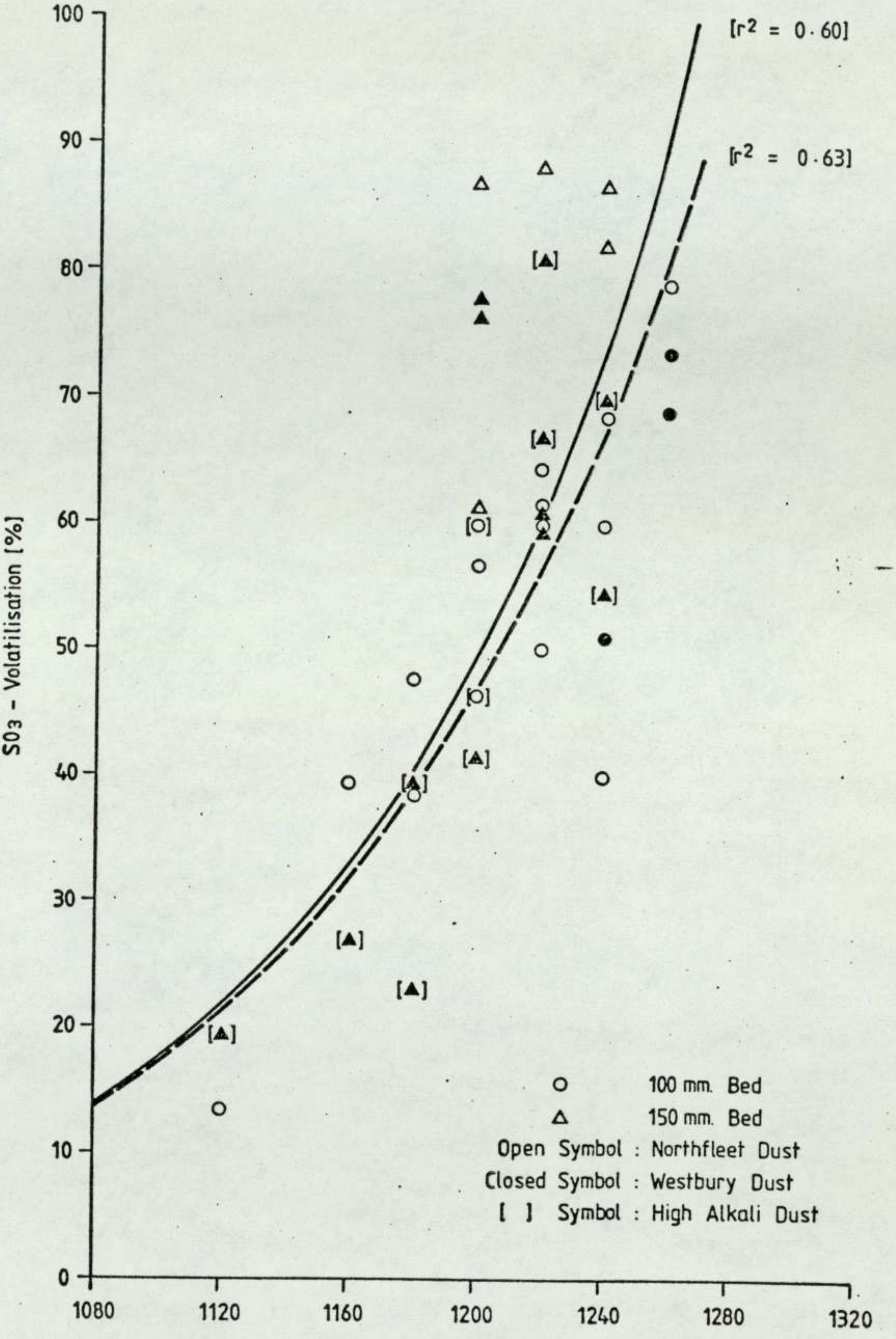


FIGURE 6.23

Effects of Calcining Temperature on the Degree of SO_3 Volatilisation

$$m_{N-K} = m_K - m_{Cl} \cdot \frac{94.2}{70.9} \qquad .....(6.1)$$

where m_{N-K} = mass of 'Nett-K_2O' volatilised (kg)

m_k = mass of K_2O volatilised (kg)

m_{Cl} = mass of Cl volatilised (kg)

and $\frac{94.2}{70.9}$ is the molecular ratio of K_2O:Cl in KCl.

Replacing m_{N-K} in the L.H.S. of equation (4.21) and putting P = 1 atm, $M_V = 94$ and $M_g = 29$, the partial pressure of 'Nett-K_2O' is given by,

$$p = \frac{m_{N-K}}{G_o} \cdot \frac{94}{29} \text{ (atm)} \qquad .....(6.2)$$

where $G_o = G_i + F_i \; (x_{CO_2} + x_{H_2O})$ .....(6.3)

The calculated partial pressures are plotted against the bed temperature in Figure 6.24, and although there is still an appreciable scatter of the data, the correlation is substantially improved. From regression analyses, the separate data for Northfleet and Westbury dust were found to be fitted best by exponential equations of the form,

$$p = a \exp (bT) \qquad .....(6.4)$$

The constants, a and b, and the coefficients of determination, r^2, derived are as follows:-

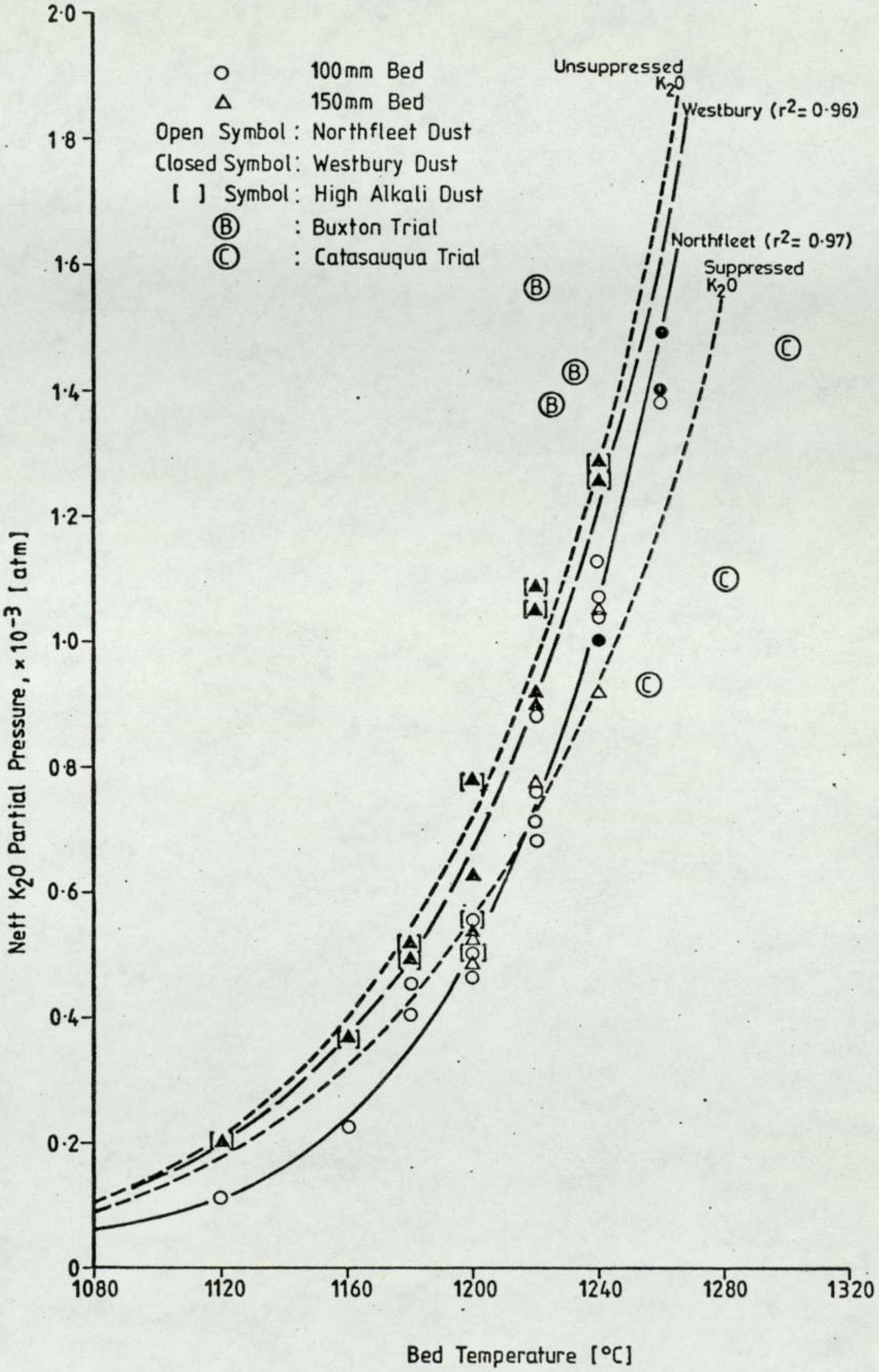


FIGURE 6.24

Correlation and Comparison of Nett-K_2O Partical Pressures

	a	b	r^2
Northfleet	1.95×10^{-13}	0.018	0.97
Westbury	1.26×10^{-11}	0.015	0.96

6.4.4 Comparison of the 'Nett-K_2O' Partial Pressure Correlation with the 300mm and 450mm Fluidised Bed Results and the Published Saturation Vapour Pressure of K_2SO_4

For the purpose of comparison, several data points derived from the 300mm fluidised bed trials at Buxton (Evans 1976 a & b) and the 450mm Pyzel bed trial at Catasauqua (Evans and Haspel, 1976) are included in Figure 6.24. Also shown are the suppressed and unsuppressed saturation vapour pressure curves of K_2O based on those of K_2SO_4 published by Hart and Laxton (1967) and discussed earlier (Section 4.4.4).

As can be seen, the Buxton data, which were derived from Northfleet dust, are approximately 50% above the present Northfleet data and are also considerably above the Westbury data and the unsuppressed K_2O vapour pressure curve. In contrast, the Catasauqua data, which were derived from Westbury dust, are all significantly below the present data and the suppressed K_2O vapour pressure curve. However, this discrepancy should not be considered to be very significant, since the evaluation of partial pressures of this magnitude is highly sensitive to the accuracy of temperature measurements and interpretation of weight loss data (Halstead, 1977). Furthermore, from the reports of the Buxton trials, it appeared that there was a significant quantity of material deposition which was not recovered for weighing and analysis. The material balances were not reported, but from the various feed and product rates, on which the three data points shown are based, an approximate material balance indicates that the material unaccounted for over various test periods was typically in excess of 20%. This would at least partially account for the discrepancy.

In the case of the Catasauqua trial, other reasons have been suggested for these discrepancies. According to Morton (1977), who examined the materials from both the present experiments and the Catasauqua trial, the dense and close-pore structure of the Pyzel product could seriously inhibit the diffusion of alkali from the particle. In addition, since the bed was operated under incipient fusion conditions, the significant quantity of liquid melt present might also hamper the diffusion of the alkali vapour as well as suppressing the effective equilibrium vapour pressure.

In comparing the present data with the K_2O saturation vapour pressure curves, it is seen that for the Northfleet dust, the data tend to lie below the suppressed vapour pressure curve at temperatures below 1220°C and gradually approach the unsuppressed vapour pressure curve towards higher temperatures . In the case of Westbury dust, the data generally follow the unsuppressed vapour pressure curve. Since most of the Westbury data were derived from the high alkali dust, the effect of Nett-K_2O concentration in the feed was examined by relating the Nett-K_2O potentially available from the feed to saturate the gas to the actual partial pressure achieved, normalised for temperature (i.e. as a ratio to the unsuppressed K_2O vapour pressure at the temperature of the test). However, due to the scatter of the data, it was not possible to draw any precise conclusions.

6.4.5 Correlation of the Na_2O Partial Pressure

As indicated earlier in this thesis, Na_2O need not be considered in the present study because of the low level present in both Northfleet and Westbury flue dust. However, for completeness and for potential application to other flue dusts, the partial pressure obtained was also evluated and plotted as a function of the bed temperature. As can be seen from Figure 6.25, the Northfleet and Westbury data fall clearly along 2 separate exponential curves. The constants and coefficients of determination are as follows:-

	a	b	r^2
Northfleet	4.11×10^{-10}	0.011	0.88
Westbury	3.42×10^{-10}	0.011	0.95

Compared with the saturation vapour pressure of Na_2O based on Na_2SO_4, both sets of data, in particular that for the Northfleet, lie above the unsuppressed vapour pressure curve. This suggests either that a greater level of decomposition was achieved or, more likely, that a proportion of Na_2O was present as NaCl, so accounting for the higher Na_2O partial pressure apparently achieved for the Northfleet dust (since there was more Cl present). If this was the case, the Nett-K_2O partial pressure calculated for the previous correlation should have been higher, particularly for the Northfleet dust. However, as the amount of Na_2O involved is relatively low, the effect is small.

6.4.6 Lime Combination Characteristics

The effect of the calcination temperature on the extent of lime combination, as reflected by the amount of residual free lime in the

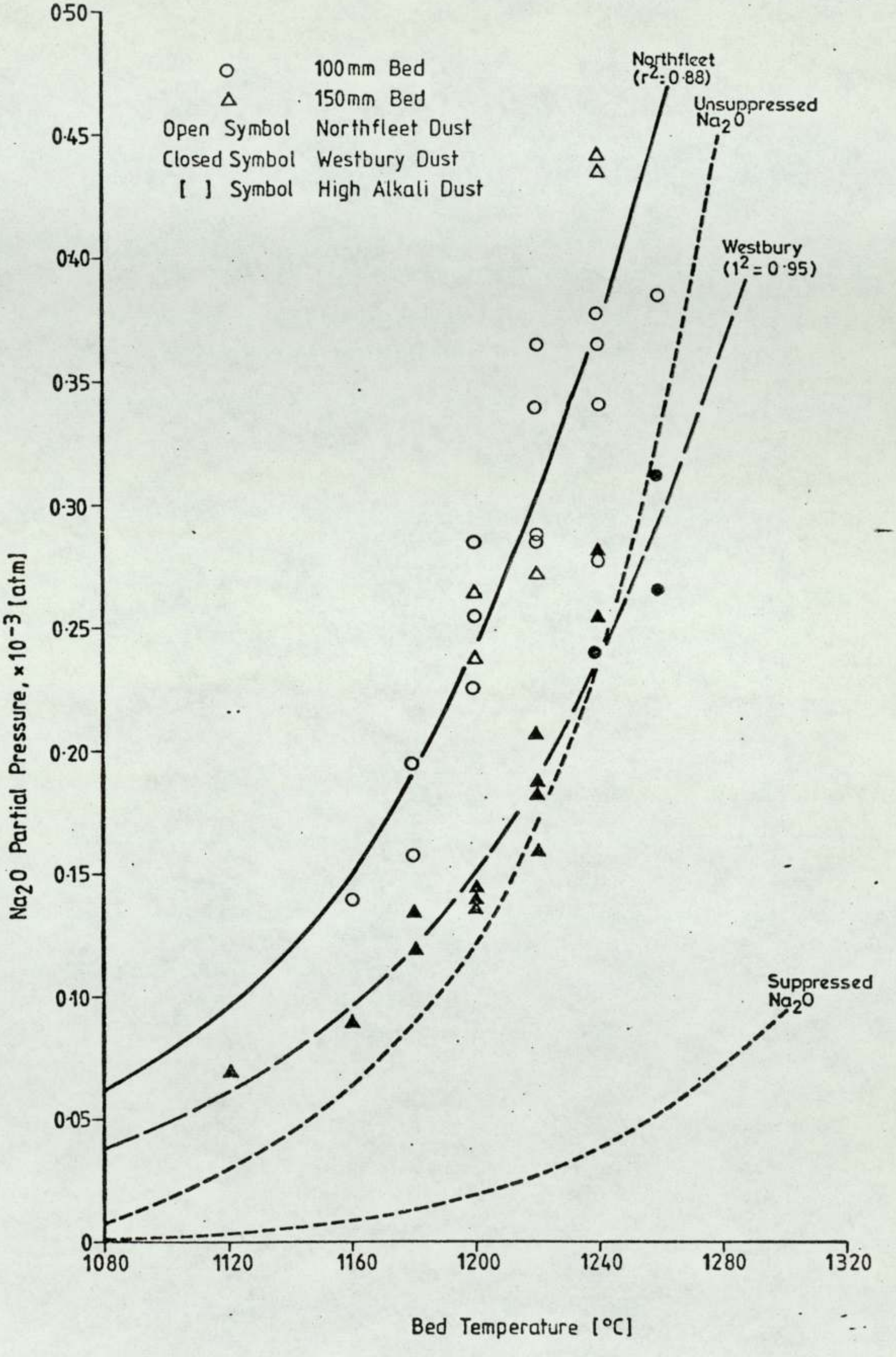


FIGURE 6.25

Correlation and Comparison of Na_2O Partial Pressures calcined product, is shown in Figure 6.26. From the scatter of the data, it appears that the extent of lime combination is fairly insensitive to the calcining temperature over the range of temperature investigated (1120-1260°C). The types of dust and the bed size, too, did not have any significant effect on the results.

The effect of material residence time was examined by plotting the residual free lime at 1200, 1220 and 1240°C against the mean solid residence time. As can be seen from Figure 6.27, the correlation was significantly improved and the data may be represented by the following empirical equation:-

$$RFL = 94 (\tau_s)^{-0.83} \qquad .....(6.8)$$

where RFL = Residual free lime (%)

and τ_s = Mean solid residence time (min)

Although this correlation is fairly weak (the coefficient of determination <0.5), this is not considered to be a serious drawback as the extent of lime combination is non-critical and it is not essential to predict the exact level of free lime.

6.5 Design Considerations

6.5.1 Scale-up of the Fluidised Bed

From the requirements of calcining Northfleet and Westbury flue dusts and the results presented here, it is evident that the scale-up of the

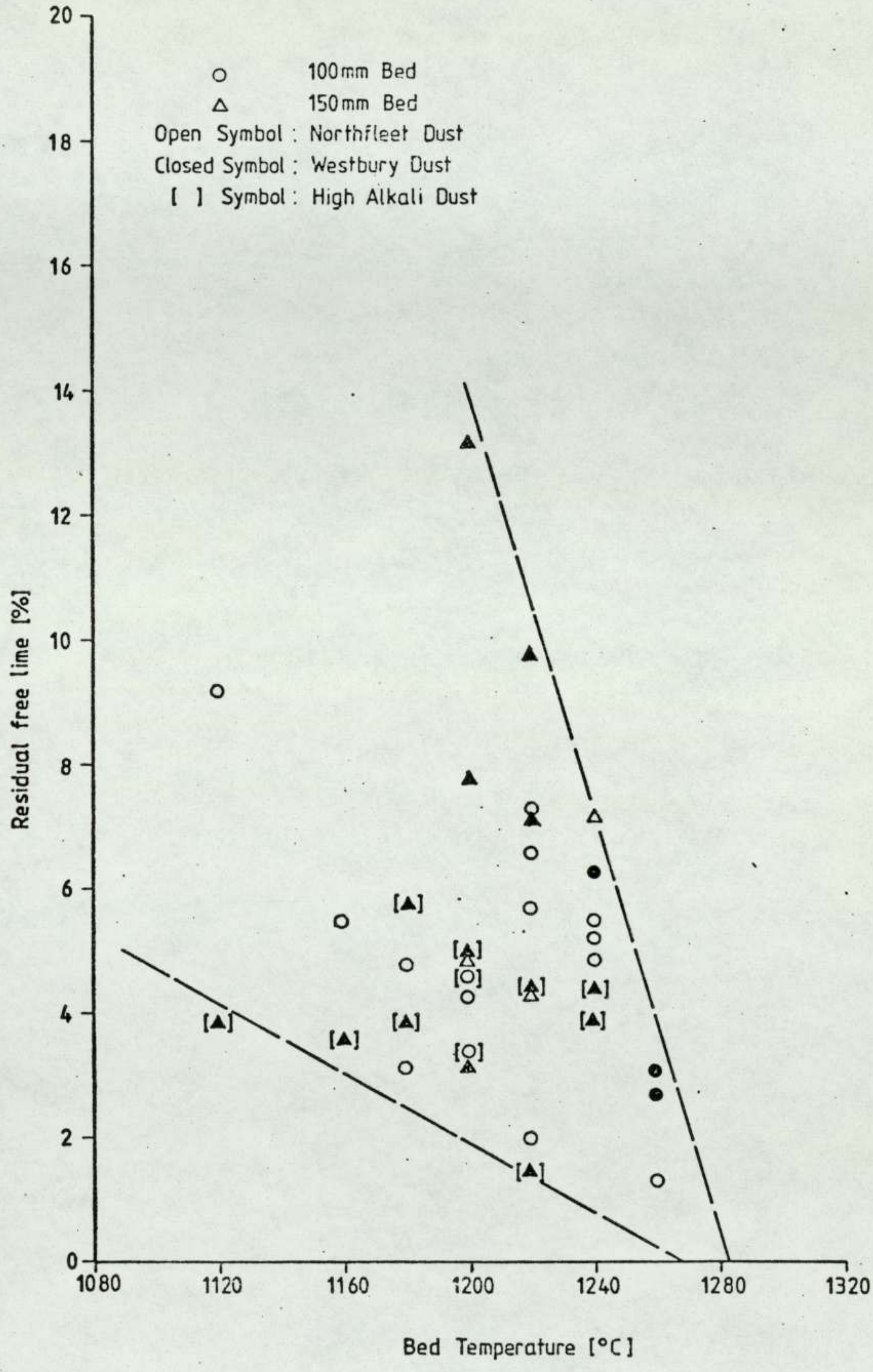


FIGURE 6.26

Effects of Calcining Temperature on Residual Free Lime of Calcined Product

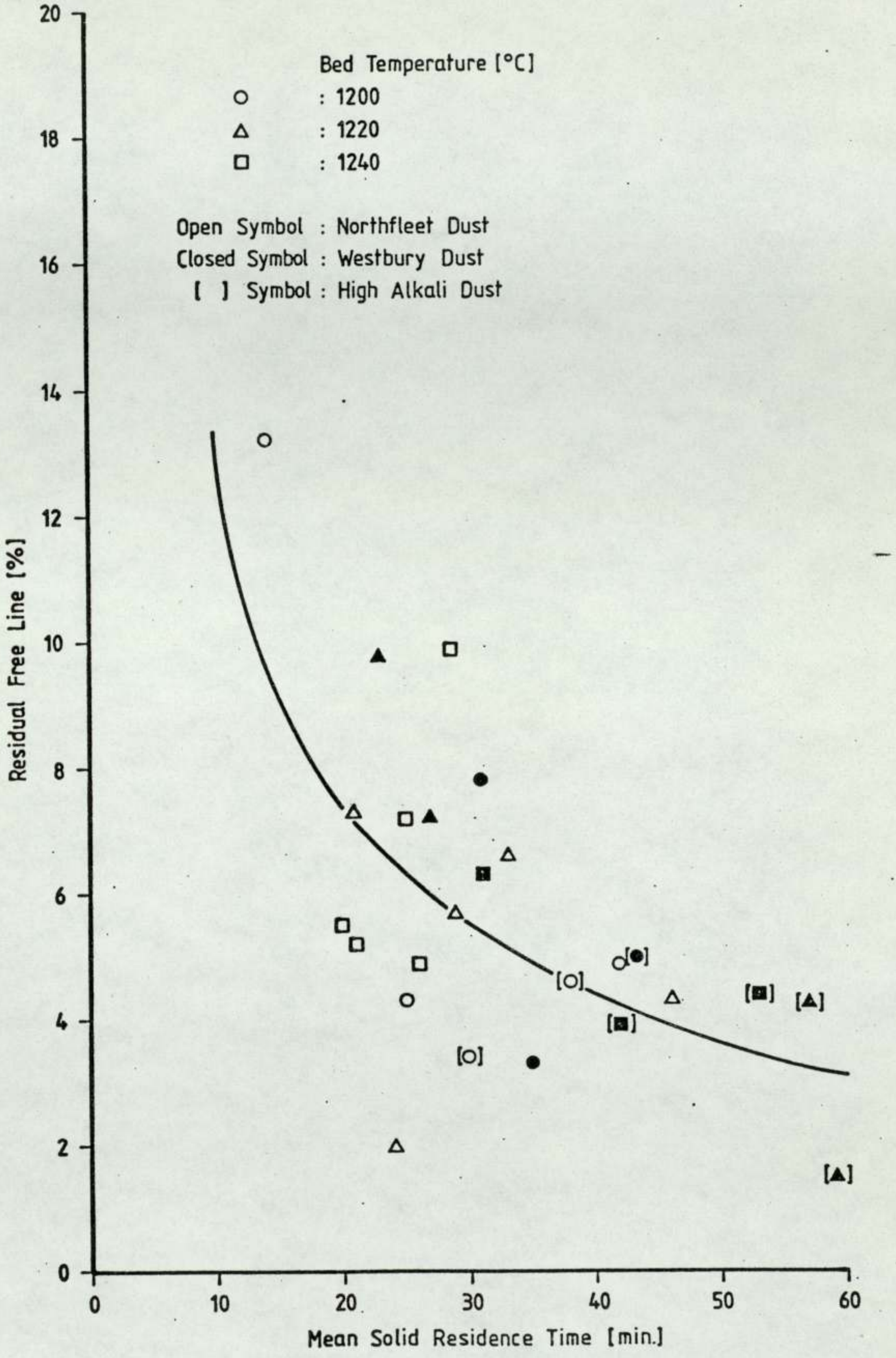


FIGURE 6.27

Effects of Mean Solid Residence Time on Residual Free Lime of Calcined Product fluidised bed is essentially determined by the amount of K_2O which must be removed. For conditions likely to be needed in a full-scale plant, the amount of K_2O removed with the indigenous Cl can be assumed to be virtually independent of the calcining temperature and is given by the following expression,

$$\Psi_K' = \Psi_{Cl} \cdot \frac{x_{Cl}}{x_K} \cdot \frac{94.2}{70.9} \qquad .....(6.9)$$

where Ψ_{Cl} = Degree of Cl volatilisation (typically 85-95%)

x_{Cl} = Mass Fraction of Cl in feed

x_K = Mass fraction of K_2O in feed

and (94.2/70.9) is the molecular ratio of K_2O:Cl in KCl.

