

THE EFFECT OF MINERAL SALTS ON DEPOSIT FORMATION
DURING FLUIDISED BED COMBUSTION OF COAL

A Thesis Submitted for the Degree of Doctor of Philosophy

by

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ABSTRACT

The mineral matter present in three UK bituminous coals has been characterised using a combination of chemical analysis, X-ray diffraction, thermal analysis and infra-red techniques. The coals were found to contain the same salts and minerals, but varying in their relative proportions. The most abundant minerals were the kaolinite and mica groups of aluminosilicates, ankerite, dolomite, calcite, pyrite and quartz. The majority of the sodium and chlorine appeared to be organically associated with the coal. As the ionisable salt content (mainly water soluble ions of Na^+ , K^+ , Ca^{2+} , Mg^{2+} , Cl^- and SO_4^{2-}) of the coals decreased, so the melting temperatures of the resultant ashes increased.

Combustion of the coals in a laboratory fluidised bed combustor has shown that condensing salts of sodium, potassium and calcium chlorides and sulphates, and possibly low melting point eutectic mixtures provide an adhesive layer, allowing capture of impinging gas borne particulates, which form deposits. Such initial salt rich deposits were significantly reduced for the coal with the lowest ionisable salt mineral content.

The study has concentrated on the effects of combustion parameters and pretreatments of the coal on the nature of the deposits formed. Deposits on above-bed surfaces were particularly affected by surface temperatures and by the use of sulphur sorbent bed materials. Maximum deposition occurred ^{on} surfaces of 450° to 700°C, whilst in-bed sulphur retention enhanced deposition of alkali chlorides. Operation at higher bed temperatures, lower oxygen partial pressures and lower fluidising gas velocities also influenced deposition. Coal blending and reduced chlorine contents were identified as possible methods of reducing gaseous emissions and deposit forming tendencies. The effects of probe material, position, coal feed rate and time were also evaluated. The results of the laboratory study have been compared with pilot plant trials using the same coals.

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ABBREVIATIONS

a.a.	As Analysed
a.d.	Air Dried
BS	British Standard
c	Condensed Phase
d.b.	Dry Basis
DTA	Differential Thermal Analysis
DTG	Differential Thermogravimetry
EDX	Energy Dispersive X-ray Analysis
EPMA	Electron Probe Microanalysis
FBC	Fluidised Bed Combustion
FT-IR	Fourier Transform Infra-red Spectroscopy
g	Gaseous Phase
HTA	High-Temperature Ash
ICPS	Inductively Coupled Plasma Spectroscopy
Kp	Equilibrium Constant
LTA	Low-Temperature Ash
MAS	Magic Angle Spinning
m.pt.	Melting Point
NMR	Nuclear Magnetic Resonance
pf	Pulverised Fuel
SEM	Scanning Electron Microscopy/Microscope
S/S	Stainless Steel
TGA	Thermal Gravimetric Analysis
Umf	Minimum Fluidising Gas Velocity
wt.	Weight
XRD	X-Ray Diffraction
~	Approximately

CHEMICAL NAMES

Anhydrite	CaSO_4
Ankerite	$2\text{Ca Mg Fe}(\text{CO}_3)_4$
Apatite	$\text{Ca}_5(\text{PO}_4)_3 (\text{F}, \text{Cl}, \text{OH})$
Bassanite	$\text{CaSO}_4 \cdot \frac{1}{2}\text{H}_2\text{O}$
Calcite	CaCO_3
Cristobalite	SiO_2 (ring structure)
Dolomite	$\text{Ca Mg} (\text{CO}_3)_2$
Gypsum	$\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$
Haematite	$\alpha\text{Fe}_2\text{O}_3$
Illite	$\text{K}_y \text{Al}_4 (\text{Al}_y \cdot \text{Si}_{8-y}) \text{O}_{20} (\text{OH})_4$ where y generally 1 to 1.5
Kaolinite	$\text{Al}_2\text{O}_3 \cdot 2\text{SiO}_2 \cdot 2\text{H}_2\text{O}$
Magnesite	MgCO_3
Magnetite	$\text{FeO} \cdot \text{Fe}_2\text{O}_3$
Marcasite	FeS_2
Mullite	$3\text{Al}_2\text{O}_3 \cdot 2\text{SiO}_2$
Muscovite (mica)	$\text{K Al}_2 (\text{Al Si}_3 \text{O}_{10}) (\text{OH})_2$
Pyrite	FeS_2
Quartz	SiO_2
Rutile	TiO_2
Siderite	FeCO_3
Tridymite	SiO_2 (ring structure)

THE EFFECT OF MINERAL SALTS ON DEPOSIT FORMATION DURING
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1. INTRODUCTION AND OBJECTIVES

Coal is the UK's greatest natural energy source and has remained dominant in spite of the rapid increase in crude oil and natural gas production during the 1960's. At this time, oil became plentiful and cheap, and nuclear power appeared to be poised for rapid growth. However, by the mid 1970's the price of oil had increased sharply, and subsequently became erratic and unpredictable. The large reserves of coal compared to other fossil fuels ensure that the former will remain a crucially important energy source for many years to come.

About 80 m tonnes of coal are sold each year to the electricity generating Boards in the UK. The Central Electricity Generating Board, CEGB, now operates 79 power stations of which 43 are coal fired plants producing over 75% of UK electricity. It has been estimated that an extra 12,000 MW per year will be required by the year 2000. The recently completed Drax power station in North Yorkshire has a total output of 4000 MW and is capable of meeting 10% of UK electricity requirements. The CEGB has recently applied for permission to build two new 1,800 MW coal fired power stations, at Fawley in Hampshire and at West Burton in Nottinghamshire. An application for a third at Kingsnorth in Kent is expected shortly. Two sites, Hams Hall in Warwickshire and Killingholme in South Humberside have been earmarked as possible locations for further coal-fired power stations.

In face of the growing awareness of the problems associated with nitrogen and sulphur oxides, and with increasing use of nuclear power, development of more efficient combustion technologies, such as fluidised bed combustion (FBC), which permit control of emissions, is essential. In the UK there are now over 110 fluidised bed boilers and furnaces with the capacity to burn over 0.65 m. tonnes of coal per annum. Pressurised FBC in combined cycle power generation systems, has the potential to provide improved electricity generating efficiency using coal.

The mineral components of some coals can, however, present problems of fouling, slagging and corrosion when the coals are burned in conventional or FBC plant. Most of these problems are attributed to the presence of alkali (Na, K) and alkaline earth (Ca, Mg) metal elements (1) and their associated chlorine (2). Such elements are the major water soluble mineral constituents and are often referred to as ionisable salts. Although present as relatively minor components of coal they are of particular importance as it is suggested they are likely species to be released during combustion (3).

Three important parameters have the potential to influence the nature and extent of deposits. Primarily, the coal's mineral constituents, in particular their mode of occurrence but, in addition, the design and mode of operation of the combustor.

The objective of this project is to investigate the mechanisms of binding (mode of occurrence) of the ionisable salt mineral components in coals and to study their release during FBC. Three UK bituminous coals were selected for the study on the basis of their varying ionisable salt mineral content and recorded performance when burned in commercial combustors. In the initial stage of the study the minerals, including the water soluble salts, were separated from these coals by low-temperature plasma ashing and aqueous extraction. The coals and the separated minerals were fully characterised (chemically and physically) and the mineralogical composition estimated using a variety of analytical techniques. These include inductively coupled plasma spectroscopy, ICPS, X-ray diffraction, XRD, microscopic techniques, Fourier-transform infra-red, FT-IR, solid state nuclear magnetic resonance spectroscopy, NMR, thermal and normative analysis.

Subsequently, the thermal behaviour of the selected coals were studied in a laboratory fluidised bed combustor and the fate of the major salt mineral components determined. The consequence of varying FBC parameters, such as probe and bed temperatures, coal feed rate, fluidising gas velocity, combustion atmosphere and time, deposit surface material and position and of bed material, on the nature and extent of initial deposition was determined.

Additionally, the influence of certain coal pretreatments such as coal chlorine content and coal blending on these deposits were investigated. The nature of the deposits formed when the coals were burned both in the laboratory and in a plant scale fluidised bed furnace, were compared.

Knowledge gained from the behaviour of the minerals as influenced by changes in combustion conditions and coal pretreatments was used to elucidate the mechanisms for the release and deposition of the ionisable salt minerals. This study indicates ways in which some of the problems caused by the presence of ionisable mineral salts might be alleviated.

2. LITERATURE SURVEY

2.1 Fluidised Bed Combustion

2.1.1 Fluidised bed combustion of coal

Initial investigations in Britain into FBC of coal were made with the objective of producing an alternative technology to pulverised fuel (pf) burning for power generation (4). In addition, using FBC technology (staged combustion and limestone beds), production of nitrogen and sulphur oxides can be reduced to meet current EEC emission standards (5).

Three main types of atmospheric FBC technology have been developed (6); two types of 'bubbling bed' (shallow and deep) and a quite different circulating principle. In the UK the shallow bed system is most widely used, generating outputs of up to 30 MW (6). Pressurised FBC in combined cycle power generation systems, which use both gas and steam turbines, has the potential to increase the efficiency of power generation above the efficiency of conventional pf stations. Programmes of work have been carried out on a pressurised system of 80 MW capacity at the Grimethorpe pressurised FBC facility (7,4).

FBC of coal on a large scale is unique in that high combustion intensities may be achieved at relatively low temperatures. The essential features of a (shallow) fluidised bed boiler are illustrated in Figure 1. Coal is continuously fed to a hot bed fluidised by the injection of preheated air to the bottom of the bed (8). The bed particles are forced upward by the air flow and exhibit many of the properties of a liquid; the bed is said to be fluidised. The critical gas velocity at which the transition from a stationary to a fluidised bed takes place is called the minimum fluidising velocity (9). During start-up the fluidising air is initially heated to 510°C, at which temperature the particles of coal are injected into the bed for combustion (10). The coal is rapidly distributed throughout the bed and burnt, producing heat for raising steam, water heating or other purposes.

Coal is supplied continuously at the rate required to meet the desired heat output. The bed temperature is controlled to about 850°C by water tubes immersed in the bed (4,11). Approximately

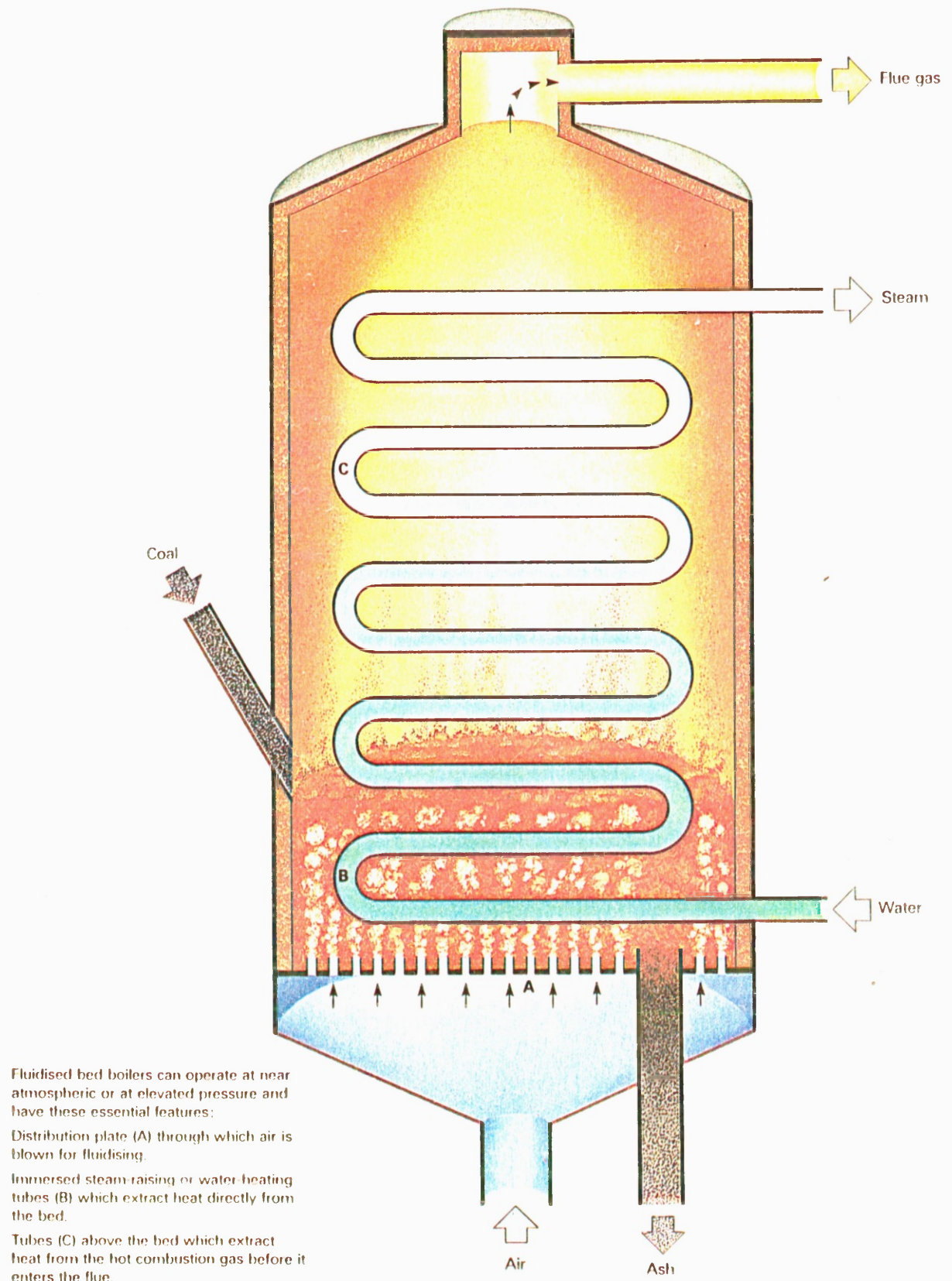


Figure 1. Features of a Fluidised Bed Boiler.

50% of the heat generated can be extracted by these tubes and the steam produced may be converted to electrical energy in a conventional steam turbine cycle. Alternatively, where the heat is required in the form of clean hot air, the tubes in the bed may be made of ceramic material through which air passes. Heat transfer tubes are also placed above the bed to extract heat from the hot combustion gases before they enter the flue.

The bed material can either be the ash formed from combustion of the coal or an inert material such as sand. The concentration of coal in the bed is small; the burning coal is surrounded by inert material and the bed temperature is relatively low, so there is little tendency for ash particles to stick together (11). Bed material is removed continuously to maintain the required level.

The ash in the bed has some capacity to absorb sulphur oxides, depending on its calcium (and sodium) content, but sulphur retention can be markedly increased by adding limestone (CaCO_3) or dolomite ($\text{CaCO}_3 \cdot \text{MgCO}_3$) to the bed. At FBC temperatures ($<900^\circ\text{C}$) the calcium carbonate forms calcium oxide which reacts with sulphur oxides produced during combustion to form calcium sulphate (10,12). Calcium sulphate is stable and retained within the bed. The magnesium carbonate present in dolomite will not react in an analogous way to form magnesium sulphate unless the bed temperature is very low ($<800^\circ\text{C}$).

Some of the finer residual char particles resulting from incomplete combustion of the coal are elutriated from the bed. This unburned char together with the finer ash, sorbent and other particulates are separated from the flue gas using cyclones, prior to release to the atmosphere. In some applications where the fluidising velocity is high, it is necessary to provide a second combustion stage for this material, either recycling it to the main bed to improve combustion efficiency or feeding it to a second bed (8). Such a system is termed a 'fast' or recycling fluidised bed (4). A comparison of the combustion conditions, ash entrainment in FBC and pf systems is summarised in Table 1.

Table 1 - Combustion Conditions in Pulverised Coal and Fluidised Bed Systems

Conditions	Pulverised - Coal Firing	Fluidised - Bed Combustion
Coal particle size, (μm)	<100	<2000
Combustion temperature $^{\circ}\text{C}$	1400-1600	800-950
Residence time of ash in combustion zone, (s)	2 - 5	10 - 1000
Flue gas velocity, (ms^{-1})	10 - 20	1 - 3
Ash entrainment in flue gas, (%)	75 - 80	40 - 60
Nature of ash entrained in gas	Chiefly spherical particles, 0.01 to 50 μm in diameter	Chiefly non- spherical particles, 0.01 to 20 μm in size
Nature of remaining ash	Sintered clinker with some fused slag, a few g to many kg	Unfused, non- spherical particles, chiefly 20-2000 μm in size

The standard fluidised bed combustor can produce hot gas at temperatures up to $\sim 1050^{\circ}\text{C}$. To meet the requirements for higher process gas temperatures (up to 1300°C), a two-bed combustor/pyrolyser has been developed (4).

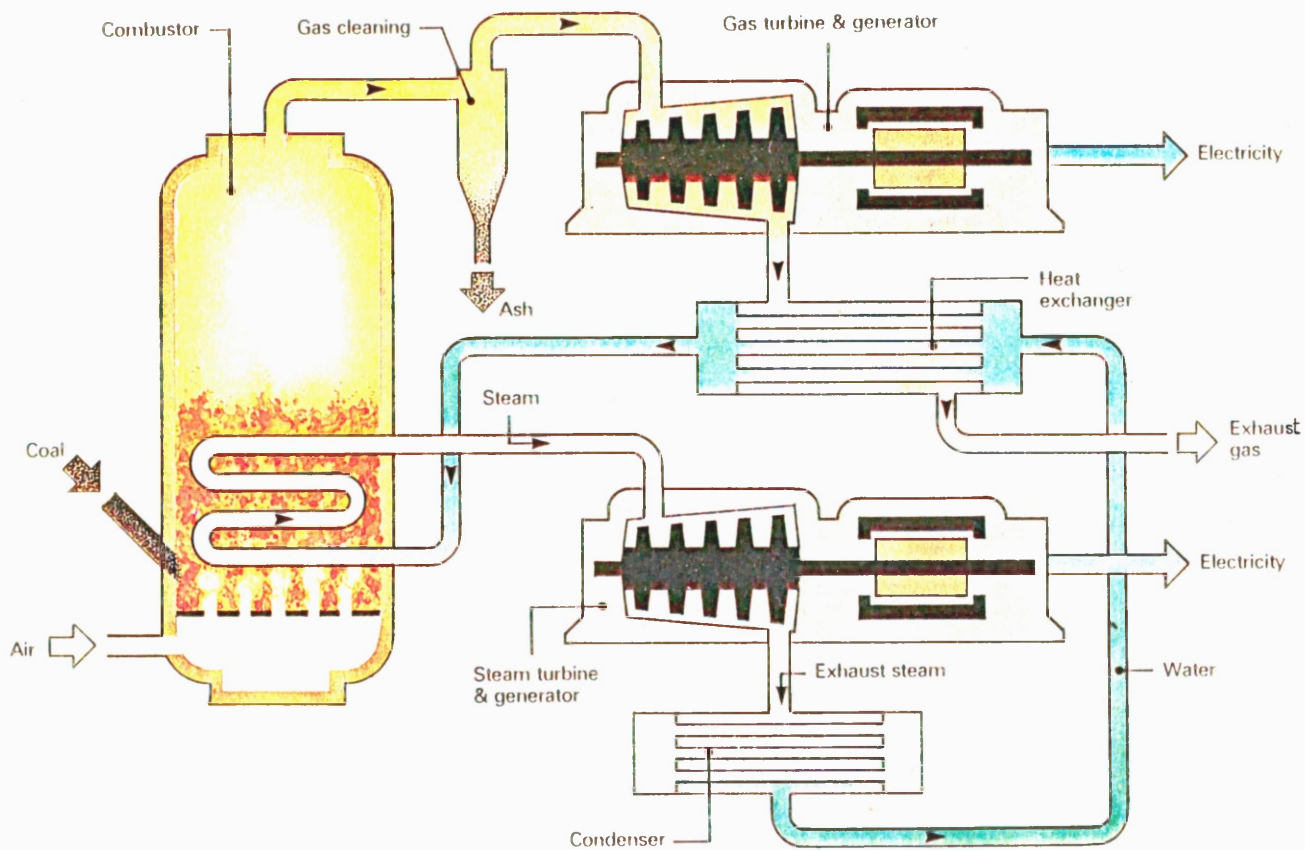
Using fluidised bed technology for coal combustion the NO_x emission level will meet the current EEC standards, however standards for NO_x emission levels are expected to become more severe in the future. Low NO_x emissions can be achieved by means of staged FBC, where the air used for combustion is separated into a primary air stream through the air distributor and the bed, and the secondary air stream supplied as overfire air above the bed surface into the freeboard. The total excess air is kept constant so the availability of oxygen in the bed to combine with the fuel nitrogen is lower thus decreasing NO_x emissions.

The 80 MW pressurised fluidised bed combustor (4,7) at Grimethorpe, Yorkshire (Figure 2) consists of a 2 m square, 8 m tall, water cooled enclosure suspended in a pressure shell (6 to 12 bar) and operates at bed temperatures between 800° and 950°C. Air for combustion and fluidisation enters the top of the pressure shell and flows down the annular space before entering the furnace through the distributor plate. Coal blended with sorbent, is supplied to the bed. The combustion heat is removed by a tube bank immersed in the fluidised bed, which forms part of a boiler system generating superheated steam. The exhaust gases are ducted into primary and secondary cyclones. The cleaned gas is cooled below 380°C in a heat exchanger and passed through the gas turbine materials test section.

2.1.2 Advantages of fluidised bed combustion

FBC technology offers a number of advantages over conventional coal combustion technology:

- a) The lower combustion temperatures of FBC enable a wide range of coal quality and types (coals with high ash, high sulphur, low rank and low ash fusion temperatures) to be burnt efficiently with a high degree of amenity (4).
- b) The thorough mixing of bed and coal particles in the fluidising bed ensures that the coal is rapidly burnt at a high rate (8). The heat distribution through the bed is uniform (no hot spots), gas-solid contact is effective (good combustion efficiency), with high heat transfer coefficients to immersed surfaces (efficient heat exchange) in an exceptionally small boiler, with lower capital costs (8,13,14).
- c) Sulphur emissions to the atmosphere can be reduced at minimal cost and with only a small loss of efficiency by the addition of limestone or dolomite to the fluidised bed (4,15).
- d) The lower combustion temperatures ensure a reduction in the formation of NO_x , by oxidation of atmospheric nitrogen.
- e) Mineral matter associated with the coal should not fuse and cause slagging problems at FBC temperatures.



The gas turbine is driven by the off-gas from a combustor supplied with high pressure air. The combustion chamber is reduced in size because of the smaller air volume and is contained in a pressure vessel.

The steam turbine is driven by steam raised in tubes immersed in the fluidised bed. By combining the two turbines in this way, electricity is generated more efficiently than in conventional systems.

Figure 2. Pressurised Fluidised Bed System for Advanced Cycle Generation of Electricity.

- f) Fouling and corrosion of above-bed heat exchange surfaces from the condensation of volatile alkalis should be less severe (16).
- g) Fluidised bed combustors are responsive to changing heat demands and the evenness of the fluidised bed temperatures enables automatic control to be more precise than in other coal-burning systems (16).

2.2 Occurrence of Mineral Matter in Coal

2.2.1 Origin of coal

Coal deposits were formed from plant materials by the action of heat and pressure over long periods. The stages of coalification involve the formation of peat, then lignite, followed by sub-bituminous coal, bituminous coal and finally anthracite. The coalification process can be regarded as a progressive elimination of oxygen in the form of carbon dioxide and water; these changes define a progressive increase in rank of the coal (17). This increase in rank is characterised physically by a decreasing porosity and an increasing gelification and vitrification. Chemically there is a decrease in the volatile matter content, as well as an increase in the percentage of carbon, a gradual decrease in oxygen content and ultimately, as the anthracite stage is approached, a marked decrease in hydrogen content (18).

2.2.2 Origin and classification of mineral matter in coal

The phrase 'mineral matter in coal' usually refers to all the inorganic material found in coal (19), whether as discrete mineral phases or as inorganic elements associated with the coal matrix. Mineral matter may become associated with coal in various ways (20).

- 1) Inorganic matter originally present in the vegetation from which the coal formed.
- 2) Dissolved or suspended matter introduced by water percolating through the decaying vegetation during the formation of coal.
- 3) Dissolved or suspended matter introduced by water percolating through cracks and fissures in the coal after its formation.

A number of systems of classifying mineral matter in coal, based on various physical features, are used:-

Terminology based on origin (21)

Syngenetic	Mineral matter introduced during the formation of coal (first and second stages of coalification).
Epigenetic	Mineral matter introduced after coalification.

Terminology based on origin and inorganic constituents (22)

Inherent	Mineral matter originating from plant material in the coal swamp.
Adventitious	Mineral matter incorporated after the deposition of plant material in the coal swamp.

Sedimentary petrology terminology (23)

Detrital	Minerals transported by water or wind and deposited in the coal swamp.
Authigenic	Minerals formed within the coal swamp or at a later stage of coalification.

The inherent mineral matter is usually less than 2% wt. of the coal and is considered to be combined chemically with the organic matter of the coal. It contains the inorganic elements essential to the existence of the plant eg. iron, phosphorus, sulphur, calcium, potassium, magnesium, silicon, aluminium, sodium, chlorine and manganese (20).

Additional mineral matter found in coal seams originates from dissolved salts and clay suspension in the swamp or flood waters. Much of this adventitious coal mineral matter is not homogeneously distributed and is frequently found to be present as deposits in cleavage and fracture cracks. The amount of adventitious mineral matter associated with deposits has been largely determined by the geological environment under which the initial coal plant residues were consolidated into the stratified seams (24). It comprises both syngenetic and epigenetic components and makes up the greater part of the total mineral matter in coal.

2.2.3 Minerals in UK coals

Coal mineralogy has been widely studied (20,25-27) and techniques for the analysis of mineral matter have recently been reviewed by Jenkins and Walker (23) and Finkelmann and Gluskoter (28). The most popular and probably the most specific method used for identifying minerals is XRD analysis. Differential thermal analysis (DTA) has been used most effectively for following changes with thermal treatment (29). These techniques are often supplemented by optical or electron microscopy and by normative analysis(20). Table 2 lists mineral species identified in different coal deposits together with their melting point data (30). The overwhelming majority of the minerals can be classified as belonging to one of four groups: aluminosilicates, sulphides, carbonates and silica (quartz). The proportions of minerals in coals vary widely. Most mechanically-mined UK bituminous coals include mineral matter composed of 80% wt. aluminosilicates and quartz, less than 15% wt. carbonates and less than 10% wt. sulphides.

a) Aluminosilicate minerals (clays)

The most abundant mineral species present are the layered aluminosilicates, [kaolinite, muscovite/illite (potassium aluminosilicates) and mixed layer illite-montmorillonites] (19,25,30-33), which for convenience are all referred to as clays in this report. Dixon et al (34) have studied the distribution of mineral species in various coal strata from East Midlands (UK) coalfields and reported that kaolinites and potassium aluminosilicates are the principal clay minerals in all sections of the seam profiles; potassium aluminosilicates frequently being the most abundant species in all strata with the exception of the coal seam. In washed coals, the clays are found mainly as finely-dispersed particles in the coal substance.

Clay minerals have largely formed by weathering of igneous rocks, the products depending on the conditions of weathering and on the basic or acidic nature of the rock itself (20). Much of the clay material is detrital and coal deposits laid down in areas that were subject to periodic flooding usually contain a great deal of clay intimately mixed with the coal (30).

Table 2 - Minerals Identified in Coal (30)

Species	Chemical formula	Melting point (K)
<u>Silica and silicates—common occurrence</u>		
Quartz	SiO_2	1983
Kaolinite	$\text{Al}_2\text{O}_3 \cdot 2\text{SiO}_2 \cdot 2\text{H}_2\text{O}$	2083
Muscovite	$\text{K}_2\text{O} \cdot 3\text{Al}_2\text{O}_3 \cdot 6\text{SiO}_2 \cdot 2\text{H}_2\text{O}$	(Mullite)
Illite	As muscovite with Fe, Ca, and Fe	
Montmorillonite	$(1-x)\text{Al}_2\text{O}_3 \cdot x(\text{MgO}, \text{Na}_2\text{O}) \cdot 4\text{SiO}_2 \cdot n\text{H}_2\text{O}$	
Chlorite	$\text{Al}_2\text{O}_3 \cdot 5(\text{FeO}, \text{MgO}) \cdot 3.5\text{SiO}_2 \cdot 7.5\text{H}_2\text{O}$	
Orthoclase	$\text{K}_2\text{O} \cdot \text{Al}_2\text{O}_3 \cdot 6\text{SiO}_2$	
Plagioclase	$\text{Na}_2\text{O} \cdot \text{Al}_2\text{O}_3 \cdot 6\text{SiO}_2$ — Albite $\text{CaO} \cdot \text{Al}_2\text{O}_3 \cdot 2\text{SiO}_2$ — Anorthite	
<u>Silicates—less common occurrence</u>		
Augite	$\text{Al}_2\text{O}_3 \cdot \text{Ca}(\text{Mg}, \text{Fe}, \text{Al}, \text{Ti}) \cdot 0.2\text{SiO}_2$	
Amphibole	Augite + Na, F, P	
Biotite	$\text{Al}_2\text{O}_3 \cdot 6(\text{MgO} \cdot \text{FeO}) \cdot 6\text{SiO}_2 \cdot 4\text{H}_2\text{O}$	
Granite	$\text{Al}_2\text{O}_3 \cdot 3(\text{CaO}, \text{MgO}, \text{FeO}, \text{MnO}) \cdot 3\text{SiO}_2$	
Epidote	$4\text{CaO} \cdot 3(\text{Al}, \text{Fe})\text{O}_3 \cdot 6\text{SiO}_2 \cdot \text{H}_2\text{O}$	
Kyanite	$\text{Al}_2\text{O}_3 \cdot \text{SiO}_2$	2083 (Mullite)
Sanidine	$\text{K}_2\text{O}_3 \cdot \text{Al}_2\text{O}_3 \cdot 6\text{SiO}_2$	
Strauroilite	$\text{Al}_2\text{O}_3 \cdot \text{FeO} \cdot 2\text{SiO}_2 \cdot \text{H}_2\text{O}$	
Tourmaline	$\text{Na}(\text{Fe}, \text{Mn})_3 \cdot 3\text{Al}_2\text{O}_3 \cdot 6\text{SiO}_2 \cdot 3\text{BO} \cdot 2\text{H}_2\text{O}$	
Zircon	$\text{ZrO}_2 \cdot \text{SiO}_2$	2825
<u>Oxides and hydrated oxides</u>		
Rutile	TiO_2^b	2100
Mangetite	Fe_3O_4	1865
Hematite	Fe_2O_3	1840
Limonite	$\text{Fe}_2\text{O}_3 \cdot \text{H}_2\text{O}$	675 ^c
Diaspore	$\text{Al}_2\text{O}_3 \cdot \text{H}_2\text{O}$	425 ^c
<u>Carbonates</u>		
Calcite	CaCO_3	1200 ^b
Aragonite	CaCO_3	1150 ^b
Dolomite	$\text{CaCO}_3 \cdot \text{MgCO}_3$	1050 ^b
Ankerite	$\text{CaCO}_3 \cdot \text{FeCO}_3$	1000 ^b
Siderite	FeCO_3	800 ^b
<u>Sulfides</u>		
Pyrite	FeS_2	1075 ^b
Marcasite	FeS_2	1075 ^b
Pyrrhotite	FeS_x	1300
Chalcopyrite	CuFeS	1300
Melnikovite	$\text{FeS}_2 + (\text{As}, \text{FeS}, \text{H}_2\text{O})$	1075 ^b
Galena	PbS	1370
Mispickel	$\text{FeS}_2 \cdot \text{FeAs}_2$	1075 ^b
Sphalerite	ZnS	
<u>Sulfates</u>		
Barytes	BaSO_4	1855
Gypsum	$\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$	1725
Kieserite	$\text{MgSO}_4 \cdot \text{H}_2\text{O}$	1395 ^b
Thenardite	Na_2SO_4	1157
Mirabilite	$\text{Na}_2\text{SO}_4 \cdot 10\text{H}_2\text{O}$	1157
Melanterite	$\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$	755 ^b
Keramolite	$\text{Al}_2(\text{SO}_4)_3 \cdot 16\text{H}_2\text{O}$	945 ^b
Jarosite	$\text{K}_2\text{SO}_4 \cdot x\text{Fe}_2(\text{SO}_4)_3$	900 ^b
<u>Phosphates</u>		
Apatite	$\text{Ca}_5\text{F}(\text{PO}_4)_3$	>1500
Evansite	$3\text{Al}_2\text{O}_3 \cdot \text{P}_2\text{O}_5 \cdot 18\text{H}_2\text{O}$	>1775
<u>Chlorides</u>		
Halite	NaCl	1074
Sylvite	KCl	1043
Bischofite	$\text{MgCl}_2 \cdot 6\text{H}_2\text{O}$	987

b denotes the decomposition temperature

c denotes loss of water

b) Sulphur containing minerals

Sulphur is a vital element for sustenance of plant life and a relative abundance of sulphur compounds are found in coal deposits and associated mineral matter. The most commonly occurring minerals of the sulphide group are pyrite and marcasite, FeS_2 , these being polymorphs, differing only in their crystallographic structure (32, 35).

Neavel (36) considered that pyrite found in peat and coal deposits had been largely formed as the result of activity of anaerobic bacteria. Sulphur originated from plant and animal protein (organic sulphur), or was brought in by sea water in the form of sulphates. Iron originated from weathered silicate minerals (37). Consequently, syngenetic pyrite deposits appear frequently in clay-bearing sediment.

The origin, form and distribution of the pyritic inclusions in coal have been studied in detail (19,20,38), largely with a view to reducing the deleterious effects of sulphur in industry and to the environment. Pyrite particles can occur in coal in a variety of forms and sizes ranging from very small crystals and framboids (finely disseminated spherical nodules), $<1 \mu\text{m}$, to large inclusions, massive lenses and veins, 10 cm. It can be structurally distinct or intimately associated with the coal structure (39).