The degree of 'Nett-K_2O' volatilisation can be obtained by replacing the equilibrium partial pressure in equation (4.23) with the correlation derived from the experiment. Assuming that P = 1 atm and M_g = 29, the degree of Nett-K_2O volatilisation is given by ($P \gg p$),

$$\Psi_K'' = \frac{94.2}{29} \cdot \frac{G_o}{F_i \cdot x_K} \cdot a \exp(bT) \times 100\% \qquad .....(6.10)$$

where the constants a and b are given in Section 6.4.3.

Combining equation (6.9) and (6.10), the overall degree of K_2O volatilisation can be expressed as follows:-

For Northfleet Dusts

$$\Psi_K = \frac{94.2}{\%K_2O}\left[\Psi_{Cl} \cdot \frac{\%Cl}{70.9} + 6.72 \times 10^{-11} \left(\frac{G_o}{F_i}\right) \exp\ (0.018\ T)\right] \quad .....(6.11)$$

For Westbury Dusts

$$\Psi_K = \frac{94.2}{\%K_2O}\left[\Psi_{Cl} \cdot \frac{\%Cl}{75.9} + 4.34 \times 10^{-9} \left(\frac{G_o}{F_i}\right) \exp\ (0.015\ T)\right] \quad .....(6.12)$$

Using the above equations, and assuming that $\Psi_{Cl} = 90\%$, the degree of K_2O volatilisation at various (G_o/F_i) ratios and temperatures of 1200-1280°C are calculated for the typical Northfleet and Westbury flue dusts shown in Table 4.1 and depicted in Figure 6.28. At a G_o/F_i ratio of 2-3, which may be regarded as typical for normal calcination, the calculated degree of K_2O volatilisation obtainable for the two dusts varied from about 55-75% and 20-55% respectively. The minimum degree of volatilisation required to achieve less than 4% K_2O in the calcined product, assuming that there is very little dust carry-over, is approximately 65% for both the dusts. In the case of Northfleet dust, this should be achieved at a temperature of between 1240°C and 1280°C. In the case of Westbury dust, however, the (G_o/F_i) for the same temperature range needs to exceed at least 4 or 5. Such a high gas:solid ratio is unlikely to be economical in practice and some other means of enhancing K_2O volatilisation is required. This is discussed in the following sections.

6.5.2 Feasibility of Enhancing Alkali Volatilisation

There are several alternative means of enhancing K_2O volatilisation, one which has already been mentioned is via the addition of $CaCl_2$ (Section 3.5.2). The effectiveness of $CaCl_2$ will depend primarily on how

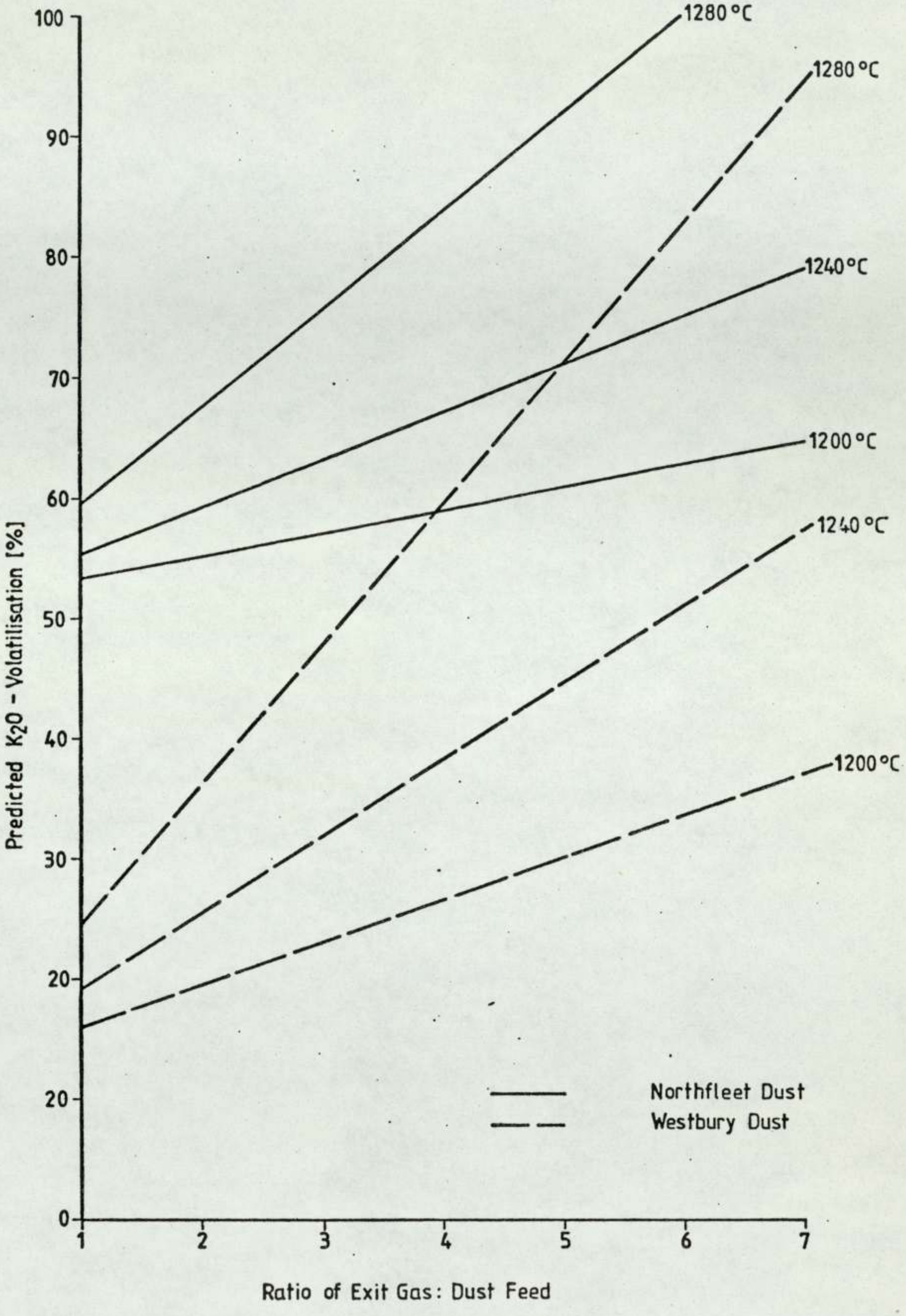


FIGURE 6.28

Predicted Degree of K_2O Volatilisation of Northfleet and Westbury Flue Dusts at Various Temperatures and Gas: Solid Ratios well it is mixed with flue dust. It can be seen from equation (3.1) that if $CaCl_2$ is fully reacted with K_2O, for every 1% of $CaCl_2$ added, 0.85% K_2O will be removed as KCl. In practice, perfect mixing may not be achieved and there may be some $CaCl_2$ not present in close proximity to K_2SO_4. Since the vapour pressure of $CaCl_2$ is relatively low (only about twice that of K_2SO_4), it may not be volatilised and this could result in an increase of the Cl level in the calcined product.

An alternative method of enhancing K_2O volatilisation is by operating the bed under a reducing condition in order to enhance the decomposition of K_2SO_4. This may be achieved by, say, staging the air supply to the bed, as was reported by Swift and Wheelock (1975) for enhancing the decomposition of calcium sulphate in a 'two-stage' fluidised bed reactor. A possible disadvantage of this approach is that other obnoxious gases such as H_2S, CO, etc., may also be generated and could present potential safety hazards.

A third possible approach is to promote the conversion of K_2SO_4 to KOH, which has a vapour pressure even higher than that of KCl, in accordance to the following reaction:-

$$K_2SO_{4(g)} + H_2O \rightleftharpoons 2KOH_{(g)} + SO_2 + \tfrac{1}{2}O_2 \qquad .....(6.13)$$

This approach has been studied by Goes and Keil (1960) and patented by Brachthauser (1968) for alkali reduction in cement burning. However, according to Halstead (1977), this reaction is unlikely to be favourable for dust calcination because of the relatively low temperature involved. This is indirectly corroberated in the present experiments as no significant KOH was found in the alkali product, in spite of a relatively high concentration of H_2O resulting from oxygen enrichment and combustion of propane.

There was no opportunity to study any of these techniques in the present investigation. However, a brief laboratory test to determine the effects of $CaCl_2$ addition and reducing condition on the alkali retention characteristics of a Westbury dust was carried out. As can be seen from Table 6.4, both of the approaches are potentially feasible. The addition of 5% $CaCl_2$ was considerably more effective but also led to a significant increase in the residual Cl of one of the test samples (where CaF_2 was also added to promote lime combination). In a fluidised bed where the residence time is variable, this may pose a greater problem. However, a detailed study is needed before passing further comment.

6.5.3 Design of the Exhaust Gas System

On the basis of the observations and various data given, the design of a fluidised bed exhaust gas system should not present any major difficulty. An important consideration to be noted is the layout of the gas duct. The length should be kept to a minimum and, as far as possible, any bend or short elbow should be avoided. It is also desirable to keep the gas velocity below about 20 m s^{-1} to reduce gas turbulence, particularly when the alkali loading is high. Instead of air quenching, it may be worth considering partial air and water cooling in order to reduce the gas quantity to be handled.

With regard to the choice of alkali collector, it is suggested that the appropriate equipment manufacturer is consulted, using the data presented

TABLE 6.4

Effects of Reducing Conditions and $CaCl_2$ Additive on Alkali Retention Characteristics of Westbury Flue Dust

% w/w	Raw Dust	Calcined Dust		Calcined (Dust + 5% $CaCl_2$)		Calcined (Dust + 5% $CaCl_2$ + 1% CaF_2)	
		Oxidising*	Reducing**	Oxidising	Reducing	Oxidising	Reducing
K_2O	6.2	5.4	3.3	1.8	0.3	2.1	0.4
Na_2O	0.69	0.7	0.6	0.4	0.23	0.4	0.25
SO_3	6.0	8.1	3.4	7.2	0.6	7.9	0.5
Cl	0.8	<0.01	<0.01	0.02	<0.01	0.15	0.02
F	0.15	0.08	0.04	-	-	0.39	0.30
Free Lime		2.8	3.7	8.2	2.9	2.4	1.5

* 20% excess air in the combustion

** 20% deficiency in air in the combustion here as a basis for discussion.

6.5.4 Reliability of the Results

The results are subjected to the usual random and systematic errors in measurements of the test conditions and in the quantifying and analysis of the materials. The magnitude of the measuring and recording instruments' errors have already been indicated (Section 5.3), however they will be compounded by additional random errors. For instance, the fluidised bed temperature over a processing period could vary by as much as 50°C over short duration, although for the tests presented, the variation tended to fall within 20°C in general.

The errors associated with quantifying the materials could arise from material spillage or accumulation, the latter may be fairly significant in some of the tests. As for material analysis, the most significant error is likely to arise from sampling and storage, rather than the analytical techniques.

It is difficult to assess the magnitude of the overall error involved but for the present requirement, it is unlikely to have any significant effect on the conclusions.

CHAPTER 7

PROCESS APPRAISALS AND RECOMMENDATIONS

Summary

An appraisal of the fluidised bed process developed during this work is presented. On the basis of calcining 300,000 t.p.a. of Northfleet flue dust and assuming that the feed to the fluidised bed calciner is dried and preheated to 100°C and that the combustion air is preheated by heat exchange with the calcined product, the fuel consumption of the process is calculated to be approximately 1200 kcal/kg of dust. The electrical power consumption of the process is estimated to be approximately 70 kWh/t of dust and the capital cost of the plant to be approximately £2.6M (in 1976).

Assuming a yield of 0.62 t calcined product and 0.1 t alkali product per tonne of dust calcined, and product values of £6.5/t for the calcined product and £15/t for the alkali product, a small return on capital (10%) is obtained when a dumping credit of £1.5/t dust is allowed: this is estimated to be the saving from ceasing the dust dumping operation. Compared with alternative processing options, it is shown that the case of converting a surplus capacity cement kiln near Northfleet Works would offer the greatest financial incentive. A leaching and crystallisation scheme involves the highest capital investment and shows a return similar to that of the present process, and two alternative Pyzel schemes which are considered, one including electricity generation and one without, appeared fairly promising on the simple evaluation carried out.

The technical merits of the various options are briefly considered and the possibilities of refining the present process are indicated. These include recrystallisation of the alkali product in order to increase its sale value, inclusion of more extensive heat recuperation systems to lower the fuel consumption and the possibility of obtaining additional cost benefits by combining the calcination process with the incineration of certain chlorinated organic wastes. A broad outline of the recommended future work is included.

7.1 Introduction

In Chapter 3, it was shown that several options appear to be technically feasible for processing Northfleet and Westbury flue dusts, viz, leaching and crystallisation, rotary kiln calcination, and the (fluidised bed) Pyzel process. Normally, the kiln option would be excluded because of the high capital cost required. However, the recent closure of a BCI cement works (Wouldham Works) near to Northfleet Works had made available a number of kilns for possible conversion to process flue dust.

In this chapter, a preliminary assessment of the techno-economical aspects of the various options for processing Northfleet flue dust are considered. The case for Westbury dust cannot be compared at this stage because of the further development work needed to enhance the K_2SO_4 volatilisation.

7.2 Preliminary Economic Evaluation of Various Options for Processing Northfleet Flue Dust

7.2.1 Bases of Evaluation

The evaluation is based on a dust throughput of 300,000 t.p.a., which is the estimated quantity of dust available from Northfleet Works when operating at full capacity, and the composition of the dust is based on that shown in Table 4.1. The data for the Pyzel process are derived from Haspel (1976), those for a possible Wouldham kiln conversion from Onions (1977) and for the leaching and crystallisation case, the operating data from Table 3.2 are applied with slight adjustment (but the yields of the alkali salts are based on the dust shown in Table 4.1, assuming that 90% of KCl and K_2SO_4 are recovered).

For the pellet-fed fluidised bed process developed here, 1200°C operation is assumed. Although it was indicated in Section 6.5.1 that a temperature of about 1250°C is probably required to produce a calcined product of $<4\%$ K_2O, this criterion is only approximate and is not considered to be critical, provided the K_2O level in the feed does not exceed 6% (refer Section 4.2.3). Assuming that virtually all the Cl present is volatilised, more than 50% of K_2O will be removed, and when allowance is made for a small amount of K_2O removal with the carry-over material, the level of K_2O in the calcined product is expected to be in the region of 4-5%.

7.2.2 Process Flowsheet and Anticipated Performance of the Fluidised Bed Option

The flowsheet of the fluidised bed process envisaged is shown in Figure 7.1 and a discussion of the design of the various plant items has been presented in previous chapters. For the present evaluation, a bag filter is assumed and the temperature of the gas available for drying is taken as 250°C. It is assumed that the feed particles are dried to 2% moisture and preheated to 100°C before feeding to the calciner. The effects of using an electrostatic precipitator or varying the degree of preheating are considered elsewhere (Khor, 1976). The heat and mass balance of the scheme, including the assumptions and data used in the calculation, is presented in Appendix F, which also gives an estimate of the electrical energy required for the major fans. A summary of the heat balance for the fluidised bed calciner is shown in Table 7.1 and as can be seen, the heat consumption is estimated to be approximately 1200 kcal (nett)/kg dust or in the terminology of U.K. cement industry, an equivalent of 18.1% 'standard coal' consumption. (A standard coal is a

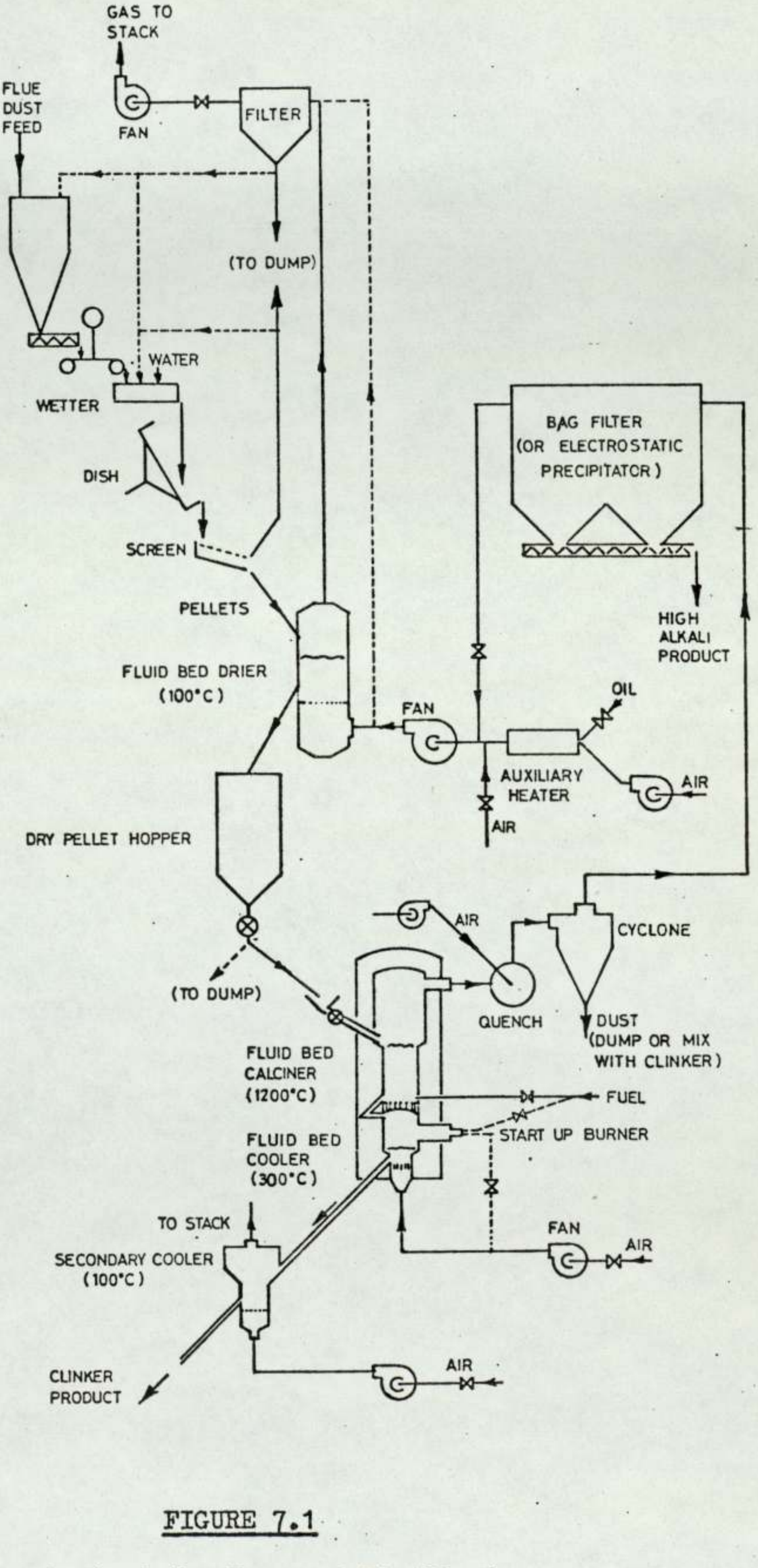


FIGURE 7.1

Flowsheet of the Proposed Fluidised Bed Calcination Process

TABLE 7.1

Summary of the Fluidised Bed Calciner Heat Balance

$$\text{Basis:- 1 kg dust feed} \xrightarrow{1200^\circ C} \begin{array}{l} \text{0.62 kg calcined product,} \\ \text{0.10 kg alkali product,} \\ \text{0.05 kg carry-over material, and} \\ \text{0.21 kg } CO_2 \text{ and 0.02 kg } H_2O \end{array}$$

Datum = 20°C

Heat Input	Kcal/kg dust	% of Heat
Coal	1203	89.3
Preheated Air (313°C)	128	9.5
Preheated Feed (100°C)	16	1.2
	1347	100.0
Heat Output		
Exhaust Gases (incl. Feed CO_2 & H_2O)	770	57.2
Theorectical Heat of Reaction	230	17.1
Calcined Product	183	13.6
Alkali & Carry-over Material	44	3.3
Heat Losses	120	8.9
	1347	100.1

notional coal with a gross calorific value of 700 kcal/kg or approximately 6650 kcal/kg nett).

The electrical energy estimated for the 5 major fans is approximately 60 kWh/t dust, Table 7.2, but in addition to this, the mixer and pelletiser are estimated to need 5 kWh/t dust. With further allowance of 5 kWh/t dust for various items of equipment not considered in detail, the total electric energy required is approximately 70 kWh/t dust.

7.2.3 Economic Comparison of the Alternative Schemes

Table 7.3 shows an economic comparison of the options which are technically feasible for processing Northfleet flue dust. The capital costs were provided by the 'Southern Area Technical Services Department' of BCI. A working capital corresponding to 10% of the capital cost is allowed in each case except for the rotary kiln conversion scheme where the capital cost shown represents only the cost of plant modification. The true capital cost was estimated to be £4.8 and this figure is used for both the working capital and maintenance allowance.

The table only compares the more readily quantifiable direct variable costs. There is no allowance for capital charges and plant depreciation or additional site utilities and services, which could vary significantly for the different schemes shown. In the case of leaching and crystallisation, an additional £4.1/t is allowed for the cost of handling and calcining the treated dust after leaching. Because of a greater quantity of alkali product produced, the yield of clinker from the leaching and crystallisation scheme after allowing for 5% dust loss in the kiln is assumed to be 60% (instead of 62% for other schemes). A credit of

TABLE 7.2

Summary of Gas Quantity, Temperature and Pressure and the Fan Power Required for the Fluidised Bed Plant

Fan	Gas Quantity (kg/kg dust)	Fan Inlet Temperature (^oC)	Fan Inlet Pressure (mm W.G.)	Fan Outlet Pressure (mm W.G.)	Fan Power (kWh/t dust)
Drier/Filter	4.20	100	-900	atm	15.0
Primary Cooler/ Calciner	1.82	20	atm	1800	10.0
Secondary Cooler	1.21	20	atm	600	2.3
Quench Air	10.55	20	atm	100	3.4
Exhaust Gases	12.79	250	-400	atm	29.1

Total = 59.8 kWh/t dust

TABLE 7.3

Economic Comparison of Various Options for Calcining 300,000 t.p.a. of Northfleet Flue Dust

OPTION		(A) Pellet-Fed Fluidised Bed Process		(B) Pyzel Process - without Electricity Generation		(C) Pyzel Process - with Electricity Generation		(D) Leaching and Crystallisation Process		(E) Conversion of Redundant Kiln	
Capital Cost		£2.56M		£2.81M		£3.70M		£5.27M		£0.93	
Working Capital		£0.26M		£0.28M		£0.38M		£0.53M		£0.48M @	
TOTAL INVESTMENT:-		£2.82M		£3.09M		£4.16M		£5.80M		£1.41M	
Operating Cost	Unit Cost	Requirement per t dust	Annual Cost (£)	Requirement per t dust	Annual Cost (£)	Requirement per t dust	Annual Cost (£)	Requirement per t dust	Annual Cost (£)	Requirement per t dust	Annual Cost (£)
Energy - Coal (std)	£25/t	0.181t	1,357,000	0.125t	938,000	0.125t	938,000	Additional Kilning*	800,000	0.15t	1,125,000
- Fuel Oil	£50/t	-	-	-	-	-	-	0.069t	1,035,000	-	-
- Electricity	1.7p/kWh	70 kWh	357,000	70 kWh	357,000	Nil	-	35 kWh	179,000	38 kWh	194,000
Labour & Supervision	£5000/ man year	12 men	60,000	8 men	40,000	8 men	40,000	16 men	80,000	20 men	100,000
Maintenance	2½% of investment	-	71,000	-	77,000	-	104,000	-	145,000	-	132,000 %
TOTAL OPERATING COST:-		£1,845,000		£1,412,000		£1,082,000		£2,239,000		£1,551,000	
Revenue	Unit Value	Yield per t dust	Annual Revenue (£)	Yield per t dust	Annual Revenue (£)	Yield per t dust	Annual Revenue (£)	Yield per t dust	Annual Revenue (£)	Yield per t dust	Annual Revenue (£)
Credit from Dumping	£1.5/t	-	450,000	-	450,000	-	450,000	-	450,000	-	450,000
Calcined Product	£6.5/t	0.62t	1,209,000	0.62	1,209,000	0.62	1,209,000	0.60	1,170,000	0.62	1,209,000
Alkali Product	£15/t	0.10t	450,000	0.10	450,000	0.10	450,000	-	-	0.10	450,000
Recrystallised KCl	£30/t	-	-	-	-	-	-	0.064	576,000	-	-
Recrystallised K_2SO_4	£45/t	-	-	-	-	-	-	0.056	756,000	-	-
TOTAL REVENUE:-		£2,109,000		£2,109,000		£2,109,000		£2,952,000		£2,109,000	
ANNUAL RETURN:-		£264,000		£697,000		£1,027,000		£713,000		£558,000	
ANNUAL RETURN ON CAPITAL:-		10.3%		24.0%		27.2%		13.5%		60.0%	
SAVINGS/t OF DUST PROCESSED		£0.88		£2.32		£3.42		£2.38		£1.86	

£1.5/t dust resulting from savings in dust dumping is also allowed.

As can be seen, all the options show a return on capital but the rate varies from 10% for the pellet-fed fluidised bed process to 60% for the conversion of Wouldham Works. As mentioned earlier, various overhead charges and certain variable costs are omitted and the figures should therefore be regarded as simple yardsticks for gross comparison. Nevertheless, it is clearly demonstrated that unless considerable improvements to the pellet-fed fluidised bed process can be made, this particular option is unlikely to be commercially viable. The technical features of the various options and, in particular, consideration for improving the fluidised bed process are discussed in the next section.

7.3 Technical Considerations

7.3.1 General Appraisal of the Alternative Schemes

Although it is evident from the previous discussion that the pellet-fed fluidised bed is financially the least attractive of the various options considered, there are a number of features which make the process potentially preferable. For instance, the process can be built in two stages to reduce the capital investment: initially the pelletisation plant can be built, simply to enable unobtrusive dumping to continue until the calcining plant becomes necessary. Compared with the Pyzel process, the pellet-fed route is considerably more flexible, as the former necessitates the bed to operate at incipient fusion temperature to ensure efficient dust accretion. Any variability of the feed composition may impair the bed performance and increase the risk of fusion. Moreover, it also appears that for the same bed temperature, the degree of K_2O removal is lower in the Pyzel process (see Section 6.4.4). The principal advantage of the Pyzel process over the present process is the greater heat recuperation which reduces the fuel consumption significantly, Figure 7.2. However, the feasibility of the heat recuperation system is still subject to some uncertainty and moreover, if proven, the recuperation system may also be adopted in the present process.