The average sulphur content of UK bituminous coals is reported to be 1.6% wt (30), of which approximately 50% is organically associated and the remainder largely present as pyrite (40).

c) Carbonate minerals

Siderite (FeCO_3) and dolomite ($\text{CaCO}_3 \cdot \text{MgCO}_3$) are formed during the first stages of coalification while calcite (CaCO_3) and ankerite ($2\text{CaCO}_3 \cdot \text{MgCO}_3 \cdot \text{FeCO}_3$) form during the later stages (41) and in bituminous coal are present mainly in joints and cleats (29). In UK coals calcite and ankerite are the principal carbonate minerals (42) and the major form of calcium and magnesium. The proportions of the components of ankerite can vary independently (43). The composition of ankerite in coals from the East Midland coalfields was however found to be relatively constant; 54% wt. CaCO_3 , 24% MgCO_3 , 20% FeCO_3 and 2% MnCO_3 (42,44).

d) Quartz

Quartz is present in all coals (19,45). It can occur in various forms ranging from rounded particles to highly angular fragments and as crystalline masses, from 1 mm to <1 μm . Recent studies (46) have suggested that quartz is primarily authigenic in origin because the relatively large grains present in coal are not likely to be washed or carried into the centre of the coal swamp.

e) Ionisable salt minerals

The ionisable salt minerals constitute that part of the mineral matter which is soluble in water. The major component species are the alkali metal cations Na^+ and K^+ , the alkali earth cations Ca^{2+} and Mg^{2+} and the anions Cl^- and SO_4^{2-} . Although present as relatively minor components of coal, they are of particular importance as it is suggested that they are likely species to be released during combustion (3).

The mode of occurrence of sodium in coal has been the subject of considerable debate. Assumptions regarding the coexistence of sodium and chlorine in coal as crystalline NaCl (47) have been superseded in light of aqueous leaching experiments (48,49). Studies (50-52) have shown differences in the rates of release of sodium and chlorine suggesting that the two elements, whilst present as ions, are largely independent. Recent pyrolysis/mass spectrometry studies (52) have established that the HCl emitted from coal is produced from brine-derived chlorides and that covalently bonded organo-chlorine structures do not exist in coal. Whilst ^{23}Na (53) NMR studies have shown the sodium to be surface-bound and hydrated with no evidence for NaCl in the raw coals. Gibb and Angus (3) have demonstrated that over 90% of the sodium in UK coals is readily removable by aqueous extraction indicating that only trace amounts are present in aluminosilicate minerals. Such evidence implies that most of the sodium in UK coals can be considered as being available for deposit formation.

In comparison, potassium has been reported to be primarily associated with the insoluble aluminosilicate minerals and the majority of calcium and magnesium are present as insoluble carbonates of calcite, dolomite and ankerite.

The majority of the chlorine in UK coals originates from sea water (50,51,55). The distribution of chlorine through the seams suggests that the majority was introduced after coal formation (epigenetic) (50) and is closely related to the occurrence of brines in deep coal measures (30). The salinity of the brine ground waters increases with depth and when they are in contact with coal-bearing strata correspondingly more chloride is taken up (50). However the high rank coals, because of their low porosity, are unable to take up large amounts of the chloride and associated cations (30). A number of theories have been expressed about the mode of occurrence of chlorine in coal, with current evidence suggesting that chlorine is mainly found in the organic coal matrix as chloride ions and not in the mineral matter (47,56,57). The nature of the chlorine-coal bond is however uncertain. The chlorine may be trapped within the porous structure as a solution (58) or associated with basic group (50). UK coals show a large variation in their chlorine content. The chlorine content of UK low rank coals varies from 0.05 to 1.0% wt. depending on their geographic locality (56), whilst for high-rank coals the chlorine content rarely exceeds 0.2% wt. (59).

Freshly mined coals usually do not contain significant quantities of sulphates (generally <0.03% wt.), however a variety of iron sulphates will form when the sulphides are oxidised in air (31).

2.3 Problems that Mineral Matter Pose in Combustion

Mineral matter has always caused problems in coal burning industries. During combustion the coal minerals undergo a variety of reactions and transformations that yield a complex mixture of solid, molten and volatile species.

Emissions of hydrogen chloride, sulphur and nitrogen oxides from coal combustion pollute the atmosphere and contribute to acid rain formation. The alkali metals in coal can cause problems of fouling and corrosion of cooler metal surfaces in the combustor (30). Other inorganic elements which can volatilize during combustion can contribute to fouling problems or condense as a submicron fume and be emitted to the atmosphere presenting potential environmental and health hazards (11,60-62).

The formation of molten slag deposits can also cause problems during combustion of certain coals. The proportion of minerals determines the melting temperature of the ash ie. its slagging propensity. Slagging in bituminous coals is generally attributed to the fluxing action of ferrous oxide on the acidic constituents (eg. Al_2O_3 , SiO_2) in the ash (63).

The abrasive property of certain minerals such as quartz and pyrite can cause erosion wear damage in the combustor depending on the size and shape of the impacting particles (30,64).

The ash related problems in pf combustors have been summarised in Table 3 (30) and give some indication of the specific difficulties to be expected with fuels of usual characteristics. For certain coals the use of additives, such as copper oxychloride, can relieve slagging problems (30,65). Sulphur oxide emissions can be reduced by high or low temperature gas cleaning but these processes are expensive and there are problems in disposing of the end products such as huge quantities of calcium sulphate rich ash or slurry (30).

In addition to the mode of occurrence and relative concentration of the coal mineral constituents, the design and mode of operation of the combustor will also influence the thermal behaviour of the minerals. Although a given coal will have characteristic inherent slagging and fouling propensities, combustors can often be designed and operating conditions adjusted to overcome these problems.

2.3.1 Mineral matter related problems in fluidised bed combustion

The lower combustion temperature of FBC, 800°C - 950°C , should reduce the problems associated with volatilisation of mineral species (1). However some ash sintering may occur if the deposit temperature exceeds 800°C (30). Alkali salts in gases derived from coal combustion can be harmful to gas turbomachinery in a pressurised FBC system, by enhancing hot corrosion and cementing deposited particulates (67,68).

Table 3 - Summary of Ash Related Problems (30)

Coal and ash characteristics	Effect on boiler operation and chimney emission	
	Adverse	Beneficial
Wet (>12% water) bituminous coals	May freeze in transport, and stick to conveyers and bunkers. May limit mill performance, hence boiler output.	
High-moisture and high-volatile sub-bituminous coals	Require large amount of heat for drying and thus need special boilers where the water pre-heater (economizer) is omitted.	Sub-bituminous coals have a high combustible volatile content and thus do not require a fine milling.
Low (<15%) combustible volatile coals	Produce high-carbon residue ash; require extra-fine milling and boilers with long flame path.	
High (>20%) ash coals	Cause abrasion and particle impaction erosion wear of fuel handling plant, mills, burners, boiler tubes and ash pipes; can also cause boiler slagging and impair performance of the electrical precipitators by ash over-loading. There may be problems of ash disposal.	High-temperature and air-heater corrosion rarely occurs with high-ash coals unless chlorine and sulfur contents are high.
Coals with quartz-rich ash (>15% quartz in ash)	Cause abrasion and erosion wear as above.	Boiler slagging and fouling should not be a major problem; some sub-bituminous coals rich in quartz but also rich in sodium constitute an exception and can cause severe fouling.
High-sulfur (>2%) coals with iron-rich (>15% Fe ₂ O ₃) ash	Cause furnace slagging in pulverized-coal-fired boilers, also fouling and corrosion of superheaters and air heaters. The coals are more suitable for cyclone firing. Emission of SO ₂ and with pyrite-associated trace elements, As, Cu, Hg, Pb, Se is high.	The ash has comparatively high surface conductance and thus the electrical precipitators should have a high catch efficiency.
Medium-sulfur (1-2%) and medium-ash (12-20%) coals	Can give some slagging, corrosion erosion and precipitation problems depending on the design and operation conditions of coal milling and boiler plant.	
Low-sulfur (<1.0%) coals	Emission of chimney solids could be high. The ash of low surface conductance is not readily captured in electrical precipitators.	There should be no significant high-temperature or acid corrosion. Emission of SO ₂ and the chalcophilic trace elements is low.
High (>0.3%) chlorine coals	Cause furnace-wall and superheater corrosion and also fouling; HCl emission is high.	The ash conductance and the performance of electrical precipitators are marginally enhanced.
Coals with calcium-rich ash (>10% CaO in ash)	Can cause superheater and reheater fouling by sintered deposits and air-heater fouling by compacted deposits.	The sulfate retention in ash is high; the SO ₂ emission is reduced correspondingly.

The non-entrained ash in the fluidised bed should not agglomerate at temperatures below 930°C and cause slag problems or affect fluidisation (30). The overall environment for in-bed tubes is less severe than with conventional equipment, although tube corrosion and wear may occur (5,69-71).

2.3.2 Effects of coal cleaning

As mined coals contain significant proportions (10-20%) of adjoining floor and roof strata (free dirt) which is comprised mainly of aluminosilicate minerals and quartz (30,72). The more reactive mineral constituents, including sodium and chlorine, are closely associated with the coal substance. Although coal sodium and chlorine species are largely water soluble, there is no significant difference in the sodium and chlorine content of washed and untreated coals received at power stations (30). This is because chlorine and sodium are attached to the organic coal matrix and also because the residence time of coal in a conventional coal washery is relatively short. Free dirt and some pyrite can be removed by density separation, to produce 'washed smalls', in order to increase the calorific value of the fuel or remove specific deleterious impurity species (pyrite). Coal cleaning can however alter the chemical composition by redistributing and concentrating the more reactive soluble material, such as salts of calcium, magnesium and sodium, which will subsequently affect their thermal behaviour (29). For certain cleaned coals the lower ash and sulphur contents result in significant benefits of reducing erosion and emissions (64). However, for other coals their slagging or fouling tendencies would increase, as the constituents that influence slagging ie iron, calcium and sodium and for fouling, sodium, are all concentrated in the coal fraction(30,72). In general low ash content, <8%, coals will tend to have high fouling and slagging propensities (72).

2.4 Behaviour of Mineral Matter during Coal Combustion

2.4.1 Chemical transformations of mineral matter

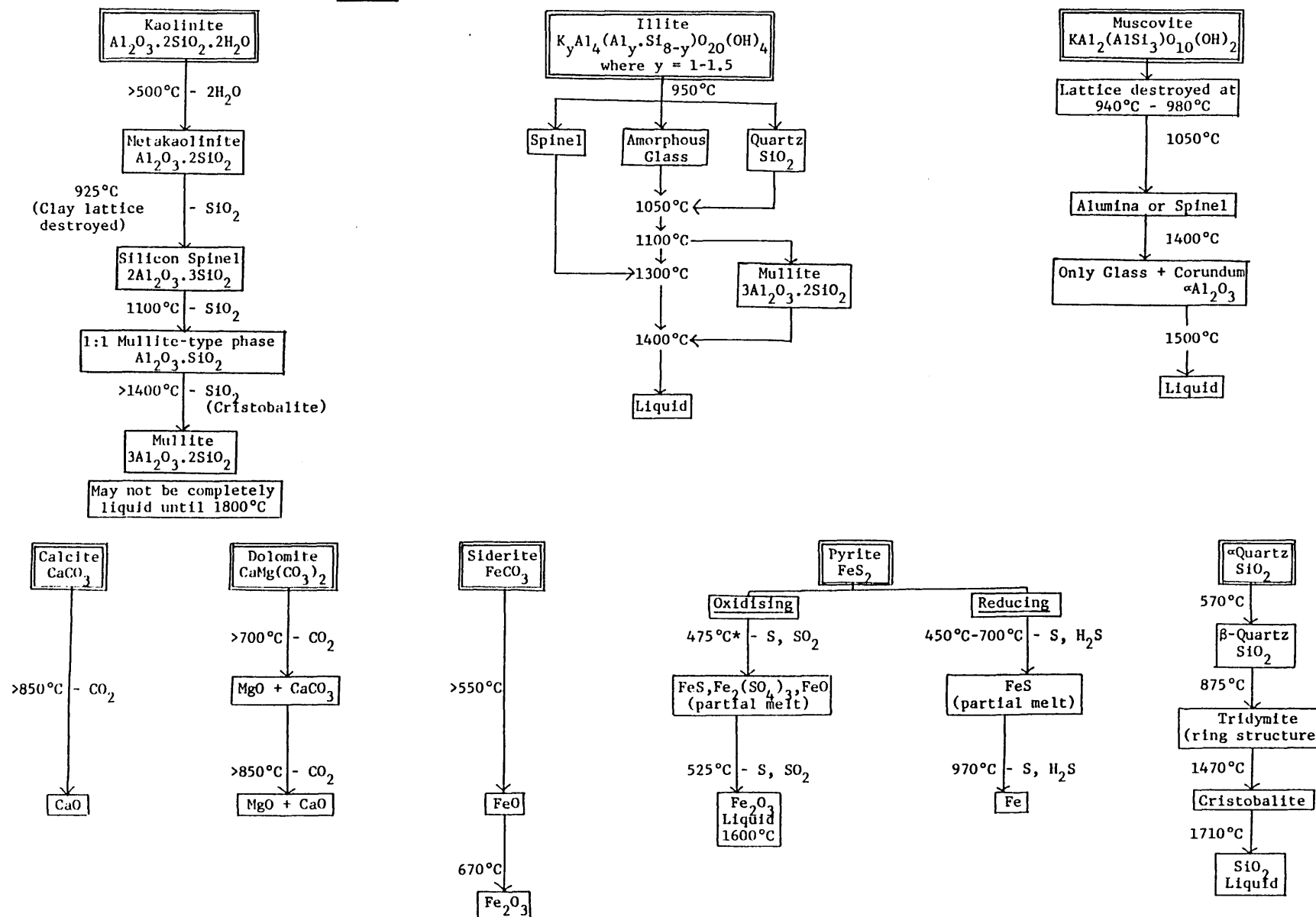
High temperature chemical transformation reactions of coal minerals in both oxidising and reducing atmospheres have received much attention (73-79). The thermal behaviour of the minerals

has usually been studied in inert atmospheres by thermal analysis techniques eg. DTA, where the heating rates are low compared to combustion processes. Padia (76) attempted to simulate combustion conditions by dropping coal particles through a laminar-flow tube furnace at temperatures from 700°C to 1560°C. The chemical transformations that the principal mineral constituents undergo in oxidising conditions are summarised in Table 4.

As the coal particles are heated there is a loss of 'inherent' water, adsorbed on the coal substance or associated with the mineral matter (aluminosilicates and gypsum) which commences at ~40°C (29). The next significant change is the decomposition of organic matter to yield complex hydrocarbon vapours (volatile matter) at temperatures over 230°C, depending on the structure of the coal. Of the elements combined organically or physically adsorbed, chlorine and sulphur are volatilised and others such as sodium and calcium will tend to remain in the char, possibly to be volatilised at a later stage of the burning particle when its temperature has risen to over ~750°C. In the early stages an appreciable proportion of the organically combined sulphur is released in the volatile organic fragments, later to be pyrolysed to yield elemental sulphur, its hydrides and eventually oxides. Chlorine is most likely volatilised as hydrogen chloride at an early stage in the flame (52). At temperatures around 330°C, pyrite first loses sulphur to form pyrrhotite (FeS) which then begins to oxidise from 500°C upwards to form haematite (Fe₂O₃) and sulphur oxides (80, 81). Dehydroxylation of 'chemically' bonded water in the aluminosilicate minerals, mainly kaolinite and illite, commence at 380°C (79).

Carbonates dissociate at temperatures between 530° and 930°C, releasing carbon dioxide. Each carbonate has a characteristic threshold temperature where thermal decomposition will commence. Decomposition of the mixed carbonates, dolomite and ankerite, takes place as a multistage reaction (76,82), the temperatures of the decarboxylation reaction being dependent on the proportions of the carbonates. During coal combustion, calcium and magnesium

Table 4 Principle Reactions Undergone by Coal Minerals during Combustion



* Temperature dependent on mineral and carbon impurities, and on concentration

oxides can react in part with sulphur gases to form sulphates (30). The remainder of the CaO and MgO is captured by aluminosilicates. Iron oxide formed in the boiler flame is also highly reactive and is readily dissolved in fused silicate particles or deposits. Iron sulphate is unstable at flame temperatures but some iron oxide will dissolve in the molten alkali-metal sulphate formed on heat exchange surfaces (discussed in Section 2.6).

Kaolinite and other clay minerals undergo a series of structural changes, of lattice destruction and phase transformation, as combustion proceeds and the temperature of the residual ash rises above 800°C. Micas and the related illites generally cleave easiest along the planes of potassium ions, (Section 4.2.1), thus enhancing alkali metal release. It has been suggested (30) that potassium can be exchanged for sodium during combustion and subsequently reacting with hydrogen chloride to form volatile potassium chloride.

The varying composition of the atmosphere surrounding the mineral matter during its heating can affect the direction and rate of many of the chemical reactions, for example, the decomposition and oxidation of pyrite and decomposition of carbonates, the latter being stabilised by the generally high partial pressure of carbon dioxide. The proximity of different mineral components and their decomposition products can also influence thermal reactions.

In addition, minerals which are more intimately associated with the coal particles during combustion (eg inherent minerals), are more susceptible to higher temperature chemical reactions, dissociation, and volatilisation (83). As a result, the inherent ash may be more available to create the conditions that can lead to a fouling problem.

2.4.2 Physical transformations of mineral matter

In addition to the chemical mineral matter transformations which can occur during combustion, accompanying physical changes take place which affect the release of the minerals into the combustion gases as fly ash and vapours. Little is reported on

such changes in FBC, most work being concerned with pf systems (76,84-88). Padia (76), and Flagan and Friedlander (86), have proposed the most widely accepted mechanism for ash agglomeration and particle break up during pf combustion. Figure 3a illustrates that during pf combustion the mineral inclusions adhere to the receding carbonaceous surface, where the surface inclusions fuse and coalesce with one another to form ash particles ranging in size from 1 to 30 μm (76,86). Particles generated by this process account for most of the mass of ash produced. The resulting melt is primarily an Al-Si-Fe-Ca-O melt, the proportions and high temperature behaviour depending on the ash composition (37). The final products are usually molten spherical ash particles which may either solidify and be carried along with the product gases or remain in the bottom of the combustor as a sintered and fused mass (30). At high temperatures in neutral or mildly reducing atmospheres, the basic constituents eg. oxides of iron, calcium and sodium, can act as fluxing agents in highly acidic (high silica content) melts; lowering the viscosity and melting point and subsequently increasing the slagging propensity of the melt.

Before solidification the ash particles may undergo other processes such as coalescence with other particles or expansion due to internal gas release to form hollow spheres known as cenospheres (89,90). However this simple mechanism predicts fly ash particles with larger median diameters than the mineral matter size distribution in coal (which typically has a mass median diameter of about 2 μm (88)) and does not account for the large number of small particles observed in fly ash (86,91). Other mechanisms by which mineral matter is released into the combustion gases as fly ash must also occur.

Inorganic elements which can volatilise during pf combustion, other than S, N, Cl and alkali metals such as Na and K, include Si, Fe, Mg, Mn, As and Sb (11). These elements are thought to mainly volatilise by chemical reduction of the oxide to the more volatile metal suboxide in the locally reducing atmosphere within a burning char particle. These species can either recondense heterogeneously on the surface of existing fly-ash particles or

FATE OF MINERAL MATTER IN COAL DURING pf COMBUSTION

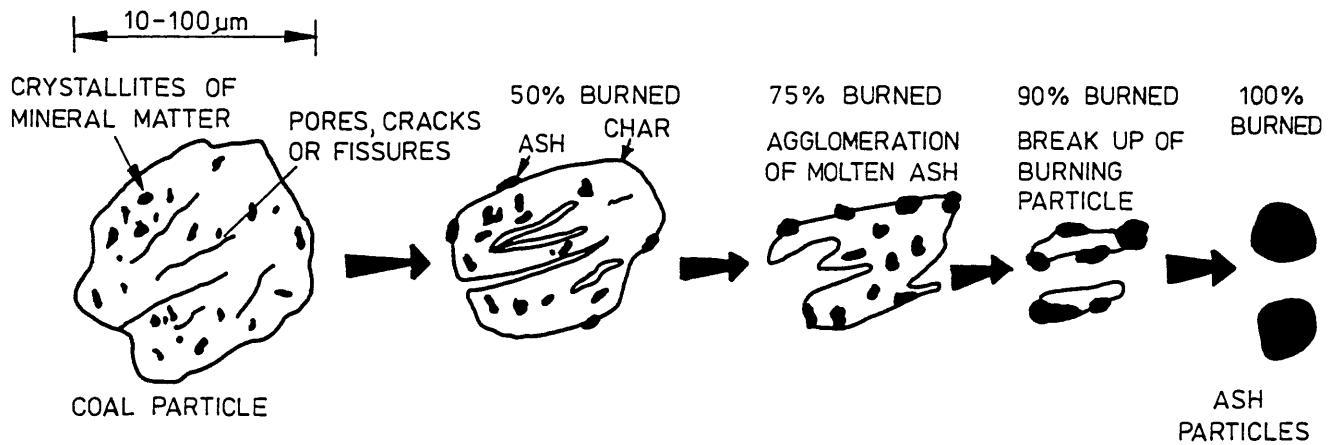


FIGURE 3a. ASH AGGLOMERATION AND PARTICLE BREAK UP DURING pf COAL COMBUSTION.

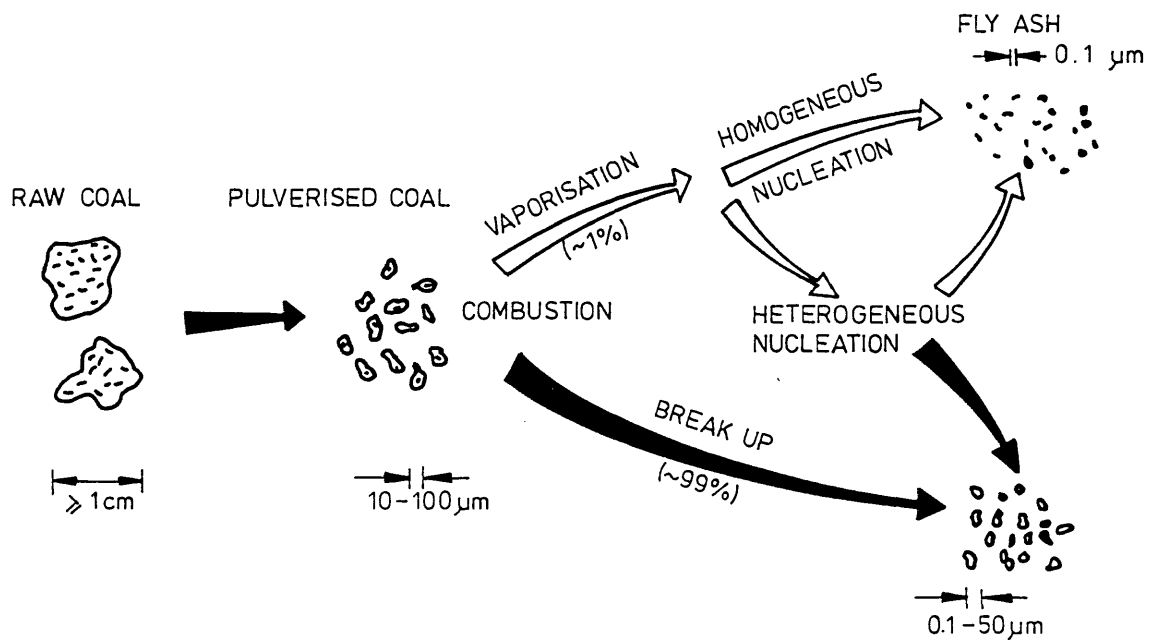


FIGURE 3b. PROCESSES WHICH CONTRIBUTE TO FORMATION OF FLY-ASH PARTICLES.

homogeneously to form new particles as they re-oxidise in the cooler combustion gases (92-94). Homogeneous nucleation forms a submicron fume of very high surface area, which grows in size to 0.05 μm (95) and accounts for 1% of the total mass of the fly ash (96). The fume may subsequently deposit on heat exchange surfaces and partly be emitted into the atmosphere (97-99). Flagan and Friedlander (95) illustrated the processes which contribute to the formation of the fly ash particles during pf combustion in Figure 3b.

The two distinct mechanisms account for the bimodal size distribution observed in the fly ash produced in pf combustion (100).

2.4.3 Thermal transformations in fluidised bed combustors

The majority of the mineral matter in UK coal is present as a dispersion of fine clay, 0.1 - 10 μm in diameter. At FBC temperatures these fine particles of ash do not agglomerate when burned. They retain their original size and can be entrained in the flue gas. Approximately 50% of the ash is entrained although the velocity of the flue gas in FBC is low and the coal feedstock is coarse compared to pf combustors (Table 1).

Raask (30) has summarised the transformations undergone by coal minerals in pf and FBC systems in Table 5. The nonsilicate mineral species in coal, mainly pyrite and carbonates, will dissociate, oxidise and may react with sulphur gases to be converted to sulphates. Chlorine will volatilise as hydrogen chloride (101) which may subsequently react with alkali elements in the coal, particularly those which were originally associated with the organic fraction (90).

The principal difference between the two combustion systems is that in the FBC ash, there is no significant reaction between silicate ash and the nonsilicate species; whereas in pf combustion fused aluminosilicates constitute an acidic media and are capable of absorbing alkali metals in the form of oxides eg. oxides of Na, Ca and Mg (30).

Table 5 - Transformations of Coal Minerals in Pulverised Fuel and Fluidised Bed Combustion (30)

Species	Pulverized-coal firing	Fluidized-bed combustion
Aluminosilicate	Dehydration, vitrification, spheroidization, and partial recrystallization; partial flame volatilization of potassium and the lithophilic trace elements; extensive sintering and coalescence on particle-to-particle contact	Dehydration and some crystal structural changes; no significant release of potassium or the trace elements; much-reduced particle sintering
Quartz	Partial vitrification	No change
Pyrite	Dissociation and oxidation to SO_2 , SO_3 , and Fe_3O_4 ; extensive volatilization of the chalcophilic trace elements	As in pulverized-coal firing, but the trace-element release is less extensive
Carbonate	Dissociation and partial capture of calcium by silicates, the remainder sulfated to CaSO_4	Dissociation and sulfation; there is no significant reaction with silicates, but the sulfate contains significant amount of CaO when lime is added to reduce SO_2 emission
Chloride	Volatilization and partial capture of sodium by silicate with a release of potassium; the released potassium and the residual volatilized sodium sulfated to K_2SO_4 and Na_2SO_4 ; chlorine present in the flue gas as HCl	Sodium chloride sulfated to Na_2SO_4 ; no significant reaction of silicates or formation of K_2SO_4 ; chlorine present in the flue gas as HCl

2.5 Behaviour of Alkalis in Fluidised Bed Combustion

2.5.1 Alkali volatilisation

The release of volatile alkali metal compounds during FBC of coal depends largely on i) the chemical state and the distribution of the alkali and other minerals in the coal (102); ii) the temperatures and local chemical environments that these phases are exposed to; iii) the time of reaction and (iv) the relative rates of different thermochemically favoured reactions (99).

Hydrogen chloride formed during combustion of UK coals, can attack the sodium and potassium compounds to form volatile chlorides (3,68,103). The temperatures of the individual char particles containing the alkalis will exceed the bed temperature by several hundreds of degrees (104). At these temperatures ($>1000^\circ\text{C}$) sodium is readily released from coal, mainly as gaseous sodium chloride into the combustion gases (Figure 4) (105,106). Figure 4 also indicates that volatilisation of sodium and potassium as their hydroxides could occur; this is particularly relevant to low chlorine American coals.

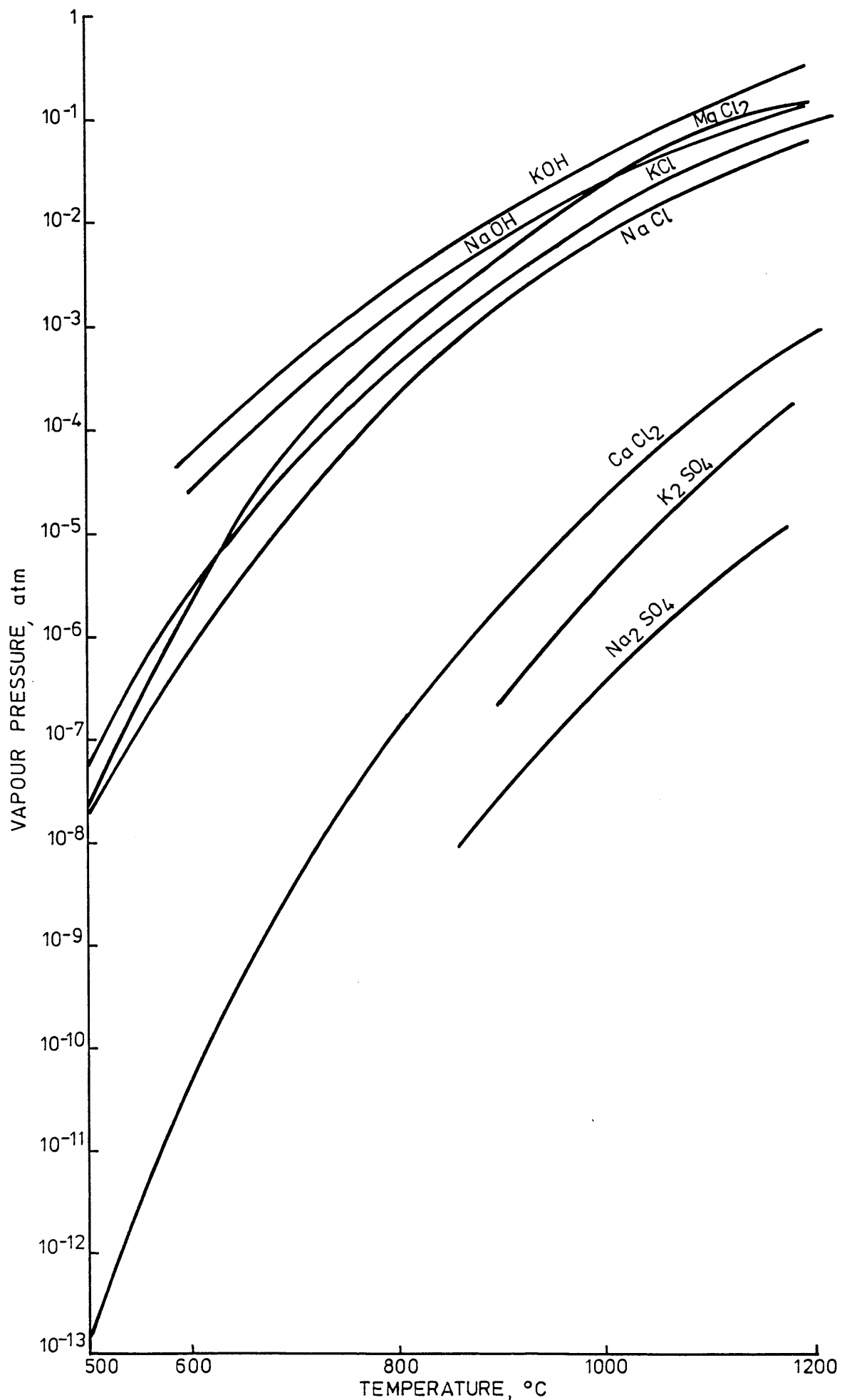


FIGURE 4. VAPOUR PRESSURES OF SODIUM, POTASSIUM, CALCIUM AND MAGNESIUM CHLORIDES, SODIUM AND POTASSIUM HYDROXIDES AND SULPHATES.

The alkali-containing clay minerals are involatile and decompose to give mullite, spinel and a glassy phase which contains the alkali (3). Volatilities for mineral type alkali compounds are unknown but thermochemical calculations indicate that potassium is likely to be released from silicates as its chloride through exchange reactions with gaseous hydrogen chloride or sodium chloride (107-111). Vapour pressure data for gaseous sodium chloride over condensed sodium sulphate and clay minerals has indicated that at FBC temperatures capture of sodium by the clay minerals could occur (112).

The saturation vapour pressures of sodium and potassium chlorides are relatively large (113), as shown in Table 6, well above concentrations typically measured in coal derived gases. Therefore in the combustion gases the alkali chlorides will largely be present in the vapour phase. In addition the effective vapour pressure of sodium chloride, in the presence of water vapour (8% v/v), can increase by factors of 1.5 to 3.5. This may be attributable to reactions occurring between condensed sodium chloride and water to form volatile sodium hydroxide (114).

10 to 50% of the total sodium present in the coal can be released into the gaseous phase during combustion (115). The release of sodium has been shown to increase with temperature and higher levels of chlorine, and to decrease with increasing pressure and higher levels of sulphur (106).

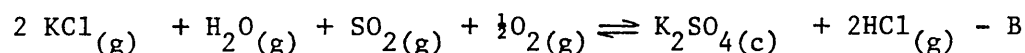
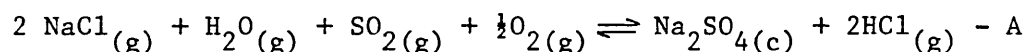
Table 6 - Estimated Saturation of Sodium and Potassium Sulphates, Chlorides and Hydroxides at 900°C

Species	Saturation vapour pressure (atms)	Concentration in ppm (wt) at 1 atm*	
		As salt	As Na or K
Na_2SO_4	2.9×10^{-8}	1.4×10^{-1}	4.0×10^{-2}
K_2SO_4	2.3×10^{-7}	1.3	6.0×10^{-1}
NaCl	2.1×10^{-3}	4.1×10^3	1.6×10^3
KCl	4.8×10^{-3}	1.2×10^4	6.2×10^3
NaOH	1.35×10^{-2}	1.8×10^4	1.0×10^4
KOH	2.3×10^{-2}	4.3×10^4	3.0×10^4

* based on mean gas molecular weight of 30

2.5.2 Alkali deposition

Chemical reactions of volatilised alkali compounds can occur with sulphur oxides in combustion gases. Thermodynamic calculations show that the majority of volatilised sulphur will be present as dioxide rather than trioxide over the temperature range experienced in FBC (Figures 5 and 6) (68,116). Estimated vapour saturation concentrations of the sulphates are well below reported total concentrations (Table 6 and Figure 4) suggesting that if the alkalis are present as sulphates they will be present predominantly as a condensed phase (113). The most likely reactions to occur in the combustion gases between sulphur dioxide and the alkali chlorides are:



where c = condensed phase, g = gaseous phase.

For reaction A, the equilibrium constant, K_p' , takes the form:

$$K_p' = [\text{p}_{\text{HCl}}]^2 [\text{p}_{\text{SO}_2}]^{-1} [\text{p}_{\text{O}_2}]^{-\frac{1}{2}} [\text{p}_{\text{H}_2\text{O}}]^{-1} [\text{p}_{\text{NaCl}}]^{-2} \quad - 1$$

where p = partial pressure

If the total system pressure is P (atms), then the ideal gas mixture assumption gives the mole fraction, x, of the species in question as:

$$x = p/P \quad - 2$$

Therefore, at thermodynamic equilibrium in reaction A, with no other reactions occurring,

$$x_{\text{NaCl}} = x_{\text{HCl}} P^{-1.25} (K_p' x_{\text{SO}_2} x_{\text{H}_2\text{O}} x_{\text{O}_2}^{\frac{1}{2}})^{-1} \quad - 3$$

These reactions appear to be very important in regulating vapour phase alkali content. Estimates for the values of the equilibrium constants obtained from the JANAF (117) thermochemical tables for the above reactions and that of sulphur trioxide

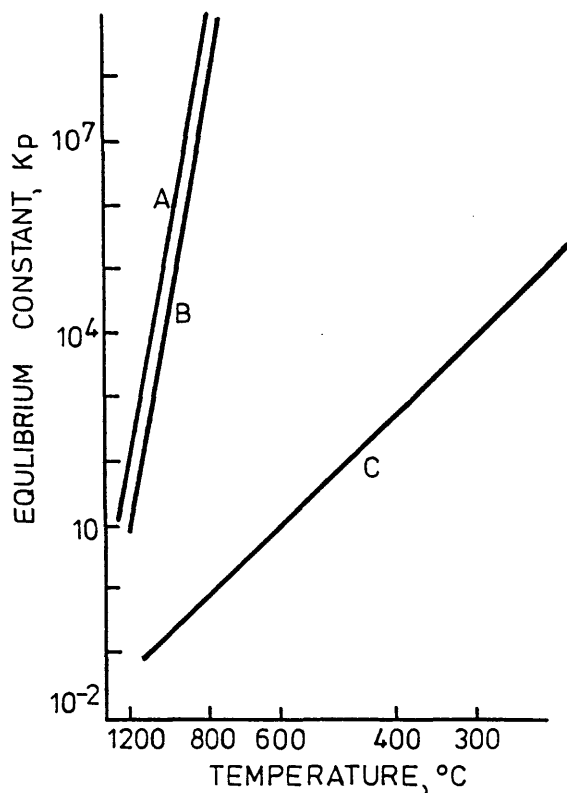


FIGURE 5. EQUILIBRIUM CONSTANTS FOR REACTIONS (A), (B) AND (C).

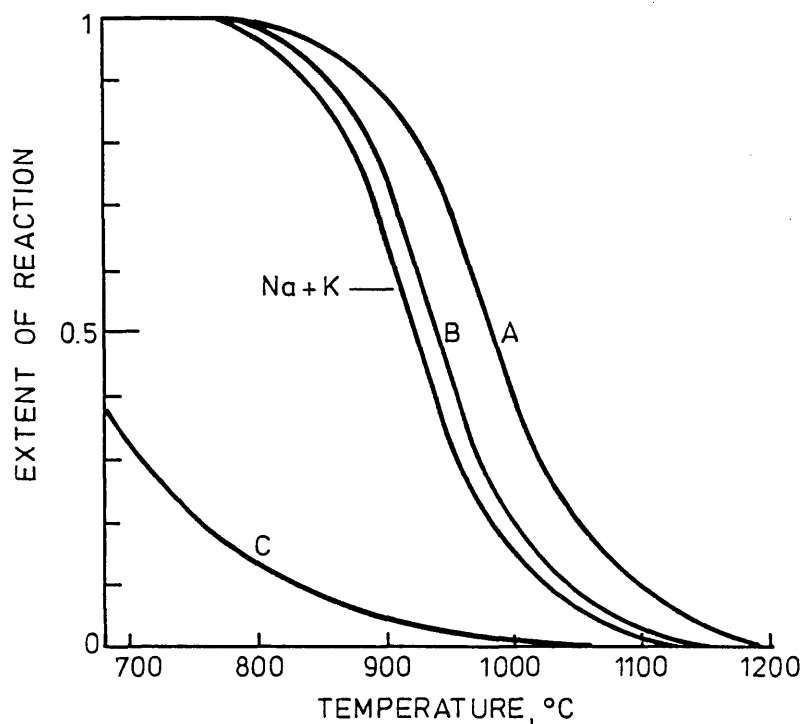
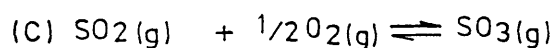
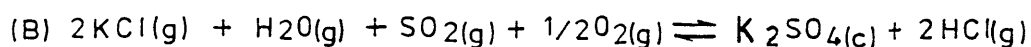
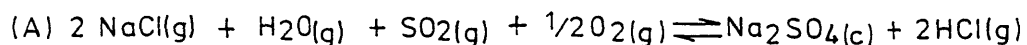


FIGURE 6. EQUILIBRIUM CONVERSION OF ALKALI CHLORIDES TO SULPHATES, REACTIONS (A), (B) AND (C), FOR GAS COMPOSITION IN TABLE 7.



formation, are shown in Figure 5. The calculated equilibrium constants for both sodium and potassium are large except at temperatures above 1000°C. Thus, under oxidising conditions in the presence of sulphur, thermodynamic equilibrium favours the formation of condensed phase sulphates rather than vapour phase chlorides. Since the alkali concentration is normally small by comparison with other vapour components in reactions A and B, the equilibrium of chloride to sulphate is largely dependent on temperature, pressure and gas composition.

Thermochemical data for standard free energy changes for the sulphonation of sodium, potassium, calcium and magnesium chlorides, at elevated temperatures were obtained from the National Physics Laboratory (NPL) and illustrated graphically in Figure 7. The results confirm data compiled by Scandrett (68) that at FBC gas temperatures, <850°C, conversion of alkali chlorides to condensed sulphates is favoured; equilibrium concentrations of alkali sulphates increasing at lower temperatures.

Figure 6 showed the predicted extent of conversion at thermodynamic equilibrium for a total system pressure of 1 atm and typical combustor flue gas of composition given in Table 7. For reactions A and B the fraction of the chloride converted, independently and for both alkalis (in the representative ratio of three moles of potassium to one of sodium), is used (118).

Table 7 - Representative Combustor Flue Gas

Component	Concentration
O ₂	3.0 vol %
CO ₂	16.1 vol %
H ₂ O	4.5 vol %
SO ₂	400 ppm
Alkali	4 to 12 ppm
N ₂	Balance

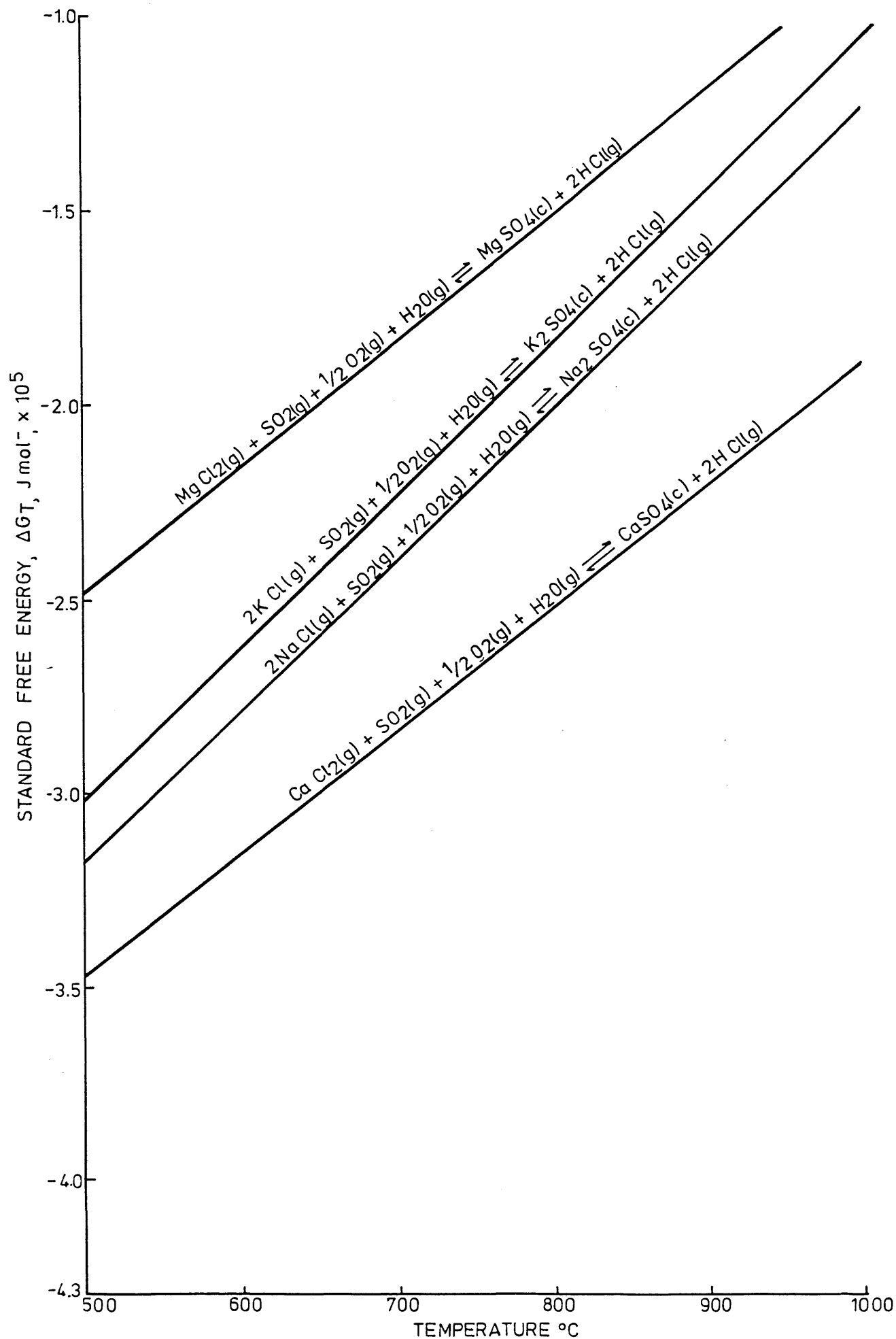


FIGURE 7. STANDARD FREE ENERGY CHANGES, ΔG_T , FOR THE SULPHONATION OF ALKALI CHLORIDES, AS A FUNCTION OF TEMPERATURE.

The graphs were calculated from the equilibrium constant in Figure 5 by using several simplifying, if unrealistic, assumptions (119). The calculations, however, indicate that below about 1000°C conversion of chlorides to condensed sulphates is substantial. On the simplified basis, the calculations suggest that for conditions typical of FBC, more than 20% of the sodium and more than 40% of the potassium are predicted to remain as gaseous chlorides at 930°C. It should be noted that these estimates are sensitive to gas composition; in particular the presence of hydrogen chloride, which was omitted from Table 7. Equation 3 and work by Singe (120) and Yaverbaum (121) have shown that the proportion of gaseous alkali chlorides will increase with hydrogen chloride concentration (typical combustion gas levels of 160 ppm correspond to a high chlorine coal).

The thermodynamic theory that excess chlorine will prevent liquid deposition has yet to be demonstrated. The theory suffers from two limitations; excess chlorine may cause formation of the $\text{NaCl}/\text{Na}_2\text{SO}_4$ mixed melt, and excess HCl may cause direct gaseous attack which destroys the protective oxide coating of the cooler metal surfaces in the combustor (115).

Depending on conditions the sulphates can condense on heat exchange tubes in the convection passes of the combustor, on entrained particulates or nucleate to form an aerosol.

2.5.3 Gettering reactions for alkali metals

Chamberlain (106) and Sverdrup and Jansson (112) have shown that alkali salt vapour pressures above clay minerals, such as those introduced with the coal and the sorbent, are much lower than those above the sulphates. It is reasonable to suppose the gaseous alkalis react with or are physically adsorbed on these clay minerals, thus retaining most of the alkali within ash particles. This has led to the deliberate introduction of 'getter' materials, such as silica, alumina and silica-alumina to form involatile species which will retain gaseous alkalis. Because of the low vapour pressures of the sulphates, the getter reactions of interest are with the alkali chlorides. Thermodynamic approaches have been used by several groups to

attempt to assess the potential of 'gettering' reactions (106,112,113,122,123). Equilibrium constants for gettering reactions for which thermochemical data are available, are shown in Figure 8 (113,123). The reactions of alkali chlorides with 'getters' are exothermic; they are favoured by increasing water vapour concentration but inhibited by HCl. Reactions with pure silica are not favoured but aluminosilicates are much more promising 'getters'.

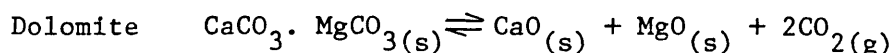
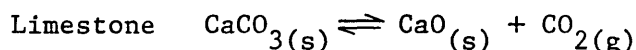
The actual performance of 'getters' has been investigated and has not always corresponded to thermodynamic predictions. The most effective sorbents eg. activated bauxite, were highly porous (124-128) suggesting that these materials acted primarily by physical adsorption of the gaseous alkali.

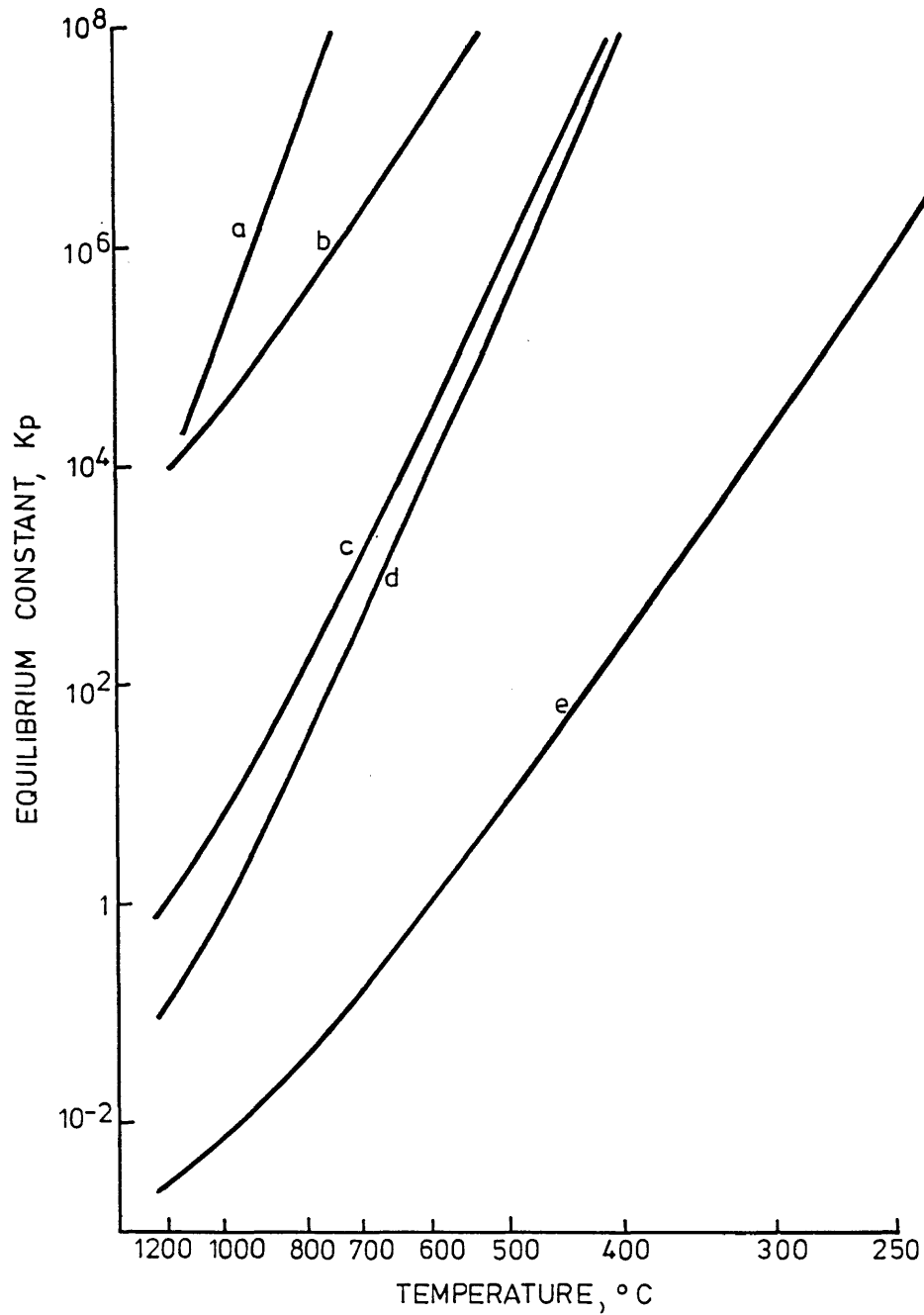
It should be noted as with all calculations based on thermochemical data, the results are subject to several major limitations. They are dependent on the accuracy of the data on which they are based (thermochemical data are notoriously difficult to obtain for the elevated temperature range of interest) and they can only estimate conditions at thermodynamic equilibrium.

2.5.4 Sulphur retention

A major attractive feature of FBC technology is the ability to capture SO₂ using limestone or dolomite as a bed material (129-131). Limestones and dolomites from different sources, however, vary considerably in their ability to capture SO₂ and studies have shown that the porosity of the calcined rock and calcium content are the major factors affecting performance as a sorbent (129,130,132,133).

At FBC bed temperatures the carbonates calcine rapidly, (individual decomposition temperatures being dependent on their crystal structures (Section 2.4.1)) causing major changes in the sorbents structure (132). The sorbent porosity increases during calcination (decrease in density) although some shrinking of the particle is often encountered:

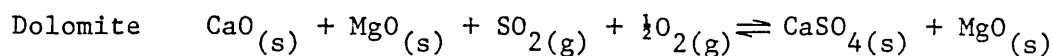
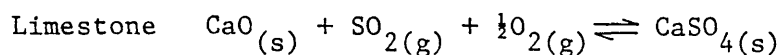




- (a) $2\text{KCl(g)} + \text{H}_2\text{O(g)} + \text{Al}_2\text{O}_3 \cdot \text{SiO}_2\text{(s)} + 5\text{SiO}_2\text{(s)} \rightleftharpoons 2\text{KA1Si}_3\text{O}_8\text{(s)} + 2\text{HCl(g)}$
 (b) $2\text{NaCl(g)} + \text{H}_2\text{O(g)} + \text{Al}_2\text{O}_3 \cdot \text{SiO}_2\text{(s)} + 5\text{SiO}_2\text{(s)} \rightleftharpoons 2\text{NaAlSi}_3\text{O}_8\text{(s)} + 2\text{HCl(g)}$
 (c) $2\text{NaCl(g)} + 2\text{SiO}_2\text{(s)} + \text{H}_2\text{O(g)} \rightleftharpoons \text{Na}_2\text{O} \cdot 2\text{SiO}_2\text{(c)} + 2\text{HCl(g)}$
 (d) $2\text{NaCl(g)} + \text{SiO}_2\text{(s)} + \text{H}_2\text{O(g)} \rightleftharpoons \text{Na}_2\text{O} \cdot \text{SiO}_2\text{(c)} + 2\text{HCl(g)}$
 (e) $2\text{KCl(g)} + \text{SiO}_2\text{(s)} + \text{H}_2\text{O(g)} \rightleftharpoons \text{K}_2\text{O} \cdot \text{SiO}_2\text{(c)} + 2\text{HCl(g)}$

FIGURE 8. EQUILIBRIUM CONSTANTS FOR CHLORIDE 'GETTERING' REACTIONS.

During sulphonation, at FBC bed temperatures, the sorbent porosity decreases:



MgO does not react with SO_2 because MgSO_4 is unstable above 775°C , at atmospheric pressure (134).

The pore structure is largely determined by calcination conditions or the reaction temperature reached during sulphonation. Other parameters which affect the pore structure of limestone particles during calcination, include the presence of sodium chloride which can induce structural rearrangement. This can lead to an optimum pore distribution for reactions with sulphur dioxide and oxygen, thus increasing the sulphur capacity of an unreactive limestone (135).

Figure 9 shows the optimum temperature range for the formation of calcium sulphate and it is evident that there is a sharp decrease in sulphur retention, in the form of CaSO_4 , as the bed temperature increases above 900°C (30). At higher temperatures the reactivity of CaO formed on the dissociation of CaCO_3 will decrease. This is due to the change in structure and porosity of the CaO (the surface area decreases) as the nonsulphated CaO crystallites sinter to larger crystals above 900°C .

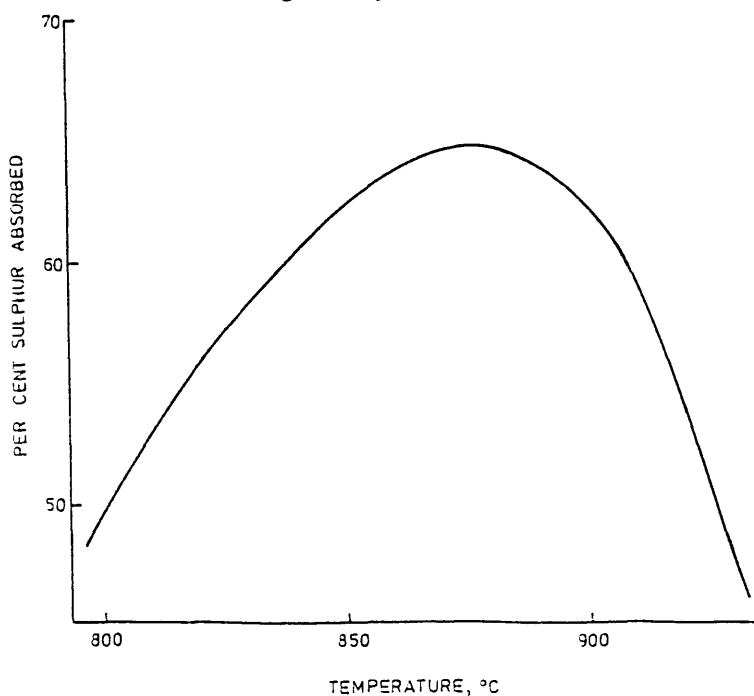


FIGURE 9 OPTIMUM TEMPERATURE FOR SO_2 ABSORPTION BY LIME.

Also as the molar volume of the sulphate is larger than either the oxide or the parent carbonate, SO_2 diffusion into the particles pore limits the reaction rate (132). Calcium sulphate blocks the pores and entire limestone particles develop exterior sulphonation shells which eventually terminate the sulphonation reaction (130). Large pores mean lower surface area but less diffusive limitations. In general, smaller particles have greater rates and effectiveness since pore length is small.

For reduction in sulphur emissions of >50%, limestone is added to fluidised beds (shallow) in a ratio of $\sim 4:1$, Ca:S. The spent limestone is removed from the bed along with the coal ash. Economically it is important to keep limestone additions low in order to minimise both limestone prices and spent limestone disposal costs.

2.6 Fouling and Corrosion of Heat Exchange Surfaces

Fouling of the heat exchange surfaces in the convection passes of a combustor occur from the build-up of deposits on the tubes resulting from the release of mineral matter from the coal during combustion (136). These deposits can inhibit, or if severe block the throughput of hot gases from the combustor, causing reduced heat exchange capability (137,138). This, in turn, results in overheating in the furnace which exacerbates the release of the minerals and increases fouling rates. Eventually the unit will have to come off load and the deposits removed manually.

The inner layers of deposits are often rich in elements capable of reacting with protective metal oxide coating at rates which constitute corrosion.

The extent of fouling by coal is largely dependent on the thermal behaviour of the coals mineral constituents, in particular the ionisable salts, although the design and mode of operation of the combustor can also influence deposition (66).

This study has concentrated on investigating the formation of high-temperature (400 to 800°C) fouling deposits, bonded to convection-heated surfaces, such as superheaters and reheaters. Other deposits formed in coal-fired boilers include slag deposits, either loosely held or strongly bonded in the radiant

section of the boiler (i.e. furnace walls) and low-temperature deposits on cooled surfaces, such as air heaters and economisers near the flue gas outlet point(139).

2.6.1 Fouling and corrosion in conventional combustion

Ash fouling of heat exchange surfaces during coal combustion has been the subject of a number of studies (30,66,138-146). For UK coals, fouling is usually initiated by the preferential deposition of alkali metal (Na and K) sulphates formed during combustion in the furnace. The low melting and hence sticky sulphate matrix acts as a "flypaper" to collect ash particles which will slowly sinter together (66,142-144,146). The sintering process may be assisted by the condensation of sulphates on ash particles to give a low melting surface layer. As the deposit accumulates the outer surface becomes insulated from the tube metal and approaches gas temperatures. If the temperature becomes sufficiently high, bulk sintering will occur. The rate of build-up of bonded and sintered deposits on surfaces between 400° and 800°C depends largely on the composition of the deposited material. However the size and temperature of the particles are also important (147). The fouling tendency of a coal has been shown to be directly proportional to its chlorine content and inversely proportional to its ash content (147), reflecting the changes in ash composition with coal wash treatment.

The mechanisms of superheater/reheater corrosion are complex and largely associated with the deposition of alkali sulphates onto the tube surface and their enrichment at the base of the porous fly ash deposit, known as 'hot salt' corrosion.

For metal temperatures above 400°C (typically experienced in superheater regions), alloys containing major additions of chromium are used as tube materials, to provide better oxidation resistance (148). In a combustion atmosphere these metal alloy surfaces will oxidise to form a protective, chromium rich oxide scale (149). The rate of growth of this oxide layer is dependent on the rate at which oxygen can diffuse through and attack the metal. The surface temperature of the deposited ash on superheater tubes is usually too low to cause appreciable

sintering and the oxidising flue gas may diffuse through the porous ash layer and sustain normal formation of the underlying protective oxide (2).

During ash build-up on the tube, sodium, potassium, calcium and magnesium sulphates formed from reactions in the combustion gases gradually accumulate by condensation at the base of the porous ash deposit (Figure 10) (30).

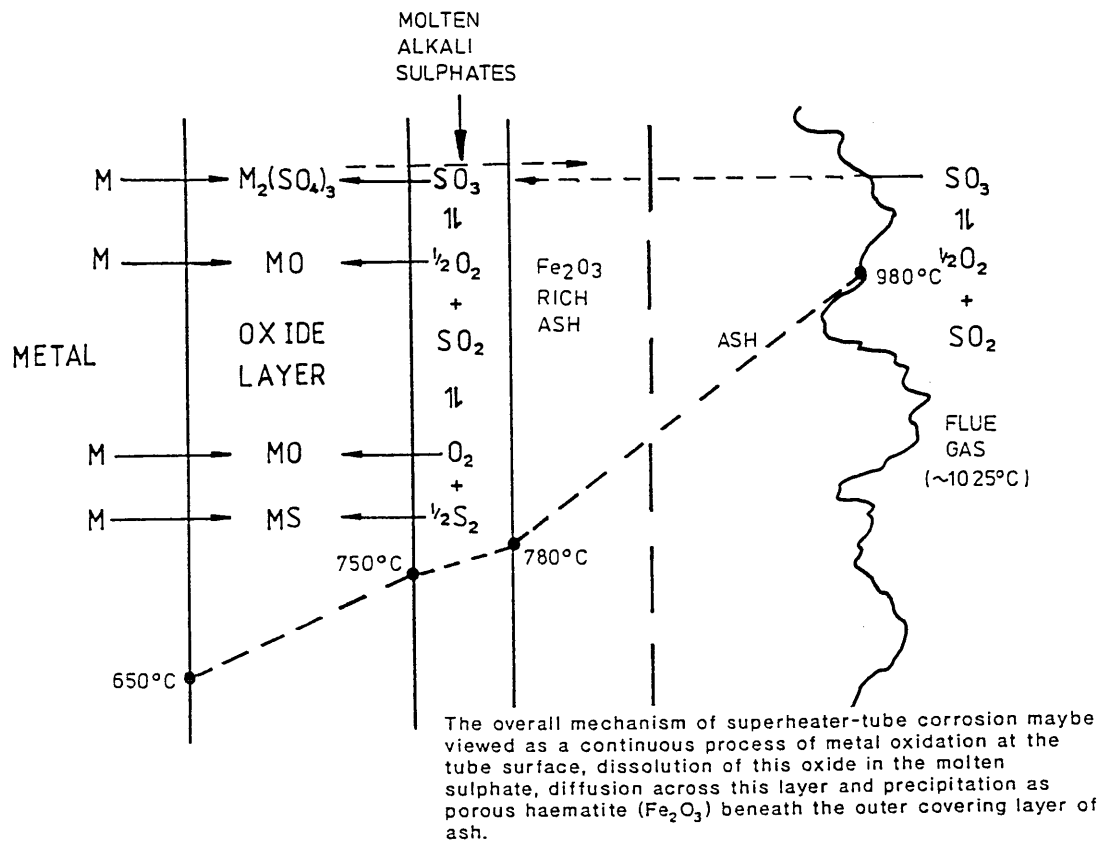
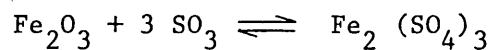


FIGURE 10. SCHEMATIC DIAGRAM FOR THE ASH DEPOSIT AND TEMPERATURE GRADIENT AT THE SURFACE OF SUPERHEATER TUBES IN A COAL-FIRED BOILER.

This mixed sulphate deposit remains molten at tube-surface metal temperatures above 600°C and forms a thin layer of extremely corrosive liquid next to the protective oxide scale (2). The molten sulphate layer contains free sulphur trioxide which can attack the protective oxide coating to form iron and chromium based sulphates eg.



A temperature gradient will exist through the molten sulphate layer, as shown in Figure 10.

The stability of the corrosion products decreases with increasing temperature giving rise to a concentration gradient for the dissolved metal ions (2). This ensures that the dissolution is effectively a continuous process with iron and chromium diffusing outward through the molten sulphate layer. At the hotter outer surface iron/chromium oxides are re-precipitated, but they no longer form a protective layer. Calcium and magnesium sulphates are less thermally stable than sodium and potassium sulphates in boiler atmospheres (Table 8) (30) and are therefore less likely to deposit and migrate through the oxide layers.

Table 8 Temperature Limits for the Thermal Stability of Alkali Sulphates in Boiler Atmospheres

	Temperature Limit for Thermal Stability, °C
K_2SO_4	1180
Na_2SO_4	1030
$CaSO_4$	880
$MgSO_4$	730

In addition the free sulphur trioxide can be reduced to sulphur, as a result of reactions at the metal oxide-molten sulphate interface. Sulphur can diffuse through the oxide layer, allowing sulphidation of the metal to proceed with reduced corrosion resistance.

The molten alkali sulphate layer acts as a fluxing agent, fluxing:

- a) the protective oxide scale, giving enhanced rates of oxidation and sulphidation.
- b) the resulting corrosion products.

The rate of these continuous transport processes determines the rate of corrosion and is highly dependent upon the temperature gradient between the hot gas and the metal surface. Consequently

for a given metal temperature, higher corrosion rates are observed at higher gas temperatures. Corrosion rates have also been shown to increase rapidly in the range 600° to 650°C, as the salts become molten (2,30,143,145,150), see Figure 11. Rates go through a maximum and fall at higher temperatures, giving a bell shaped curve. The shape of the curve reflects the stability of the complex sulphates.

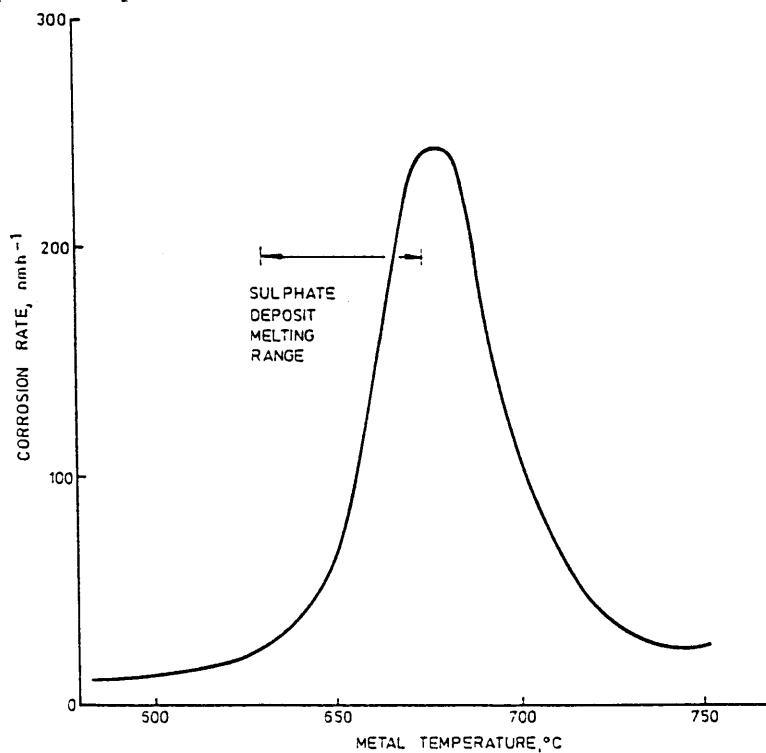


FIGURE 11. VARIATION IN CORROSION RATE WITH METAL TEMPERATURE

Hot salt corrosion can occur very rapidly, following deposition of only small quantities of molten alkali sulphates, forming characteristic scalloped shaped corrosion fronts.

Other important variables which affect the rate of corrosion include fuel chlorine content (which also indicates the likely sodium and potassium content) and concentration of gaseous sulphur trioxide formed within the outer solid ash. The latter also influences the chemical stability of the molten sulphate (30).

A strong linear correlation of the chlorine content of coal with corrosion rates has been found. This has been explained as the chlorine in coal promoting the release of the alkali metals from

the mineral matter (2). The corrosivity of the salts is particularly severe when the potassium to sodium ratio is high (147). In general some attack of the tube metal is likely to occur when the deposition rate of the total sulphates ($K_2SO_4 + Na_2SO_4$) is greater than $3 \text{ gm}^{-2} \text{ hr}^{-1}$ (147). There appears to be no direct influence of chlorine levels on superheater corrosion rates, although the presence of low concentrations of chloride ions may affect corrosivity of the molten sulphate deposit (2).