With the leaching and recrystallisation option, there is still a major area of uncertainty, viz, the handling and calcining of the sludge containing the treated dust. The process also produces a small quantity of waste liquor, comprised mainly of various unrecovered salts which would need to be disposed of or, as suggested in one of the schemes, returned to the kiln with the sludge. In addition, the large plant area and large quantity of process and cooling water required might not be readily available at Northfleet Works.

The case for converting Wouldham Works is by far the most desirable financially. However, the feasibility of the process is crucially dependent on the assumption that the rotary kiln is capable of handling the very high alkali concentration in the exhaust gases, which has yet to be proven under large scale operating conditions. In the small scale trials (Section 3.4.3), the gas volume and temperature were both considerably higher than would be expected in a production plant. Nevertheless, for the particular case of Northfleet Works where the redundant works is situated at close proximity, the option is worth pursuing further.

In the following sections, the possibilities of refining the present

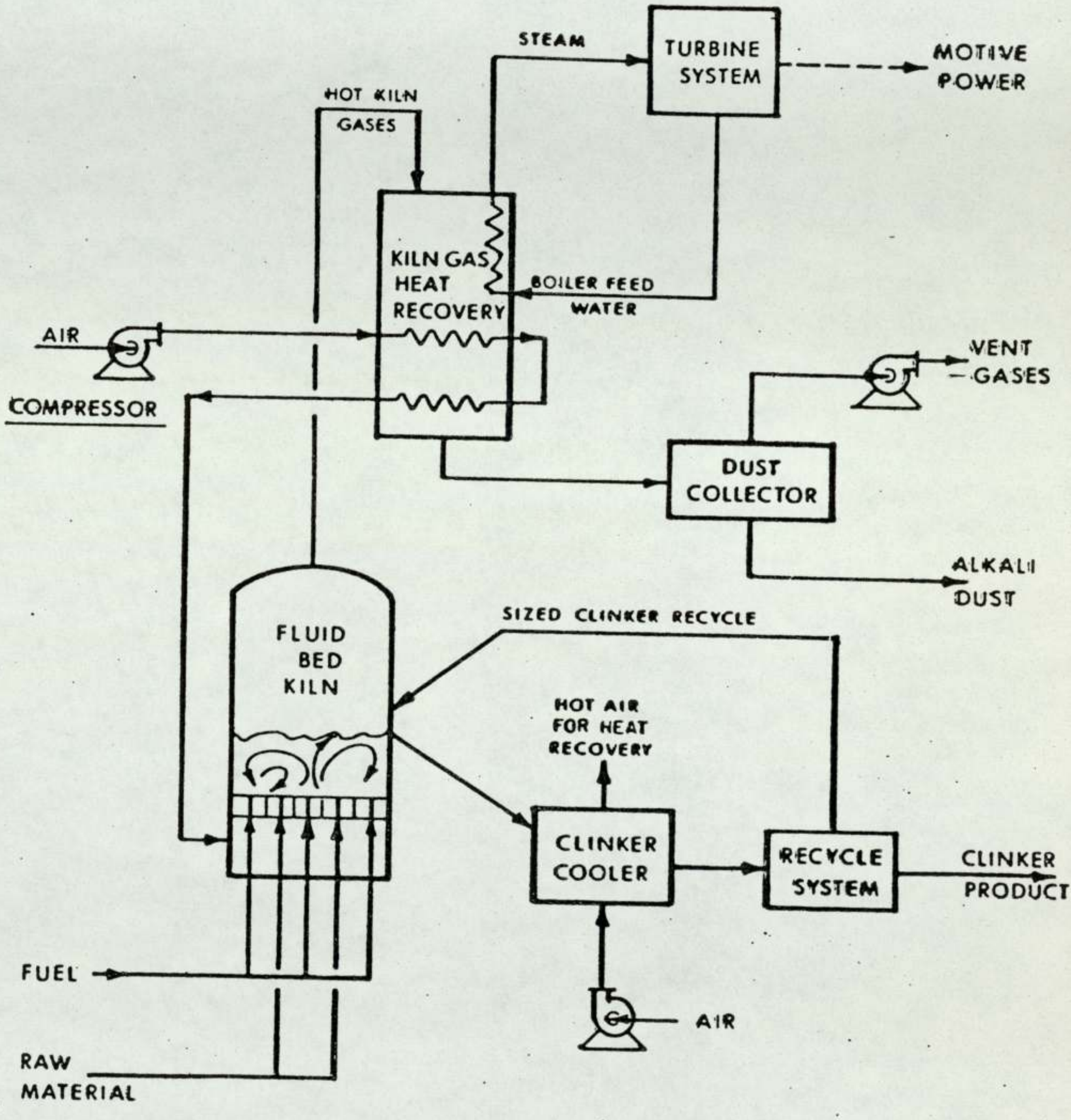


FIGURE 7.2

Pyzel Fluidised Bed Process
Incorporating Electricity Generation

process are discussed.

7.3.2 Beneficiation of the Alkali Product

It is evident from the comparative costs of alkali product and recrystallised alkali salts shown in Table 7.3 that it is possible to double the revenue from the alkali product by subjecting it to recrystallisation. The feasibility of the scheme was investigated by Evans (1977) and two methods were suggested: one based on dry alkali product collection, in which the material is first dissolved in water and then recrystallised to obtain separate fractions of relatively pure KCl (+ Na_2SO_4) and K_2SO_4, Figure 7.3, or alternatively an alkali salt solution may be obtained directly by venturi scrubbing, Figure 7.4. Based on the published solubility data of the various alkali salts involved, the heat requirement for evaporating a saturated solution of salts is estimated to be approximately 200 kcal/kg dust processed, which may be recuperated from the waste gases without additional fuel requirement, as is illustrated in the next section.

7.3.3 Potential of Heat Recuperation

From Table 7.1, it is clear that there is considerable potential for improving the fuel consumption of the fluidised bed process, which represents about 70% of the operating cost involved. One possibility which has already been mentioned is to adopt the recuperation system suggested in the Pyzel scheme (Figure 7.2). An alternative possibility is shown in Figure 7.5, where the calciner exhaust gases are partially utilised for preheating the combustion air and partially for raising steam which is then used for recrystallisation of the alkali salts. In addition, the feed is dried and preheated to a higher temperature using

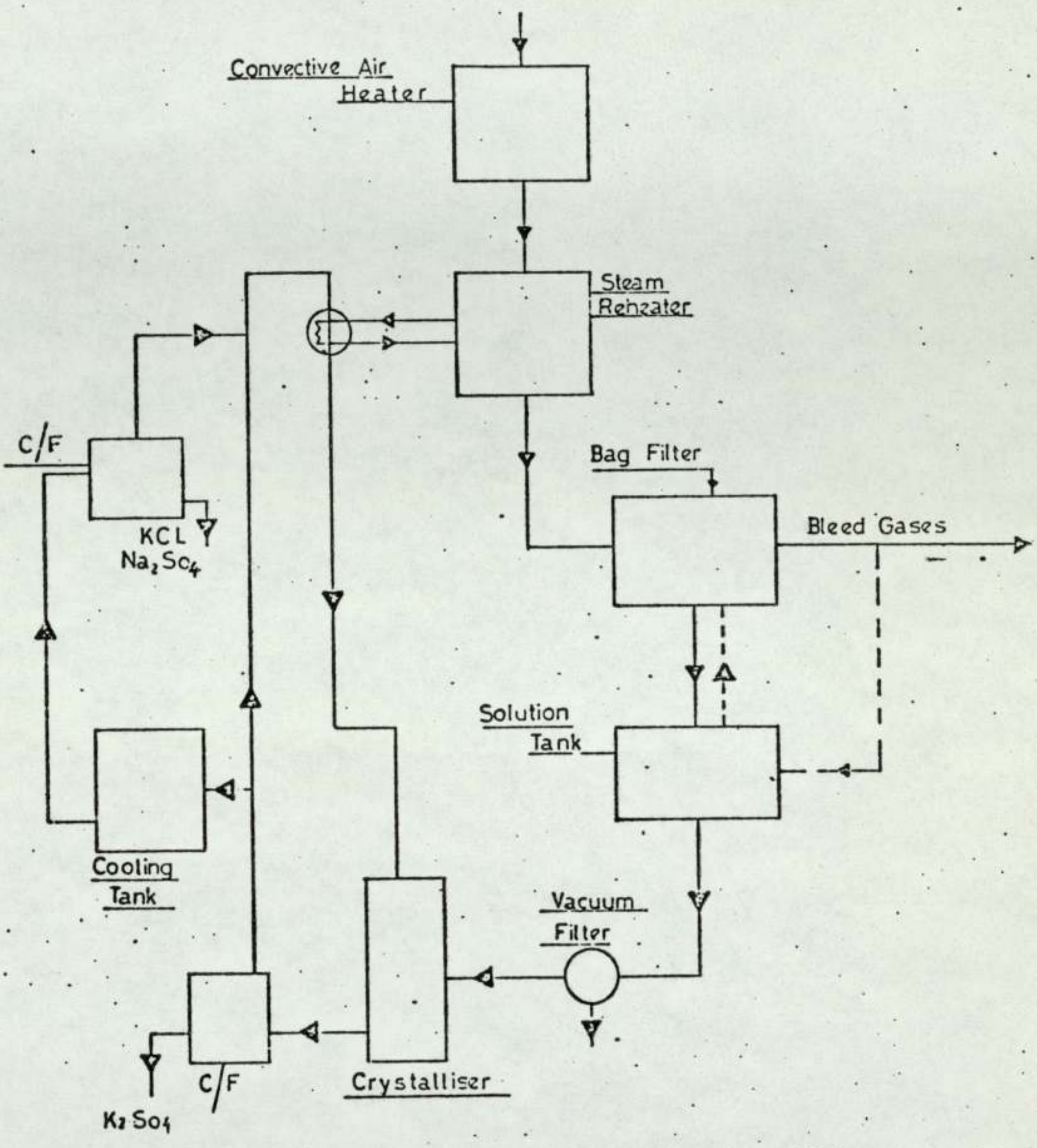


FIGURE 7.3

Proposed Scheme for Beneficiation of Alkali By-Product via Dry Collection

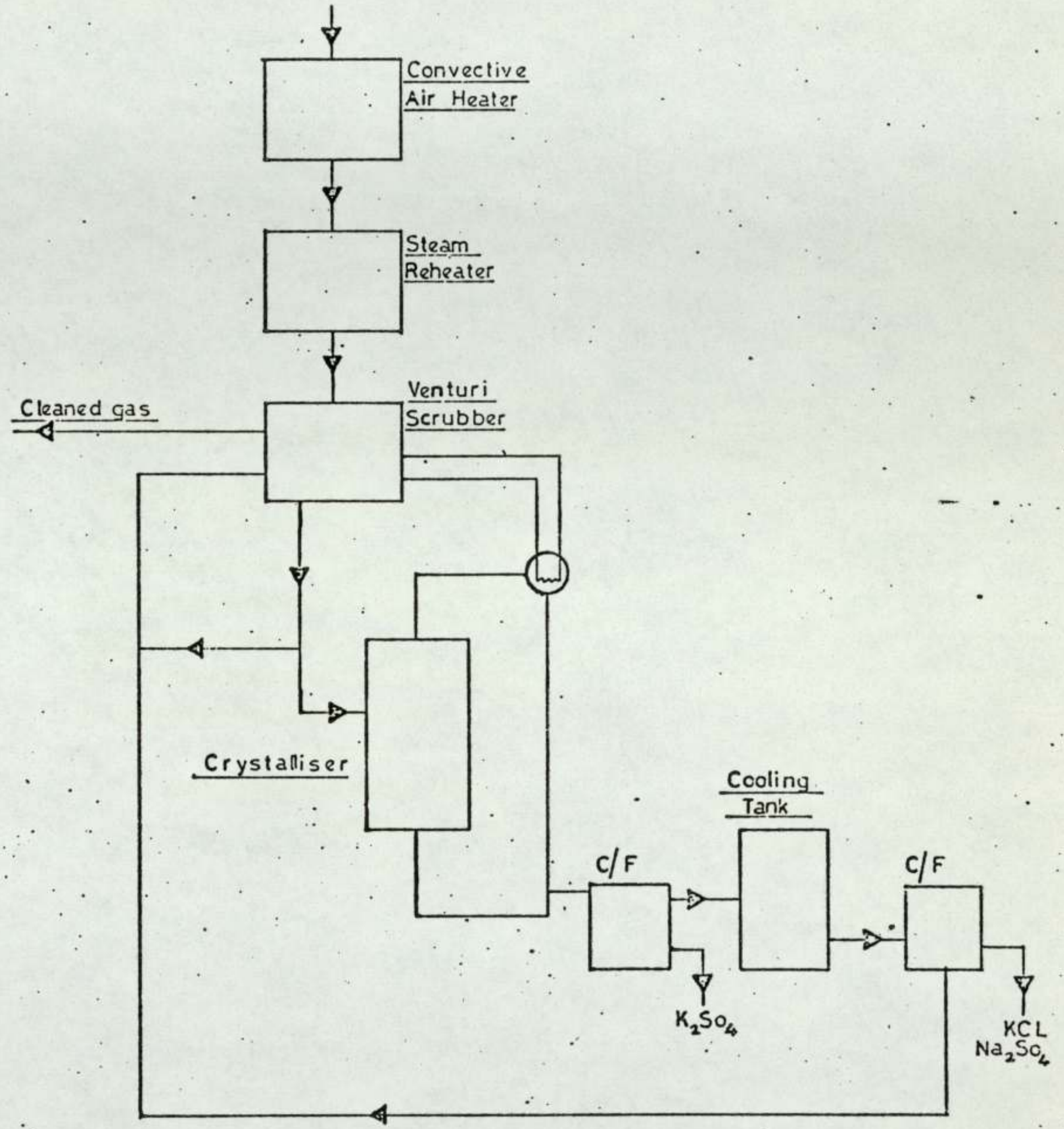


FIGURE 7.4

Proposed Scheme for Beneficiation of Alkali By-Product via Wet Collection

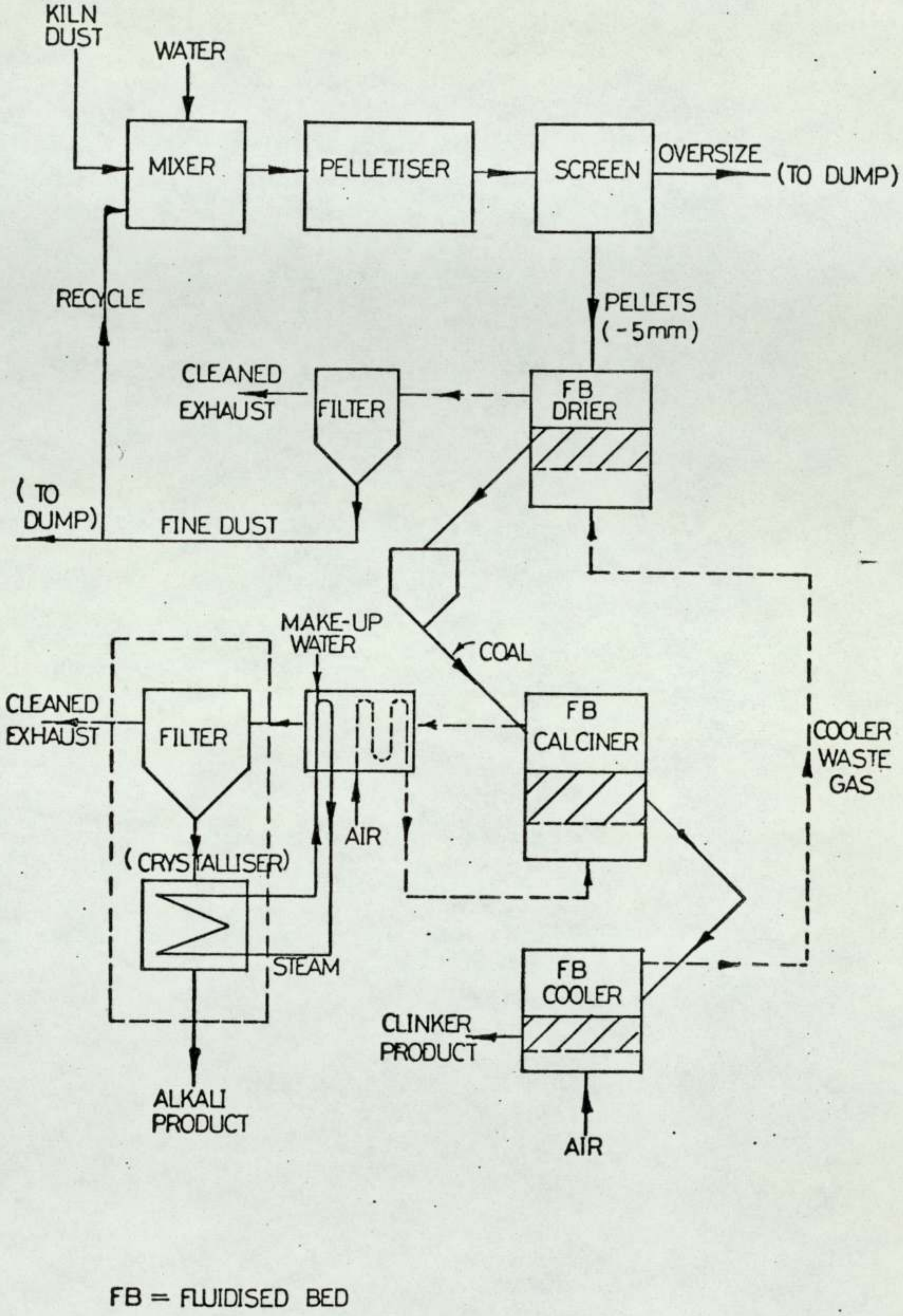


FIGURE 7.5

Proposed Scheme for Improving Heat Recuperation and Alkali By-Product Beneficiation the waste gas from the fluidised bed coolers.

Obviously, any improvement in heat utilisation will lead to a reduction in the gas:solid throughput ratio which will reduce the degree of K_2SO_4 volatilisation.

7.3.4 Combining Flue Dust Calcination with Incineration of Organic Wastes

It may be feasible to combine the calcination of flue dust with the incineration of certain chlorinated organic waste products such as carbon tetrachloride and hexachloroethane; trichloroethylene and vinyl chloride; monochlorobenzene and para-chlorotoluene; polyvinyl chloride and chlorinated polythene as well as chlorinated pesticides such as lindane and the DDT family. Apart from providing a source of income, since such wastes are usually available with credits for their disposal (which may be as much as £100/t), the wastes also have a significant calorific value and contain the Cl radical which could be effectively utilised in enhancing the volatilisation of K_2O and Na_2O.

7.4 Recommendation for Future Work

It can be seen from the previous sections that there is considerable scope for improving the fluidised bed process to make it financially viable. As far as the problems of Northfleet and Westbury Works are concerned, a first priority should be given to the investigation of the feasibility of enhancing K_2SO_4 volatilisation via $CaCl_2$ addition or by using reducing conditions, as this will reduce the calcining temperature required and thus improve the general performance of the process. Additionally, an effective heat recuperation system should be developed and the feasibility of recrystallising the alkali product into separate fractions of KCl and

K_2SO_4 investigated. If the suggestion of combining flue dust calcination with organic waste incineration can be shown to be viable, then this should supersede the priorities of the various work items indicated since it is potentially the most rewarding.

In carrying out any future experiments, particular attention should be given to obtaining a good material balance and ensuring that the variability of the bed temperature is kept to a minimum. It is recommended that a larger fluidised bed of, say, greater than 200mm diameter be used so that there is no need to rely on oxygen-enrichment to reduce the fluidisation velocity. Where practicable, the test duration should be extended and regular sampling and analysis of materials carried out during the tests. The relevance of feed composition, calcining atmosphere, solid residence time, bed temperture, etc., should be more systematically investigated. Finally, a more precise method of sampling and positive weighing of the bed inventory would also be desirable.

CHAPTER 8

CONCLUSION

A study has been made of the feasibility of simultaneously producing a low grade cement clinker and fertiliser from 1-5mm pellets of alkali-rich flue dusts derived from Northfleet and Westbury cement works by calcining in a fluidised bed. On the basis of the experiments carried out in 100mm and 150mm diameter fluidised beds, the following conclusions are drawn:-

(1) A significant proportion of alkalis (i.e. K_2O, Na_2O, Cl and SO_3) present in the dusts can be volatilised by treatment at a temperature of approximately 1200°C for about 30 min. The proportion of original alkalis retained or volatilised in these tests cannot be characterised simply as a function of the calcining temperature, as was implied in previous work. Based on evidence derived from XRD analyses and leaching and crystallisation of the dusts carried out elsewhere, the alkalis are shown to be present predominantly as KCl, K_2SO_4 and Na_2SO_4 which gave significantly different volatilisation characteristics due to the differences in vapour pressures.

(2) In the case of KCl, almost 100% volatilisation can be achieved and for the range of temperature (1120-1260°C) and mean residence time (14-59 min) investigated, the degree of volatilisation was virtually independent of either of these parameters. This is consistent with the published saturation vapour pressure of KCl which indicates that

the amount of KCl vapour which can be carried in, say, 1 kg of air at 1200°C before it becomes saturated is approximately 600 g vapour, which far exceeds the amount of KCl available from either of the dusts under normal calcining conditions. As far as the relevant product quality criterion is concerned, most of the calcined product had a Cl level considerably less than the stipulated maximum of 0.3% Cl. This limit was exceeded in some tests when there was a higher proportion of poorly calcined material which appeared to arise from a combination of low residence time and temperature, or possibly poor sampling.

(3) The volatilisation of K_2SO_4 (or 'Nett-K_2O' as is used in this thesis) is primarily controlled by the saturation vapour pressure at the bed temperature, as is supported by fairly good correlation of the experimental data. Good agreement is also obtained when the data are compared with the saturation vapour pressure of K_2SO_4 reported by Hart and Laxton (1967) and with the results of 300mm and 450mm fluidised bed experiments. As a general guide, the amount of 'Nett-K_2O' which can be carried in air before it becomes saturated is only approximately 4 g of vapour per kg of air at 1200°C, increasing to approximately 10 g at 1260°C. In the present experiments, because of the high gas:feed ratio, a considerably higher degree of K_2SO_4 volatilisation than would normally be expected in a production plant was achieved. Consequently, all the normal Northfleet and Westbury dusts which were calcined were able to meet the quality criterion of <4% K_2O in the calcined product. Prediction based on the experimental results indicates that in a full scale plant, this criterion may only be attained at approximately 1250°C for a gas:feed

ratio of 2 for a typical Northfleet dust and that at the same temperature, a gas:feed ratio of up to 5 is required for a typical Westbury dust, which is obviously unlikely to be an economical proposition. However, there is evidence to suggest that the saturation vapour pressure of K_2SO_4 may be exceeded under a reducing condition; alternatively, the amount of K_2O volatilisation may also be enhanced by adding $CaCl_2$ to the feed to convert K_2SO_4 to KCl.

(4) It is not necessary to volatilise the Na_2SO_4 because of the low concentration present. Nevertheless, for completeness, the experimental data are shown to correlate according to the vapour saturation model as in the case of K_2SO_4. Good agreement was obtained between the Westbury data and the unsuppressed saturation vapour pressure of Na_2SO_4 reported by Cubicciotti and Keneshea, (1972). However, the Northfleet data were consistently above the saturation vapour pressure, and it is thought that this was due to a small amount of Na_2O being present as NaCl.

(5) The amount of residual free lime is not a critical requirement in the situation considered at present, where the amount of calcined dust to be added to the works clinker is relatively small. However, to minimise the diluent effect of such an addition, it is suggested that the maximum free lime content of the calcined dust should be limited to 16% for Northfleet works and 9% for Westbury works. These criteria were readily achieved and typically, only 5-6% residual free lime was obtained. Within the range of conditions studied, the amount of free lime was fairly insensitive to the bed temperature but decreased as the mean residence time was increased. In order to

avoid an excessive amount of poorly calcined material, it is recommended that the fluidised bed be designed for at least 40 min residence time.

(6) There was little problem in fluidised bed operation, provided the fluidisation velocity was maintained at about 3-4 m s^{-1} and the bed temperature did not exceed 1260°C. Otherwise, there could be a risk of bed fusion as a result of poor mixing and excessive flux formation. The propensity towards bed fusion appeared also to be affected by the dust composition. Generally, the Westbury dust was found to be more susceptible to fusion than the Northfleet dust. This is thought to be due to the presence of a higher concentration of sulphates in the former dust, which enhanced the formation of the low temperature calcium and alkali sulphate eutectic melt. However, there is also some indication that part of the problem of fusion was due to the sensitivity of the small bed used for these tests to slight variability of the feed or fuel input rates. In a larger bed, a higher temperature may be feasible.

(7) There was little problem with the recovery of the alkali product provided the fluidised bed exhaust gases were adequately quenched, preferably to below 650°C, and the coarser carry-over material, which amounted to typically 5% of the feed, was pre-separated in a cyclone. Problems of build-up, which occurred in the initial experiments, are attributed to a combination of high exit gas temperature (~700°C) and dust loading (~40% of feed was lost) in the case of the calcium sulphate type (hard) build-up, and excessive turbulence and high KCl concentration in the gas stream in the case of the alkali-based

(soft) build-up. The performance of the bag filter and electrostatic precipitator achieved in these tests was unstaisfactory, but more data are now available for the proper design of either of these items of equipment for future work.

(8) Preliminary evluation of the process for calcining 300,000 t.p.a. of Northfleet dust, assuming that a yield of 62% calcined product and 10% alkali product are attainable (with 5% carry-over material), and that the theoretical heat of reaction is 230 kcal/kg, indicate a fuel consumption of approximately 1200 kcal/kg dust and an electric consumption of approximately 70 kWh/t dust. This is based on the feed being preheated to 100°C by the calciner exhaust gases and the combustion air preheated to 300°C by the calcined product. On estimated 1976 cost levels, the process is shown to provide an annual return of about £250,000 for a capital investment of £2.6M when a credit of £1.5/t dust is allowed due to savings gained from discontinuation of dumping.

(9) When compared with the alternative options which appear also to be technically feasible, viz, Pyzel process, leaching and crystallisation, and conversion of a redundant cement kiln, the eonomics of the present process are unattractive, mainly because of the high fuel consumption. However, there is considerable scope for refining the process, including better utilisation of the fluidised bed exhaust gases (possibly in combination with a scheme for fractional recrystallisation of the alkali product in order to enhance its sale value) and the possibility of combining dust calcination with incineration of certain chlorinated hydrocarbon

wastes.