2.6.2 Fouling and Corrosion in Fluidised Bed Combustion

The lower combustion temperatures of FBC ensure that fouling and corrosion of above-bed heat exchange surfaces, from the condensation of volatile alkalis, will be less severe. Little is reported on laboratory scale investigations of the mechanisms for the release and deposition of the ionisable salt minerals during FBC. Thermodynamic calculations predict, however, that contamination of above-bed heat exchange surfaces, by a sulphate melt is theoretically possible during FBC (113). The low melting alkali sulphate layer can lead to fouling problems as in pf combustion.

In FBC two forms of corrosion of above-bed metal alloy surfaces have been found:

- a) sulphidation - oxidation (69-72,151,152)
- b) hot salt corrosion (2,30)

The sulphidation-oxidation form of attack mainly occurs on in-bed metal surfaces and is thought to be a consequence of the formation of compact deposits, containing $CaSO_4$ and CaO (from coal ash or limestone/dolomite additions to the bed) on metal surfaces and of local low oxygen activity regions (69,70,153). The above-bed environment is thermodynamically oxidising in nature (providing that no significant freeboard combustion takes place) and deposits formed from elutriated bed material are loosely bonded and do not act as a barrier to the diffusion of oxygen to the metal surface (70,153). Compact deposits formed by condensing alkali metal salts within the ash, however, may prevent sufficient oxygen reaching the alloy surface. Reactions can occur within the deposits containing $CaSO_4$ and CaO , to liberate sulphur. This sulphur diffuses from the deposit through

the scale to form metal sulphides with the alloy elements (eg chromium), thus making the resulting depleted alloy susceptible to oxidation. Such corrosion is characterised by migration of sulphur into the metal ahead of the visible surface damage (154,155) and occurs preferentially along the grain boundaries (152). This is mainly due to 'sensitization' of the alloy (152) which occurs after heating to 400-700°C for ~2 hrs. Carbon and chromium diffuse through the alloy to react at the grain boundaries, forming chromium carbide. Sulphidation occurs extremely rapidly through the sensitized zones and only minute amounts of liquid alkali sulphates are needed to promote this type of attack.

A similar form of hot salt corrosion attack to that found on superheaters in pf systems may also occur (70,153). Corrosion rates, however, are likely to be lower in FBC plants due to the lower levels of volatile alkali species present.

Chlorides in coal may be troublesome depending on the chlorine content of the coal (and presumably on the use of sulphur sorbent bed materials) and may enhance the attack at the metal surface by disrupting the structure of the oxide layer (153).

2.6.3 Fouling indices

As discussed in Section (2.3), although the extent of fouling by coal varies considerably between different boiler designs and occurrences of fouling are exacerbated by higher firing rates (156), a given coal has a characteristic inherent fouling propensity. Correlations have been developed between the ash composition and observed fouling characteristics for the purpose of assessing the fouling propensity of a coal (143).

The importance of sodium sulphate deposits as precursors to fouling deposits has led to the sodium content of coals being used to predict fouling behaviour. In addition, the overall ash composition must have some influence on fouling characteristics.

The most widely accepted parameters are the fouling factors, R_f and R'_f , which are used to indicate the relative tendency of coals with bituminous or lignititious ash respectively, to cause low, medium, high or severe fouling of convection surfaces (157,158).

High-temperature ash, HTA, (Section 3.1.1) is designated as being bituminous if $\text{wt.\% Fe}_2\text{O}_3 > \Sigma \text{ wt.\% CaO} + \text{MgO}$ and lignitious if $\text{wt.\% Fe}_2\text{O}_3 < \Sigma \text{ wt.\% CaO} + \text{MgO}$.

The fouling indices are given by:

$$R_f = R_{b/a} \times \text{wt.\% Na}_2\text{O}$$

$$R_f' = \text{wt.\% Na}_2\text{O}$$

where $\text{wt.\% Na}_2\text{O}$ denotes the total concentration of sodium in the HTA and $R_{b/a}$ is the ratio of basic to acidic oxides.

$$R_{b/a} = \frac{\text{Fe}_2\text{O}_3 + \text{CaO} + \text{MgO} + \text{K}_2\text{O} + \text{Na}_2\text{O}}{\text{SiO}_2 + \text{Al}_2\text{O}_3 + \text{TiO}_2}$$

Details of these fouling parameters and their values are given in Section 4.5.

Chlorine content has been used, to a lesser extent, to predict fouling propensity. The relationship between sodium content and chlorine content, however, is far from exact and the technique less reliable.

Laboratory studies of coal ash can identify the temperature at which ash particles begin to soften and by determining the strength of sintered pellets prepared at different temperatures, a measure of the relative fouling propensity of coal can be obtained. For example, the CEGB has developed a simple index of fouling, $T_s(5)$, based on the temperature at which a prepared pellet has a given compressive strength. The lower the value of $T_s(5)$, the more likely is the coal to produce troublesome deposits (66,72).

The indices outlined may be used to establish a broad ranking of coal ash performance. No single index or combination of indices, however, has been sufficiently proven to be an accurate guide to the fouling propensity of a UK coal (156). The indices have been used mainly for US coals and there is little reported information on their applicability to British coals (156).

2.6.4 Remedial measures for dealing with ash fouling

Fouling deposits can be tolerated within a boiler provided that they are amenable to removal by sootblowers (jets of high

pressure air or steam) (30). If the deposits are fused and intractible, or cannot be reached by sootblowers, then boiler outage is necessary for cleaning.

For a given boiler, in addition to the provision of well-placed and effective sootblowers, other means that have been used to minimise fouling problems include:

- 1) Coal blending to 'sweeten' coals of high fouling propensity.
- 2) Close control of combustion conditions to minimise exceptionally high temperatures within the furnace.
- 3) The use of additives (eg magnesia) to the coal/air feed to control the formation of deposits. The mechanisms involved in the interaction of coal minerals with fuel additives, however, often have not been elucidated and many additive trials have given inconclusive results.

3. EXPERIMENTAL TECHNIQUES

3.1 Separation of Mineral Matter and Salts from Coal

3.1.1 High-temperature ash

The HTA which is the residual inorganic material when coal is raised in temperature to 815°C, was obtained by the British Standard method (159) (Appendix I).

3.1.2 Low-temperature ash

The minerals were separated from the organic coals by low-temperature plasma ashing (~150°C). Multiple 1 to 1.5g of the coals (-212 µm) were processed in glass dishes with a layer loading of about 40 mg cm⁻² using a Plasmaprep 300. The furnace was operated at 100 W 'forward' and 2-3 W 'reflected' power, 0.6 Torr vacuum at 20 ml min⁻¹ of oxygen; this gave an ashing rate of ~30 mg hr⁻¹. The ashed samples were taken down to constant weight, the period required for each sample being 100 hrs on average. Further details of the plasma ashing technique are given in Appendix I.

3.1.3 Demineralised coal

The mineral matter was removed from the coal by a technique devised by Radmacher and Mohrhauer (160), based on the extraction of the minerals with hydrofluoric and hydrochloric acids. The procedure was modified to include a preliminary extraction with dilute hydrochloric acid, to avoid the formation of insoluble calcium fluoride and this is now an International Standard Method (161).

A known weight of -212 µm coal of known moisture content was treated sequentially with dilute hydrochloric acid, concentrated hydrofluoric acid and finally concentrated hydrochloric acid at 50°C for periods of 45 mins. The residual coal was recovered after each acid digestion in a plastic filtration unit and thoroughly washed. The demineralised coal was finally dried and weighed. The amount of mineral matter extracted was the loss in weight of the coal after allowance had been made for changes in moisture content and for any adsorbed hydrochloric acid.

3.1.4 Aqueous leaching

Water soluble (ionisable) salts were obtained by two aqueous extraction procedures:

- 1) Extractions under relatively mild conditions by boiling the -212 μm coals in water, under reflux, for periods varying up to 6 hours.
- 2) More vigorous extractions by sequential wet grinding in a high speed ball mill followed by refluxing with boiling water. After 3 cycles of wet grinding (2 hour) and refluxing (2 hour) extractions were essentially complete.

The leachates from both procedures were analysed for Cl^- , SO_4^{2-} , Na^+ , K^+ , Ca^{2+} and Mg^{2+} contents by Dionex ion chromatography.

3.2 Analytical Techniques

3.2.1 Elemental analysis

The elemental compositions of the ashes expressed as oxides were determined by ICPS using a Perkin Elmer ICP/6000 spectrometer.

Water soluble cations Na^+ , K^+ , Ca^{2+} and Mg^{2+} and anions Cl^- and SO_4^{2-} were determined by ion chromatography using a Dionex 2000i Ion Chromatograph.

Sulphur is generally recognised to exist in coal in three forms namely sulphate, pyritic and organically bound sulphur compounds. Total sulphur was determined using a Leco SC-32 Sulphur Determinator. Sulphate and pyritic sulphur were determined according to BS procedures (159). At present there is no accepted method for organic sulphur which has to be determined indirectly by difference.

Phosphorus was determined colorimetrically with molybdenum blue using a Philips SP6-350 visible spectrometer according to the BS method (159).

Chlorine was determined by the BS high-temperature combustion method (159).

The concentration of iron present as carbonate was determined from an acetic acid extract of the low-temperature ash (LTA) by ICPS. Iron carbonate is soluble in acetic acid whilst pyrite and iron associated clay minerals are not. Corrections were made for the presence of haematite in the acid extract of the LTA (Appendix I). Ankerite is the major mineral in UK coals containing iron carbonate and was assumed to have the composition of 54% CaCO_3 , 24% MgCO_3 , 20% FeCO_3 and 2% MnCO_3 (20,42). The concentration of ankerite in the coal was then calculated from

the iron carbonate content of the LTA and the mineral matter content.

3.2.2 Ultimate and proximate analysis

Carbon, hydrogen, nitrogen and carbon dioxide were determined according to BS procedures (159). At present there is no reliable method for oxygen, which has to be determined by difference $((100 - (H_2O + \text{ash} + C + H + N + S)) \%)$.

Proximate analyses (moisture, ash and volatile matter) were determined using a LECO MAC-400 automatic analyser.

3.2.3 Ash fusion

Ash fusibility (159) is an empirical test to simulate the behaviour of coal ash particles when heated in reducing (or oxidising) atmospheres, and is used for judging the quality of coal with respect to furnace slagging.

The HTA was ground and, with the aid of a binder, formed into pyramidal cones. The cones were heated at 5°C min^{-1} from 1000°C under a reducing atmosphere (50:50 mixture of hydrogen and carbon dioxide) and the temperature of initial 'deformation' (IDT), formation of a 'hemisphere' (HT) and complete 'flow' (FT) were noted (159).

3.2.4 High-temperature microscopy

A few milligrams of finely ground ash were pressed into the junction of a Pt/20% Rh:Pt/5%Rh thermocouple. The thermocouple is used as a resistance heater and the device is attached to the stage of an optical microscope.

The temperature was slowly increased from room temperature to 1500°C and the melting behaviour of the ash observed.

3.2.5 X-ray diffraction

XRD was used to analyse the LTA and HTA of the three coals. Diffractograms were obtained on Siemens and Philips Diffractometers using $\text{CuK } \alpha$ -radiation, scanning from 3° to 60° (2θ) at a speed of 2° per minute. The diffractograms were indexed and the minerals identified by comparison of their interplanar spacings with those of standard minerals or data published in the ASTM index.

A quantitative procedure for analysis of LTA was devised, based on the Internal Standard method (19, 162-165). However, instead of adding a reference mineral as the internal standard, pyrite in

the LTA was quantified from its pyritic sulphur concentration and used as the internal reference. Standard mineral mixtures were prepared; the proportions of the minerals varying to provide a wide range of relative compositions. Intensity data were obtained for the reflections listed in Table 9 for each sample. Calibration curves were constructed for each mineral, from which the mineral concentrations in the coals were then calculated, as in the Internal Standard method (165).

Table 9 - 'd' Spacings used for Quantitative Determination of Minerals Present in Coal

Mineral	'd' spacing (Å)	Relative Intensity
Kaolinite	7.1	100
Muscovite Mica	1.99	45
Calcite	1.875	17
Dolomite/Ankerite	1.78	30
	2.88	100
Siderite	1.73	40
Pyrite	1.63	100
	1.91	40
Quartz	2.46	12
	4.26	35

3.2.6 Thermal analysis

The three coals and their mineral matter were analysed using a Stanton-Redcroft STA-780 Thermal Analyser. A 20-40 mg sample was heated from 20 to 1000°C at 10°min⁻¹ in air, nitrogen and carbon dioxide. Alumina was used as the reference material.

Thermal analysis data was also obtained for the minerals kaolinite, muscovite mica, montmorillonite, illite-montmorillonite, quartz, pyrite, calcite, dolomite, siderite and gypsum in nitrogen and for the three carbonates in carbon dioxide, to assist with mineral identification and interpretation of thermal analysis curves.

Data was recorded as weight loss (thermal gravimetric analysis, TGA), rate of weight change (differential thermogravimetry, DTG) and as temperature differences (differential thermal analysis, DTA) between minerals and reference.

3.2.7 Infra-red analysis

FT-IR spectra were obtained for coals 'as received' and after demineralisation, and for their HTA and LTA. Spectra were obtained for 5% mixtures of the samples in potassium bromide, using a Nicolet 5DX FT-IR spectrometer with a Barnes Diffuse Reflectance accessory. 128 scans of each sample were taken at a resolution of 4 cm^{-1} , over a wavelength range of 4000 to 400 cm^{-1} .

The minerals were identified by comparison of their spectra and absorption bands with those of minerals in Painters mineral library and other published works (166-168).

3.2.8 Petrographic analysis

The relative abundances of macerals present were obtained using a microscopic statistical point count analysis technique. The crushed coals were set in a resin matrix and a ground and polished surface prepared. The proportions of macerals were quantified from their varying reflectivity. The average value for the reflectance of the coals was also obtained.

3.2.9 Forms of pyrite

The occurrence of pyrite in the three coals was studied under an optical microscope. The coals were prepared for reflected-light microscopy as for petrographic analysis and examined in air and under oil immersion, in polarised light, at magnification increasing to 500x.

3.2.10 Pore structure

Pore structure measurements were made using a Micromeritics Digi-Sorb 2500, an automated technique for determining nitrogen adsorption and desorption isotherms at -196°C at pressures up to saturation vapour pressure. Surface area and pore volume data can vary according to sample degassing procedures and on the penetrating power of the gas adsorbed. At -196°C nitrogen cannot enter pores with entrance widths $<0.4\text{ nm}$ and the surface area obtained may be taken to refer to the area in pores with entrance widths $>0.4\text{ nm}$.

The coals were vacuum dried at 110°C for 12 hours and further degassed in the Digisorb for >4 hours at 100°C prior to analysis. The nitrogen sorption isotherms were used to calculate the BET area and pore size distribution using a slit shaped pore model (169). A n-plot analysis was carried out to obtain micropore volume and specific surface area (170).

3.2.11 Solid-state ^{23}Na and ^{27}Al nuclear magnetic resonance (NMR) spectroscopy

^{23}Na NMR spectra of the three coals, the HTA and LTA of Coal 2 and a sample of exhaustively dried Coal 1 (dried under vacuum at 100°C for 18 hours) were run at 105.8 MHz, with magic angle spinning (MAS), using a Bruker WH 400 spectrometer at the University of Warwick (53). 20 K scans were taken, at a sweep width of 50 K Hz. Chemical shifts were referenced to aqueous sodium chloride at infinite dilution.

^{27}Al NMR spectra of the three coals were obtained at 104.2 MHz under similar conditions, and referenced to dilute aqueous $(\text{Al}(\text{OH})_2)_6^{3+}$.

3.3 Laboratory Fluidised Bed Combustor

3.3.1 Coal preparation

Coals 1, 2 and 3, supplied as washed singles were air dried (ad), crushed and sieved to +180 -355 μm prior to use.

Coal pretreatment studies involved blending Coals 1 and 3 in ratios of 2:1, 1:1 and 1:2 m/m and varying the chlorine content of Coal 1. The chlorine content of Coal 1 was reduced to 0.18% (ad) by heating in a minimum free space oven under nitrogen, at 300°C, for 48 hrs. The chlorine content of Coal 1 was enhanced to 1.43% (ad) by bubbling 0.5% hydrogen chloride gas in nitrogen, through prewetted coal in a fluidised bed, at ambient temperature for 1 hr.

3.3.2 Combustion apparatus

The combustion apparatus which is shown in Figures 12 and 13 consists essentially of a gas preheater and a 70mm diameter, fluidised bed made of silica glass and containing a coal feeder and probes to collect deposits. The bed of sand is supported on a silica glass, 0 grade, sintered disc. The sand is fluidised by air preheated to 510°C and directly heated by kanthal wire wound

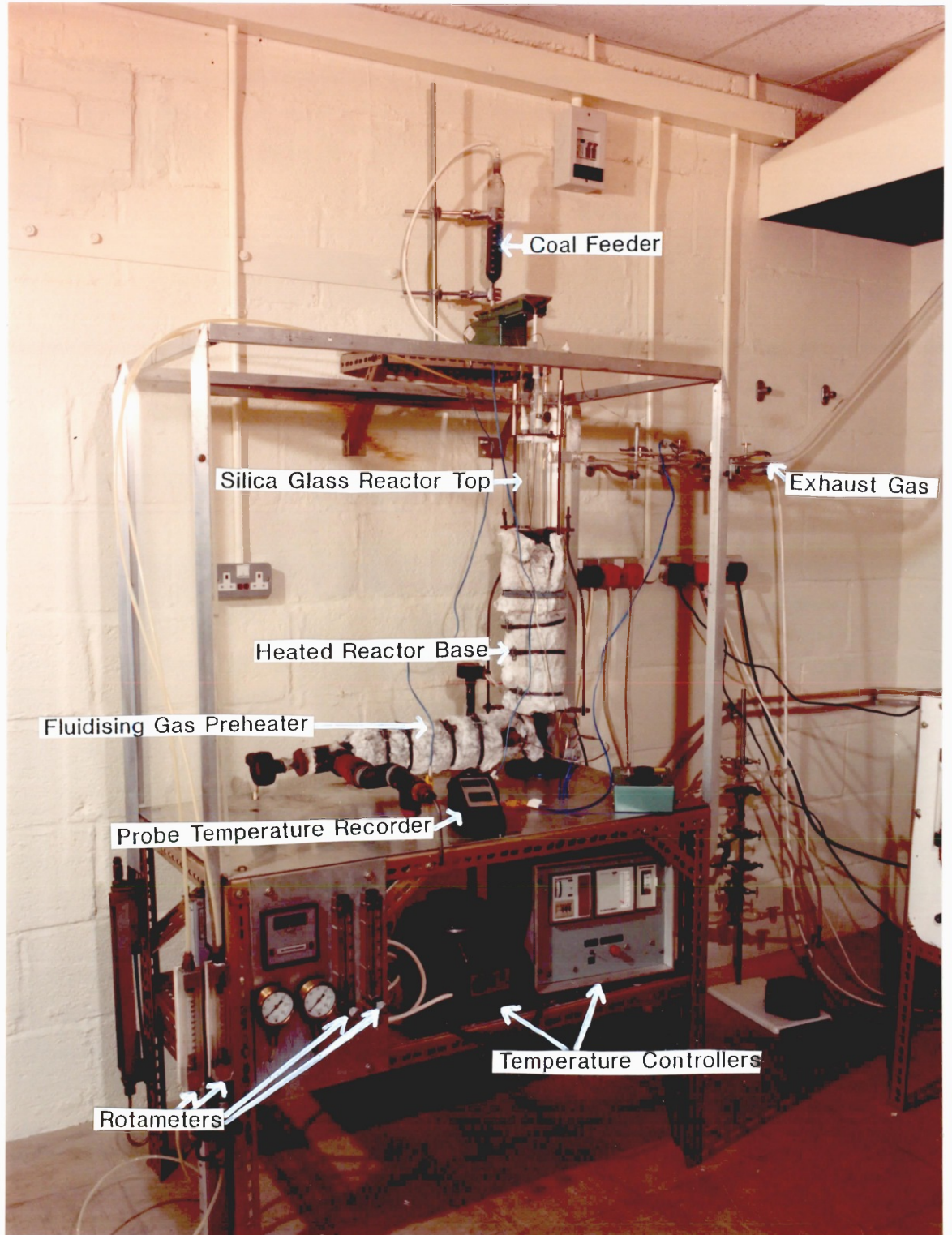


FIGURE 12. LABORATORY FLUIDISED BED COMBUSTER.

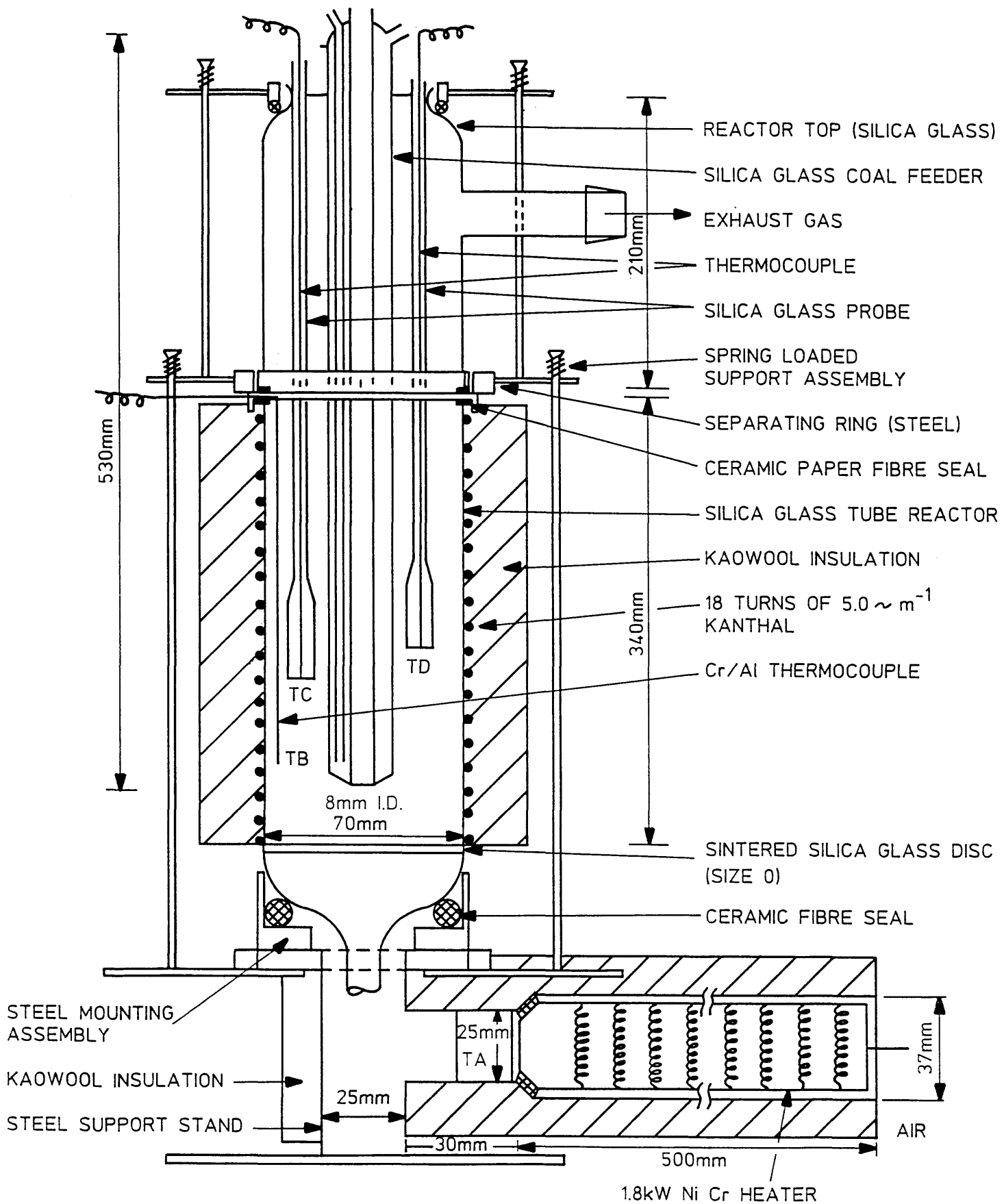


FIGURE 13. 70mm DIAMETER FLUIDISED BED COMBUSTOR

around the reactor tube. Bed temperatures are controlled and monitored via an in-bed thermocouple. The fluidised bed has a depth of ~ 130 mm, the gas velocity through the bed being about five times the minimum fluidising velocity.

Sized coal is fed at a constant rate from a vibratory feeder into the fluidised bed at a point about 40 mm below its ebullating surface. Coal blockage is avoided by using a nitrogen assisted coal feed and a nitrogen cooling jacket.

Combustion deposits are collected on the bases of silica glass probes located symmetrically around the coal feeder in the freeboard of the reactor zone. The probe bases are either fixed or detachable silica discs, both 9 mm in diameter. The temperature of the target surface is monitored by a thermocouple positioned inside the hollow probe. The required target surface temperature is attained by adjusting the height of the probe above the bed after conditions in the combustor have stabilised. The temperature difference between the inner and outer surfaces of the target were measured by fixing a thermocouple at the base of a hollow silica glass tube, at an identical height to a probe. The thermal conductivity of silica glass is very low at FBC temperatures and the temperature difference was found to be insignificant, as was the temperature variation across the target surface.

Standard operating conditions are listed in Table 10. The combustion parameters and dimensions of the laboratory scale combustor are, where possible, representative of industrial FBC.

3.3.3 Combustion parameters

Each combustion parameter was varied independently from the 'standard' operating conditions (Table 10) and deposits were collected at a range of probe surface temperatures, 400°C to 800°C.

- a) Deposition surface temperature: The effect of varying probe surface temperature, 400-800°C on the nature and extent of deposition was investigated for each of the three coals.
- b) Bed temperature: Bed temperatures were maintained variously at 850°C, 875°C, 900°C and 925°C with corresponding fluidising gas velocities of 0.173, 0.169, 0.166 and 0.162 msec⁻¹ (at room temperature) respectively.

Table 10 - Standard Operating Conditions for the
70 mm Fluidised Bed Combustor

Coal size	-	-355 +180 μm
Weight of coal	-	80 g
Coal feed rate	-	100 g hr ⁻¹
Weight of sand	-	300 g
Sand size	-	-500 +250 μm
Bed temperature	-	850°C *
Probe temperatures	-	400 to 800°C
Probe material	-	silica glass
Gas preheater temperature	-	510°C
Fluidising gas	-	air
Coal coolant and injection gas	-	N ₂
Fluidising gas velocity	-	0.173 m sec ⁻¹ (40 l min ⁻¹) at room temperature
Flue gas composition	-	oxygen 8-10%, carbon dioxide 7-9%
Silica glass probes	-	9 mm diameter

* For feed rates > 100 g hr⁻¹ the bed temperature
was maintained at 900°C.

- c) Coal feed rate: Coal feed rates of 100, 130 and 160 ghr⁻¹ were used. Bed temperatures were maintained at 900°C by reducing heat input to the reactor.
- d) Combustion atmosphere: Fluidising gas atmospheres containing lower oxygen concentrations of 15 and 10% v/v were used.

- e) Fluidising gas velocity: The effect of lowering the fluidising gas velocity from 0.17 msec^{-1} to 0.13 and 0.09 msec^{-1} (at room temperature) was investigated.
- f) Deposit growth: Deposits on three probes of surface temperatures 515 , 565 and 620°C were collected as the weight of coal combusted was increased in 100g increments, from 100 to 700g over 7hr .

Samples of deposit and bed ash were collected during an extended 20 hr run, in which 2 kg Coal 1 was burnt. The $-160 \mu\text{m}$ fractions of bed material and deposits were characterised by chemical, XRD and scanning electron microscopy (SEM) techniques.
- g) Deposit surface position: The effect of position of the probe deposit collecting surface in the freeboard was investigated using a gas cooled probe (Figure 14). A stream of nitrogen (6 l min^{-1}) cooled the inner surface by 150°C and a thermocouple attached to the outer contact surface monitored the deposition surface temperature.
- h) Deposit surface materials: Alumina probes, of similar design to the silica glass probes, were constructed from a hollow alumina tube and a 6 mm od by 1 mm thick alumina disc.

Stainless steel (s/s) type 321, was used to represent a typical material used in industrial FBC above-bed heat exchange tube banks. Probes were made by wiring s/s square stamps, 10 by 10 by 1 mm , to the base of an existing silica glass probe. The s/s stamps were pretreated by heating in the FBC, in air, at 650°C , for 2 hrs . The same three s/s stamps were used throughout the duration of the experiment. Temperature differences between inner and outer alumina and s/s deposition surfaces were monitored by thermocouples.
- i) Sulphur sorbent bed material: Ballidon limestone ($98.5\% \text{ CaCO}_3$) and Houghton dolomite ($56.8\% \text{ CaCO}_3$, $37.2\% \text{ MgCO}_3$) were heated separately in the fluidised bed reactor, in air, at 850°C , prior to use.

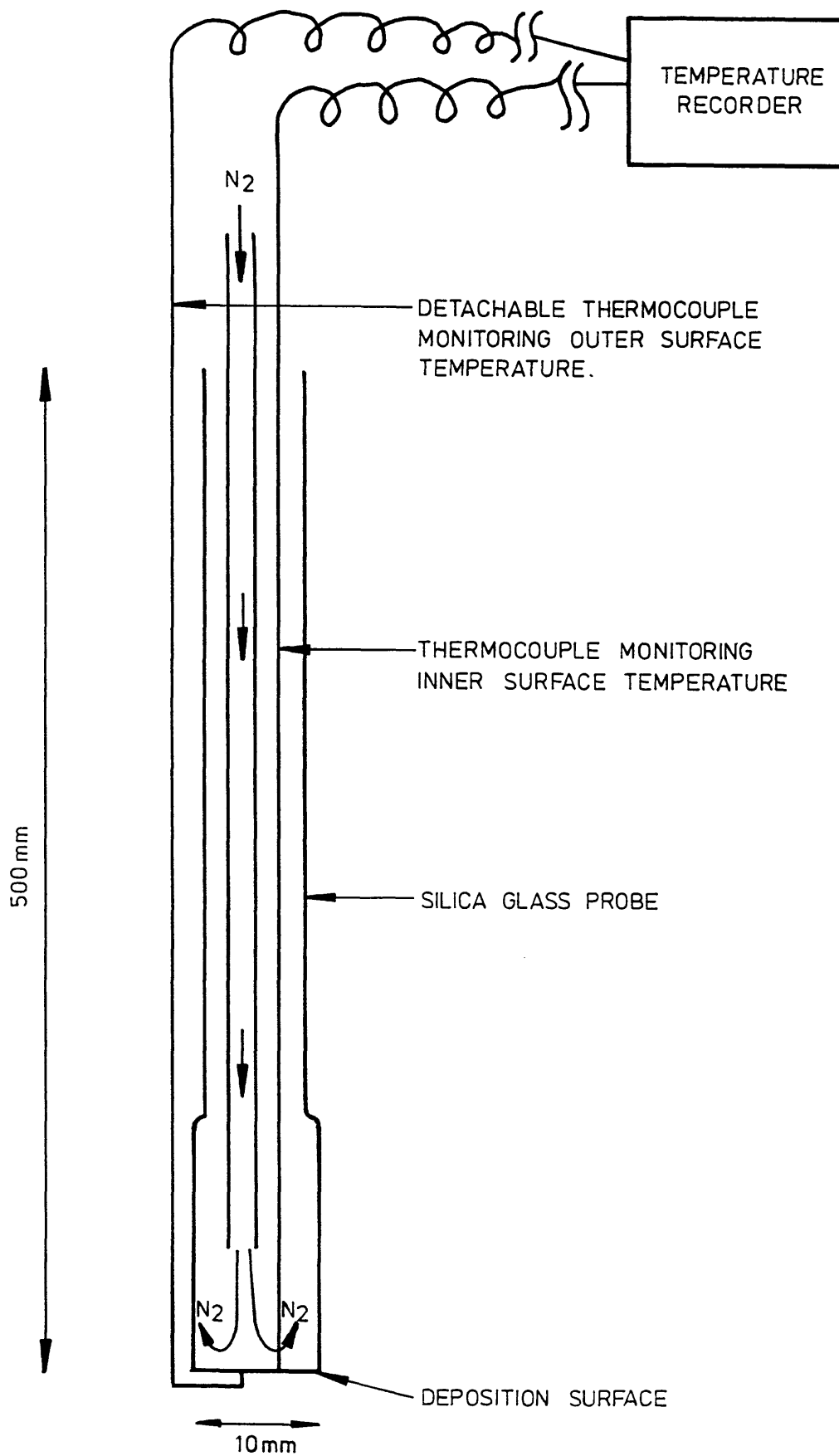


FIGURE 14. SILICA GLASS GAS COOLED PROBE

3.4 Characterisation of Combustion Products

3.4.1 Chemical analysis

The deposits were dissolved from the probes with dilute nitric acid using an ultrasonic bath. The resultant solutions were made up to 10 ml with high purity de-ionised water and their Na^+ , K^+ , Ca^{2+} , Mg^{2+} , Cl^- and SO_4^{2-} contents determined by ion chromatography and ICPS.

Chemical analysis of samples of deposits, bed and fly ash from pilot plant trials were determined by BS methods (section 3.2.1).

3.4.2 Microscopy

Deposits obtained at $\sim 600^\circ\text{C}$ on the detachable silica discs were examined using a Philips 9500 Scanning Electron Microscope (SEM) equipped with energy dispersive X-ray analysis (EDX). The deposits were coated with gold and the discs mounted directly into the microscope.

Deposits obtained from pilot plant trials were mounted in epoxy resin and a section cut perpendicular to the deposit-metal interface. This was ground and polished, coated with carbon and examined at magnifications up to 5K. Semi-quantitative chemical analysis of the layers across the deposit were obtained by electron probe microanalysis (EPMA) using a JEOL model JSM35 SEM. The morphology of the pilot plant deposits was studied by reflected light microscopy. Polished sections of specimens were prepared as for examination by EPMA and were studied prior to the carbon coating procedure.

3.4.3 X-Ray diffraction

Deposit and bed ash samples were analysed qualitatively by XRD using Siemens and Philips Diffractometers (Section 3.2.5). The major phases present were identified by comparing the observed interplanar spacings with those of compounds listed in the ASTM index.

3.4.4 Gas analysis

Exhaust gas from the laboratory combustor was analysed for H_2 , O_2 , N_2 , CO , CO_2 and CH_4 by gas chromatography using a Carle Analytical Gas Chromatograph.