(10) Finally, an important contribution of this thesis which should not be overlooked is that it provided a basis for any further work on flue dust processing to be carried out and it also presents a considerable amount of previous, hitherto unpublished work on flue dust processing. Additionally, the saturation vapour pressure model presented may find application in the study of alkalis in cement manufacture and the general concept of the present work may be usefully applied to other minerals or wastes processing particularly when they involve the volatilisation or decomposition of low volatile components.

APPENDIX A

Glossary of Terms and Definitions

A.1 Cement Quality Factors

(a) Lime Saturation Factor (L.S.F.)

The general aim of cement burning is to produce a clinker with as high a C_3S content as is possible. The potential for this can be expressed as the Lime Saturation Factor which is defined in B.S.12 as:-

$$\text{L.S.F.} = \frac{(\text{CaO}) - 0.7(\text{SO}_3)}{2.8(\text{SiO}_2) + 1.2(\text{Al}_2\text{O}_3) + 0.65(\text{Fe}_2\text{O}_3)} \times 100\% \qquad .....(\text{A.1})$$

where each symbol in brackets refers to the % (by weight of total cement) of the oxide, excluding any contained in the insoluble residue. The expression is derived from studies of the equilibrium combination of the materials involved and assumes that the whole of SO_3 present to be in combination with CaO and that there is no free lime present. When the L.S.F. = 100%, the maximum proportion of SiO_2 present is potentially as C_3S and as L.S.F. decreases, the proportion of SiO_3 as C_3S decreases and that as C_2S increases concomittantly.

(b) Lime Combination Factor (L.C.F.)

In the previous section, the word potentially with respect of C_3S content is used because in all normal cement there is invariably a content of free lime, i.e. lime not in combination with any other component and therefore not contributing to the production of C_3S. To take account of this, an additional factor known as the Lime Combination Factor is often included:-

$$\text{L.C.F.} = \frac{(CaO) - 0.7(SO_3) - (\text{Free CaO})}{2.8(SiO_2) + 1.2(Al_2O_3) + 0.65(Fe_2O_3)} \qquad .....(A.2)$$

Thus with an L.C.F. = 100%, the maximum possible proportion of SiO_2 is as C_3S.

(c) Silica Ratio (S/A+F or S/R)

This is the ratio of SiO_2 content to the sum of Al_2O_3 and Fe_2O_3, i.e.

$$S/A{+}F = S/R = \frac{\%\ SiO_2}{\%\ Al_2O_3 + \%\ Fe_2O_3} \qquad .....(A.3)$$

The full significance of this factor is outside the scope of this discussion but simply from a compositional point of view it follows that the higher the silica ratio the higher is the proportion of C_2S and C_3S, other factors being unchanged.

(d) Alumina-Iron Ratio (A/F)

This is the ratio of Al_2O_3 content to Fe_2O_3 content, i.e.:-

$$A/F = \frac{\%\ Al_2O_3}{\%\ Fe_2O_3} \qquad .....(A.4)$$

The ratio determines the proportion of C_3A to C_4AF in cement, the higher the ratio the higher is the proportion of C_3A.

A.2 Definitions of Performance Parameters for Flue Dust Calcination

(a) Degree of Alkali Retention = $\dfrac{\text{Amount of Alkali in Calcined Product}}{\text{Amount of Alkali in Feed}}$

$$= \frac{F_o . x_o}{F_i . x_i} \times 100\% \qquad .....(A.5)$$

(b) Degree of Alkali Volatilisation = $\frac{\text{Amount of Alkalis Volatilised}}{\text{Amount of Alkalis Input}}$

$$= \frac{F_i . x_i - F_o . x_o - \Sigma F_e x_e}{F_i . x_i} \times 100\% \qquad .....(A.6)$$

(c) Alkali Collection Efficiency = $\frac{\text{Amount of Alkali Collected}}{\text{Amount of Alkali Volatilised}}$

$$= \frac{F_a . x_a}{F_i . x_i - F_o . x_o - \Sigma F e x_e} \times 100\% \qquad .....(A.7)$$

(d) Material Yield = $\frac{\text{Amount of Material Obtained}}{\text{Amount of Feed Input}} \times 100\%$ .....(A.8)

A.3 Meanings of the Fluidised Bed Operating Factors

(a) Fluidisation Velocity, $U_o = \frac{\Sigma G_i}{A_t} \times \frac{(T_b + 273)}{273} \text{ m s}^{-1}$ .....(A.9)

(b) Bed Inventory, $W = A_t \; \Delta P_B$

$$= A_t \; (\Delta P_o - \Delta P_D) \text{ kg} \qquad .....(A.10)$$

(c) Mean Residence Time, $\tau_s = \frac{W}{F_o + F_e} \times 60 \text{ min.}$ .....(A.11)

APPENDIX B

Experimental Investigation of the Alternative Methods of Feed Production for Fluidised Bed Calcination

B.1 Introduction

Since flue dust is a very fine material (refer Figure 4.1), it is necessary to agglomerate it to form larger particles for fluidised bed calcination. Various methods of feed production were investigated and the preferred method was to pre-wet the dust followed by dish pelletisation and fluidised bed drying of the wet pellets. The properties required of the wet pellets for processing in a fluidised bed drier and of the dried pellets for processing in a fluidised bed calciner cannot be defined accurately. According to Thyer (1974), an acceptable particle size distribution of the feed is between 0.5mm and 5mm (shaded area in Figure B.2) and, from various tests carried out in BCI, a minimum crushing strength of 300 g wet and 600 g dry for 3mm pellets may be adopted as a rough guide for the strength requirement.

B.2 Pre-wetting and Pelletisation of Flue Dust

This method of pelletisation is fairly familiar to cement manufacturers in connection with either Lepol kilns or dust dumping. However, the pellets produced usually have a size range of 5-25mm. The feasibility of producing smaller pellets was initially examined at BCI Research Division using a Lodige-Morton mixer and dish pelletiser to treat Northfleet flue dust. It was shown that pellets within the size range of 0.5-5mm could be produced. In the calcination trials in Australia (Section 3.5.3), a suitable feed of Northfleet flue dust was produced without a dish pelletiser by using either a 2-pass pelletisation in a peg mixer (320mm (D) x 1230mm (L)) or a paddle mixer for pre-wetting followed by pelletisation in the peg mixer. However, the throughputs obtained were low, averaging about 12 kg/h by the first method and just over 100 kg/h by the second.

In early 1975, a large-scale trial was carried out in a 40 t/h fly-ash pelletisation plant on hire from Lytag Ltd., Tilbury, Figure B.1. Northfleet flue dust was pre-wetted and pelletised under various conditions to determine the optimum design parameters (Evans, 1975 a). It was established that consistent and good quality pellets of 0.5-5mm diameter could be produced with minimal supervision by the addition of about 18% water in the peg mixer at a dust throughput of about 6 t/h. The typical particle size distribution obtained is shown as line D in Figure B,2, which is clearly within the recommended size range. Incorporation of pulverised coal fuel in the pellets was also achieved without difficulty, by adding the coal as a slurry to the peg mixer. However, attempts to pelletise the dust using only the peg mixer were unsuccessful, producing a substantial proportion of fines (up to 40% < 0.6mm) and oversize (up to 20% >4.8mm).

Further trials covering both Northfleet and Westbury dusts were made in BCI Research Division at Barnstone using a similar rig (Evans, 1976 b). There was generally little difference found for the two dusts. The main operational problem was a high wear rate of pegs in the mixer. Wear rates of the order of 1mm per 10 h were observed on tungsten carbide tips used in the Lytag machine and 0.1mm/10 h on harder steel tips in the Barnstone

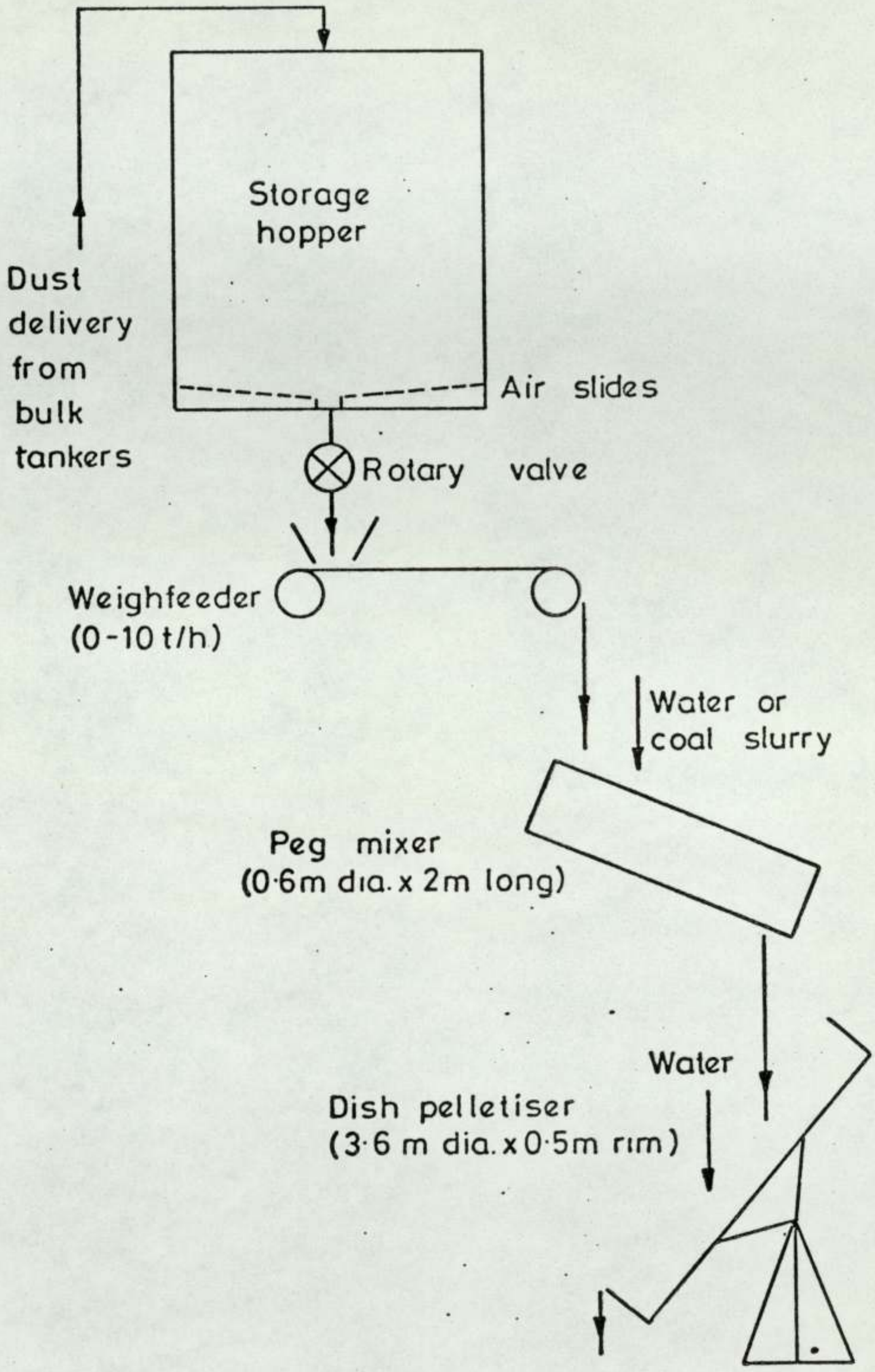


FIGURE B.1

Schematic of Lytag Pelletisation Plant, Tilbury machine. In a production plant, experimentation with different tip materials and peg clearance would probably reduce the wear rates, but regular maintenance might well be required.

It should be mentioned that several alternative types of mixer have been considered (e.g. Ajax, Frenkel, Morton, Oakes), but were generally found to be less satisfactory. The mixers either inadequately pre-wetted the material or gave rise to severe build-up within the equipment due to the presence of cementitious and crystalline components in flue dust which, on being wetted, cause certain hydration reactions to occur, leading to the formation of syngenite and other cementitious substances. In a peg mixer, permanent build-up of such substances is avoided by the continuous flexing action of the neoprene casing and the continuous sweeping of the casing by the spirally arranged pegs, Figure B.3.

B.3 Alternative Method of Producing Water-Bound Pellets

Further to the attempt during the Lytag trial to produce water-bound pellets directly from the peg mixer, a trial was carried out using a more sophisticated high speed blade mixer called the 'Schugi Flexomix'. A salient feature of the mixer is that the vertical mixing chamber, which is fabricated of neoprene, is subjected to continuous deforming and cleaning action from the outside by an oscillating cage of nylon rollers.

In a trial carried out at Amsterdam (Evans, 1975 b), the mixer was found to be capable of adequately wetting both the Northfleet and Westbury flue dusts at a moisture level of 19-20%, with no apparent sign of any permanent build-up of material. However, the pellets obtained were mainly in the size range of 0.1-2mm, Figure B.2. (For the purpose of comparison,

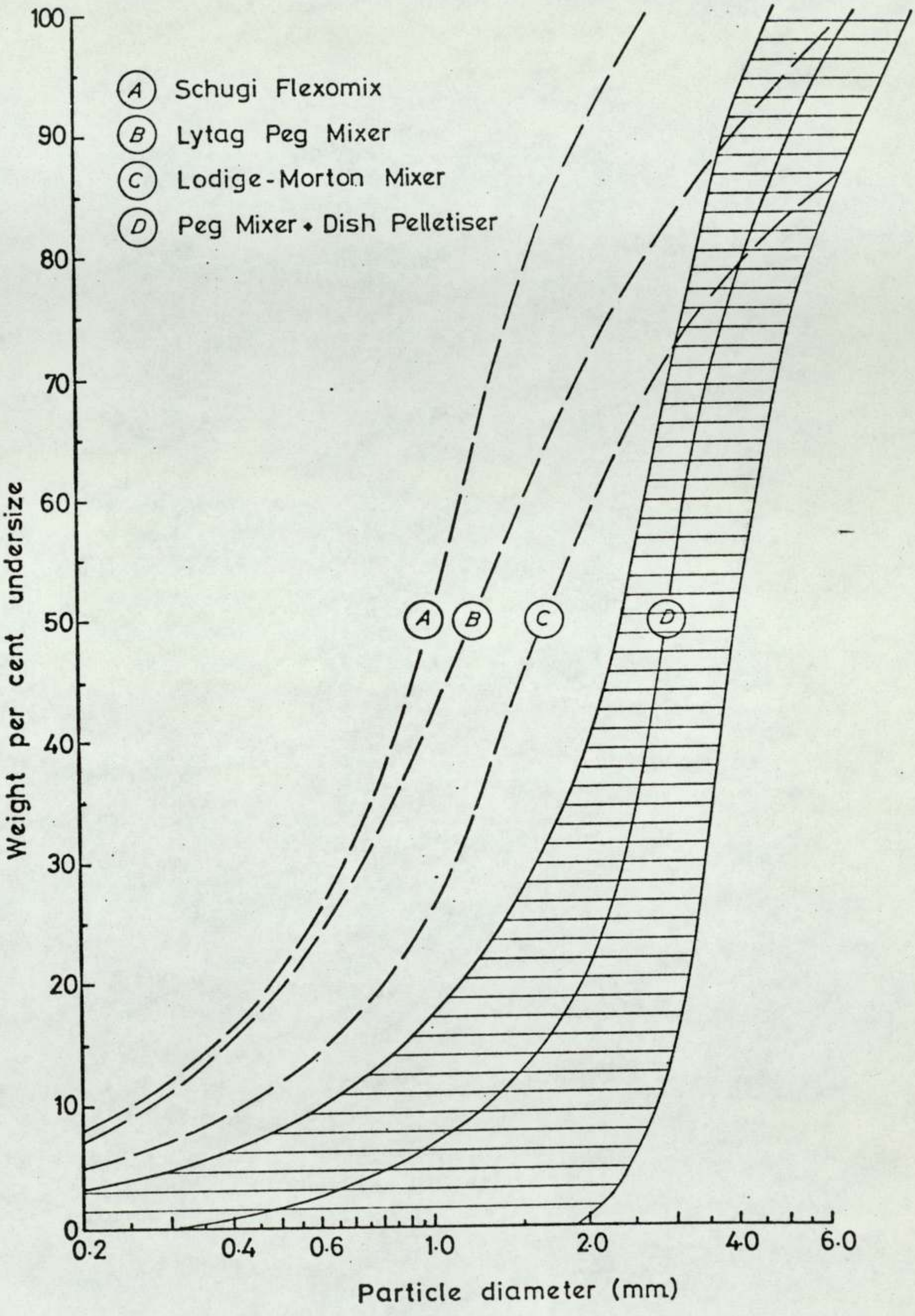


FIGURE B.2

Particle Size Distribution of Flue Dust Pellets Produced by Different Methods

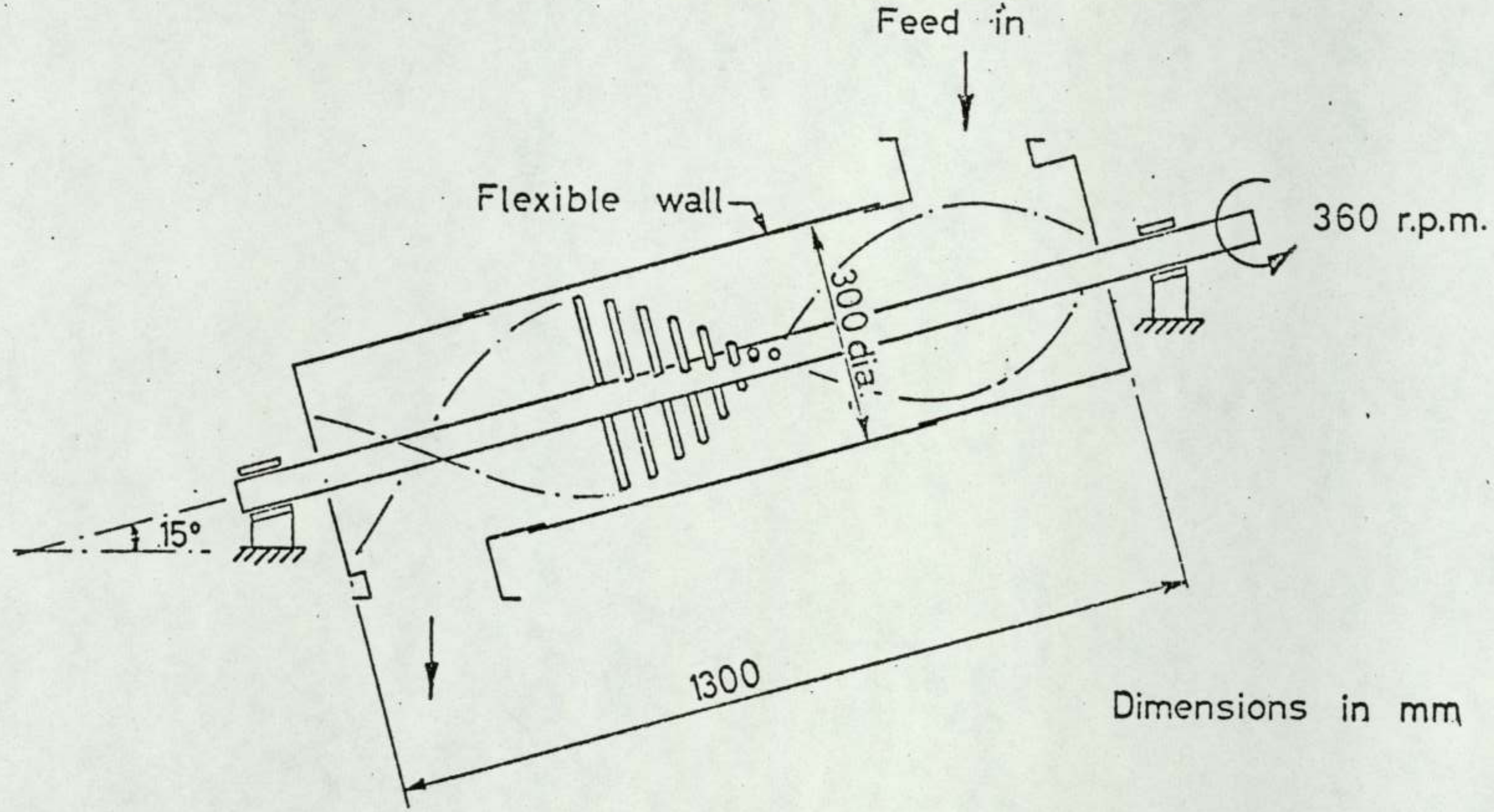


FIGURE B.3

Details of the Peg Mixer

particles obtained from a Lodige-Morton mixer and a peg mixer are also shown). In addition, the power consumption was found to be excessively high (5-7 kWh/t in the pilot plant unit) and because of the very high speed utilised (1500-200 r.p.m.), the rates of blade wear would also be expected to be high.

B.4 Drying of Water-Bound Pellets

The drying of water-bound pellets is desirable not only to reduce the overall heat requirement of the process but also to minimise the risk of pellet decrepitation. The increased risk of decrepitation when flue dust pellets are suddenly exposed to high temperatures have previously been observed under laboratory conditions, which also established that decrepitation could be largely avoided by preheating at temperatures below about 200°C. During the calcination trial in Australia, Northfleet dust pellets were successfully dried in the 300mm diameter fluidised bed at temperatures of 120-180°C with no apparent problem. Subsequent tests carried out at Barnstone in a 150mm, 380mm and 750mm diameter fluidised beds, Figure B.4, confirmed the problem-free operation (Boon and Evans, 1975; Evans, 1976 a & b).

From the 150mm fluidised bed tests, a relationship between the dust loss and pellet strength was also obtained, Figure B.5. It can be seen that provided the crushing strength of dried pellets was more than about 350 g (on a 3mm dried pellet), a dust loss of less than 10% could be expected. In terms of the green pellet strength, this would correspond to about 100-200 g, a target readily achieved in the Lytag trial. (The green pellets generally gained strength on storage, roughly doubling in strength in 48 hours, and also gained strength after drying, from 50-300% increase).

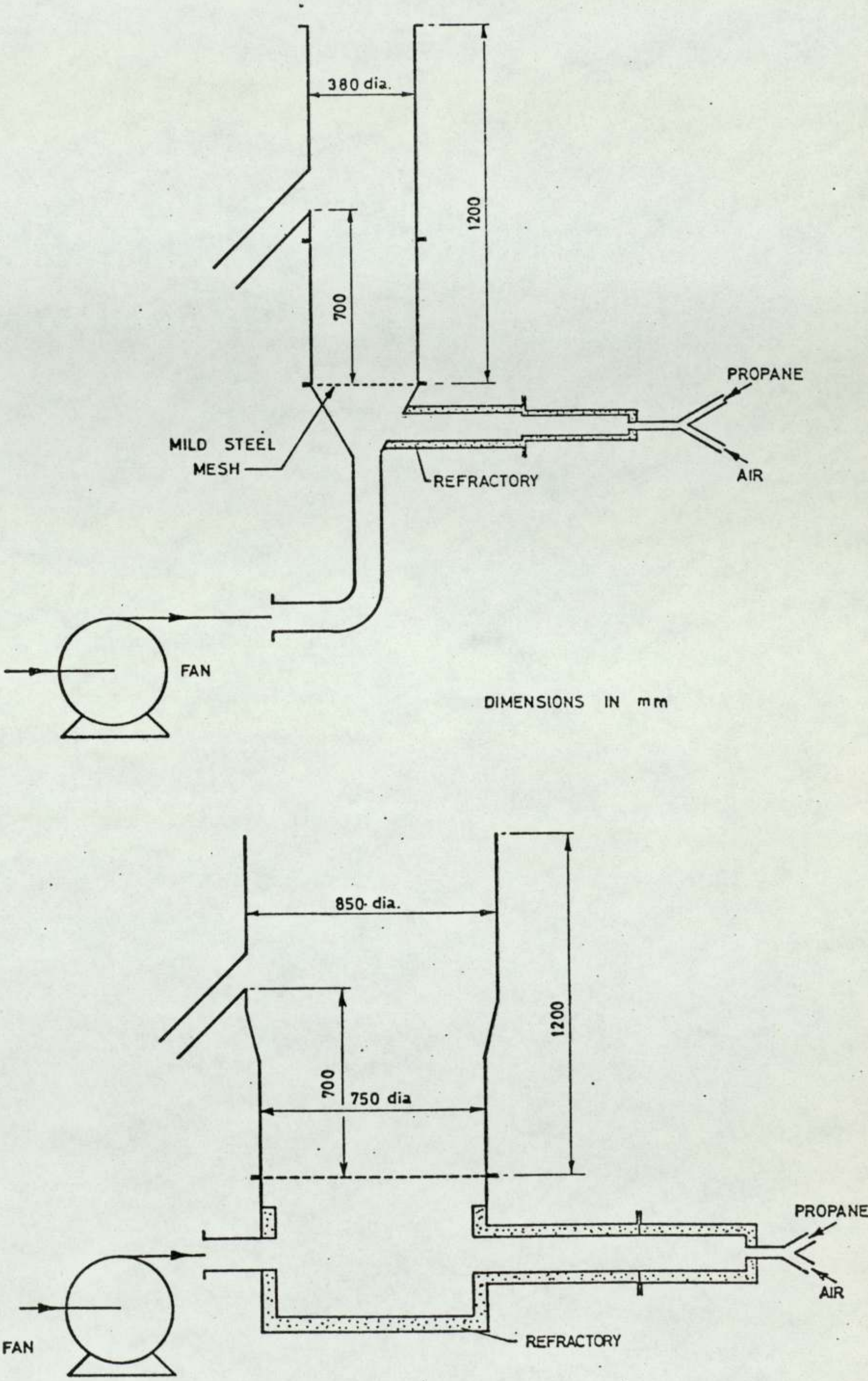


FIGURE B.4

The 380mm Diameter and 750mm Diameter Fluidised Beds Used in the Drying Experiments

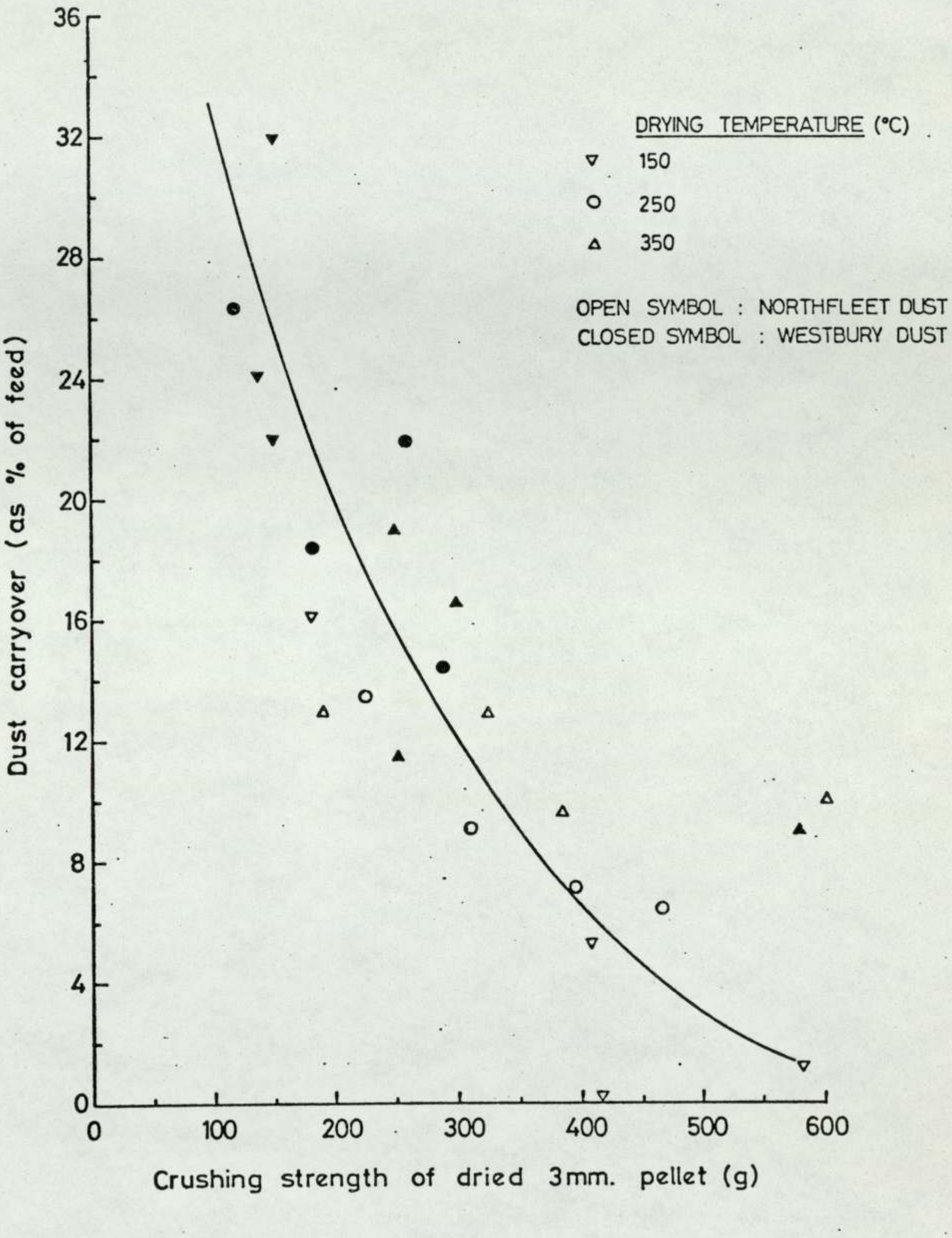


FIGURE B.5

Relationship Between Dust Carry-over and Pellet Strength in Fluidised Bed Drying

In the 150mm fluidised bed, the residual moisture of pellets after 10 minutes drying at 100-350°C was typically about 1%. In the 750mm bed, which has a maximum throughput of about 1000 kg/h, the pellets were dried from about 11-16% inlet moisture to about 2% residual moisture for 8-12 minutes heating at 80-120°C. The fluidisation velocity was typically about 1.5-2 m/s and the dust loss was estimated to be of the order of 5-15%.