3.5 Bomb Combustion

3.5.1 Coal preparation

Coals 1 and 3, supplied as washed singles, were air dried, ground and sieved to $-212\ \mu\text{m}$ prior to use.

Blends of Coals 1 and 3 (2:1, 1:1 and 1:2 m/m) and a sample of Coal 1 with a reduced chlorine content, were also used. The chlorine content of Coal 1 was reduced to 0.24% m/m ad, see Section 3.3.1.

3.5.2 Aqueous extraction

The $-212\ \mu\text{m}$ coals were ground in a Glen Creston high speed ball mill to an estimated particle size of $\sim 70\% < 75\ \mu\text{m}$. The water soluble constituents were extracted by refluxing with boiling deionised water for 2 hours. The leachates were analysed for Na^+ , K^+ , Ca^{2+} , Mg^{2+} , Cl^- and SO_4^{2-} by Dionex Ion Chromatography.

3.5.3 Bomb combustion and ash analysis

1 g of coal ($-212\ \mu\text{m}$) was placed in a 7 ml nickel crucible and fired under 30 atmospheres of oxygen in the pressure vessel of an adiabatic bomb calorimeter. The vessel was charged with 5 ml of deionised water before firing and this together with the crucible and its contents was transferred to plastic containers and analysed for water soluble Na^+ , K^+ , Ca^{2+} , Mg^{2+} , Cl^- and SO_4^{2-} by Dionex Ion Chromatography.

Ash produced by bomb combustion of the coals was examined using a Philips 9500 SEM equipped with EDAX. The ash samples were mounted on aluminium stubs and coated with gold prior to examination.

4. CHARACTERISATION OF COALS AND ASHES

4.1 Coals

4.1.1 Proximate, ultimate and alkali/alkaline earth metal analysis.

The proximate, ultimate and alkali/alkaline earths analyses for the three coals are given in Table 11 together with calorific value and coking properties.

The coal classification system used by British Coal classifies coal according to the degree of metamorphism (ie. rank). Volatile matter and Gray King coke type is chosen as the criteria of rank. Analyses for the three coals indicate they are all of similar rank, ie. bituminous with high volatile content, weakly caking properties. Coal 3 has a slightly higher rank.

The decrease in sodium, calcium and chlorine contents from Coals 1 to 3 is consistent with their observed fouling tendencies in industrial combustion trials, Coal 1 having the higher fouling propensity. The ash, potassium and sulphur contents, however, increase from Coal 1 to 3.

4.1.2 Thermal analysis

The thermal analyses of the three coals were recorded in both air and nitrogen and the results are summarised in Table 12. Typical thermal analysis curves for Coal 3, in air, are illustrated in Figure 15.

Water is released endothermically, possibly along with small amounts of volatile organic species, at temperatures up to 200°C. In air all three coals combusted in two stages as the volatile hydrocarbons underwent oxidation/combustion, followed by the rapid oxidation of the remaining fixed carbon. Peaks for Coal 1 were observed to occur at some 20 to 40°C below those for Coals 2 and 3, indicating a greater reactivity possibly related to a more open pore structure (Section 4.1.6).

In nitrogen, pyrolysis takes place after an initial release of water. The maximum rates of weight loss occurred at temperatures of about 70°C and 460°C with smaller losses to 1000°C. Coal 3 exhibited a complicated series of endothermic reactions at 470-570°C and a broad one at 770°C; these may be partially

Table 11 Coal Analyses

	Coal		
	1	2	3
BC Coal Rank Code No.	802	802	702
<u>Proximate analysis % m/m</u>			
Moisture, ad	8.0	6.1	4.7
Ash, ad	3.1	4.9	5.2
Volatile matter, daf	39.9	40.1	38.4
<u>Calorific value</u>			
kJ/kg (db)	32,220	31,980	32,220
<u>Coking properties</u>			
BS Swelling number	1	1	3½
Gray-King coke type	D	D	E
<u>Ultimate analysis % m/m</u>			
C]	82.6	82.9	83.2
H] dmmf	5.3	5.2	5.4
O]	9.1	8.9	8.0
N]	1.6	1.6	1.7
Cl]	0.8	0.7	0.3
CO ₂]	0.5	0.5	0.1
S Total] db	0.84	1.09	1.65
S pyritic]	0.17	0.34	0.65
S SO ₄]	0.02	0.02	0.03
S organic]	0.65	0.73	0.97
<u>Alkaline/alkaline earths</u>			
% m/m db			
Na	0.18	0.10	0.11
K	0.01	0.08	0.10
Ca	0.47	0.38	0.13
Mg	0.08	0.10	0.04

ad - air dried
db - dry basis
daf - dry ash free
dmmf - dry mineral matter free

Table 12 Thermal Behaviour of Coals

Sample	Atmosphere	DTA	DTG (Maxima rate of weight change)	Interpretation
Coal 1	Air	Minor endotherm at 70°C	Weight loss at 70°C	Release of water and possibly a small amount of volatile organic species.
		Major exotherm at 330°C	Small weight gain at 260°C Weight loss at 330°C	Chemisorption of oxygen (exothermic) Oxidation/combustion of volatile hydrocarbons.
		Major exotherm at 470°C	Weight loss at 470°C	Oxidation of remaining fixed carbon
	N ₂	Broad endotherm at 70°C	Weight loss at 70°C	Loss of water (and volatile organic species).
		Broad endotherm at 490°C	Weight loss at 490°C	Pyrolysis of coal and possibly decomposition of pyrite/dehydroxylation of the clay minerals.
Coal 2	Air	Minor endotherm at 70°C	Weight loss at 70°C	Loss of water (and volatile organic species).
		Major exotherm at 350°C	Small weight gain at 250°C Weight loss at 350°C	Chemisorption of oxygen. Oxidation/combustion of volatile hydrocarbons.
		Major exotherm at 500°C	Weight loss at 500°C	Oxidation of remaining fixed carbon.
	N ₂	Endotherm at 60°C	Weight loss at 70°C	Loss of water (and volatile organic species).
		Endotherms at 440°, 500°C	Weight loss at 440°, 500°, 550° and 750°C	Pyrolysis of coal and possibly decomposition of pyrite/dehydroxylation of the clay minerals.
Coal 3	Air	Major exotherm at 350°C	Small weight gain at 280°C	Chemisorption of oxygen.
		Major exotherm at 510°C	Weight loss at 350°C	Oxidation/combustion of volatile hydrocarbons.
			Weight loss at 510°C	Oxidation of remaining fixed carbon.
	N ₂	Endotherm at 70°C	Weight loss at 60°C	Loss of water (and volatile organic species).
		Endotherms at 470°, 520°, 570° and 770°C	Weight loss at 460°C	Pyrolysis of coal and possibly decomposition of pyrite/dehydroxylation of the clay minerals

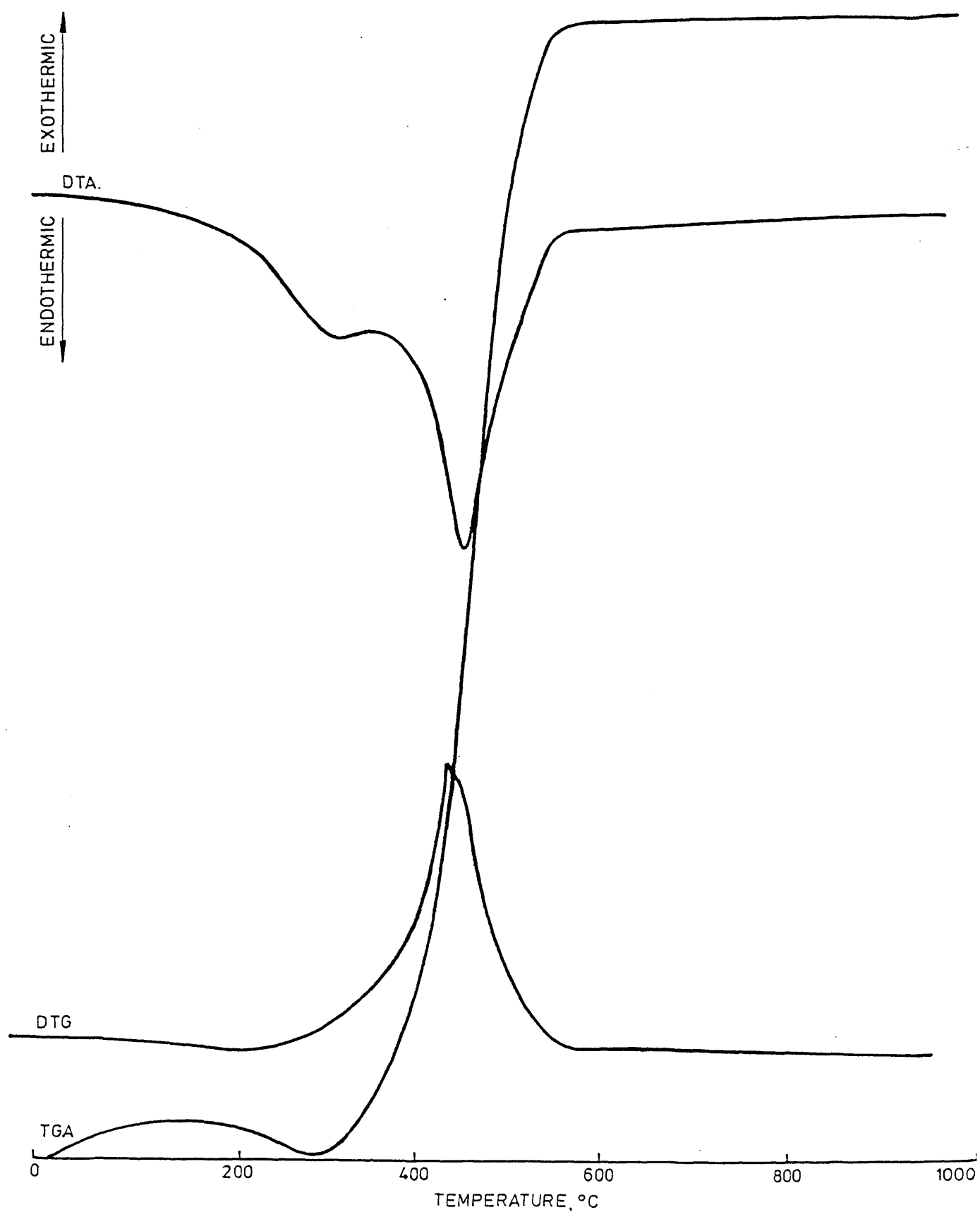


FIGURE 15. THERMAL ANALYSIS CURVES FOR COAL 3
(in air)

attributable to the decomposition of pyrite and the dehydroxylation of the clay minerals. These reactions were shown to a lesser degree by Coals 1 and 2.

The shape of the burning profile, which basically is the DTG curve of the coal in air, provides an assessment of the rank of the coal (171). In general, the peaks representing the release of volatile hydrocarbons are broader and at lower temperatures in the burning profile of the lower rank lignitic coals than for higher rank bituminous coals and anthracites. The results in Table 12 confirm that Coal 3 is the higher rank coal.

4.1.3 Infra-red spectroscopy

The FT-IR spectra for the three coals and for the demineralised coals are shown in Figures 16 and 17 respectively.

The assignment of the most characteristic bands in the infra-red spectra of coals is well established (168) (Figure 16). Figures 16 and 17 show all the main coal bands to be almost identical in absorbance although there are some minor differences in the shape and comparative absorbancies of the C-H band at about 3200 cm^{-1} . This may be attributable to small differences in the water content of the coals.

The band at 1605 cm^{-1} is characteristic of aromatic C-H and carbonyl groups. The shape and relative intensity of the band change as a function of rank (168).

The major differences in Figure 16 are in the areas where mineral matter would be expected, ie. at about 1030 cm^{-1} and below 600 cm^{-1} . Coal 1 appears to contain relatively less mineral matter (ie. kaolinite minerals) than Coals 2 and 3.

The absence of any new band near 1700 cm^{-1} (C=O stretching region) in the spectrum of the demineralised sample indicates that no significant oxidation of the organic component occurred during acid treatment.

4.1.4 Petrographic analysis

The maceral group analysis and reflectance measurements are given in Table 13.

The reflectance of vitrinite increases with rank and the mean random reflectance is a measurement of the degree of coalification, confirming that Coal 3 is of slightly higher rank. Coal 1 contains the highest proportion of vitrinite macerals.

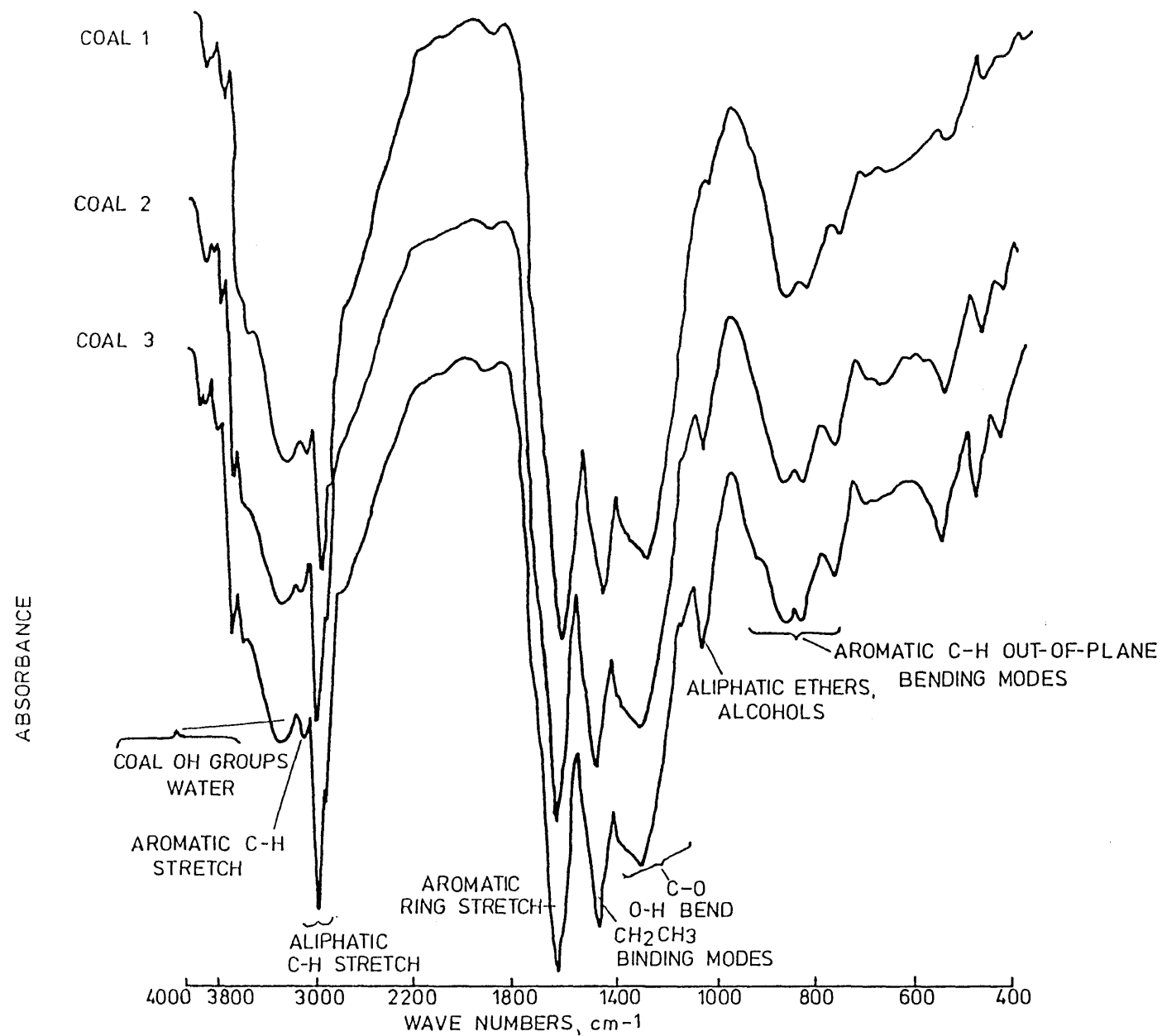


FIGURE 16. FTIR SPECTRA OF THE COALS

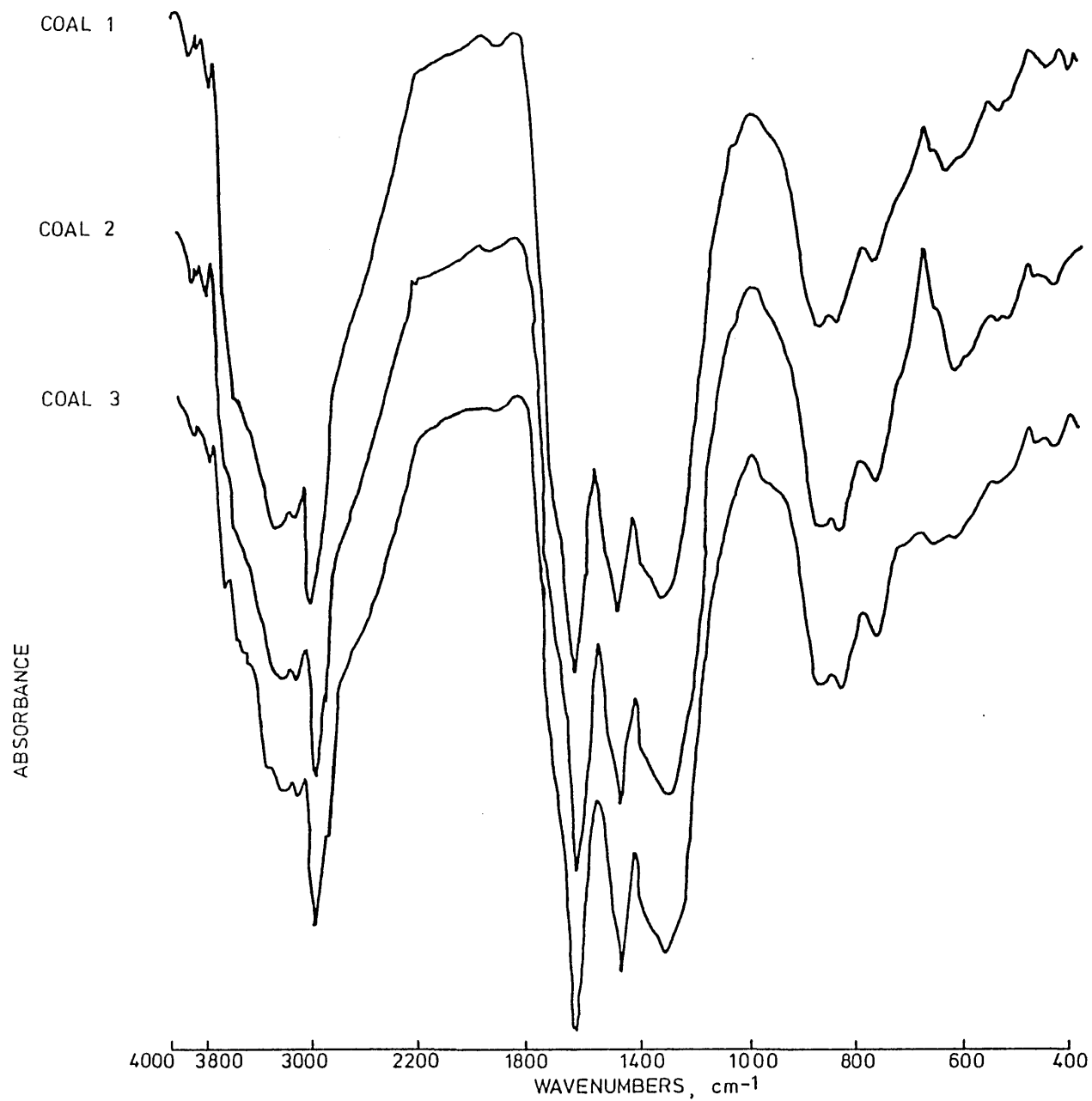


FIGURE 17. FTIR SPECTRA OF THE DEMINERALISED COALS

Table 13 Maceral Group Analysis, expressed as vol.%

Coal Maceral Groups and Minerals	1	Coal 2	3
Vitrinite	72	59	66
Exinite	5	7	6
Inertinite	21	31	24
Mineral Phases	1	4	4
Mean Random Vitrinite Reflectance, % reflected	0.63	0.66	0.72

4.1.5 Forms of pyrite

Pyrite is a highly reflective mineral and was found to be present in the coals as either fine concretions (single particles speckled in the coal macerals), framboids (spherical agglomerations), crystals (angular solid particles) or cleats (in cracks and fissures). It appeared most abundantly as fine concretions and framboids (<40 μm diameter) associated with the coal macerals ie. syngenetic in all three coals. Photomicrographs illustrating the occurrence of pyrite in Coal 3 are presented in Figures 18a to d. Pyrite was more abundant in Coals 2 and 3, than in Coal 1, appearing mainly as multiple agglomerations in the former and singularly in the latter. A higher proportion of pyrite occurred as larger crystals in Coal 1. Some pyrite appeared to be intimately associated with the clay minerals in Coal 3.

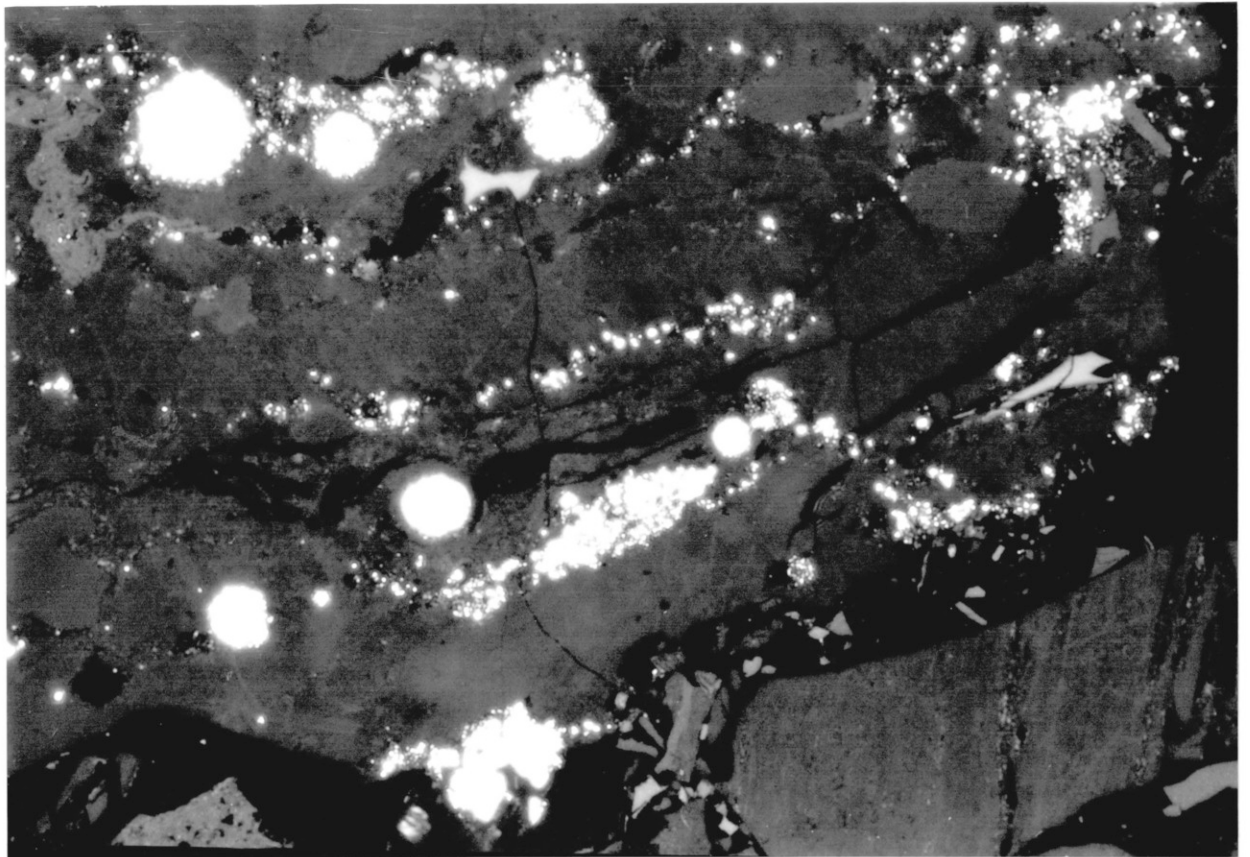
4.1.6 Pore structure

The surface areas and volumes for ranges of pore widths are given in Table 14.

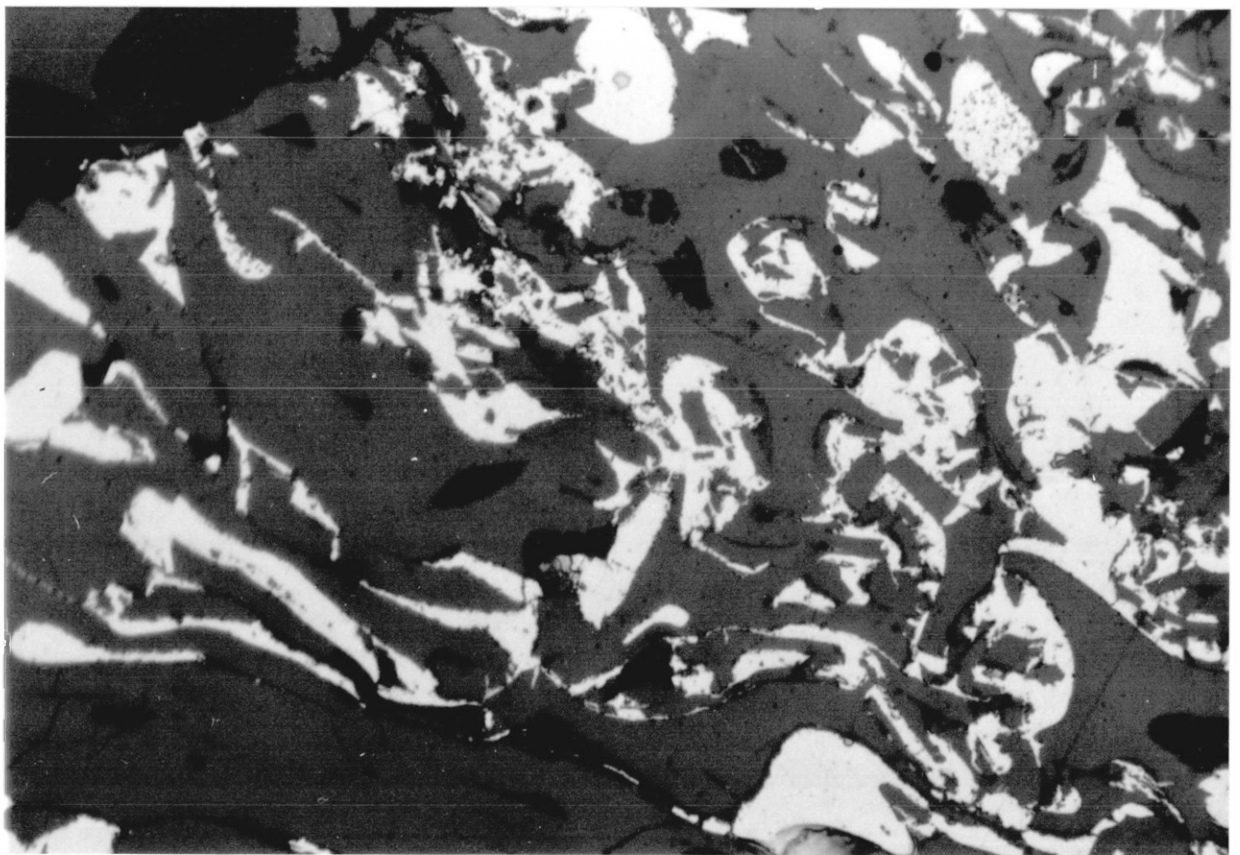
The data shows that Coal 1 has the most developed and more extensive pore structure with Coals 2 and 3 showing a similar but much lower porosity. The main difference between the coals lies in the micropore region (<2 nm) with Coals 2 and 3 showing no measurable value in this width range.

The majority of sodium and chlorine in UK coals originates from sea water and is introduced after the coal formation. Interestingly Coal 1 contains the highest concentration of sodium, calcium and chlorine. Presumably the greater porosity of Coal 1 enables it to take up larger amounts of the halides.

(a)



(b)

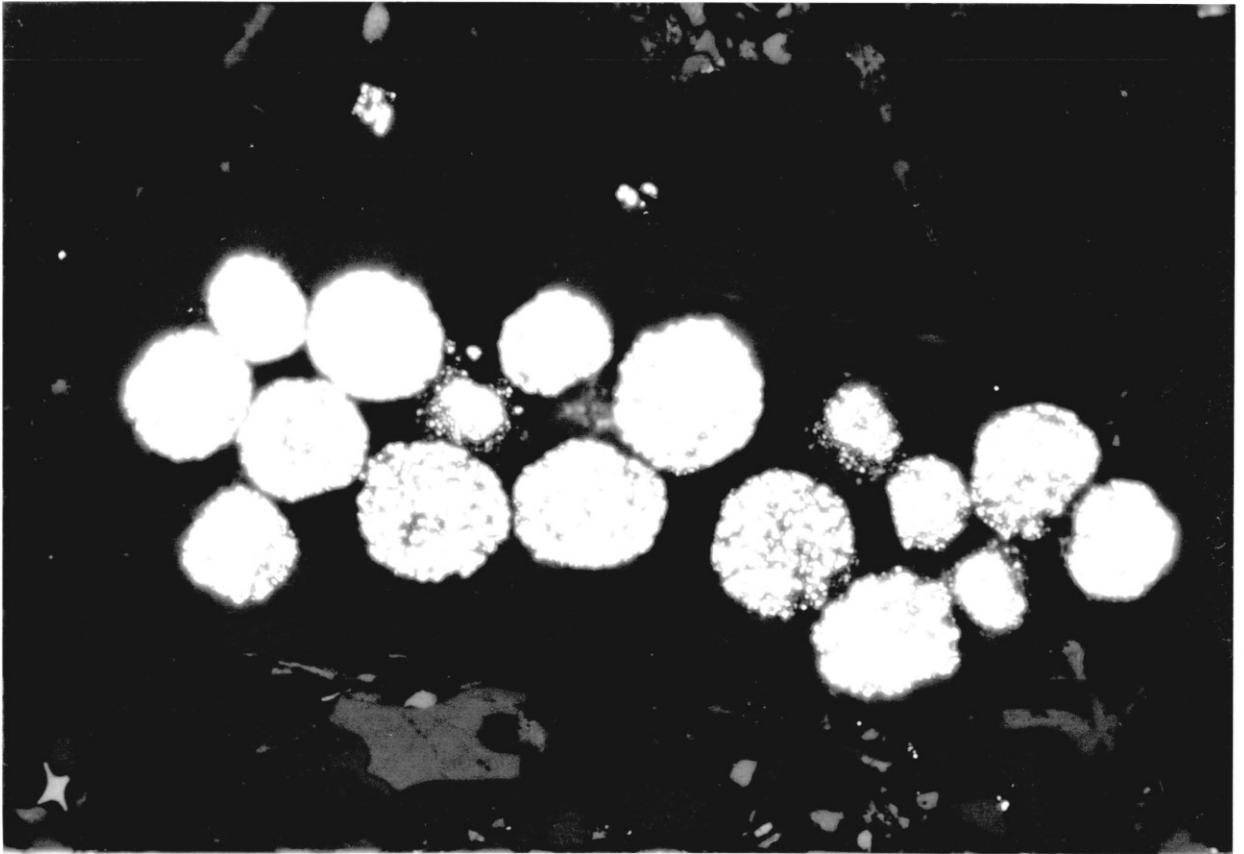


Figures 18a and b. Photomicrographs of Coal 3 Illustrating the Occurrence of Pyrite.

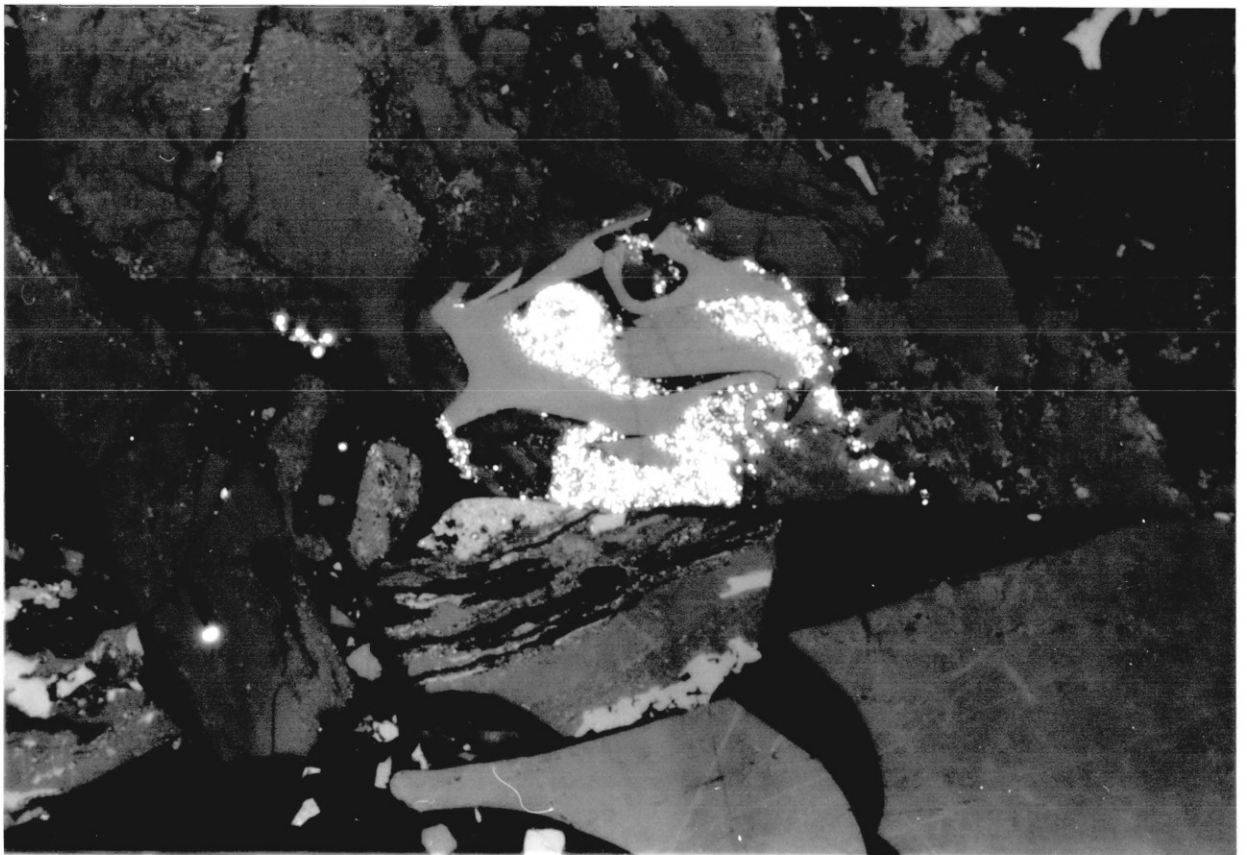
(a) as fine and framboidal concretions and as crystals associated with the coal macerals/minerals.