B.5 Feasibility of Direct Production of Dry Calciner Feed

The feasibility of producing dry agglomerates of flue dust which can be processed directly in a fluidised bed calciner has also been considered. The method suggested involves compacting flue dust between high pressure rolls to obtain a 'sheet' of 1-2mm thickness which is then crushed, e.g. in a jaw crusher, and screened to produce 'flakes' of the required size range (Srikandarajah, 1976). Flakes of Northfleet flue dust were produced for testing in the present study, and there was generally no significant difference in their calcining behaviour.

The main advantages of this method of agglomeration are simplicity as well as greater consistency and stability of properties, which are often difficult to achieve in a dish pelletiser. However, the capital and operating costs were found to compare unfavourably with those of the pelletisation method. It is estimated that for a 10 t/h unit, the cost (1976) of installing a roll compactor is in the order of £150,000 compared to £60,000 for the pelletiser circuit while the operating costs are, respectively, about £4/t and £1/t. Hence, most of the tests were carried out with pellet feed.

APPENDIX C

Calculation of the Phase Composition of Northfleet and Westbury Flue Dusts and Calcined Product

C.1 Bases and Assumptions

The compositions of the dust feed and calcined product used as the bases of calculation are given in Table C.1. The composition of the feed is identical to that given in Table 4.1 while that of the calcined product is estimated according to the following assumptions:-

(i) For 1 kg of dust calcined, approximately 0.65 kg of calcined product is obtained.

(ii) The calcined product contained 4% K_2O and 0.3% Cl as specified by the calcining requirement (section 4.2.3).

(iii) 50% of the original Na_2O and SO_3 in the dust feed are retained in the calcined product.

(iv) All the CO_2 and H_2O are volatilised after calcining.

The phase compositions are calculated by stoichiometry and the approach adopted for both the feed and calcined product are essentially identical, as is shown below, except that in the case of the dust feeds no attempt was made to determine the argillaceous and clinker phases.

TABLE C.1

Chemical Composition of Northfleet and Westbury Flue Dust Feed and Calcined Product Used for Calculating the Phase Compositions and the Theoretical Heat of Reaction

Basis:- 1 kg dust → 0.65 kg Calcined Product

(Wt. %)	Northfleet		Westbury	
	Feed (1 kg)	Calcined Product (0.65 kg)	Feed (1 kg)	Calcined Product (0.65 kg)
SiO_2	13.3	20.5	13.2	20.3
Al_2O_3	4.3	6.6	4.5	6.9
Fe_2O_3	1.9	2.9	1.8	2.8
CaO	40.0	61.5	39.8	61.2
MgO	0.7	1.1	0.5	0.8
K_2O	7.9	4.0	7.6	4.0
Na_2O	1.0	0.8	0.9	0.7
Cl	3.4	0.3	0.8	0.3
SO_3	5.3	4.1	8.4	4.0
CO_2	21.0	0	21.0	0
H_2O	2.0	0	2.0	0
Total	100.8	101.8	100.5	101.5

C.2 Phase Compositions of the Flue Dust Feed

C.2.1 Northfleet Flue Dust

1) Assume Cl is present wholly as KCl,

Amount of KCl present = $3.4 \times \frac{74.55}{35.45} = \underline{7.15\%}$

K_2O left = 7.9 - 4.52 = 3.38%.

2) Assume remaining K_2O as K_2SO_4,

Amount of K_2SO_4 present = $3.38 \times \frac{174.2}{94.2} = \underline{6.25\%}$

SO_3 left = 5.3 - 2.87 = 2.43%.

3) Assume Na_2O is present wholly as Na_2SO_4,

Amount of Na_2SO_4 present = $1.0 \times \frac{142}{62} = \underline{2.52\%}$

SO_3 left = 2.43 - 1.29 = 1.14%.

4) Assume remaining SO_3 as $CaSO_4$,

Amount of $CaSO_4$ present = $1.14 \times \frac{136}{80} = \underline{1.94\%}$

CaO left = 40 - 0.8 = 39.2%.

5) Assume MgO is present wholly as $MgCO_3$,

Amount of $MgCO_3$ present = $0.7 \times \frac{84.3}{40.3} = \underline{1.46\%}$

CO_2 left = 21 - 0.76 = 20.24%.

6) Assume remaining CO_2 as $CaCO_3$,

Amount of $CaCO_3$ present = $20.24 \times \frac{100.1}{44} = \underline{46.05\%}$

CaO left = 39.2 -25.8 = 13.4%.

7) The remaining CaO is present as free lime (up to 5%), $Ca(OH)_2$, and in combination with the SiO_2, Al_2O_3 and Fe_2O_3 as clinker dust while the remainder of SiO_2, Al_2O_3 and Fe_2O_3 are probably present in their natural states (Sprung, 1966). For the present purpose, it is unnecessary to proceed any further.

C.2.2 Westbury Flue Dust

1) Assume Cl is present wholly as KCl,

$$\text{Amount of KCl present} = 0.8 \times \frac{74.55}{35.45} = \underline{1.68\%}$$

K_2O left = 7.6 - 1.06 = 6.54%.

2) Assume remaining K_2O as K_2SO_4,

$$\text{Amount of } K_2SO_4 \text{ present} = 6.54 \times \frac{174.2}{94.2} = \underline{12.09\%}$$

SO_3 left = 8.4 - 5.55 = 2.85%.

3) Assume Na_2O is present wholly as Na_2SO_4,

$$\text{Amount of } Na_2SO_4 \text{ present} = 0.9 \times \frac{142}{62} = \underline{2.29\%}$$

SO_3 left = 2.85 - 1.16 = 1.69%.

4) Assume remaining SO_3 as $CaSO_4$,

$$\text{Amount of } CaSO_4 \text{ present} = 1.69 \times \frac{136}{80} = \underline{2.87\%}$$

CaO left = 39.8 - 1.18 = 38.62%.

5) Assume MgO is present wholly as $MgCO_3$,

$$\text{Amount of } MgCO_3 \text{ present} = 0.5 \times \frac{84.3}{40.3} = \underline{1.05\%}$$

CO_2 left = 21 - 0.55 = 20.45%.

6) Assume remaining CO_2 as $CaCO_3$,

Amount of $CaCO_3$ present $= 20.45 \times \frac{100.1}{44} = \underline{46.53\%}$

CaO left = 38.62 - 26.07 = 12.55%.

7) The remaining CaO, SiO_2, Al_2O_3 and Fe_2O_3 are assumed to be present in various phases as indicated for Northfleet flue dust.

C.3 Phase Compositions of the Calcined Product

C.3.1 Northfleet Calcined Dust

1) Assume Cl is present wholly as KCl,

Amount of KCl present $= 0.3 \times \frac{74.55}{35.45} = \underline{0.63\%}$

K_2O left = 4.0 - 0.40 = 3.60%.

2) Assume remaining K_2O as K_2SO_4,

Amount of K_2SO_4 present $= 3.60 \times \frac{174.2}{94.2} = \underline{6.66\%}$

SO_3 needed $= 3.6 \times \frac{80}{94.2} = 3.06\%$.

3) Assume Na_2O is present wholly as Na_2SO_4,

Amount of Na_2SO_4 present $= 0.8 \times \frac{142}{62} = \underline{1.83\%}$

SO_3 needed $= 0.8 \times \frac{80}{62} = 1.03\%$.

(SO_3 present = 3.06 + 1.03 = $\underline{4.09\%}$).

N.B. Strictly speaking, the K_2O and Na_2O should have been balanced according to the amount of SO_3 present and any excess K_2O and Na_2O is assumed to be absorbed in the clinker complex.

4) Assume Fe_2O_3 is fully reacted to C_4AF,

Fe_2O_3 present $= 2.9\%$

Al_2O_3 absorbed $= 2.9 \times \frac{101.94}{159.68} = 1.85\%$

CaO absorbed $= 2.9 \times \frac{4 \times 56.08}{159.68} = 4.07\%$

Amount of C_4AF formed $= 2.9 - 1.85 + 4.07 = \underline{8.82\%}$

Al_2O_3 left $= 6.6 - 1.85 = 4.75\%$.

CaO left $= 61.5 - 4.07 = 57.43\%$

5) Assume remaining Al_2O_3 is fully reacted to C_3A,

CaO absorbed $= 4.75 \times \frac{3 \times 56.08}{101.94} = 7.84\%$

Amount of C_3A formed $= 4.75 + 7.84 = \underline{12.59\%}$

CaO left $= 57.43 - 7.84 = 49.59\%$.

6) Assume a free lime of 5% and the remaining lime (= 44.59%) is present either as C_2S and any excess CaO will react with C_2S to form C_3S,

SiO_2 present $= 20.5\%$

CaO absorbed in $C_2S = 20.5 \times \frac{2 \times 56.06}{60.09} = 38.25\%$

Excess $CaO = 44.59 - 38.25 = 6.34\%$

C_2S required for excess $CaO = 6.34 \times \frac{172.25}{56.08} = 19.47\%$

Amount of C_3S formed $= 6.34 + 19.47 = \underline{25.81\%}$

Amount of C_2S formed $= 20.5 + 38.25 - 19.47 = \underline{39.28\%}$.

(Note:- If the free lime is assumed to be 10%, then excess $CaO = 1.34\%$

and C_2S required for excess $CaO = 1.34 \times \frac{172.25}{56.08} = 4.12\%$

Amount of C_3S formed $= 1.34 + 4.12 = \underline{5.46\%}$

Amount of C_2S formed $= 20.5 + 38.25 - 4.12 = \underline{54.63\%}$).

C.3.2 Westbury Calcined Dust

1) Assume Cl is present wholly as KCl,

Amount of KCl present = $0.3 \times \frac{74.55}{35.45} = \underline{0.63\%}$

K_2O left = $4.0 - 0.40 = 3.60\%$.

2) Assume remaining K_2O as K_2SO_4,

Amount of K_2SO_4 present = $3.60 \times \frac{174.2}{94.2} = \underline{6.66\%}$

SO_3 neded = $3.60 \times \frac{80}{94.2} = 3.06\%$.

3) Assume Na_2O is present wholly as Na_2SO_4,

Amount of Na_2SO_4 present = $0.7 \times \frac{142}{62} = \underline{1.60\%}$

SO_3 needed = $0.7 \times \frac{80}{62} = 0.90\%$

(Amount of SO_3 present = $3.06 + 0.90 = \underline{3.96\%}$).

4) Assume Fe_2O_3 is fully reacted to C_4AF,

Fe_2O_3 present = 2.8%

Al_2O_3 absorbed = $2.8 \times \frac{101.94}{159.68} = 1.79\%$

CaO absorbed = $\frac{4 \times 56.08}{159.68} = 3.93\%$

Amount of C_4AF formed = $2.8 + 1.79 + 3.93 = \underline{8.52\%}$

Al_2O_3 left = $6.9 - 1.78 = 5.11\%$

CaO left = $61.2 - 3.93 = 57.27\%$.

5) Assume remaining Al_2O_3 is fully reacted to C_3A,

CaO absorbed = $5.11 \times \frac{3 \times 56.08}{101.94} = 8.43\%$

Amount of C_3A formed = $5.11 + 8.43 = \underline{13.54\%}$

CaO left = $57.27 - 8.43 = 48.84\%$.

6) Assume free lime present = 5% and remaining CaO (= 43.84%) is present as C_2S and any excess CaO will react with C_2S to form C_3S,

SiO_2 present = 20.3%

CaO absorbed in C_2S = $20.3 \times \frac{2 \times 56.08}{60.09} = 37.89\%$

Excess CaO = 43.84 - 37.89 = 5.95%

C_2S required for excess CaO = $5.95 \times \frac{172.25}{56.08} = 18.28\%$

Amount of C_3S formed = 5.95 + 18.28 = $\underline{24.23\%}$

Amount of C_2S formed = 20.3 + 37.89 - 18.28 = $\underline{39.91\%}$.

(<u>Note</u>:- If free lime is assumed to be 10%, then excess CaO = 0.95%

and C_2S required for excess CaO = $0.95 \times \frac{172.25}{56.08} = 2.92\%$

Amount of C_3S formed = 0.95 + 2.92 = $\underline{3.87\%}$

Amount of C_2S formed = 20.3 + 37.89 - 2.92 = $\underline{55.27\%}$.

TABLE C.2

Calculated Phase Compositions of Northfleet and Westbury Flue Dust Feed and Calcined Product

Calculated Compositions (%)	Northfleet		Westbury	
	Feed (1 kg)	Calcined Product (0.65 kg)	Feed (1 kg)	Calcined Product (0.65 kg)
KCl	7.2	0.6	1.7	0.6
K_2SO_4	6.3	6.7	12.1	6.7
Na_2SO_4	2.5	1.8	2.3	1.6
$CaSO_4$	1.9	Assume Wholly Decomposed	2.9	Assume Wholly Decomposed
$MgCO_3$	1.5		1.1	
$CaCO_3$	46.1		46.5	
C_4AF	5-10	8.8	5-10	8.5
C_3A		12.6		13.5
C_2S		39.3-54.6		39.9-55.3
C_3S		25.8-5.5		24.2-3.9
Free Lime (Assumed)	3-5	5-10	3-5	5-10
Others (By difference)*	26.5-19.5	-	25.4-18.4	-
Total	100	100.6	100	97.7

* Mainly argillaceous raw material, $Ca(OH)_2$, etc.

APPENDIX D

Determination of the Rate Controlling Stage of Heat Transfer in Fluidised Bed

D.1 Classification of Stages of Heat Transfer

According to Gelperin and Einstein in Davidson and Harrison (1971), heat transfer in a fluidised bed may be divided into 3 stages, i.e.;

(i) supply of heat to (or take-off from) the system by fluid flows or solid particles (the "thermal balance problem");

(ii) heat transfer from the fluid flow to the surface of the solid particles, or conversely (the "external problem");

(iii) propagation of heat within the solid particle (the "internal problem").

The overall rate of heat transfer is governed by the slowest stage which can be determined by the following criteria.

D.2 Boundaries Between the Individual Stages of Heat Transfer

A characteristic of the first stage is that when the gas leaves the fluidised bed its temperature is the same as that of the solid particles, and it is true if the bed is high enough, i.e.. $L_f \leqslant L_a$. This equality is observed when

$$\dot{\phi}_1 = \frac{U_o \cdot C_{pg} \cdot \rho_g \cdot d_p}{h_p \cdot L_f \cdot (1-\epsilon_f)} \longrightarrow 0 \qquad \text{.....(D.1)}$$

Assuming total mixing of the solid particles and piston flow of the gas through the bed this expression is satisfied with an error $\not> 2\%$ when $\phi_1 \leqslant 1.5$, $\not> 5\%$ when $\phi_1 \leqslant 2$, and $\not> 10\%$ when $\phi_1 \leqslant 2.6$. In the converse relation the second stage becomes governing.

Demarcation between the second and third stages consists of assessing the quantity

$$Bi = \frac{h_p}{k_p} \cdot \left(\frac{d_p}{2}\right) \qquad \text{.....(D.2)}$$

When $Bi < 0.25$ the internal thermal resistance of the particle may be neglected and heating (or cooling) of the particle should be considered as taking place with no internal temperature gradient. On the other hand, when $Bi > 20$ the problem is treated as purely internal, the rate of heat transfer from the fluid to the particle does not limit the process.

Finally, demarcation between the "thermal balance" and "internal" problems depends on the value of

$$\phi_2 = \frac{U_o \cdot C_{pg} \cdot \rho_g \cdot d_p^2}{k_p \cdot L_f \cdot (1-\epsilon_f)} \qquad \text{.....(D.3)}$$

When $\phi_2 < 0.5$ the problem may be considered as a thermal balance problem; otherwise allowance must be made for the internal thermal resistance of the particles.

D.3 Application to the Present Problem

Assuming that the flue dust pellets have a mean diameter, d_p, of 2mm and that the fluidised bed is operating at a temperature of 1200°C and a fluidisation velocity, U_o, of 3 m s^{-1}. According to Kunii and Levenspiel, (1969), the heat transfer coefficient, h_p, can be calculated from

$$Nu_p = 0.03 \; Re_p^{1.3} \qquad \text{.....(D.4)}$$

$$\text{where} \quad Nu_p = \frac{h_p \cdot d_p}{k_g} \qquad \text{.....(D.5)}$$

$$\text{and} \quad Re_p = \frac{d_p \cdot U_o \cdot \rho_g}{\mu} \qquad \text{.....(D-6)}$$

Taking the properties of gas as those of air at 1200°C,

$$Re_p = \frac{2 \times 10^{-3} \times 3 \times 0.24}{5.5 \times 10^{-5}} = \underline{26.14}$$

$$\therefore \quad h_p = 0.03 \; (26.14)^{1.3} \; \frac{2.15 \times 10^{-5}}{2 \times 10^{-3}}$$

$$= \underline{22.44 \times 10^{-3} \text{ kcal } s^{-1} \; m^{-2} \; {}^\circ C^{-1}}$$

From equation (D.1), putting $\epsilon_f = 0.5$,

L_f(m)	ϕ_1
0.1	0.34
0.3	0.11
0.5	0.07

The present experiments were all conducted with a fluidising bed height of >0.1m and therefore, the process is clearly governed by "thermal balance", i.e. stage (i). This is further substantiated by calculating the values of Bi and ϕ_2 as follows.

Assuming that the thermal conductivity of flue dust, k_s, is the same as limestone and that the pellet has a porosity, ϵ_p, of 0.4, the thermal conductivity of the pellets, k_p, can be estimated as follows (Perry and Chilton, 1973):

$$\frac{k_p}{k_s} = \frac{\gamma \cdot \epsilon_p^{2/3} + 1 - \epsilon_p^{2/3}}{\gamma(\epsilon_p^{2/3} - \epsilon_p) + 1 - \epsilon_p^{2/3} + \epsilon_p} \quad \text{.....(D.7)}$$

where $\gamma = \frac{k_g}{k_s} = \frac{2.15 \times 10^{-5}}{5 \times 10^{-4}} = \underline{0.043}$

From equation (D.7),

$$\frac{k_p}{k_s} = 0.56$$

$$\therefore \quad k_p = 0.56 \times 10^{-4}$$

$$= \underline{2.78 \times 10^{-4} \text{ kcal m}^{-1} \text{ s}^{-1} \text{ °C}^{-1}}$$

From equation (D.2),

$$\text{Bi} = \frac{22.44 \times 10^{-3} \ . \ 1 \times 10^{-3}}{2.78 \times 10^{-4}} = \underline{0.081}$$

From equation (D.3),

L_f(m)	ϕ_2
0.1	0.055
0.3	0.018
0.5	0.011

Hence, the internal thermal resistance of the particle may be neglected.

APPENDIX E

Experimental Data and Mass Balance

TABLE E.1

Input Variables of the 100mm (Tests 1-18) and 150mm (Tests 19-36) Fluidised Bed Experiment

Test Number	Type of Dust Feed⊗	Weight of Dust Processed (kg)	Processing Duration (min)	Fluidisation/Combustion Gas and Fuel Input						Quench Air (l min^{-1})
				Pilot Burner		Compressed Air (l min^{-1})	Oxygen (l min^{-1})	Injector Cooling Air (l min^{-1})	Fuel Oil (ml min^{-1})	
				Propane (l min^{-1})	Air (l min^{-1})					
1	N-P	6.8* + 22.5	370	17	430	400	0	0	40	200
2	N-P	4.0 + 19.7	170	10.5	250	0	140	0	50	500
3	N-P	4.0 + 9.7	120	9.5	220	0	160	0	55	500
4	W-P	3.0 + 8.0	90	9.5	230	0	125	0	50	650
5	W-P	2.0 + 9.0	100	9.5	230	0	140	0	35	500
6	N-P	27.4	230	9.5	220	0	100	0	25	600
7	N-P	24.0	190	9.0	175	0	100	0	18	400
8	N-P	8.0	110	9.5	225	0	130	0	35	400
9	N-P	9.8	130	9.5	225	0	85	0	30	400
10	N-P	18.0	140	9.0	220	0	100	0	25	380
11	(N-F)	1.6	50	10.0	230	0	80	0	30	250
12	(N-F)	6.7	120	8.5	200	0	80	0	28	540
13	N-P	13.0	145	9.5	225	0	80	0	30	500
14	N-P	12.0	140	9.0	210	0	70	0	30	600
15	W-P	15.8	225	8.2	190	0	70	0	30	450
16	N-F	18.4	290	8.0	200	0	70	0	30	420
17	N-F	7.9	150	8.1	200	0	75	0	30	500
18	N-F	6.2	110	8.5	200	0	70	0	30	450
19	W-P	5.9	60	8.0	200	475	0	50	65	700
20	W-P	16.0	165	9.0	220	400	50	50	65	700
21	W-P	10.0	110	9.0	220	350	90	50	65	750
22	W-P	17.0	105	8.5	200	425	70	70	65	800
23	N-F	12.0	165	9.0	210	300	60	50	65	450
24	N-P	21.6	180	9.0	210	300	60	50	65	450
25	N-P	18.0	160	9.0	210	300	60	50	75	750
26	N-P	11.3	160	8.0	200	250	50	50	50	300
27	N-P	11.5	170	8.0	200	400	55	50	62	400
28	(W-P)	6.0	70	9.0	220	400	50	50	65	250
29	(W-P)	16.0	270	8.0	200	400	40	60	65	400
30	(W-P)	16.0	295	9.0	210	410	25	90	65	700
31	(W-P)	30.0	325	8.0	200	475	20	90	55	300
32	(W-P)	15.0	180	8.0	200	410	30	90	45	300
33	(W-P)	18.0	265	Preheated with an Electric Furnace		535	0	35	50	300
34	(W-P)	22.6	310			550	0	25	40	300
35	(W-P)	22.5	300			550	0	25	40	300
36	(W-P)	16.7	160			530	0	25	50	300

⊗ N : Northfleet; W : Westbury; P : Pellet; F : Flakes;
( ) : High Alkali Dust.

* In Tests 1-5, the bed was initially established by feeding in precalcined pellets.

TABLE E.2

Operating Conditions of the 100mm and 150mm Fluidised Beds

(N.A. = Not Available)

Test Number	Average Temperature				Exit Gas $[O_2]$ (%)	Pressure Drop		Weight of Calcined Product (kg)
	Hot Box (°C)	Fluidised Bed (°C)	Freeboard (°C)	Bed Exit (°C)		Distributor Only (mm W.G.)	Distributor + Bed (mm W.G.)	
1	N.A.	1120	N.A.	1100	N.A.	220	360	7.5
2	N.A.	1260	N.A.	1020	13	130	410	13.5
3	N.A.	1220	N.A.	960	9	200	450	9.3
4	N.A.	1260	N.A.	820	5	150	400	7.5
5	N.A.	1260	N.A.	660	18	100	350	6.6
6	N.A.	1240	N.A.	660	N.A.	60	240	12.2
7	N.A.	1160	N.A.	600	N.A.	550	750	~~1~~3.7
8	N.A.	1180	N.A.	560	N.A.	400	550	4.3
9	N.A.	1180	N.A.	600	N.A.	720	950	6.0
10	N.A.	1240	1000	560	15	450	650	9.2
11	N.A.	1200	900	600	18	100	180	0.7
12	N.A.	1200	980	500	19	80	220	4.5
13	N.A.	1240	1080	540	18	70	250	7.5
14	N.A.	1200	1160	580	16	40	200	5.8
15	N.A.	1240	1060	480	16	350	530	6.4
16	N.A.	1220	1000	400	N.A.	180	360	11.8
17	N.A.	1220	900	540	6	160	300	4.9
18	N.A.	1220	960	540	8	100	220	4.1
19	750	1220	1100	960	0	50	150	3.4
20	750	1200	1100	860	6	200	300	8.6
21	750	1200	1020	800	4	200	300	4.8
22	650	1220	1060	760	7	220	340	8.8
23	800	1200	1160	900	2	200	240	7.3
24	800	1240	1000	760	3	250	350	12.7
25	780	1240	940	660	5	250	350	9.6
26	750	1220	980	700	5	160	260	6.0
27	740	1200	960	680	N.A.	60	150	6.0
28	750	1180	1020	500	N.A.	50	170	3.5
29	710	1240	1080	900	8	200	320	8.3
30	730	1220	1060	800	13	80	180	7.4
31	700	1240	1060	520	12	110	240	14.0
32	650	1200	960	460	15	80	210	6.0
33	630	1220	1000	660	18	350	490	7.7
34	530	1180	960	700	15	310	450	12.7
35	520	1160	980	580	14	280	430	11.6
36	550	1120	940	740	13	260	420	9.8

TABLE E.3

Operating Conditions of the Quench and Cyclone Systems

(Ngl = Negligible, N.D. = Not Determined)

Test Number	Quench Vessel		Drop-out Vessel Material (kg)	Cyclone				
	Temperature (°C)	Material Build-up (kg)		Inlet Temperature (°C)	Outlet Temperature (°C)	Pressure Drop (mm W.G.)	Material Collected (kg)	Material Build-up (kg)
1	700	1.46		650	400	220	10.7	0.36
2	700	0.16		500	240	150	1.0	0.16
3	700	0.12		570	300	150	0.5	Ngl
4	650	Ngl		500	400	120	0,4	0.08
5	550	0.03		500	400	100	0.5	Ngl
6	650	0.04	3.5	250	150	80	0.5	Ngl
7	600	0.58	Ngl	130	50	30	0.42	0.07
8	550	0.26	0.21	100	40	35	0.05	Ngl
9	550	0.13	0.05	120	50	30	0.003	Ngl
10	400	0.50		350	230	50	1.73	Ngl
11	450	0.01		270	160	40	0.09	Ngl
12	320	0.04		310	300	100	0.18	Ngl
13	370	Ngl		340	320	110	0.44	Ngl
14	450	0.25		350	330	75	1.45	Ngl
15	400	0.19		340	320	60	2.8	Ngl
16	280	Ngl		270	270	40	0.45	Ngl
17	350	0.05		340	300	120	0.67	Ngl
18	410	0.09		310	290	130	0.5	Ngl
19	500	N.D.		450	450	20	0.54	N.D.
20	540	N.D.		480	460	20	1.12	N.D.
21	500	N.D.		400	400	25	0.9	N.D.
22	450	N.D.		420	400	12	0.81	N.D.
23	550	N.D.		580	540	9	0.22	N.D.
24	430	N.D.		300	350	12	0.16	N.D.
25	400	N.D.		330	270	45	0.35	N.D.
26	600	N.D.		500	450	11	0.2	N.D.
27	500	N.D.		400	350	5	0.5	N.D.
28	500	N.D.		400	350	10	0.4	N.D.
29	500	N.D.		550	490	11	2.9	N.D.
30	600	N.D.		500	520	15	2.0	N.D.
31	500	N.D.		440	420	13	3.8	N.D.
32	400	N.D.		400	400	9	3.5	N.D.
33	500	N.D.		400	380	15	3.5	N.D.
34	500	N.D.		450	430	18	2.1	N.D.
35	500	N.D.		420	400	12	3.6	N.D.
36	500	N.D.		440	440	14	2.2	N.D.

TABLE E.4

Operating Conditions of the Alkali Collectors

(N.D. = Not Determined)

Test Number	Type of Collector*	Applied Power (E-P only)		Inlet Temperature (°C)	Outlet Temperature (°C)	Pressure Drop (mm W.G.)	Weight of Material Collected (kg)	Collection Efficiency ⊗ (%)
		Current (mA)	Voltage (kV)					
1								
2								
3								
4								
5								
6								
7								
8								
9								
10	B-F	-	-	200	20	170	0.59	42
11	B-F	-	-	200	20	175	0.13	40
12	B-F	-	-	200	30	90	0.52	47
13	B-F	-	-	200	20	145	0.73	64
14	E-P	3	28	200	80	65	0.23	26
15	E-P	2	26	220	90	75	0.41	41
16	B-F	-	-	130	60	145	0.80	34
17	B-F	-	-	170	60	280	0.79	79
18	E-P	1	28	250	100	65	0.03	4
19	E-P	2	30	380	200	70	0.24	30
20	E-P	2	30	300	220	130	0.86	42
21	E-P	2	25	280	200	25	0.35	30
22	E-P	2	28	280	220	100	0.50	32
23	E-P	2	28	300	200	85	0.55	34
24	E-P	2	28	300	150	50	0.54	16
25	B-F	-	-	250	100	260	0.85	30
26	B-F	-	-	230	70	120	1.1	57
27	E-P	4	32	220	190	40	1.2	61
28	E-P	3	34	250	180	30	0.4	52
29	E-P	2	33	370	250	50	1.3	34
30	E-P	3	32	300	200	40	1.5	45
31	E-P	3	30	320	230	35	1.7	32
32	E-P	3	30	260	190	30	1.3	67
33	E-P	3	28	250	140	30	N.D.	-
34	E-P	3	30	290	110	30	N.D.	-
35	E-P	3	30	240	90	40	N.D.	-
36	E-P	3	30	250	100	40	N.D.	-

* B-F : Bag Filter; E-P : Electrostatic Precipitator.

⊗ Refer Appendix D for definition.

TABLE E.5

Chemical Analyses of the Flue Dust Feed (and Precalcined Pellets) Used in the Experiments

(N.D. = Not Determined)

Test Number	K_2O (%)	Na_2O (%)	Cl (%)	SO_3 (%)	CaO (%)	CO_2 (%)	H_2O (%)	L.O.I. at 950°C (½-1 hr) (%)
1	1.94*/4.44	0.46/0.65	0.44/2.20	0.55/2.02	40.33	22.2	5.5	32.2
2	0.85/6.32	0.35/0.65	0.05/2.48	0.95/3.60	41.35	22.8	4.0	31.1
3	0.67/6.40	0.32/0.77	0.44/2.46	0.72/3.50	41.74	21.9	3.6	29.8
4	1.24/6.00	0.41/0.75	0.09/1.52	1.10/5.00	39.06	23.6	3.5	30.8
5	1.20/6.60	0.40/0.60	0.04/1.61	1.10/3.95	41.30	22.6	3.6	31.0
6	5.50	0.75	2.14	3.70	40.32	23.3	3.6	31.8
7	5.50	0.60	2.44	3.78	37.38	25.9	3.9	34.4
8	5.25	0.67	2.30	3.56	39.48	23.6	4.5	32.2
9	6.00	0.65	2.10	4.53	39.90	23.4	4.4	31.9
10	6.40	0.70	2.52	4.65	41.72	22.4	4.3	31.1
11	13.44	1.15	6.33	5.80	35.84	19.2	1.6	31.4
12	13.50	1.22	6.25	5.48	36.26	18.8	1.9	32.5
13	6.50	0.72	2.42	3.83	39.76	24.1	4.4	32.2
14	5.15	0.70	2.27	3.01	38.92	25.3	4.4	N.D.
15	5.55	0.69	1.27	4.27	39.20	23.8	4.4	29.7
16	8.40	1.10	3.61	4.46	41.44	21.0	1.6	23.4
17	7.75	1.20	3.41	4.04	41.58	21.0	1.4	N.D.
18	9.75	1.16	3.41	5.92	42.00	20.8	1.3	N.D.
19	6.60	0.82	0.70	4.52	39.34	24.4	3.8	27.9
20	4.75	0.68	1.37	5.95	39.06	21.1	1.9	29.1
21	5.00	0.68	1.29	5.26	34.86	18.1	11.1	N.D.
22	5.75	0.70	1.64	4.80	39.20	19.9	7.0	34.0
23	8.45	1.15	3.78	5.28	40.88	19.0	1.9	29.1
24	7.60	1.10	3.33	5.98	37.81	23.7	2.0	33.2
25	7.90	1.10	3.28	5.88	37.95	22.8	2.0	31.9
26	7.70	1.10	3.44	6.10	38.10	21.9	2.1	25.7
27	7.65	0.93	3.48	6.06	37.25	22.3	1.7	31.7
28	11.50	1.20	1.99	11.20	32.74	20.7	1.3	26.9
29	11.40	1.30	2.21	12.20	33.56	18.9	1.4	26.8
30	11.30	1.20	1.85	11.75	32.86	19.6	2.9	27.2
31	11.90	1.30	1.72	11.85	32.90	19.5	2.8	27.1
32	11.40	1.20	1.71	12.26	31.50	19.0	2.0	26.5
33	11.40	1.20	2.16	12.08	32.34	20.80	0.9	26.5
34	11.40	1.20	2.16	12.08	32.34	20.80	0.9	26.5
35	11.40	1.20	2.16	12.08	32.34	20.80	0.9	26.5
36	11.40	1.20	2.16	12.08	32.34	20.80	0.9	26.5

* Analysis of the precalcined pellets used to establish the initial bed.

TABLE E.6

Chemical Analyses of the Calcined Product

Test Number	K_2O (%)	Na_2O (%)	Cl (%)	SO_3 (%)	CaO (%)	Free Lime (%)
1	1.45	0.37	0.17	0.65	64.60	9.16
2	0.67	0.32	0.04	0.72	64.95	1.27
3	1.24	0.41	0.09	1.10	63.17	1.97
4	1.20	0.40	0.04	1.10	63.84	2.73
5	1.60	0.40	0.04	1.53	62.86	3.10
6	1.48	0.64	0.02	1.65	63.00	5.46
7	3.50	0.67	0.50	3.15	60.49	5.46
8	2.25	0.57	0.42	2.24	59.92	4.82
9	3.75	0.67	0.04	4.23	59.22	3.10
10	2.90	0.52	0.27	3.26	64.22	5.15
11	5.30	0.95	0.73	3.38	60.20	4.62
12	7.20	0.95	0.81	3.81	54.32	3.41
13	2.47	0.62	0.10	2.26	60.43	4.90
14	2.00	0.55	0.66	1.56	57.96	4.34
15	2.47	0.47	0.04	2.46	61.64	6.25
16	3.25	0.85	0.13	2.38	60.90	6.59
17	2.45	0.82	0.22	2.12	61.32	5.67
18	3.70	0.86	0.13	3.30	60.76	7.27
19	3.15	0.60	0.05	1.92	60.96	7.21
20	1.35	0.53	0.07	1.28	62.16	7.83
21	1.13	0.49	0.10	1.07	64.12	3.24
22	2.60	0.60	0.16	2.70	61.88	9.75
23	2.40	0.70	0.22	3.00	62.58	13.15
24	1.55	0.65	0.09	1.64	61.54	7.18
25	1.10	0.52	0.16	0.75	60.46	8.93
26	0.50	0.79	0.11	0.97	64.06	4.31
27	0.50	0.31	0.04	0.67	64.34	4.85
28	10.10	1.05	0.19	11.80	48.26	5.75
29	4.50	0.85	0.18	5.06	56.36	4.39
30	2.75	0.61	0.10	2.30	60.48	4.25
31	7.10	0.95	0.03	8.12	52.64	3.94
32	8.30	1.10	0.02	9.56	49.98	4.96
33	2.80	0.70	0.06	2.84	36.95	1.49
34	9.80	1.25	0.28	10.56	47.18	3.94
35	10.50	1.50	0.37	12.60	47.18	3.94
36	11.20	1.40	0.64	13.20	46.53	3.89

TABLE E.7

Chemical Analyses of the Cyclone (and Drop-out) Material

Test Number	K_2O (%)	Na_2O (%)	Cl (%)	SO_3 (%)	CaO (%)	Free Lime (%)
1	0.81	0.32	0.04	0.56	65.14	13.63
2	2.78	0.42	0.60	1.90	59.12	5.61
3	5.35	0.78	1.23	3.48	58.45	1.23
4	5.25	1.75	1.18	5.50	52.78	3.01
5	3.00	0.70	0.66	2.21	60.76	8.96
6	1.95*/18.3	0.55/1.9	0.36/6.1	1.52/11.3	38.64/61.6	6.76/11.22
7	10.25	1.07	4.00	8.36	43.43	7.41
8	1.85/16.9	0.4/1.3	0.9/1.3	8.39/11.1	46.25/39.4	1.97/5.6
9	14.25/16.75	1.3/1.12	4.95/8.1	9.85/10.75	40.18/39.18	5.75/0.78
10	7.40	1.00	3.05	8.46	39.48	12.06
11	16.25	1.22	5.10	12.88	37.38	2.59
12	28.75	4.00	31.00	9.24	11.34	0.79
13	13.50	1.32	6.73	7.00	45.78	8.39
14	4.30	0.75	1.19	3.58	57.40	10.53
15	6.30	1.10	0.61	5.88	54.46	10.7
16	14.25	1.85	6.77	10.20	32.58	4.0
17	4.15	1.20	2.11	2.59	20.33	2.31
18	13.50	1.49	3.48	8.64	41.72	4.96
19	11.00	0.67	1.16	7.60	37.66	1.52
20	7.50	0.98	1.09	10.12	49.84	10.2
21	7.25	1.09	1.09	7.25	51.94	13.13
22	9.00	3.25	1.86	10.36	49.00	9.52
23	11.60	1.30	2.90	11.32	41.86	7.13
24	13.80	1.60	2.98	12.88	33.70	1.07
25	23.60	2.70	6.15	19.50	29.17	4.96
26	11.90	1.40	3.56	10.92	37.80	5.46
27	10.40	1.20	2.70	10.20	40.42	6.56
28	22.80	4.20	2.83	25.80	22.58	2.14
29	9.10	1.60	1.21	8.20	42.76	2.42
30	9.80	1.18	0.55	9.12	43.82	2.45
31	12.20	1.10	0.54	12.60	45.50	6.23
32	12.60	1.65	0.48	14.30	43.82	7.04
33	17.50	1.70	0.58	14.20	39.31	3.61
34	16.51	2.10	0.50	15.56	42.98	4.82
35	13.80	1.40	0.46	14.54	44.30	4.51
36	15.60	2.00	0.52	14.88	41.70	3.42

TABLE E.8

Chemical Analyses of the Quench and Cyclone Deposits

Test Number	Quench Vessel						Cyclone					
	K_2O	Na_2O	Cl	SO_3	CaO	Free Lime	K_2O	Na_2O	Cl	SO_3	CaO	Free Lime
1	11.5	1.20	4.90	16.8	40.54	2.4	18.4	1.60	7.70	19.6	32.78	1.4
2	24.0	2.24	8.44	11.0	35.12	1.42	29.12	2.56	7.72	14.6	12.27	2.69
3	26.0	1.50	14.60	9.6	33.0	1.63	-	-	-	-	-	-
4	-	-	-	-	-	-	14.25	2.25	6.2	12.1	26.18	0.73
5	23.75	1.87	7.90	18.80	29.4	0.19	-	-	-	-	-	-
6	31.00	2.60	16.05	21.0	24.5	2.31	-	-	-	-	-	-
7	17.75	2.92	4.50	12.70	39.94	1.73	24.6	1.92	13.6	12.16	27.07	3.75
8	11.04	1.19	5.03	11.44	41.66	3.16	-	-	-	-	-	-
9	12.34	1.29	5.07	10.63	43.31	5.09	-	-	-	-	-	-
10	9.7	0.96	5.9	9.6	34.86	1.75	17.75	1.37	9.0	15.2	12.32	2.25
11	25.62	1.55	7.15	18.16	26.46	2.19	-	-	-	-	-	-
12	17.50	1.72	9.42	19.38	36.40	1.01	-	-	-	-	-	-
13	-	-	-	-	-	-	-	-	-	-	-	-
14	7.70	1.20	2.42	5.52	50.86	1.29	-	-	-	-	-	-
15	5.15	0.85	1.67	5.22	-	-	-	-	-	-	-	-
16	-	-	-	-	-	-	-	-	-	-	-	-
17	6.50	1.16	2.80	5.28	29.12	0.39	-	-	-	-	-	-
18	6.95	1.12	2.37	5.95	52.08	3.15	-	-	-	-	-	-

TABLE E.9

Chemical Analyses of the Alkali Product

Test Number	K_2O (%)	Na_2O (%)	Cl (%)	SO_3 (%)	CaO (%)	Free Lime (%)
1						
2						
3						
4						
5						
6						
7						
8						
9						
10	54.00	3.60	31.00	13.60	1.40	0.28
11	49.93	3.89	27.37	16.93	1.89	<0.1
12	52.41	4.63	37.53	5.19	1.90	0.08
13	53.89	4.93	31.33	16.37	1.05	0.03
14	53.00	3.80	27.70	18.46	2.10	0.06
15	55.70	3.85	23.52	22.08	0.84	0.11
16	50.37	4.16	30.32	13.06	0.72	<0.1
17	47.00	4.80	26.38	15.95	3.50	0.28
18	44.50	4.80	29.61	15.60	1.82	<0.1
19	26.50	2.17	8.71	20.80	0.28	<0.1
20	44.50	3.30	6.95	21.20	0.28	<0.1
21	36.10	3.10	12.50	28.30	1.12	<0.2
22	43.00	3.10	23.30	25.10	0.20	<0.1
23	56.30	4.17	24.27	21.50	0.42	0.08
24	45.50	4.50	18.39	29.80	0.30	0.11
25	49.50	6.50	24.75	21.00	0.14	0.10
26	47.00	5.05	22.21	23.60	0.85	0.03
27	44.50	4.05	19.25	26.90	0.99	0.06
28	39.50	7.50	17.50	6.50	0.56	<0.1
29	43.50	4.00	8.13	38.40	0.47	<0.1
30	52.50	3.50	6.52	38.00	0.56	0.06
31	42.25	2.50	13.73	30.17	0.42	0.17
32	48.50	3.00	14.41	29.00	0.56	0.14
33	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.
34	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.
35	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.
36	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.

TABLE E.10

Overall Material Balance for the 100mm (Tests 1-18) and 150mm (Tests 19-36) Fluidised Bed Experiment

(N.A. = Not Available, N.D. = Not Determined)

Test Number	Input		Output			Deposit and Build-up Materials (kg)	$CO_2 + H_2O$ of Dust Feed (kg)	Material Unaccounted	
	Pre-calcined Feed (kg)	Dust Feed (kg)	Calcined Product (kg)	Carry-over Material (kg)	Alkali Product (kg)			Weight (kg)	As % of Input
1	6.8	22.5	7.5	10.7	N.A.	1.82	6.23	3.05	10
2	4.0	19.7	13.5	1.0	N.A.	0.32	5.28	3.60	15
3	4.0	9.7	9.3	0.5	N.A.	0.12	2.47	1.31	10
4	3.0	8.0	7.5	0.4	N.A.	0.08	2.17	0.85	8
5	2.0	9.0	6.6	0.5	N.A.	0.03	2.36	1.51	14
6	0	27.4	12.2	4.0	N.A.	0.04	7.37	3.79	14
7	0	24.0	13.7	0.42	N.A.	0.65	7.15	2.08	9
8	0	8.0	4.3	0.26	N.A.	0.26	2.25	0.88	11
9	0	9.8	6.0	0.05	N.A.	0.13	2.72	0.90	9
10	0	18.0	9.2	1.78	0.59	0.52	4.81	1.10	6
11	0	1.6	0.7	0.09	0.13	0.01	0.33	0.34	21
12	0	6.7	4.5	0.18	0.52	0.04	1.39	0.07	1
13	0	13.0	7.5	0.44	0.73	Ngl	3.71	0.62	5
14	0	12.0	5.8	1.45	0.23	0.25	3.56	0.71	6
15	0	15.8	6.4	2.8	0.41	0.19	4.46	1.54	10
16	0	18.4	11.8	0.45	0.80	Ngl	4.16	1.19	6
17	0	7.9	4.9	0.67	0.79	0.05	1.77	-0.28	-4
18	0	6.2	4.1	0.5	0.03	0.09	1.37	0.11	2
19	0	5.9	3.4	0.54	0.24	N.D.	1.66	0.06	1
20	0	16.0	8.6	1.12	0.86	N.D.	3.68	1.74	11
21	0	10.0	4.8	0.9	0.35	N.D.	2.92	1.03	10
22	0	17.0	8.8	0.81	0.50	N.D.	4.57	2.32	14
23	0	12.0	7.3	0.22	0.55	N.D.	2.51	1.42	12
24	0	21.6	12.7	0.16	0.54	N.D.	5.55	2.65	12
25	0	18.0	9.6	0.35	0.85	N.D.	4.46	2.74	15
26	0	11.3	6.0	0.2	1.1	N.D.	2.71	1.29	11
27	0	11.5	6.0	0.5	1.2	N.D.	2.76	1.04	9
28	0	6.0	3.5	0.4	0.4	N.D.	1.32	0.38	6
29	0	18.0	8.3	2.9	1.3	N.D.	3.65	1.85	10
30	0	16.0	7.4	2.0	1.5	N.D.	3.60	1.50	9
31	0	30.0	14.0	3.8	1.7	N.D.	6.69	3.81	13
32	0	15.0	6.0	3.5	1.3	N.D.	3.15	1.05	7
33	0	18.0	7.7	3.5	N.D.	N.D.	3.91	2.26	16
34	0	22.6	12.7	2.1	N.D.	N.D.	4.90	2.90	13
35	0	22.5	11.6	3.6	N.D.	N.D.	4.88	2.42	11
36	0	16.7	9.8	2.2	N.D.	N.D.	3.62	1.08	6

TABLE E.11

Mass Balance on K_2O Component for the 100mm (Tests 1-18) and 150mm (Tests 19-36) Fluidised Bed Experiment

(N.A. = Not Available, N.D. = Not Determined, Ngl = Negligible)

Test Number	Input	Output			Amount Volatilised		Amount Recovered From Filter (g)	Amount Unaccounted	
	Dust Feed (g)	Calcined Product (g)	Carry-over Material (g)	Deposits & Build-ups (g)	Weight (g)	Weight (%)		Weight (g)	Weight (%)
1	1131*	116	87	234	695	61.4	N.A.	-	-
2	1279*	90	28	85	1076	84.1	N.A.	-	-
3	648*	115	27	31	474	73.2	N.A.	-	-
4	517*	90	21	11	395	76.3	N.A.	-	-
5	618*	106	15	7	490	79.3	N.A.	-	-
6	1507	181	160	12	1154	76.6	N.A.	-	-
7	1320	480	43	120	677	51.3	N.A.	-	-
8	420	97	12	29	282	67.2	N.A.	-	-
9	588	225	8	16	339	57.7	N.A.	-	-
10	1152	267	132	52	701	60.9	319	383	33.3
11	215	37	15	3	161	74.7	65	96	44.7
12	905	324	52	7	522	57.7	247	215	30.4
13	845	185	59	Ngl	600	71.1	393	207	24.5
14	618	116	62	19	420	68.0	122	299	48.3
15	877	158	176	10	533	60.7	228	304	34.7
16	1546	384	64	Ngl	1098	71.0	403	695	45.0
17	612	120	28	3	461	75.3	371	90	14.7
18	605	152	68	6	379	62.7	13	366	60.5
19	389	107	59	N.D.	223	57.2	64	100	30.4
20	760	116	84	N.D.	560	73.7	383	177	23.3
21	500	54	65	N.D.	381	76.1	126	254	50.8
22	978	229	73	N.D.	676	69.1	215	461	47.1
23	1014	175	26	N.D.	813	80.2	310	504	49.7
24	1642	197	22	N.D.	1423	86.7	246	1177	71.7
25	1422	106	83	N.D.	1234	86.8	421	813	57.2
26	870	30	24	N.D.	816	93.8	517	299	34.4
27	880	30	52	N.D.	798	90.7	534	264	30.0
28	690	354	91	N.D.	245	35.5	158	87	12.6
29	1052	374	100	N.D.	1578	76.9	566	1013	49.4
30	1808	204	196	N.D.	1409	77.9	788	621	34.3
31	3570	994	464	N.D.	2112	59.2	718	1394	39.1
32	1710	498	441	N.D.	771	45.1	631	141	8.2
33	2052	216	613	N.D.	1224	59.6	N.D.	-	-
34	2576	1245	389	N.D.	954	37.0	N.D.	-	-
35	2565	1218	497	N.D.	850	33.1	N.D.	-	-
36	1904	1098	343	N.D.	465	24.3	N.D.	-	-

* Includes contribution from the precalcined feed.

TABLE E.12

Mass Balance on Na_2O Component for the 100mm (Tests 1-18) and 150mm (Tests 19-36) Fluidised Bed Experiment

(N.A. = Not Available, N.D. = Not Determined, Ngl = Negligible)

Test Number	Input	Output			Amount Volatilised		Amount Recovered From Filter (g)	Amount Unaccounted	
	Dust Feed (g)	Calcined Product (g)	Carry-over Material (g)	Deposits & Build-ups (g)	Weight (g)	Weight (%)		Weight (g)	Weight (%)
1	178*	28	34	23	92	52.0	N.A.	-	-
2	142*	43	4	8	87	61.3	N.A.	-	-
3	87*	38	4	2	44	49.9	N.A.	-	-
4	72*	30	7	2	34	46.3	N.A.	-	-
5	62*	26	4	1	32	50.9	N.A.	-	-
6	206	78	29	1	98	47.5	N.A.	-	-
7	144	92	5	18	25	17.4	N.A.	-	-
8	54	25	2	3	25	45.7	N.A.	-	-
9	64	40	1	2	21	33.2	N.A.	-	-
10	126	48	18	5	55	43.9	22	33	26.1
11	18	7	1	Ngl	11	57.0	5	5	29.6
12	82	43	7	1	31	38.0	24	7	8.6
13	94	47	6	Ngl	41	44.1	36	5	5.7
14	84	32	11	3	38	45.5	9	30	35.1
15	109	30	31	2	47	43.1	16	31	28.4
16	202	100	8	Ngl	94	46.3	33	61	29.9
17	95	40	8	1	46	48.5	38	8	8.4
18	72	35	8	1	28	39.2	1	27	37.2
19	48	20	4	N.D.	24	50.4	5	18	37.5
20	109	46	11	N.D.	52	48.0	28	24	21.9
21	68	24	10	N.D.	35	51.0	11	24	35.0
22	119	53	26	N.D.	40	33.5	16	24	20.5
23	138	51	3	N.D.	84	60.9	23	61	44.3
24	238	83	3	N.D.	152	64.2	24	128	54.0
25	198	50	9	N.D.	139	70.0	55	83	42.1
26	124	47	3	N.D.	74	59.6	56	19	14.9
27	107	19	6	N.D.	82	77.0	49	34	31.6
28	72	37	17	N.D.	18	25.6	15	3	4.8
29	234	71	18	N.D.	146	62.4	52	94	40.2
30	192	45	24	N.D.	123	64.2	53	71	36.9
31	390	133	42	N.D.	215	55.1	43	173	44.4
32	180	66	58	N.D.	56	31.1	39	17	9.4
33	216	54	68	N.D.	94	43.5	N.D.	-	-
34	271	159	44	N.D.	68	25.1	N.D.	-	-
35	270	174	50	N.D.	46	17.0	N.D.	-	-
36	200	137	44	N.D.	19	9.5	N.D.	-	-

* Includes contribution from the precalcined feed.