(b) as larger crystals and as cleats.

(c)



(d)



Figures 18c and d. Photomicrographs of Coal 3 Illustrating the Occurrence of Pyrite.

(c) as framboids.

(d) as concretions (both fine and framboidal) associated with the coal macerals/minerals.

The influence of the pore structure characteristics of the coals on the ease of leaching of the ionisable salts is reported under Section 4.1.7.

Table 14 Pore Structure Data

Pore Widths (in nm)	Coal		
	1	2	3
<u>Total pore volume, mm³ g⁻¹ in pore width range</u>			
0.4 - 2	34	0	0
2 - 4	2	12	19
4 - 60	8	9	10
<u>Total pore areas, m² g⁻¹ in pore width range</u>			
2 - 4	1	11	15
4 - 60	1	1	2
2 - 60	2	12	17
>0.4	37	12	18
<u>Average Pore Width in nm</u>			
	2.4	3.5	3.3

4.1.7 Aqueous extraction

Extraction data for the removal of water soluble salts from the coals by the two aqueous extraction procedures are compared as a histogram in Figure 19.

Calculated mg moles of charge for each ion, for each extraction condition and for each coal are given in Table 15. Summed values to give charge balances are also given in the Table.

Carbon dioxide contents of the coal residues from the sequential grinding/leaching cycles are given in Table 16 and are compared with the values present originally in the coals.

Table 15 Ion Balances in Extract Solutions

Coal	Treatment	* mg moles of charge x 100						Imbalance	
		Anions		Cations					
		Cl ⁻	SO ₄ ²⁻	Na ⁺	K ⁺	Ca ²⁺	Mg ²⁺	Summation	%
1	Reflux	150.4	0.8	67.8	0.5	93.5	24.2	+34.8	18.7
2	1 hr	81.4	4.8	30.0	0.8	46.0	19.2	+9.8	10.2
3		42.2	19.6	26.1	0.8	31.0	5.0	+1.1	1.7
1	Reflux	165.6	0.8	69.1	0.5	88.5	22.5	+14.2	7.8
2	2 hr	91.0	5.0	30.0	0.8	53.0	21.7	+9.5	9.0
3		46.5	19.0	26.5	0.8	34.5	5.8	+2.1	3.1
1	Reflux	187.6	1.0	71.7	0.5	105.0	27.5	+16.1	7.9
2	6 hr	112.1	5.2	29.1	0.8	67.0	29.2	+8.8	7.0
3		54.4	18.3	26.5	0.5	38.0	6.7	-1.0	1.4
1	Three	103.1	1.3	32.6	0.5	72.0	20.0	+20.7	16.5
2	grinding/	87.0	3.5	19.1	1.5	62.5	25.0	+17.6	16.3
3	reflux cycles	44.5	9.8	20.0	2.6	26.0	5.8	+0.1	0.3

* Defined as $\frac{\text{mass of ion (mg) in extract solution}}{\text{relative atomic mass}} \times \text{charge} \times 100$

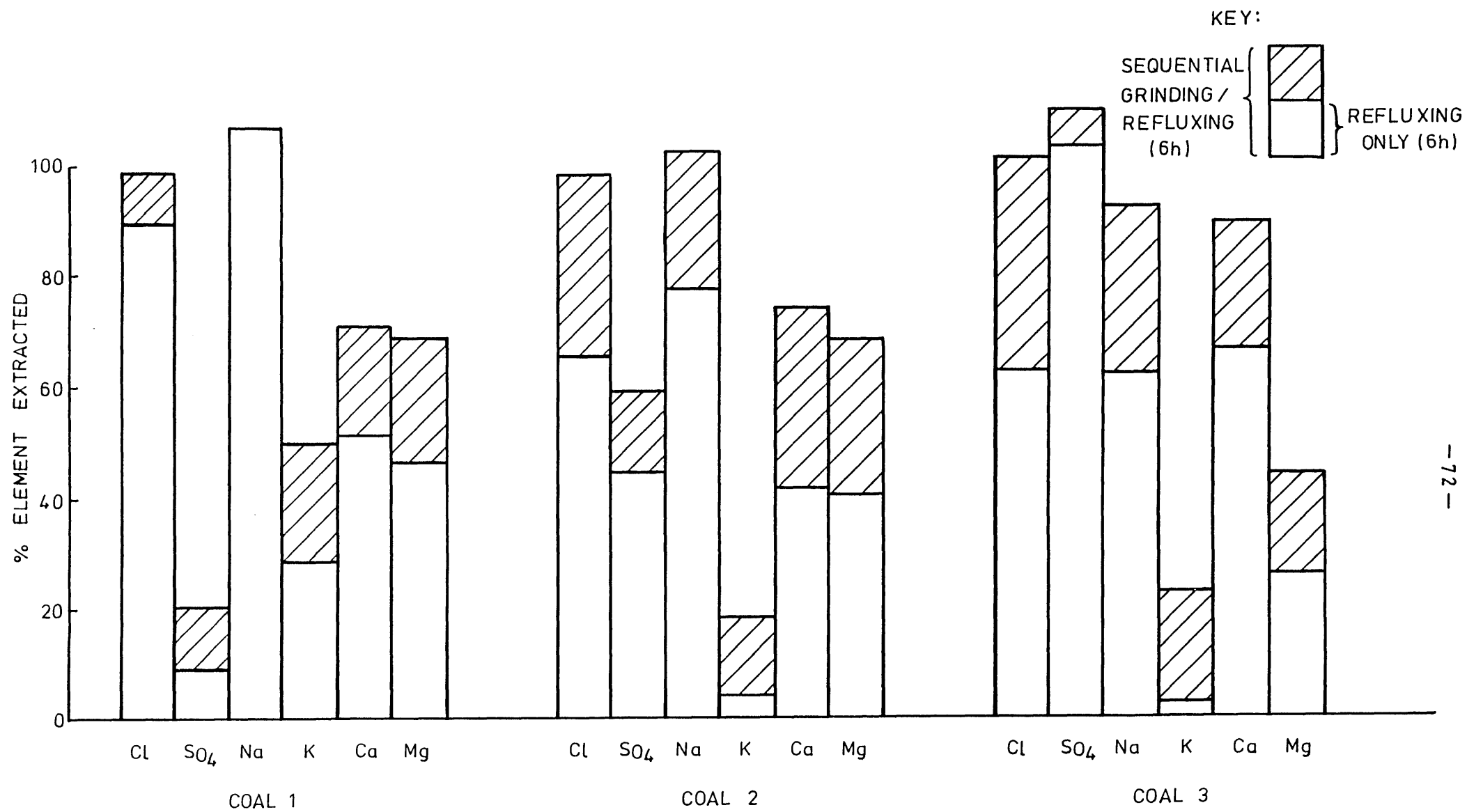


FIGURE 19. HISTOGRAM OF AQUEOUS EXTRACTION DATA.

Table 16 Carbon Dioxide Content of Coals
and Extracted Residues

Coal	% wt of Coal (ad)	
	Carbon dioxide content before extraction	Carbon dioxide content after extraction
1	0.47	0.15
2	0.51	0.14
3	0.10	0.14

The major components of the aqueous leachates are the anions Cl^- and SO_4^{2-} , the alkali metal cations Na^+ and K^+ and the alkali earth cations Ca^{2+} and Mg^{2+} .

The ion balances achieved for these species in the leachates are reasonable showing that contributions by other ions are relatively insignificant. The concentrations of the ions in the leachates reflect their concentrations in the coals, the extent of extraction being enhanced by fine grinding. The histogram of the aqueous extraction data shows that all of the Na^+ and, with extended grinding and leaching, all of the Cl^- can be washed from the three coals. However, considerable proportions of the other major leachate components appear to be fixed in the mineral/coal matrix even after vigorous leaching.

The results are consistent with the theory that both sodium and chlorine are present in the three coals as ions associated with the organic fraction of the coal and are distributed over the coal surface thus being readily accessible to water. The sodium and chlorine released by fine grinding/leaching are probably trapped in otherwise inaccessible pores. The ease of extraction of these ions in Coal 1 is clearly a function of its more open porous structure.

The low levels of leachable potassium suggests that the element is present predominantly associated with insoluble micaceous clays although Coal 1 may contain a small proportion of

organically associated potassium. The increase in its release on fine grinding may result from induced physical changes in the micaceous minerals rendering weakly bound potassium water soluble or possibly by ion exchange reactions releasing some species and fixing others.

The principal calcium and magnesium containing minerals in the coals are the insoluble carbonates, namely calcite, dolomite and ankerite, together with some sulphates and aluminosilicates. The unexpectedly high level of removal of both calcium and magnesium during water leaching suggests that there may have been some decomposition of the carbonate minerals, (Table 16 confirms this) possibly brought about by the simultaneous release of chlorine as hydrogen chloride.

Sulphate is a minor component and the more common sulphate minerals eg. gypsum, are water insoluble. However, water soluble sulphates and mixed sulphates of iron, sodium and magnesium are almost certainly present in the coals as a result of weathering and aqueous oxidation of the more common sulphides.

Release of a large proportion of the ions is probably a function of ionic dimensions and the particle and pore size distributions of the coals being leached. However, in a matrix as complex as coal there exists the possibility that some ions are formed during leaching either by mild oxidation or by breakdown of insoluble minerals. The possibility of ion-exchange reactions occurring, releasing some species and fixing others, also exists. Enhanced release by fine grinding resulted in ionisable salt removals of 1.4, 1.1 and 0.7% wt for Coals 1, 2 and 3 respectively. This represents reductions in overall mineral matter of 34, 18 and 10% wt.

A correlation has been shown to exist between the proportion of water soluble alkalis and their potential volatility (30,172). These results indicate that a larger proportion of the alkali species present in Coal 1 will be released during combustion.

4.1.8 Solid-state ²³Na and ²⁷Al nuclear magnetic resonance spectroscopy

²³Na MAS-NMR signals were observed for the three coals, as listed in Table 17. The intensity of the signals varied in the expected

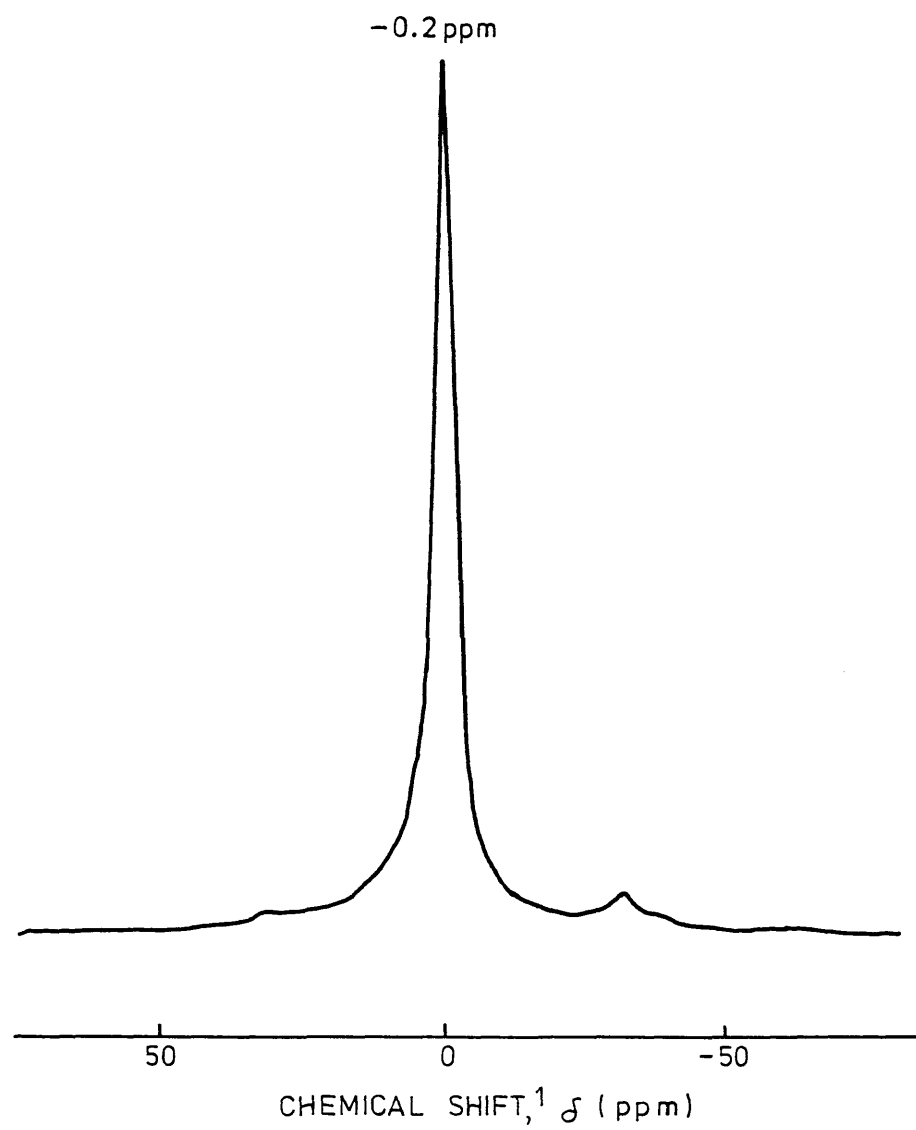
manner with their 'ash-determined' sodium content. All the ^{23}Na resonances were single sharp peaks with comparable chemical shifts to aqueous Na^+ . However, the resonances broadened substantially when the spectrum was obtained without spinning, which excludes the possibility of a local liquid environment. Linewidths with spinning were 200-400 Hz and spinning sidebands were negligible as shown for Coal 1 in Figure 20. This indicates a relatively symmetrical co-ordination environment for the bound Na^+ .

Table 17 ^{23}Na MAS-NMR Spectral Data for Raw and Dried Coals

Coal	<u>Raw Coal</u>		<u>Dried Coal</u>	
	δ^* (ppm)	Linewidth (ppm)	δ^* (ppm)	Linewidth (ppm)
1	-0.2	2	-5.2	45
2	-0.1	2		
3	0.0	2		

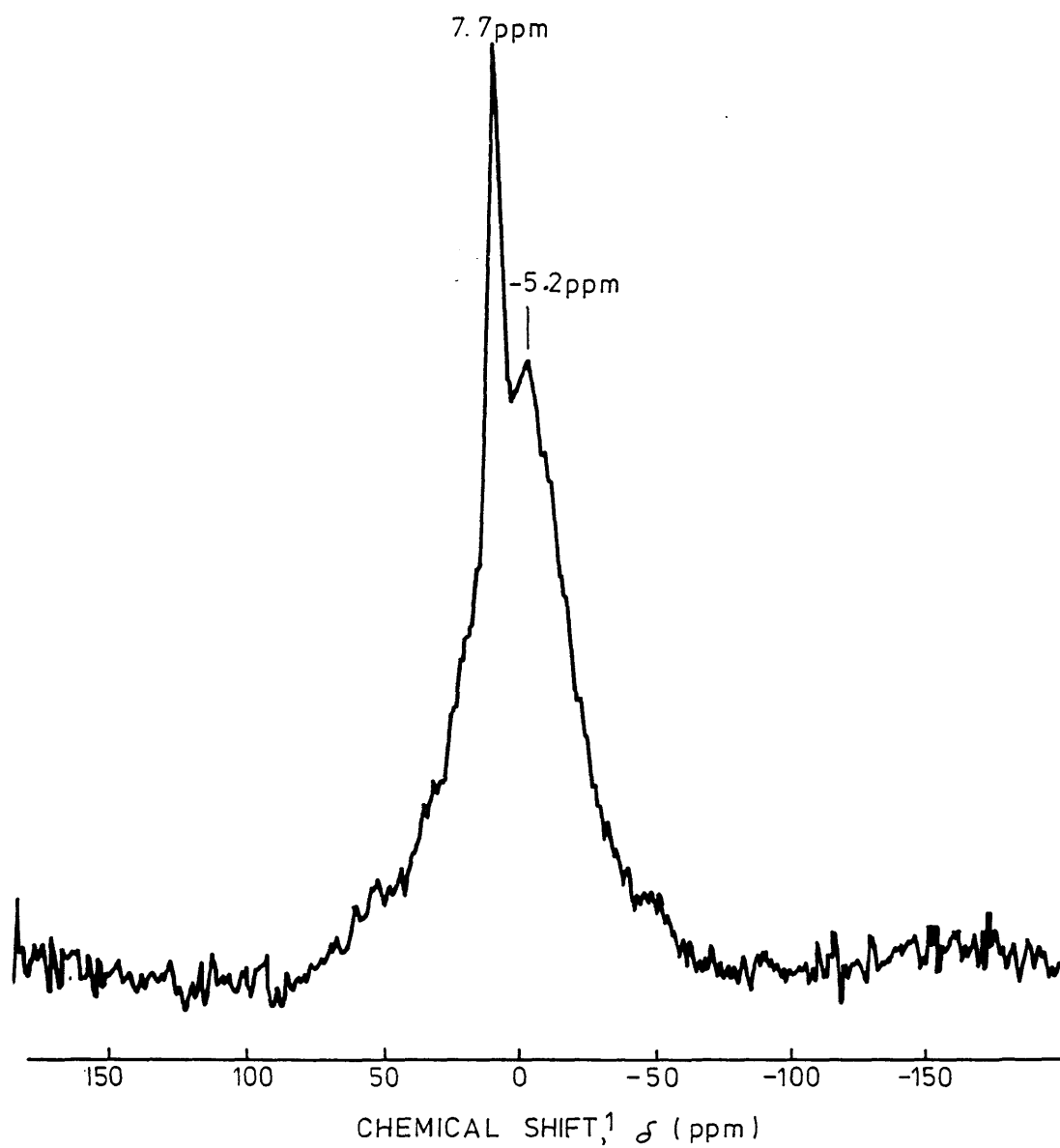
* referenced to $\text{Na}^+_{\text{aq}} = 0$ at infinite dilution

The ^{23}Na MAS-NMR spectrum of exhaustively dried Coal 1 is shown in Figure 21. Intensive drying should reduce or even eliminate the amount of water bound to surface Na^+ . The resulting Na^+ co-ordination environment is likely to have reduced symmetry and this is evidenced by the order of magnitude increase in observed linewidth. However sidebands were present, but not large, showing that the individual Na^+ environments were not highly unsymmetrical. The increase in linewidth may partially arise from chemical shift heterogeneity, especially as the chemical shifts themselves vary substantially. In fact the narrow



1. REFERENCED TO $\text{Na}^+\text{aq} = 0$, AT INFINITE DILUTION

FIGURE 20. ^{23}Na MAS-NMR SPECTRUM OF COAL 1 (RAW).



1. REFERENCED TO $\text{Na}^+_{\text{aq}} = 0$, AT INFINITE DILUTION.

FIGURE 21. ^{23}Na MAS-NMR SPECTRUM OF COAL 1 (DRIED).

linewidth component at +7.7δ, constituting about 4% of the total area (Figure 21), probably arises from crystalline NaCl. These changes were reversible upon rehydration.

²³Na chemical shifts for the three coals (Table 17) are similar to expected resonances from hydrated Na⁺ ions bound either by H-bonding or possibly at one co-ordination site, to a single organic group such as phenoxide or carboxylate (173). Neither the line widths nor the small scatter of chemical shifts are consistent with aqueous Na⁺. Thus sodium appears to be present in the coals as fully hydrated Na⁺ ions rigidly bound to single organic functional groups on the pore surface.

²⁷Al MAS-NMR spectra of the three coals showed weak resonances, whose relative intensity was consistent with their mineral content (Table 18). Linewidths varied significantly (3000-8000 Hz) and chemical shifts were consistent with the presence of both octahedrally and tetrahedrally co-ordinated Al³⁺.

Table 18 ²⁷Al MAS-NMR Spectral Data for Raw Coal

Coal	Octahedral		Tetrahedral	
	Al Resonance δ* (ppm)	Area %	Al Resonance δ* (ppm)	Area %
1	+1.6	>95	+71	<5
2	+2.3	85	+69	15
3	+2.1	80	+70	20

* referenced to Al³⁺_{aq} = 0

The major aluminosilicate species in UK coals are reported to be kaolinite, illite and muscovite (42). Kaolinite consists of a tetrahedral layer of silicon atoms in four fold co-ordination with oxygen (silica layer) joined by common oxygen atoms to a octahedral layer of aluminium atoms arranged in six fold co-ordination with oxygen or hydroxyl groups (gibbsite layer)

(174). These kaolinite units are linked by 'hydroxyl' bonds, where a H atom of an OH group acts as a bridge between two adjacent O atoms.

Muscovite basically consists of two silica layers condensed with one gibbsite layer. Isomorphous substitutions of Al^{3+} for Si^{4+} in the tetrahedral units take place. The electrical neutrality is maintained by the introduction of tightly bonded interlayer potassium ions which hold the negatively charged units together.

Illites are structurally similar to the micas consisting of two silica layers condensed with a gibbsite layer, but with less substitution of Al^{3+} for Si^{4+} than in muscovite. This leads to the presence of less interlayer potassium holding the units together, and therefore less well ordered units.

The proportion of tetrahedrally to octahedrally co-ordinated aluminium therefore gives some indication of the proportion of kaolinite to illite/muscovite in each coal. Table 18 indicates that the majority of aluminosilicates in Coal 1 are present as kaolinite whilst Coals 2 and 3 contain increasing proportions of illite/muscovite.

4.2 High-Temperature Ash

4.2.1 Elemental analysis

The elemental analyses of the HTA are given as percentage weights on the ash in Table 19. The decrease in sodium, calcium and magnesium contents from Coal 1 to 3 correlate with their reported fouling and corrosion characteristics. Conversely their iron and potassium contents increase. Although total sulphur increases from Coal 1 to 3, a decrease in the relative proportions of sulphur retained in the HTA as sulphate was observed.

4.2.2 Ash fusion

The ash fusion test is used to predict the behaviour of the mineral matter during combustion and the results listed in Table 20 indicate that the ashes from Coals 1 and 2 fuse and flow at lower temperatures than those for Coal 3. This suggests that Coals 1 and 2 present a greater potential for deposition problems than Coal 3, as confirmed in practice.

Table 19 Coal Ash Analyses

Element	Wt % on ash					
	Coal 1		Coal 2		Coal 3	
	HTA	LTA	HTA	LTA	HTA	LTA
Na	5.3	4.2	1.9	1.5	2.1	1.6
K	0.25	0.2	1.5	1.2	1.9	1.5
Ca	14.1	10.1	7.3	5.6	2.4	1.9
Mg	2.5	1.9	1.9	1.6	0.7	0.5
Fe	7.8	6.0	10.7	8.8	11.4	8.6
Ti	0.38	0.28	0.42	0.32	0.6	0.46
Mn	0.17	0.13	0.18	0.15	0.04	0.03
Al	8.4	5.5	11.8	8.8	14.8	11.3
Si	8.4	5.9	14.7	11.4	19.2	14.9
S (retained as SO ₄)	9.0	ND	4.2	ND	1.2	ND
P	0.26	0.21	0.36	0.26	0.09	0.07

ND - Not determined

Table 20 Standard Ash Fusion Temperatures and Behaviour Observed with High-Temperature Microscope

Melting behaviour	Coal 1		Coal 2		Coal 3	
	HTA	LTA	HTA	LTA	HTA	LTA
<u>Ash fusion</u>						
Deformation temperature, °C	1100	1110	1090	1070	1190	1180
Hemisphere temperature, °C	1140	1140	1140	1120	1230	1250
Flow temperature, °C	1280	1290	1300	1310	1300	1320
<u>High-temperature microscopy</u>						
Solidus temperature, °C	1010	1040	1050	1100	1080	1120
Liquidus temperature, °C	1300	1260	1265	1260	1280	1280

Since the physical behaviour of the ash during heating is thought to be related to its alkali metal content, the fusion test is sometimes taken as a measure of the alkalis present. The trends observed for total alkali/alkaline earths (Na, K, Ca, Mg) contents in Coals 1, 2 and 3 (0.74, 0.66 and 0.38 %m/m db respectively) can be correlated with that observed for their ash fusion characteristics.

4.2.3 High-temperature microscopy

The melting behaviour of the HTA as studied under the high-temperature microscope is compared with ash fusion data in Table 20. The trends observed for the solidus and liquidus temperatures, the temperature at which the initial appearance of a liquid phase and last trace of a crystalline phase are observed, are comparable with that of the ash fusion deformation and flow temperatures respectively. At the deformation temperature significant partial melting of the ash has occurred, consequently these temperatures are generally higher than their respective solidus temperatures.

4.2.4 X-Ray diffraction

The major phases identified in the three HTA were oxides of silicon, aluminium, iron and magnesium, calcium and iron sulphates and possibly calcium carbonate.

4.2.5 Infra-red spectroscopy

The FT-IR spectra of the HTA are shown in Figure 22. The absorption bands at 1160, 700 and 610 cm^{-1} are characteristic of sulphates. The relative intensities of these bands correlates with their sulphur contents (Table 11). Bands other than those mentioned are probably attributable to oxides of elements in Table 19.

It is surprising still to see a band at 3640 cm^{-1} in the spectrum of Coal 1, presumably due to water of crystallization. The broad bands at 1630 and 3200 cm^{-1} are probably due to the presence of small amounts of adsorbed water in the samples.

4.2.6 Solid state ^{23}Na nuclear magnetic resonance spectroscopy

The ^{23}Na MAS-NMR spectrum of the HTA from Coal 2 is shown in Figure 23. This differs markedly from Figures 20 and 21 with broad peaks at chemical shift +8.9 and -15.4 δ , also with

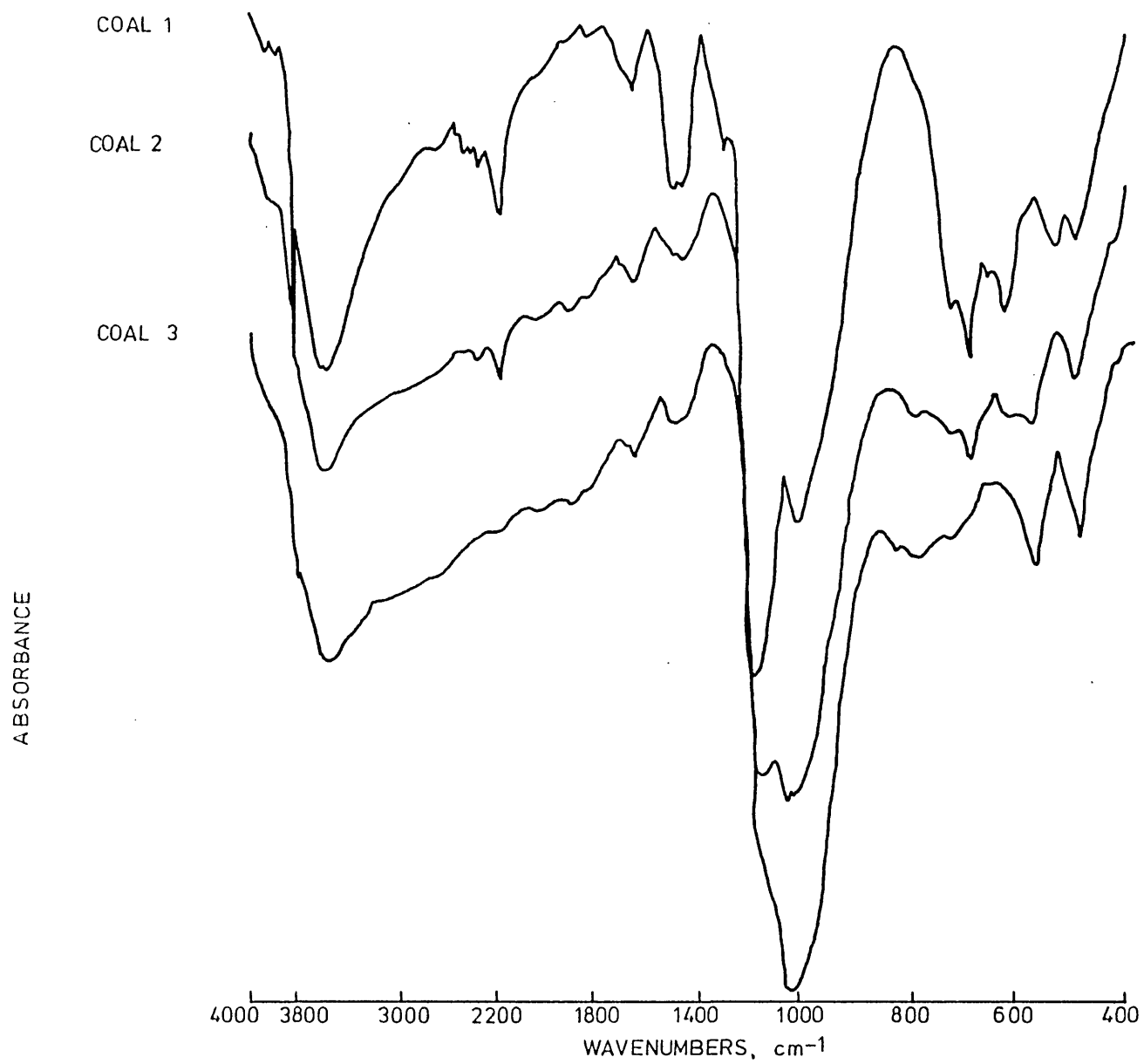
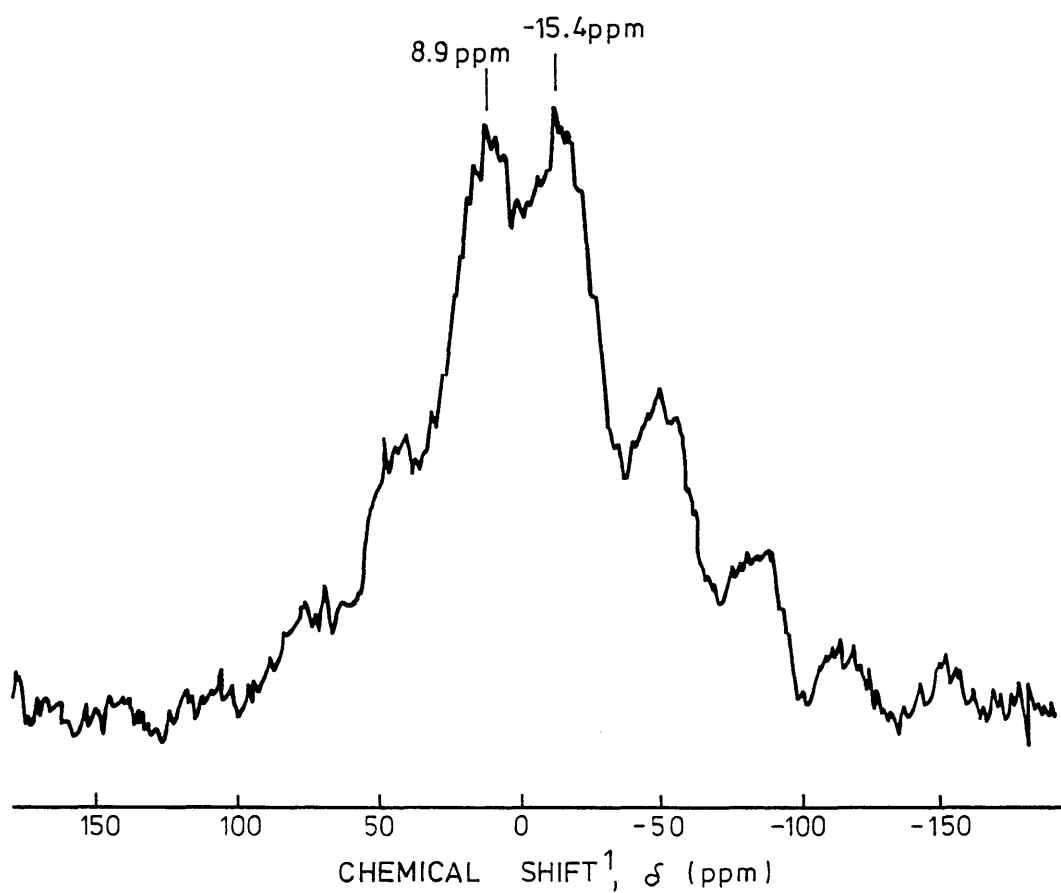


FIGURE 22. FT-IR SPECTRA OF HIGH-TEMPERATURE ASHES



1. REFERENCED TO $\text{Na}^+ \text{aq} = 0$, AT INFINITE DILUTION.

FIGURE 23. ^{23}Na MAS-NMR SPECTRUM OF HTA FROM COAL 2.

substantial sidebands. The high-temperature ashing procedure destroys the original Na^+ environment and is thought to form sodium oxide and to a lesser degree sodium sulphate. This is consistent with the HTA spectrum of Coal 2, where the Na^+ environment is unsymmetrical and different from the original Na^+ environment in the coal.

4.3 Low Temperature Ash

4.3.1 Mineral matter content

The mineral matter contents of coals can be determined by both direct and indirect methods. The latter involves applying calculation procedures to the proximate, ultimate and ash analyses: the most widely used is the Parr (175) formula, which permits calculation of the mineral matter content from the yield of ash and total sulphur (see Appendix I). More elaborate formulae allow for the decomposition of carbonates and the various forms of sulphur (176,177). However, all these formulae necessarily make assumptions about the nature of the mineral matter.

The mineral matter may also be determined indirectly by normative analysis (see Section 4.4) although this also requires assumptions about the composition of the minerals present.