TABLE E.13

Mass Balance on Cl Component for the 100mm (Tests 1-18) and 150mm (Tests 19-36) Fluidised Bed Experiment

(N.A. = Not Available, N.D. = Not Determined, Ngl = Negligible)

Test Number	Input	Output			Amount Volatilised		Amount Recovered From Filter (g)	Amount Unaccounted	
	Dust Feed (g)	Calcined Product (g)	Carry-over Material (g)	Deposits & Build-ups (g)	Weight (g)	Weight (%)		Weight (g)	Weight (%)
1	525*	13	4	99	409	77.8	N.A.	-	-
2	491*	5	6	26	453	92.4	N.A.	-	-
3	256*	8	6	18	224	87.5	N.A.	-	-
4	124*	3	5	5	112	89.8	N.A.	-	-
5	146*	3	3	2	137	94.3	N.A.	-	-
6	586	2	43	6	534	91.1	N.A.	-	-
7	586	69	17	36	465	79.4	N.A.	-	-
8	184	18	5	13	147	80.1	N.A.	-	-
9	206	2	3	7	194	94.3	N.A.	-	-
10	454	25	54	31	343	75.7	183	160	35.3
11	101	5	5	1	91	89.7	36	55	54.6
12	419	37	56	4	323	77.1	195	299	71.3
13	315	8	30	Ngl	278	88.2	229	49	15.5
14	272	4	17	6	246	90.2	64	182	66.8
15	201	3	17	3	178	88.6	96	81	40.6
16	664	15	31	Ngl	618	93.1	243	376	56.6
17	269	11	14	1	243	90.2	208	35	12.9
18	211	5	17	2	187	88.2	9	178	84.0
19	41	2	6	N.D.	33	80.7	21	12	29.3
20	219	6	12	N.D.	201	91.7	60	141	64.4
21	129	5	10	N.D.	114	88.7	44	104	80.3
22	279	14	15	N.D.	250	89.5	117	133	47.8
23	454	16	6	N.D.	431	95.1	133	298	65.6
24	719	11	5	N.D.	703	97.7	99	604	83.9
25	590	15	22	N.D.	554	93.8	210	344	58.2
26	389	7	7	N.D.	373	96.5	244	131	33.7
27	400	2	14	N.D.	384	96.0	231	153	38.3
28	119	7	11	N.D.	101	84.9	70	31	26.1
29	398	15	35	N.D.	348	87.4	106	242	60.9
30	296	7	11	N.D.	278	93.8	98	180	60.7
31	516	4	21	N.D.	491	95.2	233	258	50.0
32	257	1	17	N.D.	239	93.0	187	51	19.8
33	389	5	20	N.D.	364	93.6	N.D.	-	-
34	488	36	11	N.D.	442	90.6	N.D.	-	-
35	486	43	17	N.D.	427	87.8	N.D.	-	-
36	361	63	11	N.D.	287	79.4	N.D.	-	-

* Includes contribution from the precalcined feed.

TABLE E.14

Mass Balance on SO_3 Component for the 100mm (Tests 1-18) and 150mm (Tests 19-36) Fluidised Bed Experiment

(N.A. = Not Available, N.D. = Not Determined, Ngl = Negligible)

Test Number	Input	Output			Amount Volatilised		Amount Recovered From Filter	Amount Unaccounted	
	Dust Feed (g)	Calcined Product (g)	Carry-over Material (g)	Deposits & Build-ups (g)	Weight (g)	Weight (%)	(g)	Weight (g)	Weight (%)
1	492*	50	60	316	66	13.4	N.A.	-	-
2	747*	97	19	41	590	79.0	N.A.	-	-
3	368*	102	17	12	237	64.4	N.A.	-	-
4	433*	83	22	10	319	73.6	N.A.	-	-
5	378*	101	11	6	260	68.8	N.A.	-	-
6	1014	201	110	8	694	68.5	N.A.	-	-
7	907	432	35	82	358	39.5	N.A.	-	-
8	285	96	23	30	136	47.6	N.A.	-	-
9	444	254	5	14	171	38.5	N.A.	-	-
10	837	300	151	51	335	40.0	80	75	11.5
11	93	24	12	2	56	60.1	22	34	36.3
12	367	171	17	8	171	46.7	27	144	41.5
13	498	170	31	Ngl	298	59.8	120	178	35.8
14	361	90	52	14	205	56.8	42	162	45.0
15	675	157	165	10	343	50.8	91	252	37.4
16	821	281	46	Ngl	494	60.2	105	389	47.5
17	319	104	17	3	195	61.1	126	69	21.6
18	367	135	43	5	183	49.9	. 5	178	48.5
19	267	65	41	N.D.	160	60.1	50	110	41.2
20	952	110	113	N.D.	729	76.5	182	546	57.4
21	526	51	65	N.D.	409	77.8	99	310	59.0
22	816	238	84	N.D.	494	60.6	126	369	45.2
23	634	219	25	N.D.	390	61.5	118	271	42.8
24	1292	208	21	N.D.	1063	82.3	161	902	69.8
25	1058	72	68	N.D.	918	86.8	179	708	66.9
26	689	58	22	N.D.	609	88.4	260	350	50.7
27	697	40	51	N.D.	606	86.9	323	283	40.6
28	672	413	103	N.D.	156	23.2	26	130	19.4
29	2196	420	238	N.D.	1538	70.1	499	1039	47.3
30	1880	170	182	N.D.	1527	81.2	570	957	50.9
31	3555	1137	479	N.D.	1939	54.5	513	1427	40.1
32	1839	874	501	N.D.	765	41.6	377	388	21.1
33	2174	219	497	N.D.	1459	67.1	N.D.	-	-
34	2730	1341	390	N.D.	1069	38.9	N.D.	-	-
35	2718	1462	523	N.D.	733	27.0	N.D.	-	-
36	2017	1294	327	N.D.	396	19.6	N.D.	-	-

* Includes contribution from the precalcined feed.

APPENDIX F

Heat Balance and Fan Power Calculation

F.1 Assumptions

The following assumptions are used in the calculations:-

a) 1 kg dust → 0.62 kg calcined product

→ 0.05 kg carry-over material

→ 0.10 kg alkali product

→ 0.21 kg CO_2

→ 0.02 kg H_2O

b) Heat of reaction, $\Delta H_r' = 230$ kcal/kg dust.

c) Heat losses, $q_L = 10\%$ of the fuel or heat input.

For simplicity, it is assumed that only coal is fired in the calciner and the effect of coal ash is ignored. A 5% excess air is allowed. The data used for the calculations are given in Table F.1.

F.2 Heat Balance for the Fluidised Bed Calciner and Primary Cooler

For 1 kg of dust feed, the various heat input and output streams of the calciner are as follows:-

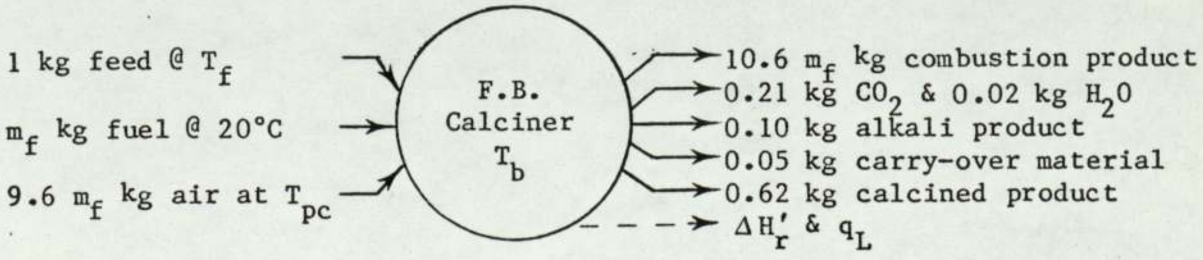


TABLE F.1

Data Used for the Heat Balance

Temperature of Calciner = 1200°C

Fuel Type = Bituminous Coal (Type 602)

Nett Calorific Value = 6344 kcal/kg

Stoichiometric Air = 9.17 kg/kg coal

Actual Air Requirement = 9.6 kg/kg coal (@ 5% excess)

Mean Specific Heats, c_p (kcal/kg)

(°C) c_p	20 (Datum)	100 (Drier)	250 (Bag Filter)	1200 (Calciner)
Dust Feed	0.19	0.20	0.21	0.26
Calcined Product (& Carry-over Dust)	0.17	0.19	0.20	0.25
Alkali Product	-	-	-	0.25 (Assumed)
Air	0.24	0.24	0.24	0.27
Combustion Products	0.24	0.25	0.26	0.29
CO_2	0.20	0.21	0.23	0.28
H_2O Vapour	0.44	0.45	0.46	0.53

Theoretical Heat of Reaction at 20°C = 230 kcal/kg dust

Latent Heat of Vapourisation of Water at 20°C = 586 kcal/kg water

Latent Heat of Fusion of the Alkali Product ≃ 80 kcal/kg alkali

Taking a datum temperature of 20°C,

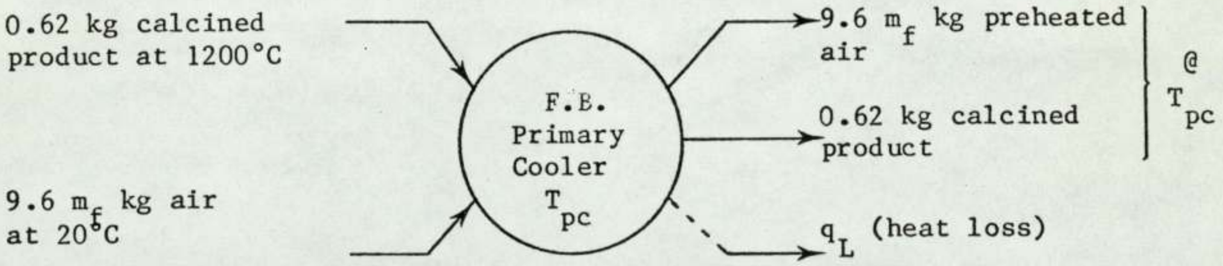
$$\text{Heat in, } q_i = 1 \times 0.2\ (T_f - 20) + 6344 \times m_f + 9.6\ m_f \times 0.24\ (T_{pc} - 20)$$

$$\text{Heat out, } q_o = 10.6\ m_f \times 0.29 \times (T_b - 20) + (0.21 \times 0.28 + 0.02 \times 0.53 + 0.10 \times 0.25 + 0.05 \times 0.25 + 0.62 \times 0.25)\ (T_b - 20) + 230 + 0.1 \times 6344\ m_f$$

For $T_f = 100$°C and $T_b = 1200$°C, the heat balance for the calciner becomes,

$$2082\ m_f + 2.3\ m_f\ (T_{pc} - 20) = 523 \qquad \text{.....(F.1)}$$

The temperature of the preheated air is determined from the heat balance over the primary cooler, i.e.,



Assume heat loss = 10% of heat in,

$$0.9\ [0.62 \times 0.25\ (1200 - 20)] = 0.62 \times 0.20\ (T_{pc} - 20) + 9.6\ m_f \times 0.24\ (T_{pc} - 20)$$

$$\therefore \quad (T_{pc} - 20) = \frac{165}{0.62 \times 0.2 + 9.6\ m_f \times 0.24} \qquad \text{.....(F.2)}$$

Substitute equation (F.2) in (F.1),

$$2082\ m_f + 2.3\ m_f \left(\frac{165}{2.3\ m_f + 0.124} \right) = 523$$

i.e. $$4789\ m_f^2 - 566\ m_f - 65 = 0 \qquad .....(F.3)$$

Solving the quadratic equation and taking the positive root gives,

m_f = 0.19 kg coal/kg dust

$\equiv$ <u>1203 kcal/kg dust</u>

and T_{pc} = <u>313°C</u>

The effects of varying T_f and T_b on m_f and T_{pc} can be readily calculated from the above equations.

F.3 Fan Power Calculation

F.3.1 Bases and Assumptions

Figure F.1 shows the major fan and the pressure or suction required for the process. The electric energy required to drive the fan can be calculated from the ideal gas laws for gas compression,

$$\text{Work done, } W' = \frac{1}{\eta} \cdot \frac{\gamma}{\gamma-1} \cdot p_1 V_1 \left[\left(\frac{p_2}{p_1} \right)^{\frac{(\gamma-1)}{\gamma}} - 1 \right] \text{J} \qquad .....(F.4)$$

where η = efficiency which is assumed to be 0.7

$\gamma = \frac{c_p}{c_v}$ = 1.4 for air

p_1, p_2 = inlet ant outlet pressure (atm)

V_1 = volume of gas at inlet temperature T (m^3)

The equation can be expressed in terms of the fan power, W,″

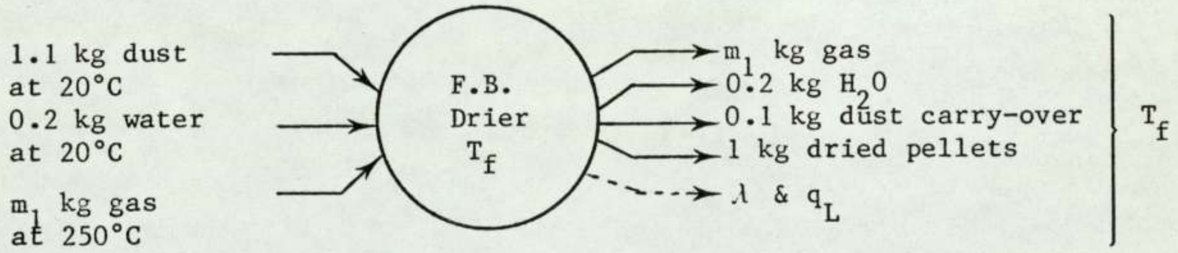
$$W'' = 0.1407\, p_1 V_1 \left[\left(\frac{p_2}{p_1}\right)^{\frac{2}{7}} - 1 \right] \text{ kWh} \qquad .....(F.5)$$

The quantity of gases involved is obtained from a heat and mass balance for the equipment involved.

F.3.2 Determination of Gas Quantity

a) The Fluidised Bed Drier

Assume that the drying gas is at a temperature of 250°C and that the drier operates at 100°C, the heat and mass balance per 1 kg of dried pellet produced is as follows:-



For T_f = 100°C and taking a datum of 20°C,

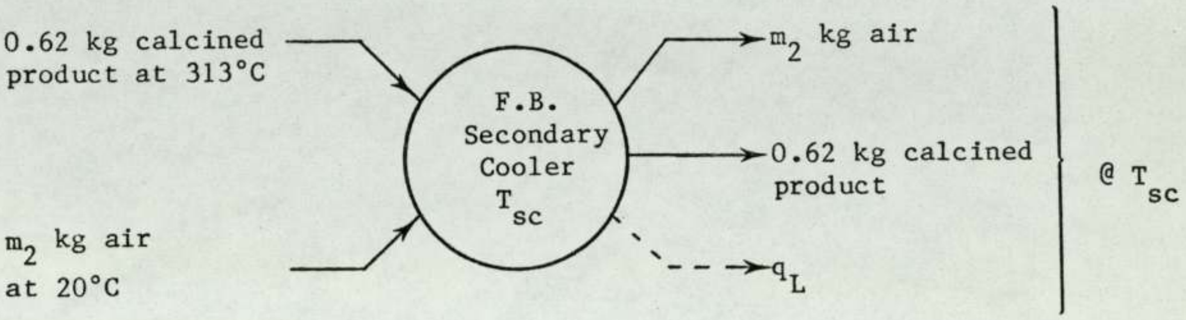
Heat in, $q_i = m_1 \times 0.26 \times 230$

Heat out, $q_o = (m_1 \times 0.25 + 0.2 \times 0.45 + 1.1 \times 0.20) \times 80 +$
$0.2 \times 586 + 0.1\,(m_1 \times 0.26 \times 230)$

$$\therefore \quad m_1 = \frac{142}{33.82} = \underline{4.20 \text{ kg gas/kg dried dust pellet}}$$

b) The Secondary Cooler

From previous calculations, the temperature of calcined product from the primary cooler is 313°C. The amount of air at 20°C required to cool the product to 100°C is given



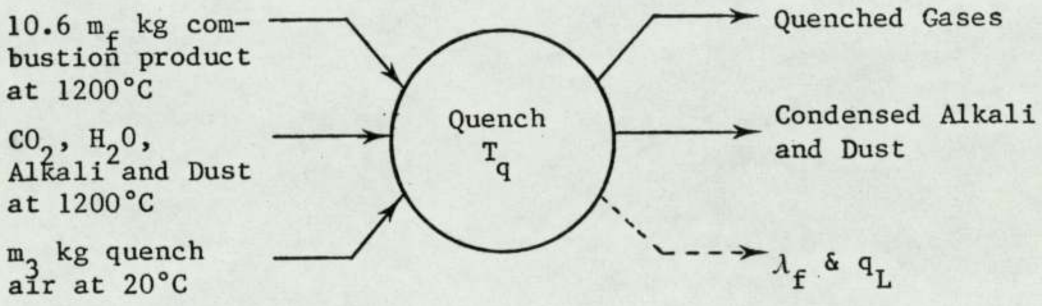
Assume $T_{sc} = 100°C$ and $q_L = 10\%$ of heat input,

$$0.9\ (0.62 \times 0.20 \times 293) = 0.62 \times 0.19 \times 80 + m_2 \times 0.24 \times 80$$

$$m_2 = \underline{1.21 \text{ kg air/kg dust calcined}}$$

c) The Air Quench

Assume that the gas is quenched to 250°C,



From Section F.2,

Heat in, $q_i = 814$

Heat out, q_o = $(2.01 \times 0.26 + 0.21 \times 0.23 + 0.02 \times 0.46 +$
$0.15 \times 0.25 + m_3 \times 0.24) \times 230 +$
$0.1 \times 80 + 0.1 \times 814$

$\therefore \quad m_3$ = <u>10.35 kg air/kg dust calcined</u>

On the basis of the gas quantity and temperature determined and the pressure or suction shown in Figure F.1, the fan power required is shown in Table 7.2.

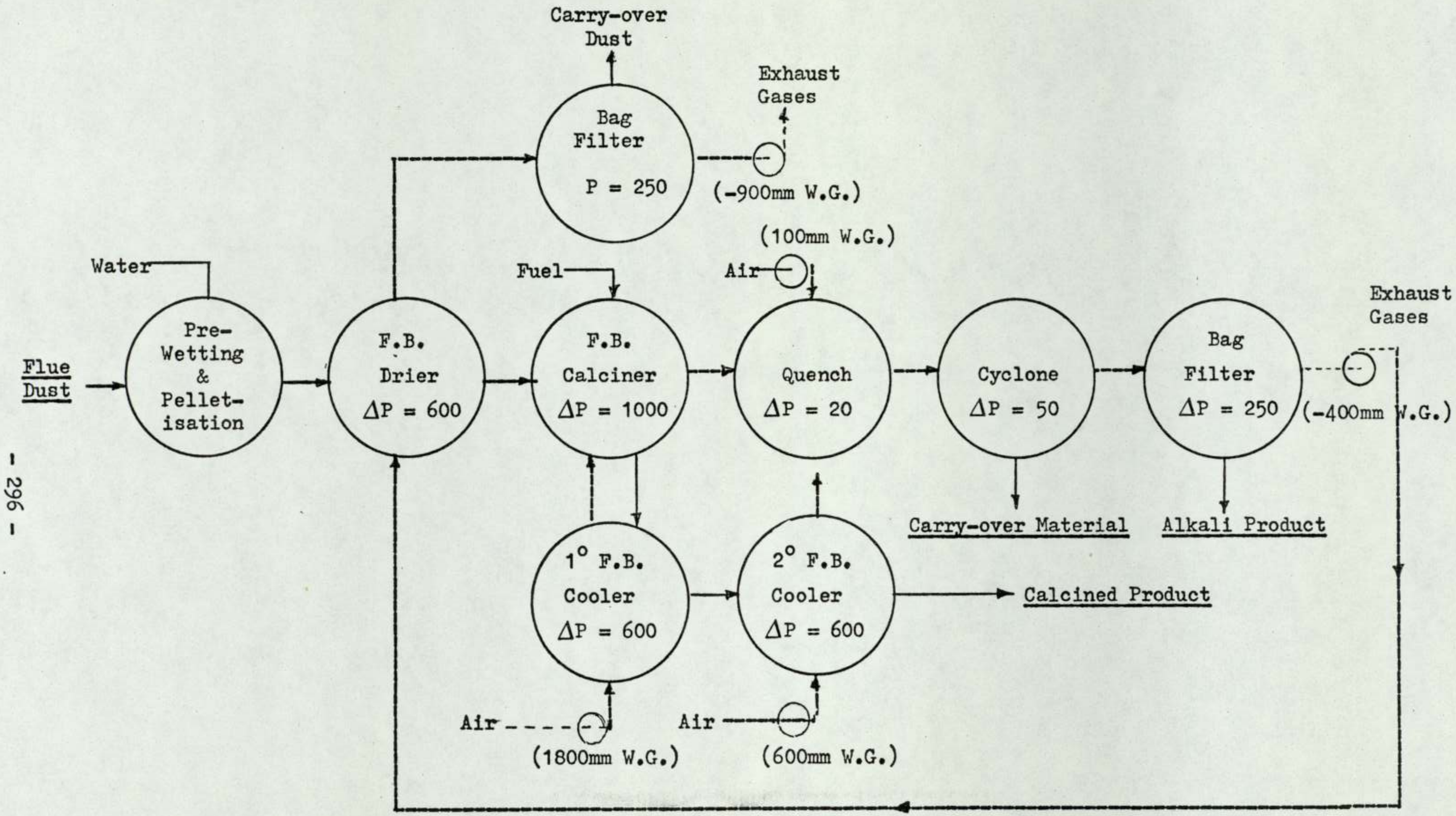


FIGURE F.1

Estimated Fan Pressure or Suction of the Fluidised Bed Process

APPENDIX G

Publication of the Present Work

'Processing of Kiln Dust'

By

B. Tettmar, J.H. Khor, S. Gregory

(Paper presented to the '1977 VDZ Congress')

VDZ-Kongreß '77

Verein Deutscher Zementwerke e.V., Düsseldorf

Verfahrenstechnik der Zementherstellung

Process Technology of Cement Manufacturing

Technologie des processus de la production du ciment

BAUVERLAG GMBH · WIESBADEN UND BERLIN
Macdonald & Evans · Estover, Plymouth, Devon.

ing orifice. The diverted kiln gas enters a mixing chamber where forced ambient air quenches the kiln gas from 920 to 500° C. An air-atomized single-nozzle water spray further cools and conditions the gas to 280° C before it enters the bypass gas precipitator [5]).

The clinkering system has been operated at 1500 t/d, limited by the existing raw grinding capacity. Installation of a Loesche Roller Mill for raw material grinding was completed this summer to allow full usage of the system. The kiln is fired by coal and/or oil; at present oil is used in the calciner. A Loesche Roller Mill coal system for calciner firing should be in operation shortly.

An initial evaluation of the process, conducted in April, 1976, indicated that the apparent effect of the bypass on alkali reduction was in reasonable conformity with laboratory volatility projections. As shown in Figure 5, the calculated and measured clinker alkali levels are in approximate agreement at a bypass of 30 to 35 percent.

Table 1 indicates the chemical characteristics of feed, bypass dust, preheater dust, and clinker in April, 1976. Bypass dust, expressed as a percentage of clinker produced, was then at about 15 percent. Based on estimates of the bypass percentage (25 to 40 percent), it was concluded that the bypass dust rate was excessive for the gas rate in use. Furthermore, the low ignition loss of the bypass dust implies the presence of significant quantities of calcined material.

A substantial reduction in dust loss was obtained by removing an obstruction in the feed pipe, with the result that waste dust rates of the order of 6–8 percent are now obtained. A further effort to conserve raw material and improve bypass performance by installation of an enclosed refractory feed pipe, extending through the feed hood into the kiln, did not provide any significant further benefit after several months of operation.

Data is summarized in Table 2 corresponding to plant operation in October 1976, following the feed end modifications. The quantity of by-pass dust has been reduced from 209 to 115 metric t/d. The quality of this dust, in terms of alkali content, has been improved from an Na_2O equivalent level of 4.69% to 7.4%. Thus, provision for smooth unobstructed flow of feed i the kiln has reduced the quantity of feed re-entrained in the k gas stream and diverted to the by-pass, while sustaining essent the same alkali removal rate. Since the by-pass dust is wasted, important to minimize its kiln feed content both from the sta point of the quantity of dust to be handled, and the value of heated, partially-calcined kiln feed.

The product from this plant is required to conform to stringe regulations on the acceptable cement alkali level. The low kiln capacity and unusually long kiln have resulted in low feed end temperatures, promoting an alkali cycle within the kiln. In or to maintain the alkali in the vapor phase beyond the kiln, chl addition was instituted. Therefore, more stable and controlla alkali reduction resulted with chloride addition to the system when operating at reduced capacity and with variable feed alk Addition of up to 0.2 percent of calcium chloride to the raw grinding system, increasing kiln feed chloride to about 0.1 pe cent, has allowed reasonably consistent low alkali (less than 0.6 percent Na_2O equivalent) cement production from this system. Under these conditions, Stage IV chloride concentrat is generally held to 0.2 percent, and no preheater coating or plugging problem has resulted.