The most reliable direct methods of determining mineral matter are the acid demineralisation procedure (Section 3.1.3) and low-temperature (plasma) ashing (Section 3.1.2). Both methods are based on separating the coal from the mineral matter. The acid demineralisation procedure involves dissolving the mineral matter in acid and measuring the weight loss. Allowances are made for changes in moisture content, residual ash, pyrite (not completely dissolved in treatment) and adsorbed hydrochloric acid. In the low-temperature ashing procedure the organic coal is removed, by oxidation, and the mineral matter content is calculated from the weight of the ash (178). Corrections are made for the moisture content and residual organic carbon. However, unaccounted for changes in the minerals may occur due to dehydration or oxidation. Data derived by these procedures are included in Table 23 for comparison purposes (Section 4.4).

4.3.2 Elemental analysis

The elemental analysis of the LTA have been compared with those obtained for their HTA in Table 19. The differences in the composition of respective LTA and HTA are due to the loss of the more volatile inorganic constituents (i.e. the release of CO_2 , SO_2 and H_2O from the carbonate, sulphide and clay minerals), during the high-temperature ashing procedure (Appendix I). Normalisation of the alkali metals indicates that negligible amounts of Na, K, Ca, Mg, Fe, Ti, Mn, Al and Si are lost during the heating of the LTA from 150 to 815°C.

4.3.3 X-Ray diffraction

The mineral phases identified from the diffractograms of the LTA are quantified in Table 21. A typical diffractogram from Coal 2 is illustrated in Figure 24. The most abundant mineral detected in these ashes was kaolinite. Muscovite, pyrite, quartz, ankerite, dolomite, calcite, anhydrite and bassenite were also detected. The concentrations of kaolinite, muscovite, pyrite and quartz increase from Coal 1 to 3 whilst those of dolomite/ankerite and calcite decrease. Anhydrite (CaSO_4) and bassenite ($\text{CaSO}_4 \cdot \frac{1}{2}\text{H}_2\text{O}$) were also identified and represent original gypsum ($\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$) which was dehydrated by the low-temperature ashing process.

Sodium sulphate is the most likely sodium-bearing compound to be present in the LTA. However it would probably be in the form of fine crystallites (<0.1µm size) dispersed throughout the LTA making it difficult to detect by XRD. No sodium-bearing components have been identified in the LTA.

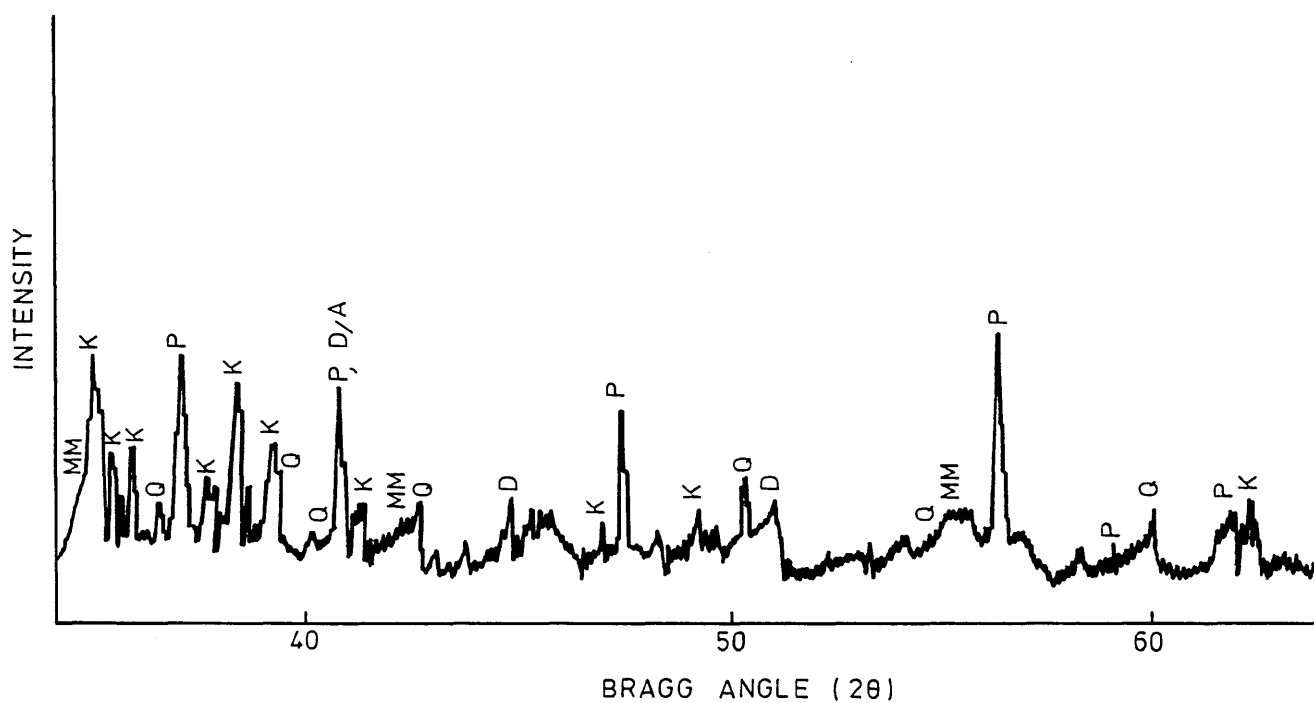
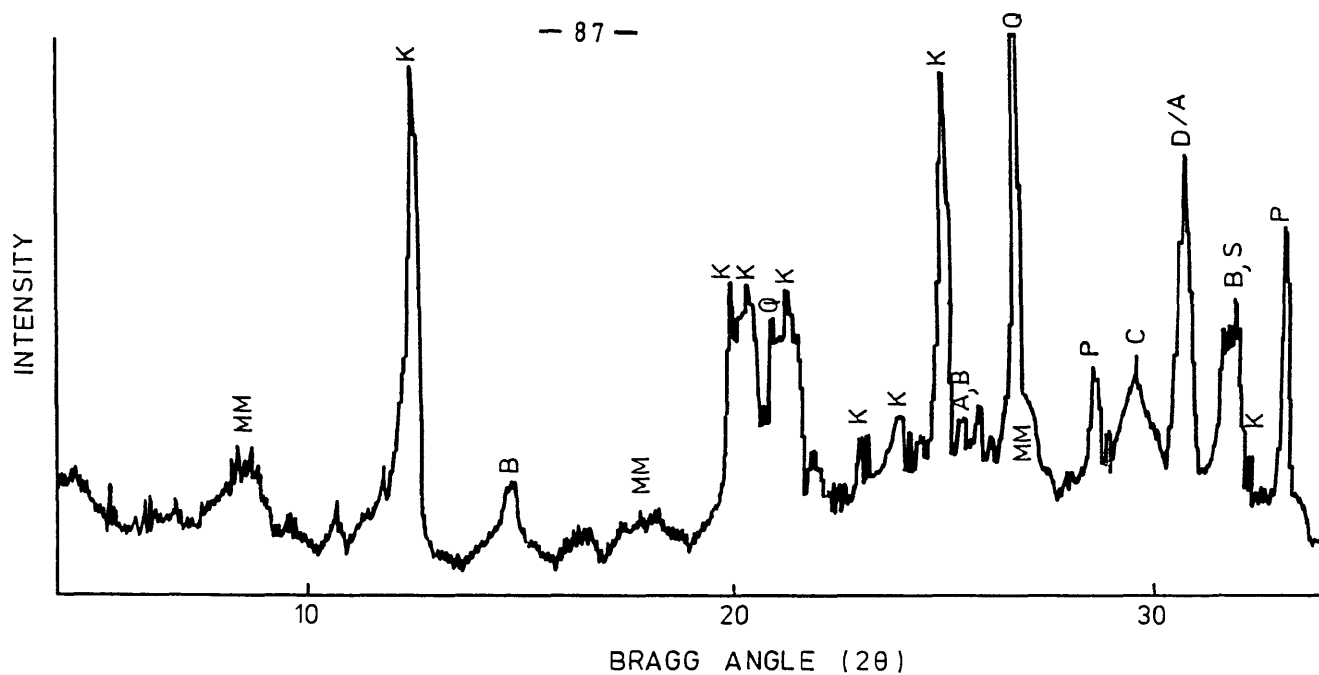
It should be noted that the XRD lines attributed to muscovite also correspond to the clay mineral illite, which is a more likely constituent of the mineral matter in UK coals (179). Mineral standards for illite were unobtainable.

XRD is considered to be the best method for mineral identification and application of XRD procedures has proved successful for the analyses of a number of mineral phases in LTA e.g. calcite and quartz. However its application to the quantification of clays is somewhat more difficult, largely due to preferred orientation effects and the selection of appropriate mineral standards. Interpretation of XRD analysis of LTA can

Table 21 Mineral Concentrations Determined by x-ray Diffraction Analysis

Mineral	Wt %					
	Coal 1		Coal 2		Coal 3	
	In mineral matter	In coal (ad)	In mineral matter	In coal (ad)	In mineral matter	In coal (ad)
Kaolinite	26.2	1.08	30.1	1.90	43.7	2.97
Muscovite	2.0	0.08	1.8	0.11	5.4	0.37
Calcite	12.3	0.51	<2	<0.1	2.3	0.15
Dolomite]	21.4	0.88	17.3	1.09	6.4	0.43
Ankerite]						
Siderite	0.14	0.005	3.0	0.19	<0.1	<0.005
Pyrite ^(a)	6.8	0.28	7.8	0.49	15.6	1.06
Quartz	<1.5	<0.1	3.2	0.20	6.3	0.43

a - Pyrite concentration calculated from pyritic sulphur content of low-temperature ash



ANHYDRITE, A
 BASSANITE, B
 CALCITE, C
 DOLOMITE / ANKERITE, D/A

KAOLINITE, K
 MUSCOVITE MICA, MM.
 PYRITE, P
 QUARTZ, Q
 SIDERITE, S

FIGURE 24. DIFFRACTION PATTERN OBTAINED FROM LTA OF COAL 2
USING $\text{Cu (K}\alpha\text{)}$ RADIATION.

also be misleading for organically associated elements which are present in the LTA as inorganic salts.

4.3.4 Thermal analysis

Figures 25, 26 and 27 show the DTA results from heating the LTA in air, nitrogen and carbon dioxide respectively and Figure 28 shows the weight variations as a function of temperature in nitrogen resulting from physical and chemical changes to the mineral matter. Table 22 summarises the major thermal events when heated in the three atmospheres.

The clay minerals begin to release adsorbed or interlayer water at low temperatures and in several stages, with endotherms and maximum weight losses at about 80 and 140°C. Dehydroxylation of the clay minerals is characterised by a series of endotherms between 300 and 550°C. These events however, are partially masked by the exothermic oxidation of pyrite in air to ferric oxide or the endothermic decomposition in nitrogen to pyrrhotite (FeS). Endothermic lattice destruction and exothermic phase changes of the clay minerals commenced at 700°C upwards for the micas and from 1000°C for kaolinites. The carbonate minerals decomposed from 550°C exhibiting a complex series of broad endotherms and weight losses. These effects generally appeared at higher temperatures with an atmosphere of carbon dioxide.

Comparison of the magnitude of these thermal events for the LTAs confirmed the compositional mineral trends of an increase in the clay minerals and pyrite from Coal 1 through to Coal 3 with a corresponding decrease in the carbonate minerals.

Reactions between evolved gases, such as sulphur oxides, with residual minerals were evident from differences in weight loss in oxidising and reducing atmospheres. Thermal events for the decomposition of carbonate minerals in oxidising atmospheres were diminished. This may be due to sulphur oxides, produced from the oxidation of pyrite, reacting with the decomposing carbonate minerals and forming calcium and magnesium sulphates.

Quantitative measurements of complex mineral mixtures are difficult, particularly for minor and non-thermally active components. Peak superposition is also a problem, however analysis in different atmospheres can help with the interpretation of the results.

Table 22 Thermal Behaviour of Low Temperature Ashes

<u>Major Thermal Events</u>				
Sample	Atmosphere	DTA	DTG (Maxima rate of weight change)	Interpretation
Coal 1	Air	Endotherms at 70° and 130°C Endotherm at 330°C Minor exotherms at 360° and 530°C and broad exotherm at 440°-470°C. Endotherms at 650°, 760° and 840°C.	Weight loss at 70° and 130°C Weight loss at 500°C Weight losses at 640° and 800°-880°C.	Release of adsorbed and interlayer water mainly from clay minerals. Dehydroxylation of clay minerals. Oxidation of pyrite and endothermic dehydroxylation of clay minerals. Decomposition of carbonate minerals and lattice destruction of micaceous clay minerals.
	N ₂	Endotherms at 70° and 140°C Endotherm at 360°C Endotherms at 540°, 690° and 730°C. Endotherms at 750°, 840°, 870° and 920°C	Weight losses at 70° and 140°C Weight losses at 540°C and 690°-750°C. Weight loss at 830°C	Release of adsorbed and interlayer water mainly from clay minerals. Dehydroxylation of clay minerals. Decomposition of pyrite and dehydroxylation of clay minerals. Decomposition of carbonate minerals and lattice destruction of micaceous clay minerals.
	CO ₂	Endotherms at 80° and 140°C Endotherm at 260°C Endotherms at 470°, 540°, 610° and 720°C. Endotherms at 780° and 870°C	 NR	Release of adsorbed and interlayer water mainly from clay minerals. Dehydroxylation of clay minerals. Decomposition of pyrite and dehydroxylation of clay minerals. Decomposition of carbonate minerals and lattice destruction of micaceous clay minerals.
Coal 2	Air	Endotherms at 80° and 140°C Endotherm at 300°C Exotherms at 350°, 430° and 510°C. Endotherms at 580° and 730°C	Weight loss at 80° and 140°C Weight loss at 500°C. Weight loss at 700° and 800°C	Release of adsorbed and interlayer water mainly from clay minerals. Dehydroxylation of clay minerals. Oxidation of pyrite and endothermic dehydroxylation of clay minerals. Decomposition of carbonate minerals and lattice destruction of micaceous clay minerals.

Table 22 (continued) Thermal behaviour of low temperature ashes

Sample	Atmosphere	Major Thermal Events		Interpretation
		DTA	DTG (Maxima rate of weight change)	
Coal 2 (contd)	N ₂	Endotherms at 80° and 150°C Endotherm at 320°C. Endotherms at 520°, 540°, 600° and 660°-730°C Endotherm at 840°C	Weight loss at 80° and 150°C Weight loss at 510° and 680°-720°C Weight loss at 840°C	Release of adsorbed and interlayer water mainly from clay minerals. Dehydroxylation of clay minerals. Decomposition of pyrite and dehydroxylation of clay minerals. Decomposition of carbonate minerals and lattice destruction of micaceous clay minerals.
	CO ₂	Endotherms at 80° and 140°C Endotherm at 320°C Endotherms at 520°, 540°, 700° and 780°C Endotherms at 850° and 880°C	NR	Release of adsorbed and interlayer water mainly from clay minerals. Dehydroxylation of clay minerals. Oxidation of pyrite and dehydroxyl- ation of clay minerals. Decomposition of carbonate minerals and lattice destruction of micaceous clay minerals.
Coal 3	Air	Endotherms at 70° and 130°C Major exotherm at 430°C Endotherms at 630° and 680°C	Weight losses at 70° and 130°C Weight loss at 470°C Weight losses at 580° and 650°C	Release of adsorbed and interlayer water mainly from clay minerals. Oxidation of pyrite and endothermic dehydroxylation of clay minerals. Decomposition of carbonate minerals and lattice destruction of micaceous clay minerals.
	N ₂	Endotherms at 490°, 530°, 550° and 580°C Endotherm at 740°C	Large weight loss at 500°C	Decomposition of pyrite and dehydroxylation of clay minerals. Decomposition of carbonate minerals and lattice destruction of micaceous clay minerals.
	CO ₂	Endotherms at 80° and 140°C Endotherm at 330°C Endotherms at 490°, 530°, 550° and 570°C Endotherm at 760° and 940°C	NR	Release of adsorbed and interlayer water mainly from clay minerals. Dehydroxylation of clay minerals. Decomposition of pyrite and dehydroxylation of clay minerals Decomposition of carbonate minerals and lattice destruction of micaceous clay minerals.

NR = Not Recorded

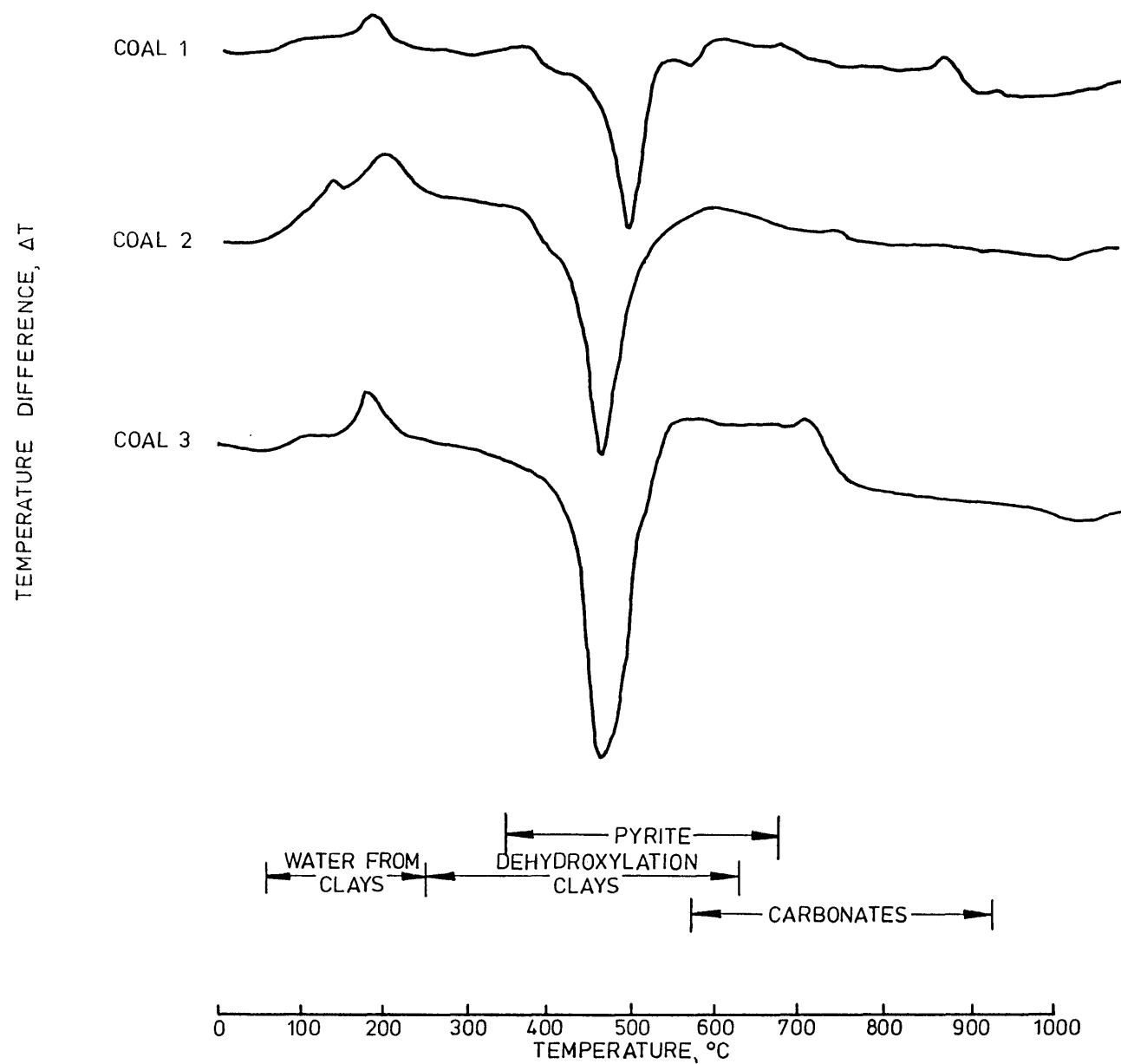


FIGURE 25. DIFFERENTIAL THERMAL ANALYSIS OF THE LOW TEMPERATURE ASHES
(IN AIR)

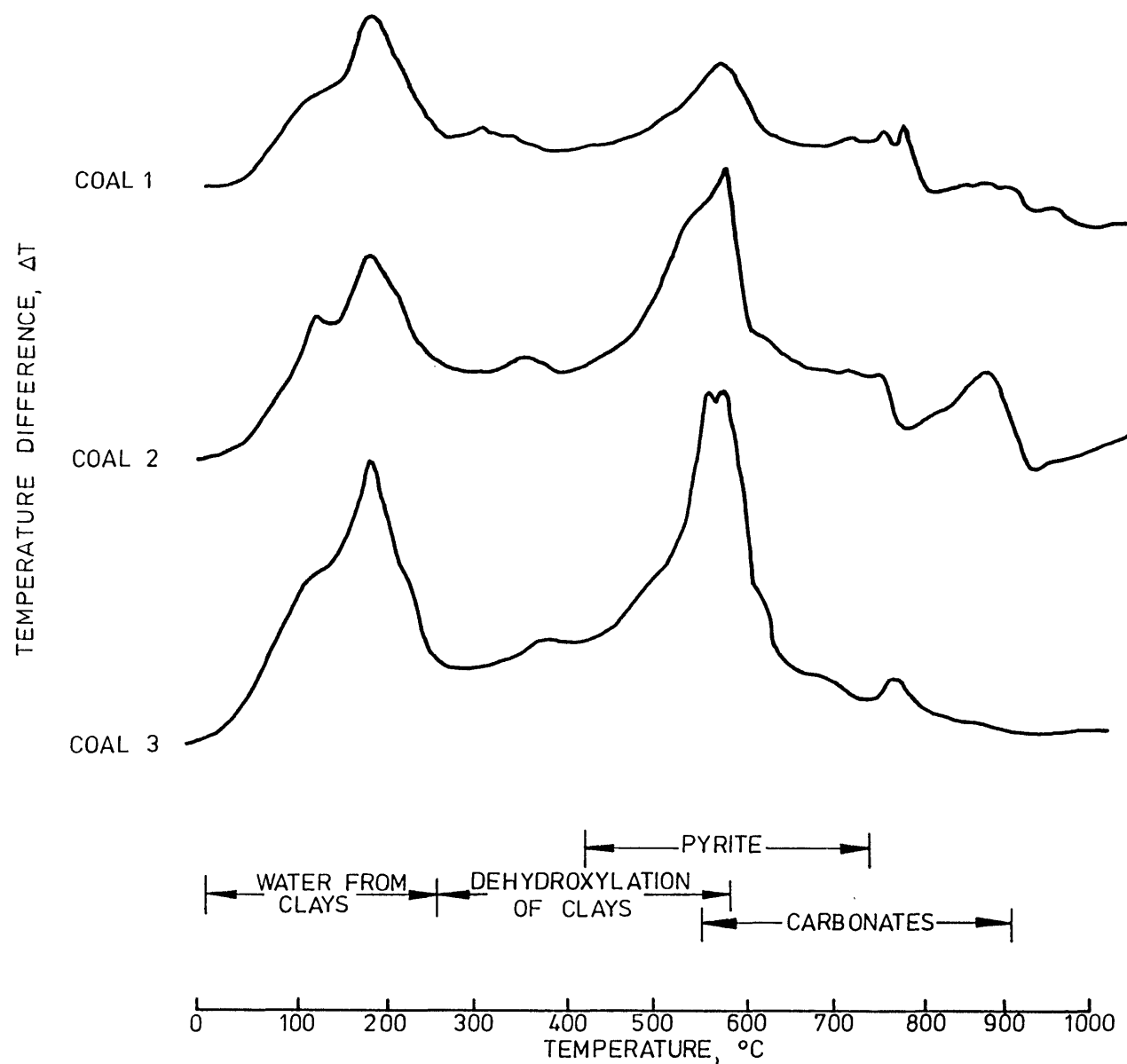


FIGURE 26. DIFFERENTIAL THERMAL ANALYSIS OF THE LOW TEMPERATURE ASHES
(IN NITROGEN).

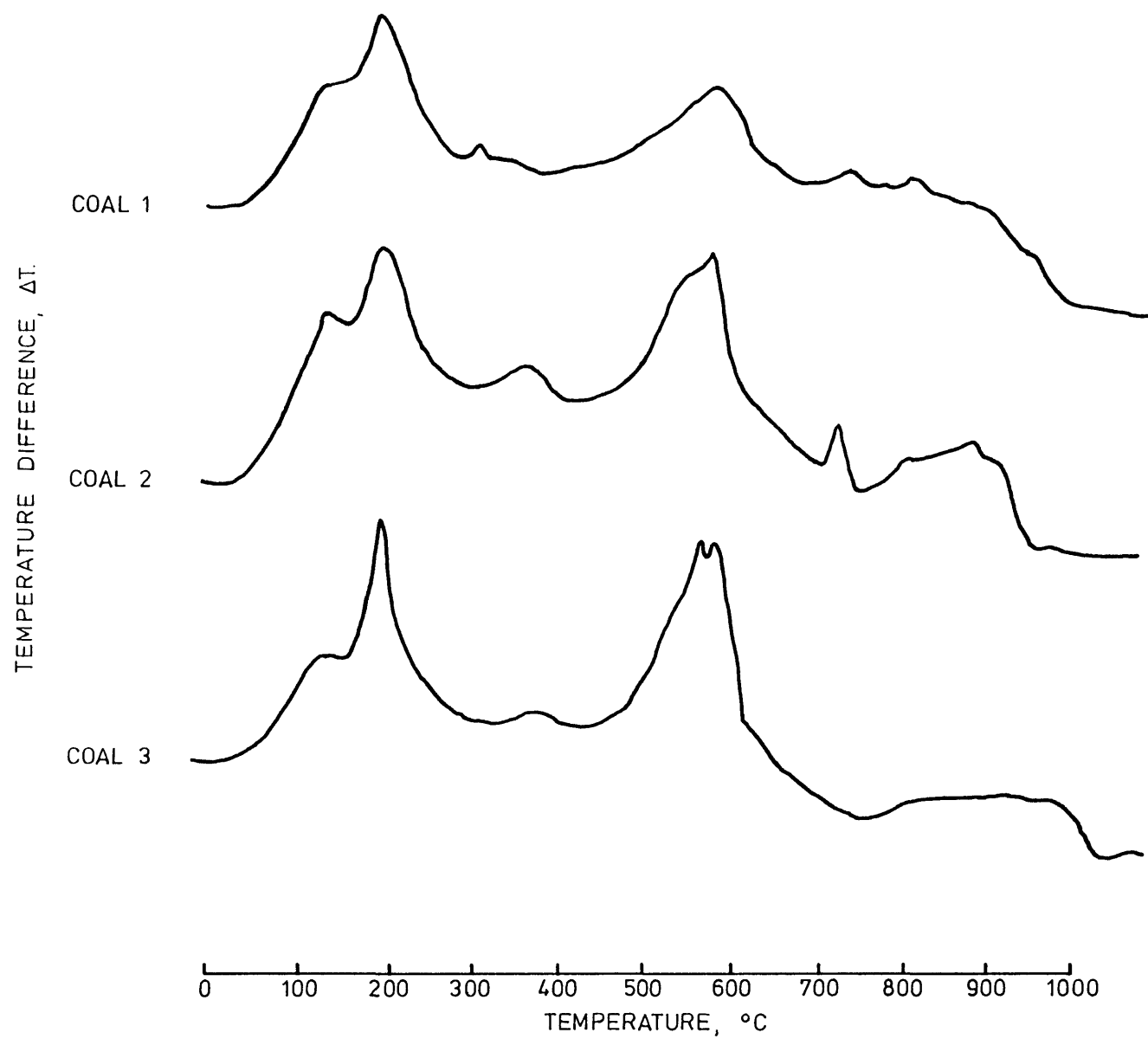


FIGURE 27. DIFFERENTIAL THERMAL ANALYSIS OF THE LOW TEMPERATURE ASHES
(IN CARBON DIOXIDE).

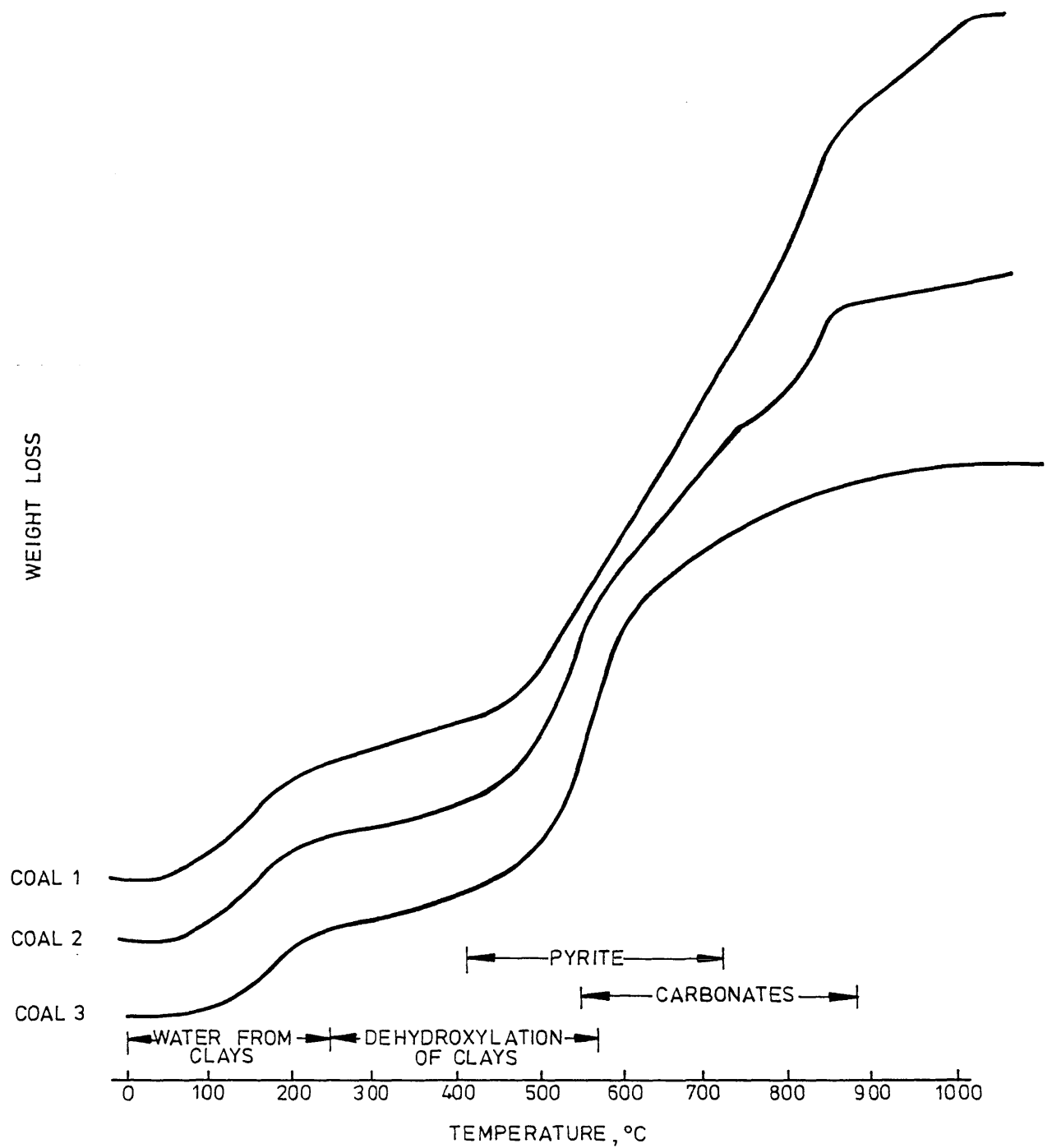


FIGURE 28. THERMAL GRAVIMETRIC ANALYSIS OF LOW TEMPERATURE ASHES.
(IN NITROGEN).

4.3.5 Infra-red spectroscopy

FT-IR studies have provided additional information on the mineral changes which can occur during low-temperature ashing. The major bands in the LTA spectra (Figure 29) are due to kaolinite. Application of the FT-IR technique of spectral subtraction to "remove" these bands can be difficult due to minor variations in the mineral structure of kaolinite and to the non-availability of appropriate mineral standards. Consequently identification of other mineral bands is limited. The relative intensity of the carbonate band at 1430 cm^{-1} confirms the compositional mineral trends in Tables 21 and 23. The additional band at 1180 cm^{-1} in the LTA spectrum of Coal 1 are due to inorganic sulphates. Comparison of the difference spectrum for Coal 1, as received and demineralised, with the LTA spectrum (Figure 30), indicates that mineral changes had taken place on ashing. The 1180 cm^{-1} band was negligible in the difference spectrum. The results suggest that during low-temperature ashing, reactions occur between organically associated cations i.e. the majority of sodium in the coals, and sulphur gases formed from the oxidation of organically bound sulphur, to form alkali sulphates. Sulphate determinations on the coal and its LTA have confirmed this and imply that fixation of other inorganic cations, as sulphate, also occur. Corresponding difference spectra for the lower sodium content Coals 2 and 3 show relatively little changes from their LTA. The spectra of the HTA showed marked changes from those of their LTA due to thermal degradation of the minerals and to reactions taking place between minerals during the high temperature ashing procedure.

4.3.6 Ash Fusion

Ash fusion data for the LTA are listed in Table 20 (Section 4.2.2). Interestingly, the LTA and HTA from each coal have practically identical ash fusion characteristics. Clearly the presence of ionisable salts and the lack of heat alteration of the insoluble minerals does not affect the high temperature behaviour under the conditions of the ash fusion test.