The current temporary low system capacity has required that calciner efficiency be held at a very low level for a pre-calcine (apparent calcination is 60 to 65 percent) in order to absorb some of the heat released in the kiln. However, operation of t flash furnace at its design condition of 90 per .ent cancinatio was achieved easily in initial testing.

The special circumstances involved in adapting an existing kil to rapid process initiation (a shorter kiln by 20 to 40 meters would have been preferred) and the need to operate at reduce capacity, have imposed some engineering compromises. Nonetheless, the operation and control of the calciner has fully confirmed expectations, and the degree of alkali reduction available exceeds that of any known suspension preheater cement kiln.

Processing of kiln dust

Traitement de la poussière du four

By **B. Tettmar, J. H. Khor,** Barnstone, Nottinghamshire, Great Britain, and
S. Gregory, Birmingham, Great Britain

Summary

Various means of processing 300,000 t/year of kiln dust from 2 wet process works in UK have been examined. The alkali content of the dust (K_2O approx 7%) is too high to permit recycling, and the dust is now having to be dumped. This represents a waste of raw materials and fuel, and is subject to environmental contraints. After reviewing

Résumé

On a étudié 2 méthodes pour traiter 300.000 t poussière de four rotatif de 2 cimenteries à voie h en Grande Bretagne. La teneur en alcali de la pou (environ 7% K_2O) est trop élevée pour permettre introduction et il faut par conséquent la déposer, représente un gaspillage de matière première et de

einen brauchbaren niedrigen Alkaligehalt (unter 0,6% Na_2O-Äquivalent) des Zements. Unter diesen Bedingungen läßt sich die Chlorid-Konzentration allgemein bei 0,2% halten, und Ansätze im Vorwärmer oder Verklumpungen traten nicht ein.

Die derzeit geringe Kapazität des Systems brachte es mit sich, daß die Leistung des Calcinierers auf einer niedrigen Stufe gehalten werden muß (Calcination 60—65%), um einen Teil der im Ofen freiwerdenden Wärme aufzunehmen. In anfänglichen Versuchsverfahren war allerdings die Möglichkeit einer 90%igen Calcinierung nachgewiesen worden.

Die besonderen Umstände bei der Anpassung eines vorhandenen Ofens an ein neues Verfahren (ein um 20 bis 40 m kürzerer Ofen wäre vorzuziehen gewesen) und die Notwendigkeit, mit verringerter Leistung zu fahren, brachten einige technische Probleme mit sich. Aber der Betrieb und die Kontrolle des Calcinierers haben die Erwartungen voll erfüllt, und das Ausmaß der Verringerung der Alkalimenge übertrifft das aller bekannten Vorwärmeröfen.

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Aufbereitung von Ofenstaub

Von **B. Tettmar, J. H. Khor**, Barnstone, Nottinghamshire/Großbritannien, und
S. Gregory, Birmingham/Großbritannien

Zusammenfassung

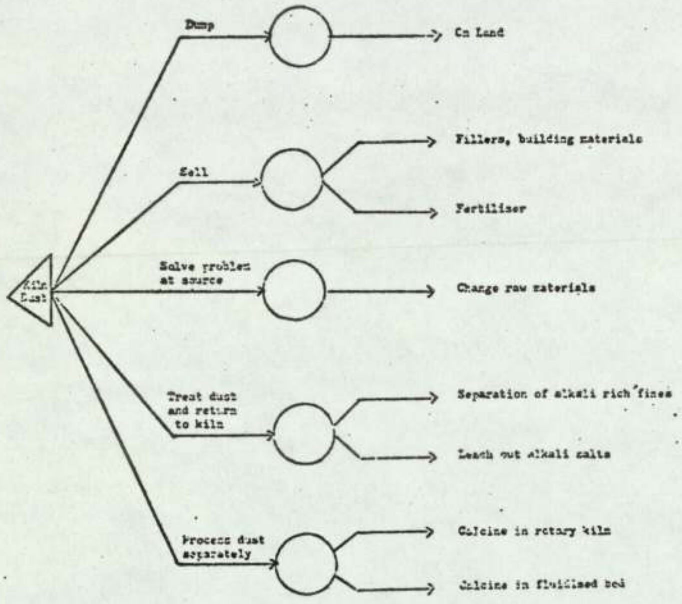
Es wurden verschiedene Methoden zur Behandlung von 300 000 t/Jahr Drehofenstaub von zwei Naßwerken in Großbritannien untersucht. Der Alkaligehalt des Staubes (ca. 7% K_2O) ist zu hoch, um eine Wiedereinführung zu erlauben, und der Staub muß daher gelagert werden. Das bedeutet eine Verschwendung von Rohmaterial und Brennstoff und verursacht Schwierigkeiten mit der Umgebung. Nach Betrachtung der verschiedenen Möglichkeiten zur Behandlung des Staubes wurden Untersuchungen im Labor und in einer Versuchsanlage unternommen, um eine Kalzination zu entwickeln, die einen brauchbaren Klinker und ein Düngemittel mit 45% K_2O liefert. Es ergab sich dabei ein Arbeitsverfahren, bei dem im Fließbett der Staub in kleinen Granalien kalziniert wird. Es ist geplant, eine Anlage für 10 t/h zu bauen.

the different options for treatings the dust, laboratory and pilot plant work was undertaken on developing calcination processes yielding a usable clinker, and a high alkali product containing 45% K_2O for fertiliser use. A process in which dust is made in small pellets which are then calcined in a fluidised bed has been developed. Consideration is being given to building a 10 t/h plant.

bustible et des difficultés avec l'environnement. Ap avoir considéré les différentes possibilités de traitem de la poussière, on a entrepris des essais en laboratoire dans une station d'essai pour développer un procédé calcination qui livrerait un clinker utilisable et un engr à 45% de K_2O. Il en est résulté une méthode consistan calciner la poussière en lit fluidisé en petits granules. prévoit de construire une installation pour 10 t/h.

1. Introduction

Large quantities of dust are collected from the waste gases of all cement kilns. This dust represents a significant proportion as high as 7 or 8 % of the raw materials quarried and of the fuel burnt. Potash, soda, chloride and sulphur from the raw materials and fuel concentrate in the dust. Disposal of the dust by blending with cement is not permissible within B.S.12. Recycling to the kiln is possible, providing chemical conditions permit and in dry processes the dust can usually be blended with kiln feed; on the other hand in a wet process, adding dust to the slurry may thicken it unduly, so insufflation or a scoop system is used instead.



Ofenstaub kiln dust

Die verschiedenen Verfahren von oben nach unten: Lagerung auf Halde / Verkauf als Füller, Baumaterial, Düngemittel / Lösung des Problems von Grund auf: Wechsel der Rohmaterialien / Behandlung des Staubs und Wiederaufgabe in den Ofen: Abtrennung des alkalireichen Feinanteils; Auslaugung der Alkalisalze / Getrennte Verarbeitung des Staubes: Calcination im Drehofen bzw. im Fließbett.

Bild 1: Möglichkeiten zur Behandlung von alkalireichem Staub

Fig. 1: Options for treating high alkali dust

However, the alkali level may be such that to recycle would mean making clinker with an excessive alkali content, and also cause build-ups in the kiln system and particularly with high chloride levels, difficulties with the gas cleaning equipment. 300,000 t/year of dust (see Table 1 for analyses) from two wet process works in U.K. operated by Blue Circle Group have to be dumped for these reasons. This dumping is costly, care has to be taken to avoid low level air pollution when moving the dust to the tip and, because of the risk of water pollution due to rain-water leaching out alkali salts, only certain land can be used for tipping. Various schemes for overcoming the need to dump have been examined, and extensive experiments have been made on calcination processes for converting dust to a clinker and a high alkali product suitable for fertiliser use.

2. Alternative to dumping

Alternative to dumping can be classified into four groups (see Fi

1) Sale of dust appears attractive, yielding income with little capital investment. Potential applications are as industrial fillers, media for acidic waste treatment, potash containing agricultural lime, and for landfill and soil stabilisation. In practice, (in U.K.) limited sales only can be achieved because of the relatively high cost of handling and transport.

2) Using raw materials or fuels with lower volatile contents coul ameliorate the problem at source. However, changing raw materi is rarely feasible and changing fuel can involve cost penalties. Mo coals contain appreciable levels of chlorine, so changing from oil to coal may lead to more chlorides in the dust.

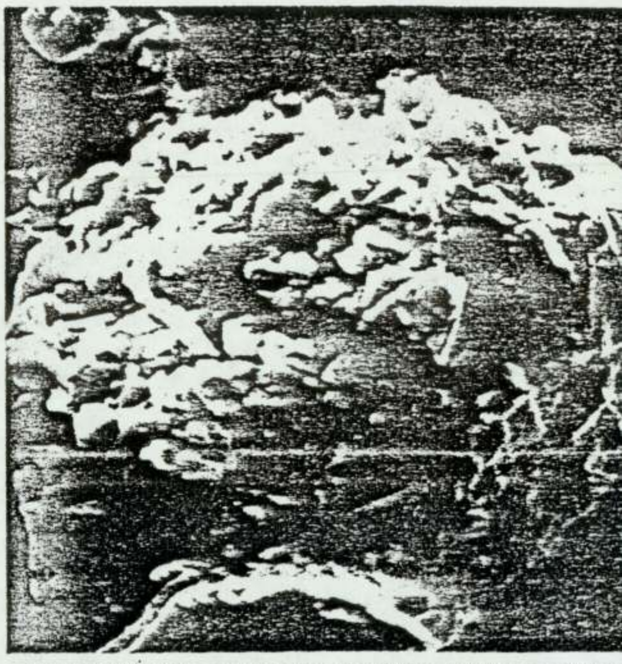


Bild 2: Rasterelektronenmikroskopische Aufnahme eines m Alkalisalzkristallen bedeckten Calcitteilchens (4000fach)

Fig. 2: Scanning electron micrograph of calcite particle coat with crystals of alcali salts

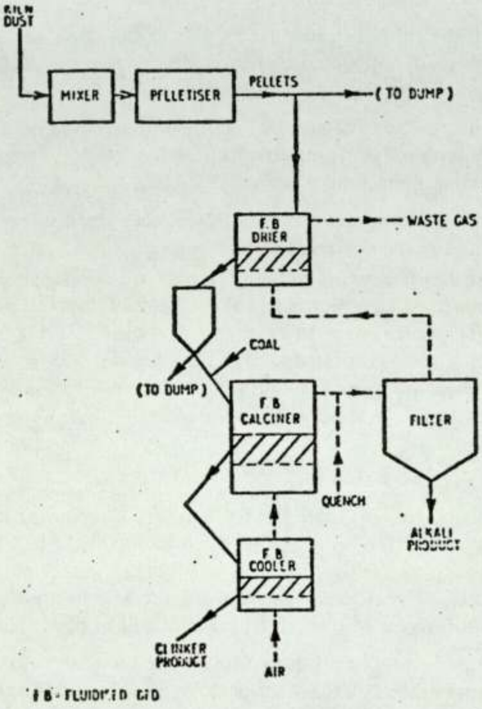
3) Methods of treating the dusts to remove some alkali salts, to allow full or partial return of the dust to the kiln, were investiga Classification of the dusts into a fine fraction and a coarse fract did not give sufficient separation since the bulk of the alkali salt occur as surface deposits on the dust particles as can be seen in figure 2. Leaching, while capable of high efficiency removal of alkali salts, which can subsequently be purified by crystallisatio leaves the dust as a wet cake which is difficult to feed to the kil also capital cost and site area are very large.

4) Calcination of the dust, either in a fluidised bed or a rotary kiln, will remove a large proportion of the alkali salts by volatili tion and convert the dust to a useable clinker.

The alkali salts can be collected as a product for application as a fertiliser.

1. Einleitung

Aus den Abgasen aller Zementöfen werden große Mengen Staub abgeschieden. Dieser Staubanteil macht bis zu 7—8 % der Rohmaterialmenge und des Brennstoffs aus, er enthält Kalium, Natrium, Chlorid und Schwefel. Eine Beseitigung des Staubes durch Vermischen mit dem Zement ist nach BS 12 nicht erlaubt. Eine Wiederaufgabe in den Ofen ist möglich, wenn die chemischen Bedingungen es zulassen, und bei Trockenöfen kann der Staub auch mit dem Aufgabegut vermischt werden. Andererseits kann beim Naßverfahren die Staubzugabe den Schlamm in unzulässiger Weise versteifen, so daß nur ein Einblasen des Staubs oder seine Beseitigung möglich ist.



Ofenstaub	kiln dust
Granulieranlage	pelletiser
zum Lager	to dump
Abgas	waste gas
Fließbett-Trockner	F. B. drier
Kohle	coal
Calcinierer	calciner
Kühlung	quench
Kühler	cooler
Luft	air

Bild 3: Calcinier-Verfahren für Granalien aus Ofenstaub

Fig. 3: Process for calcining pellets of kiln dust

Indessen kann der Alkaligehalt so hoch sein, daß eine Wiederaufgabe des Staubs im Klinker einen zu hohen Alkalianteil hervorruft. Er würde auch Anbackungen im Ofen verursachen, und bei hohen Chloridgehalten könnten Schwierigkeiten bei der Abgasreinigung auftreten. Von zwei Werken der Blue-Circle-Gruppe mußten aus diesen Gründen jährlich 300 000 t Staub gelagert werden (Tabelle 1), was hohe Kosten verursacht. Dabei muß vermieden werden, daß beim Transport die Umgebung verstaubt und bei der Auslaugung des Staubs durch Regen Alkalisalze in den Boden gespült werden, weshalb sich nur bestimmte Landflächen für die Lagerung eignen. Es wurden verschiedene Methoden zur Überwindung dieser Schwierigkeiten überlegt und ausgedehnte Versuche durchgeführt, um durch einen Calcinationsprozeß den Staub zu Klinker zu brennen und dabei ein kalireiches Material als Düngemittel zu gewinnen.

2. Alternativen zur Staubdeponie

Die Alternativen, den Staub auf Halde zu kippen, können in vier Gruppen aufgeteilt werden (Bild 1):

1.) Zunächst erscheint der Verkauf des Staubes sinnvoll, da er ohne viel Kapitaleinsatz Geld bringt. Mögliche Verwendungen wären: industrielle Füllstoffe, Mittel zur Behandlung säurehaltiger Abfälle, Düngekalk mit Kaligehalt, Verfüllungen und Bodenstabilisierungen. Praktisch bestehen in Großbritannien nur beschränkte Verkaufsmöglichkeiten, und zwar wegen der relativ hohen Behandlungs- und Transportkosten.

2.) Die Verwendung von Rohmaterialien oder Brennstoffen mit weniger flüchtigen Anteilen könnte die Frage von Grund auf lösen. Aber es ist selten möglich, das Rohmaterial zu wechseln, und ein Wechsel des Brennstoffes kann höhere Kosten zur Folge haben. Viele Kohlen enthalten beachtliche Mengen Chlor, so daß ein Wechsel von Öl zu Kohle zu mehr Chloriden im Staub führen kann.

3.) Es wurden Verfahren überprüft, aus dem Staub einige Alkalisalze zu entfernen, um den Staub ganz oder teilweise dem Ofen wieder zuzuführen. Eine Unterteilung des Staubs in eine feine und eine grobe Fraktion ergab keine ausreichende Trennung, da die Hauptmenge der Alkalisalze als oberflächliche Ablagerung auf den Staubteilchen zu finden ist (Bild 2). Auslaugungsverfahren, welche sehr wirkungsvoll Alkalisalze herauslösen, die anschließend durch Kristallisation gereinigt werden könnten, hinterlassen den Staub als einen nassen Filterkuchen, der schwer in den Ofen aufzugeben ist; außerdem sind Kapitalbedarf und Geländekosten sehr groß.

4.) Calcination des Staubes, entweder im Fließbett oder im Drehofen, verflüchtigt einen großen Teil der Alkalisalze und verwandelt den Staub in einen brauchbaren Klinker. Die Alkalisalze können zur Verwendung als Düngemittel gewonnen werden.

3. Calcination

Vorüberlegungen zeigten, daß die Calcination ein brauchbarer Weg ist, und 1974 wurden die Arbeitsbedingungen sowohl für einen Drehofen wie für ein Fließbett ermittelt. Man entschied sich für das Fließbett, da es weniger Anlagekapital und weniger Platz erfordert. Andererseits kann sich der Umbau eines außer Betrieb befindlichen Drehofens billiger als ein neues Fließbett erweisen. Deshalb wurden auch Versuche in dieser Richtung vorgenommen.

Bei den Planungen für ein Fließbett sollte das Verfahren so ablaufen, daß der Staub zu Pellets von 1—5 mm granuliert und in einem mit Kohle gefeuerten Fließbett bei 1200—1250 °C calciniert wird (Bild 3).

Der reine Wärmebedarf für die Calcination des Staubes und die Verflüchtigung der Alkalisalze liegt bei etwa 1260 KJ/kg (300 kcal/kg). Die in das Fließbett von 1250 °C einzublasende Kohlenmenge beträgt 0,13—0,25 kg/kg Staub, abhängig von der Vorwärmung der Verbrennungsluft. Der Gasdurchfluß liegt bei dieser Temperatur bei 9—17 m^3/kg Staub. Wenn Rohstaub verwendet wird, muß die Geschwindigkeit im Fließbett unter 0,02 cm/s bleiben, um ein zu starkes Herausblasen des Feinen zu vermeiden. Die Leistung pro m^2 Querschnitt würde bei bester Vorwärmung der Luft nur 0,08 kg/h betragen. Dagegen erlaubt die Verwendung von Granalien eine brauchbare Fließbett-Geschwindigkeit, die bei 3-mm-Granalien 3,5 m/s betragen kann, was einer Leistung von bis zu 1,4 t/h m^2 entspricht. Noch höhere Leistungen könnten mit größeren Granalien erreicht werden, aber der Druckabfall würde sehr groß werden. Die Granalien können entweder vor der Aufgabe auf das Bett hergestellt werden oder unter Verwendung von Klinkergrieß, an dem der in das Bett eingeblasene Staub anhaftet, wie beim Pyzel-Prozeß [1, 2]).

3. Calcination

A preliminary appraisal showed that calcination was a viable option and in 1974 work started to define the required operating conditions, using either a rotary kiln or a fluidised bed. The latter has a lower capital cost and occupies less space, so most attention has been directed to it. However, conversion of an out-of-use kiln may prove cheaper than building a new fluidised bed, so experiments were made also on the kiln process.

Work on fluidised beds was aimed at developing a process in which dust is formed into 1-5mm pellets which are then calcined in a direct coal fired bed operating at 1200 - 1250°C, Fig. 3.

The net heat of reaction to clinker the dust and to volatilise the alkali salts is about 300 kcal/kg. The coal which has to be injected into a bed operating at 1250°C is 0.13 - 0.25 kg/kg of dust, depending on degree of combustion air preheat, giving a gas flow at temperature of 9 m^3 - 17 m^3/kg of dust. Using raw dust, fluidising velocity would have to be below 0.02 cm/s to avoid excessive elutriation and capacity per m^2 of cross-section of bed would be only 0.08 kg/h, with maximum preheat. Forming pellets of dust permits a practical fluidising velocity. With a 3 mm dia. pellet, a fluidising velocity of 3.5 m/s can be used, giving a capacity of up to 1.4 t/h m^2. Higher capacities could be achieved with larger pellets but pressure drop would become excessive.

Pellets can be made either before feeding to the bed, or by providing clinker seeds on which dust blown into the bed adheres, as in the Pyzel process 1, 2).

A process in which pellets are pre-formed was chosen as pellets are a more convenient material to store or dump than raw dust. Hence, a plant could be built in two stages; first a pelletisation section to allow easier dumping followed by a calciner when dumping is no longer possible.

4. Development work on process

Pilot plant tests have been made to obtain design data for the process. Two methods of forming feed have been examined. One is to mix dust and water, pelletise in a dish, and dry the pellets in a fluidised bed, waste gases from the calciner. Pellets of moisture contents of 11 - 14 % have to be cured for up to 24h before drying; but by increasing the water content pellets can be made with sufficient strength to be dried immediately. A 3 mm dia. pelle
a crushing strength in excess of 10 N (= 1 kg). Mixing and pell
trials have been made at up to 9 t/h and drier trials at 1 t/h. T
method is to press dry dust between rolls to form sheets whic
then crushed to flakes. The capital cost of this equipment is h
than for dish pelletisation.

Calcination tests have been made in fluidised beds of 100 mm
150 mm dia. and 300 mm dia. The 2 smaller beds were fired
oil. On the largest bed, some runs were made successfully with
lump coal fed in with pellets. For the dust shown in Table 1,
tests have established that about 70 % of the alkali salts could
volatilised and clinker with 5 % free lime produced at a
temperature of 1225°C: with a mean solide retention time of
minutes and a fluidising velocity of 3.5 m/s.

All the chloride and a proportion of the sulphate were remov
more sulphate could be removed by increasing gas flow but th
would raise capital and operating costs.

Additions of 5 % and 10 % calcined dust to cement grinds hav
shown no significant effect on 28 day concrete strengths, alth
setting times tend to be slightly extended.

Alkali salts in the off-gases are collected by cooling the gases
filtering the condensed fume. Rapid quench systems which
substantially avoid build-ups have been developed. Bag filters
proved to be effective in collecting the fume: electrostatic
precipitators need to be operated at over 350°C and very low
velocity to give satisfactory efficiency. With dust A (Table 1),
typical analysis of the fume collected in filters is 47 % K_2O,
Na_2O, 24 % SO_3, 22 % Cl.

5. Proposed large scale plants

Outline designs for 2 t/h, 5 t/h and 10 t/h plants have been pr
Consideration is now being given to erecting a 10 t/h plant to
process all the dust made at one Works. Clinker output will be
45,000 t/year, representing a 7 % increase in the Works capaci
6,000 t/year of high alkali product will be produced.

Experiments on a pilot kiln have shown that similar products
those made in a fluidised bed can be obtained. For the second
an economic comparison is being made of building a 30 t/h fl
bed calciner or converting a rotary kiln located at a nearby sh
down Works.

Gewählt wurde das Verfahren der Granalienherstellung, da sich Granalien leichter lagern lassen als Staub. Die Anlage konnte nun in zwei Stufen gebaut werden, zuerst eine Granulieranlage mit Zwischenlager und dann der Calcinierer.

4. Verfahrens-Entwicklung

Um genauere Daten zu erhalten, wurden halbtechnische Versuche durchgeführt; dabei wurden zwei Verfahren untersucht. Das eine bestand darin, Staub und Wasser zu mischen, Granalien herzustellen und sie im Fließbett unter Verwendung von Abgas des Calcinierers zu trocknen. Granalien mit Wassergehalten von 11—14 % müssen bis zu 24 Std. vor dem Trocknen gelagert werden. Aber bei erhöhtem Wasseranteil lassen sich Granalien herstellen, welche genügend Festigkeit haben, um sofort getrocknet zu werden. Eine 3-mm-Granalie hat eine Bruchfestigkeit von mehr als 10 N (1 kg). Misch- und Granulierversuche wurden mit bis zu 9 t/h und Trockenversuche mit 1 t/h durchgeführt. Das andere Verfahren besteht darin, den trockenen Staub zwischen Walzen zu Platten zu pressen, die dann in Stücke gebrochen werden. Die Anlagekosten sind aber in diesem Fall höher als bei der Granulation.

Die Calcinierung wurde in Fließbetten von 100, 150 und 300 mm ∅ durchgeführt, wobei die zwei kleineren Fließbetten mit Öl gefeuert wurden. Bei dem größten Fließbett waren einige Versuche mit Kohlebrocken erfolgreich, die gleichzeitig mit den Granalien aufgegeben wurden. Beim Staub nach Tabelle 1 zeigten die Versuche, daß etwa 70 % der Alkalisalze verflüchtigt werden konnten und daß sich ein Klinker mit 5 % freiem Kalk bei einer Temperatur von 1225 °C bei einer mittleren Aufenthaltszeit von 40 min und einer Gasgeschwindigkeit im Fließbett von 3,5 m/s herstellen ließ.

TABELLE 1
Ofenstaub-Analysen

Table 1
Kiln dust analyses

	Werk A	Werk B
SiO_2	13,0	15,8
Al_2O_3	2,3	4,8
Fe_2O_3	2,1	1,3
CaO	38,1	40,7
MgO	0,8	0,6
CO_2	21,1	21,3
K_2O	7,8	6,2
Na_2O	1,1	0,6
Cl	3,5	0,7
SO_3	6,2	5,7
Anderes*)	4,8	2,5

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*) Kristallwasser, Spurenelemente u. a.

*) combined water, trace elements a. o.

Das gesamte Chlorid und ein Teil des Sulfats wurden ausgetrieben; höhere Sulfatanteile konnten bei erhöhtem Gasdurchfluß ausgetrieben werden, jedoch bei erhöhten Anlage- und Betriebskosten.

Zumahlungen von 5 und 10 % calciniertem Staub zu Zement ergaben keine sichtbare Wirkung auf die 28-Tage-Festigkeiten, wenn auch die Erstarrungszeiten dazu neigten, länger zu werden.

Die Alkalisalze in den Abgasen wurden durch Kühlung der Gase und Filtration gewonnen. Es wurden dazu Schnellkühlsysteme entwickelt, bei denen Anbackungen vermieden wurden. Schlauchfilter haben sich bei der Gewinnung als wirkungsvoll erwiesen. Elektrische Staubabscheider müssen bei Temperaturen über 350 °C und mit sehr geringer Gasgeschwindigkeit gefahren werden, wenn sie wirksam sein sollen. Bei Staub A (Tabelle 1) war die typische Analyse des aus dem Abgas abgeschiedenen Materials: 47 % K_2O, 5 % Na_2O, 24 % SO_3 und 22 % Cl.

5. Vorschläge für eine Betriebsanlage

Es wurden Pläne für Anlagen von 2, 5 und 10 t/h entworfen. Beabsichtigt ist der Bau einer Anlage von 10 t/h, um den gesamten Staub eines Werkes zu verarbeiten. Der Klinkeranfall wird 45 000 t/Jahr betragen, d. h. 7 % Zunahme der Werkskapazität, und außerdem sollen 6000 t/Jahr an hochalkalihaltigem Produkt hergestellt werden.

Ähnliche Produkte wie im Fließbett lassen sich nach Vorversuchen auch in einem Drehofen gewinnen. Für das zweite Werk wurde ein rechnerischer Vergleich für einen 30-t/h-Fließbett-Calcinierer durchgeführt bzw. für den Umbau eines Drehofens in einem benachbarten stillgelegten Werk.

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