4.3.7 High-temperature microscopy

The results obtained for the melting behaviour of the LTA, as studied under the high-temperature microscope, are also given in

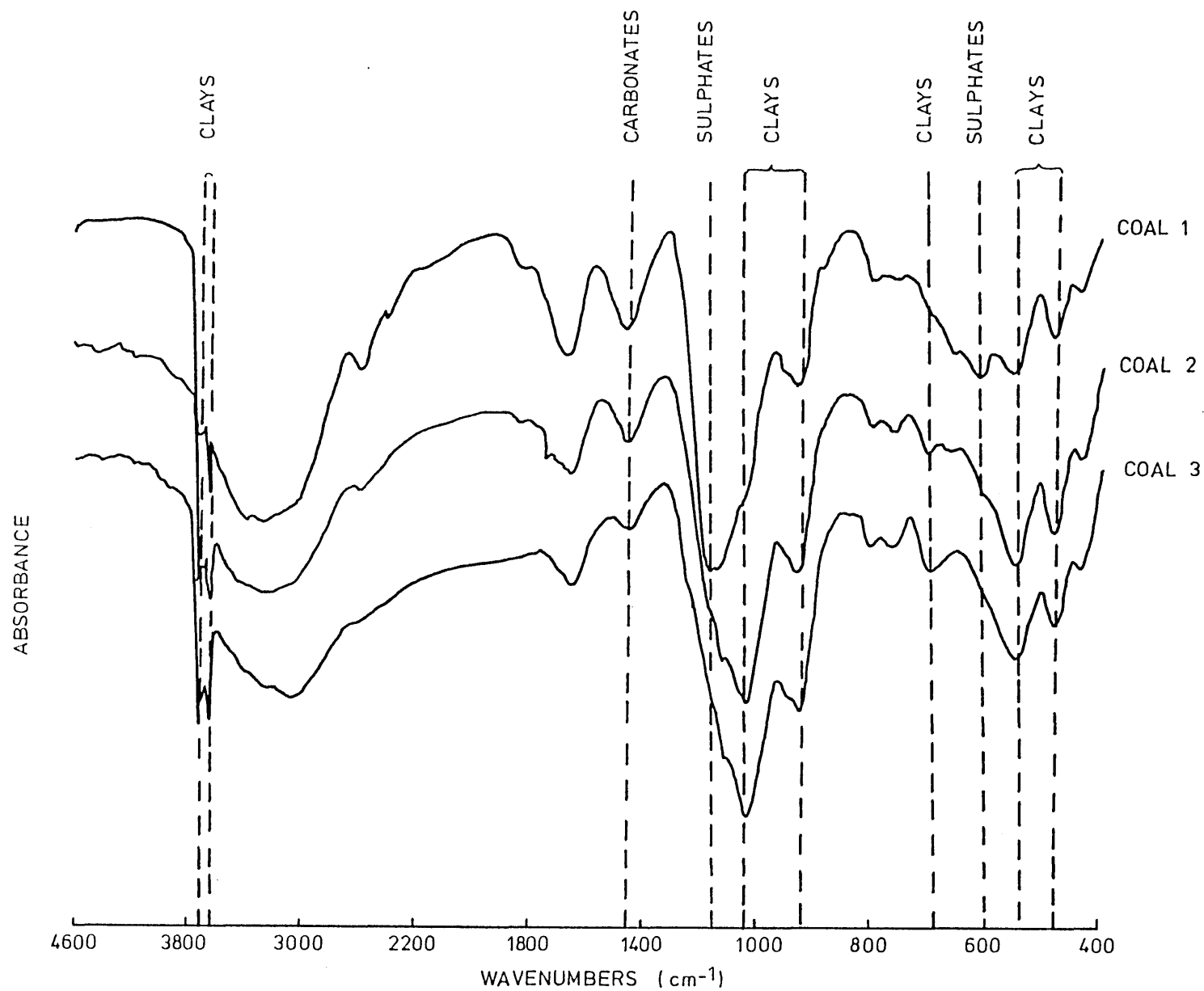


FIGURE 29. FTIR SPECTRA OF THE LOW TEMPERATURE ASHES.

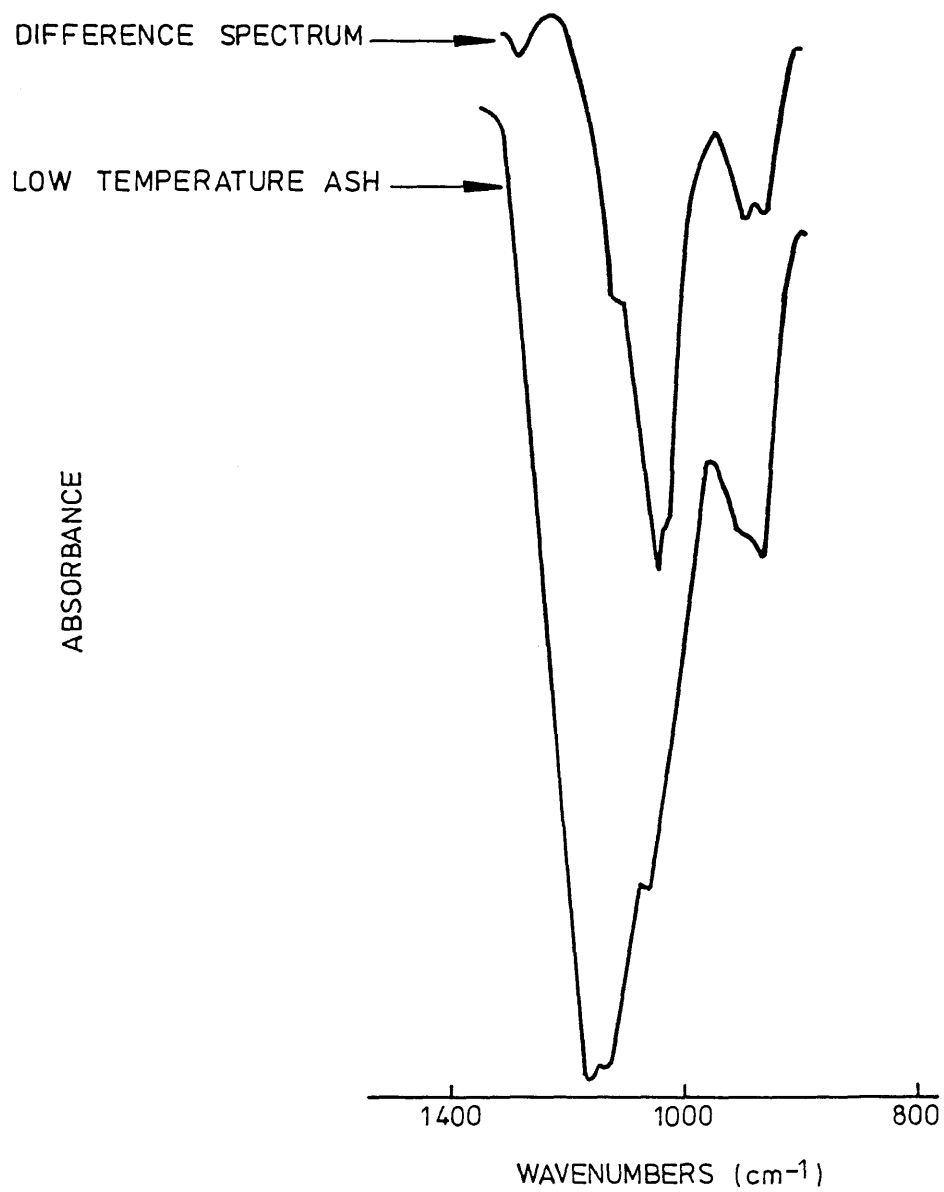


FIGURE 30 . FTIR SPECTRA OF COAL 1 MINERAL MATTER.

Table 20. The solidus temperature as determined by high-temperature microscopy provides a more accurate indication of the appearance of an initial liquid phase than the ash fusion deformation temperature. However duplicate analyses are required as the former only uses very small quantities of sample. Small variations in the melting characteristics of the LTA and HTA were considered to be insignificant.

4.3.8 Solid-state ^{23}Na nuclear magnetic resonance spectroscopy

The ^{23}Na MAS-NMR spectrum of the LTA from Coal 2 is shown in Figure 31. This also differs markedly from Figures 20 and 21, especially in the increased intensity of the sidebands. Thus the sodium environment is now much less symmetrical, even though the chemical shift of -7.3δ and width of 25 ppm are comparable to those of dried Coal 1.

The change in the spectra upon low-temperature ashing is consistent with the destruction of the original co-ordination sites and mineralisation of sodium into a variety of unsymmetrical sites.

4.4 Normative Analysis

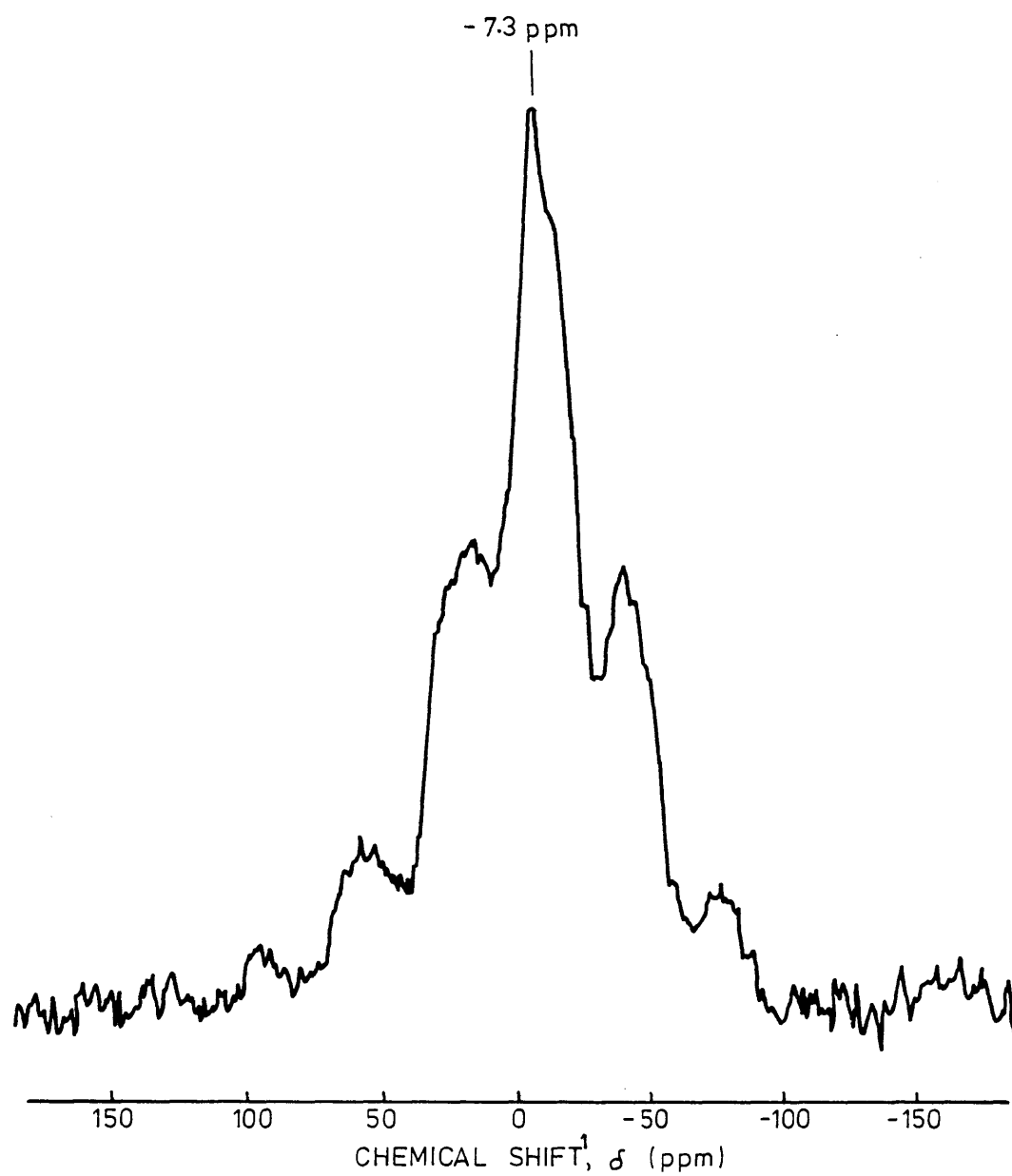
The concentrations of the respective minerals as calculated by the normative analysis method (20), are given in Table 23 (for details of the method see Appendix II).

Ankerite concentrations, calculated from the iron carbonate content of the LTA and the mineral matter content (Section 3.2.1), are 0.68, 0.84 and 0.5 wt % in Coals 1, 2 and 3 (a.d.) respectively and these compare favourably with those reported in Table 23. Corrections were made for the presence of other acetic acid soluble iron species in the LTA and for siderite in Coal 2. The concentration of quartz, calcite, ankerite/dolomite and kaolinite in the three coals are comparable with the XRD analyses (Table 21). The mica concentration of the mineral matter will have been underestimated by both methods. In the normative analysis procedure, the potassium content of muscovite was used for quantification purposes as the structure of illite (which contains less potassium and is the more likely mica constituent) has not been completely elucidated.

Table 23 Mineral Content of Coals 1, 2 and 3 Calculated by the Normative Analysis Method

% Mineral (air dried basis)	Coal 1		Coal 2		Coal 3	
	In coal	In mineral matter	In coal	In mineral matter	In coal	In mineral matter
Kaolinite	1.17	28.5	2.04	32.7	2.74	40.3
Mica	0.08	2.0	0.73	11.7	1.02	15.0
Calcite	0.49	12.0	0.20	3.2	<0.02	<0.15
Ankerite	0.73	17.8	0.94	15.0	0.46	6.8
Siderite	<0.01	<0.25	0.24	3.8	<0.01	<0.15
Dolomite	0.25	6.1	0.29	4.6	0.05	0.7
Pyrite	0.30	7.3	0.60	9.6	1.16	17.1
Quartz	<0.01	<0.25	0.26	4.2	0.43	6.3
Gypsum	0.11	2.7	0.11	1.8	0.16	2.4
Rutile	0.02	0.5	0.03	0.5	0.05	0.7
Apatite	0.04	1.0	0.10	1.6	0.03	0.4
Sodium (Calculated as Na ₂ SO ₄ in LTA)	0.51	12.4	0.30	4.8	0.35	5.1
% Total mineral matter (Normative analysis method)	3.72		5.84		6.47	
% Total mineral matter (Parr formula)	4.1		6.2		6.8	
% Total mineral matter (Direct - LTA procedure)	4.1		6.6		6.6	
% Total mineral matter (Direct - Acid leaching procedure)	ND		6.3		6.8	

ND - Not determined



1. REFERENCED TO $\text{Na}^+_{\text{aq}} = 0$, AT INFINITE DILUTION.

FIGURE 31. ^{23}Na MAS-NMR SPECTRUM OF LTA FROM COAL 2.

The concentrations of pyrite, mica, kaolinite and quartz increase from Coal 1 to 3 whilst calcite, dolomite and sodium (calculated as sulphate) decrease.

The total concentration of mineral matter calculated from the normative method and determined by the Parr (175) formula compare favourably.

Normative analysis can only be considered as yielding hypothetical mineralogical compositions as it is often difficult to ascribe entirely certain elements to specific minerals. The procedure is unable to account for substitution and solid solutions.

4.5 Fouling and Slagging Parameters

Numerous indices (157) have been used for judging the quality of coal with respect to furnace fouling and slagging. The most widely accepted indices are the slagging factor, R_s , and fouling factors, R_f and R_f' . Details of these parameters are given in Appendix III.

Coal 1 has a lignitic type ash and Coals 2 and 3 bituminous type ashes. Consequently R_s and R_f are only applicable to Coals 2 and 3. R_f' , based solely on the sodium oxide content of the HTA is thought to be more applicable to Coal 1.

The results obtained for the three coals (Table 24) indicate that Coal 3 exhibits the lowest fouling and slagging tendencies. These data correspond with the reported behaviour of these coals in industrial combustion trials.

The extent of fouling and slagging during coal combustion is governed by combustor design and mode of operation in addition to the nature of the fuel. The variety and complexity of the interdependence of the operational factors make these effects difficult to study and quantify. Consequently, it is not always possible to determine the exact cause of any slagging or fouling problems. Coals will, however, have characteristic inherent slagging and fouling propensities which, in the form of indices may be used to establish a broad ranking of coal ash deposition behaviour.

It should be noted, however, that no single index or combination of indices has been sufficiently proven to date to be an accurate guide to the fouling and slagging propensity of an unfired coal.

Table 24 Slagging and Fouling Parameters

Coal	Slagging Factor Rs	Predicted extent of slagging	Fouling Rf	Factors Rf'	Predicted extent of fouling
1	NA	-	NA	7.1	Severe
2	0.7	Medium	1.6	NA	Severe
3	0.6	Low/Medium	1.0	NA	High

NA - Not applicable

4.6 Summary of Characterisation of Coal and Ashes

The three coals studied have been shown to be of similar rank, Coal 3 being slightly higher. Examinations suggest that the coals contain the same salts and minerals which vary in their relative proportions. Increasing ash fouling and corrosion propensities of the coals correlate with increasing chlorine, sodium and calcium contents.

Although no single analytical technique has yielded a comprehensive component analysis of the total mineral matter, an order for their abundance has been established. XRD, FT-IR and thermal analysis of the LTA have shown that the most abundant mineral components are the kaolinite and mica groups of aluminosilicates, quartz, pyrite and the carbonates, calcite, dolomite and ankerite. These and smaller concentrations of gypsum, rutile, apatite, siderite and sodium (as sodium sulphate) have been quantified by normative analysis, XRD and other chemical methods. All methods gave comparable results; the most comprehensive being normative analysis.

A number of trends for the mineral composition of the three coals have been established. The relative proportions of kaolinite, mica, pyrite and quartz are seen to increase from Coal 1 to 3 whilst those of dolomite, ankerite and calcite decrease.

Solid state NMR and microscopic examinations have yielded useful information as to the nature of sodium and aluminium, and the distribution of pyrite. The majority of pyrite in the three washed coals is intimately associated with the coal macerals (syngenetic); appearing most abundantly as fine concretions and framboids (<40 μm diameter).

The nature and amounts of ionisable salts isolated from the finely ground coals by boiling water has been quantified. The major ions which can be aqueously extracted from the coals are Na^+ , K^+ , Ca^{2+} , Mg^{2+} , Cl^- and SO_4^{2-} . Fine grinding enhances the release of the salts and enables significant proportions of the inorganic mineral matter to be removed; 34, 18 and 10 wt.% for Coal 1, 2 and 3 respectively. Virtually all the Na^+ and Cl^- can be leached from the coals and a high proportion of Ca^{2+} can also be removed. Sodium and chlorine appear to be present in the coals as ions attached to surfaces within the coals porous structure. The greater porosity of Coal 1 enhances the ability to adsorb Na^+ and Cl^- on the coal surface which presumably can be correlated to the potential volatility of these elements during combustion and to their fouling tendencies.

The empirical fouling and slagging parameters calculated for the coals are also consistent with their observed fouling and slagging trends.

The ash fusion and high-temperature microscopy results show that the ashes from Coals 1 and 2 fuse and flow at lower temperatures than those for Coal 3.

5. CHARACTERISATION OF DEPOSITS FORMED DURING FLUIDISED BED COMBUSTION

5.1 Effects of Varying Fluidised Bed Combustion Parameters

5.1.1 Probe surface temperature

The influence of deposition temperature on the mass of dilute acid soluble sodium, potassium, calcium, magnesium, chloride and sulphate deposited per m^2 are reported in Tables 25 to 27 and shown graphically in Figures 32 to 34.

Blank values obtained for these ions, from probe washings of experiments carried out under similar conditions, in which no coal was combusted, were all $<0.1 \text{ gm}^{-2}$. Duplicate analyses typically varied by $<20\%$ and showed that repeatable values could be obtained providing conditions in the combustor remained relatively constant. The majority of the results reported are averages and all graphs showing deposition concentrations as a function of temperature, represent smoothed data. Ion balances for the monitored elements in the deposits are reasonable (typical % imbalance $<20\%$), showing that contributions from other ions are relatively minor.

The major dilute acid soluble components of the initial deposits are chlorine, sulphate, sodium, potassium, calcium and to a lesser extent magnesium. The deposits from Coal 1 were significantly richer in these components than those from either Coal 2 or Coal 3 (Figures 32 to 34). Maximum deposition occurred at probe surface temperatures of between 500°C and 650°C ; $\sim 30^\circ\text{C}$ higher for sulphate ions than for chlorides, for Coal 1.

Electron micrographs of the initial deposits formed at 600°C (together with EDX analyses) show the relatively heavy deposits formed by Coal 1 (Figures 35 to 38) to be predominantly crystalline, consisting of cubic crystals of sodium, potassium and calcium chlorides and 'rectangular' (monoclinic) crystals of calcium and sodium sulphates. Calcium chloride and potassium sulphate were also detected. Interestingly a high proportion of the cubic crystals had rounded edges suggesting a partially fused state and were firmly attached to the probe surface (Figure 35). Figure 37 illustrates the important role that sodium and potassium chloride, and to a lesser extent calcium and sodium

Table 25 Deposition of Soluble Sodium, Potassium, Calcium, Magnesium, Chloride and Sulphate from Coal 1

Deposition Temperature, °C	DEPOSIT CONTENT, $\text{gm}^{-2} \times 10^{-2}$					
	Na	K	Ca	Mg	Cl	SO ₄
435	45	<10	30	<10	35	130
560	110	80	50	<10	90	405
515	260	150	275	15	220	760
550	330	145	490	30	320	1,150
565	350	160	675	35	430	1,350
575	390	125	690	40	300	1,470
610	440	100	615	45	125	1,500
620	410	90	555	45	140	1,215
625	375	80	520	45	125	1,165
640	330	70	345	15	65	1,040
685	215	40	40	<10	<10	630
710	50	<10	<10	<10	<10	185

Table 26 Deposition of Soluble Sodium, Potassium, Calcium, Magnesium, Chloride and Sulphate from Coal 2

Deposition Temperature, °C	DEPOSIT CONTENT, $\text{gm}^{-2} \times 10^{-2}$					
	Na	K	Ca	Mg	Cl	SO ₄
410	20	15	<10	<10	<10	15
460	40	15	<10	<10	<10	110
465	50	15	<10	<10	<10	90
470	60	40	<10	<10	10	70
515	60	40	10	10	15	85
525	105	20	10	10	20	165
590	65	30	<10	<10	25	120
650	80	40	10	<10	10	120
705	35	40	10	<10	10	35
720	65	<10	<10	<10	<10	130
735	50	15	<10	<10	<10	80

Table 27 Deposition of Soluble Sodium, Potassium, Calcium, Magnesium, Chloride and Sulphate from Coal 3

Deposition Temperature, °C	DEPOSIT CONTENT, $\text{gm}^{-2} \times 10^{-2}$					
	Na	K	Ca	Mg	Cl	SO ₄
435	<10	<10	<10	<10	<10	<20
460	<10	<10	<10	<10	<10	<20
515	35	20	<10	<10	15	80
550	40	30	<10	<10	20	95
565	50	35	<10	<10	20	130
575	55	40	<10	<10	20	160
610	60	40	10	<10	15	175
620	60	40	10	<10	15	165
625	60	35	10	<10	15	160
640	50	30	<10	<10	15	140
685	25	20	<10	<10	10	80
710	15	10	<10	<10	<10	50

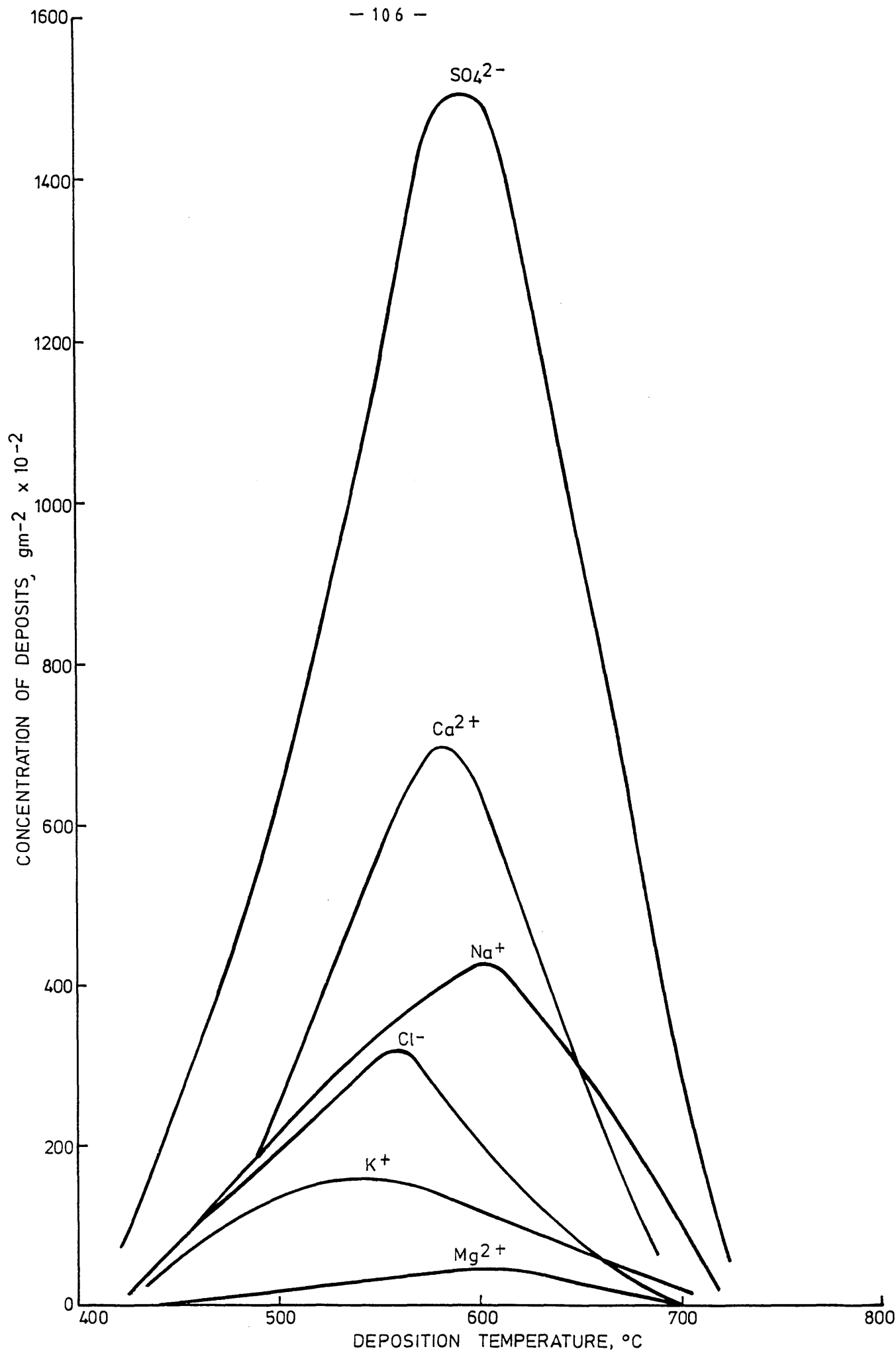


FIGURE 32. DEPOSITION OF SOLUBLE SODIUM, POTASSIUM, CALCIUM, MAGNESIUM, CHLORIDE AND SULPHATE FROM COAL 1.

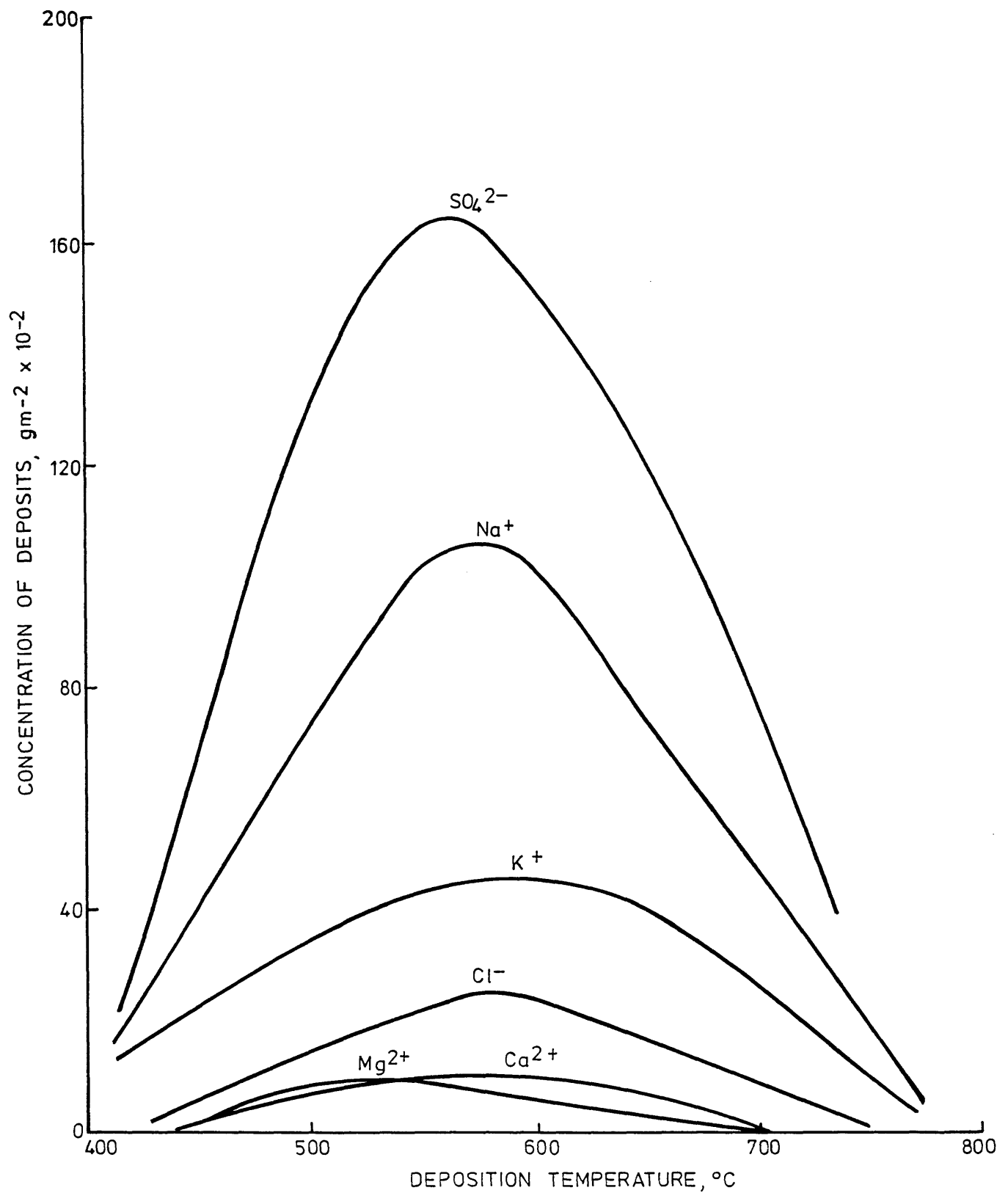


FIGURE 33. DEPOSITION OF SOLUBLE SODIUM, POTASSIUM CALCIUM
MAGNESIUM, CHLORIDE AND SULPHATE FROM COAL 2

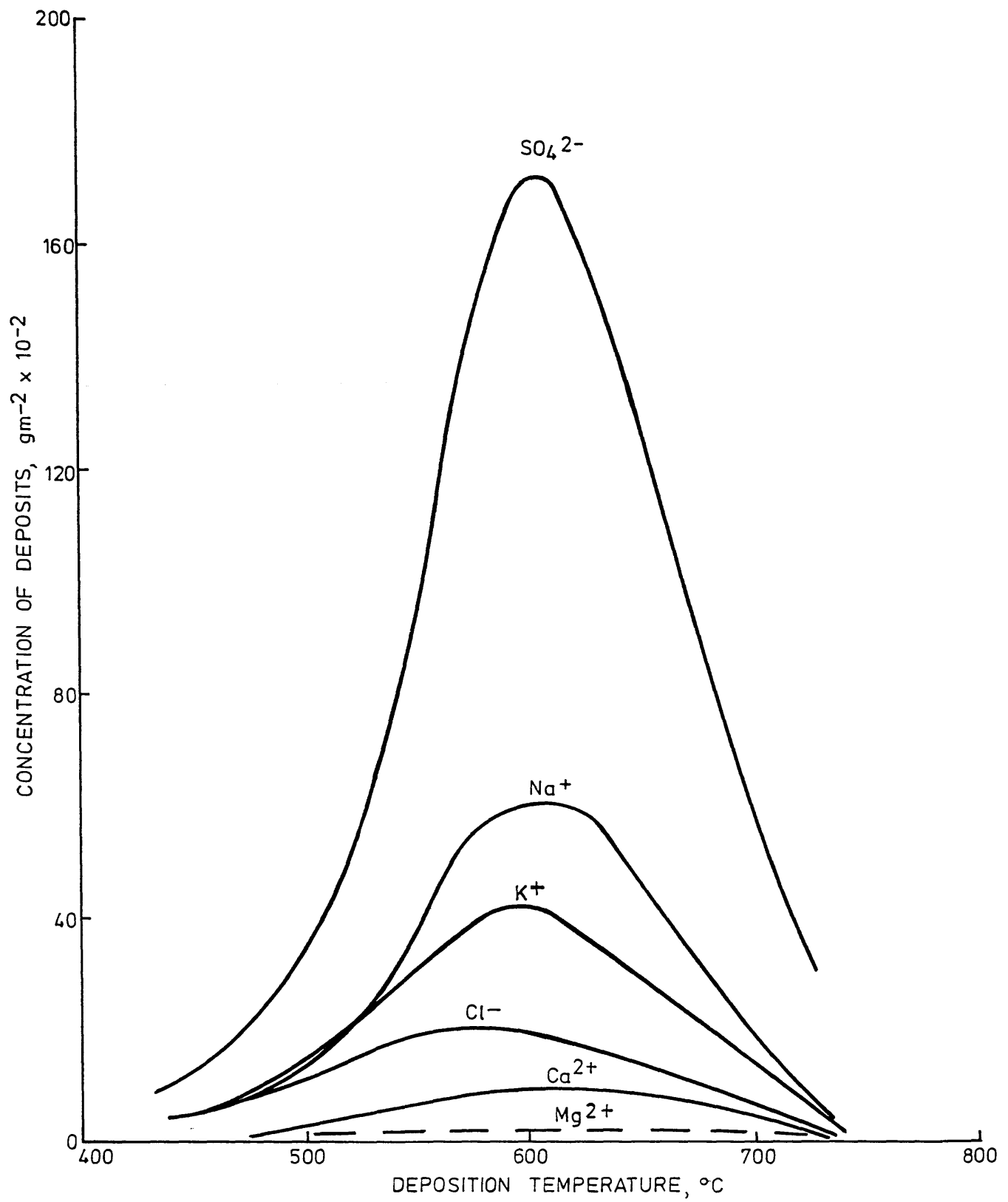


FIGURE 34. DEPOSITION OF SOLUBLE SODIUM, POTASSIUM, CALCIUM, MAGNESIUM, CHLORIDE AND SULPHATE FROM COAL 3.

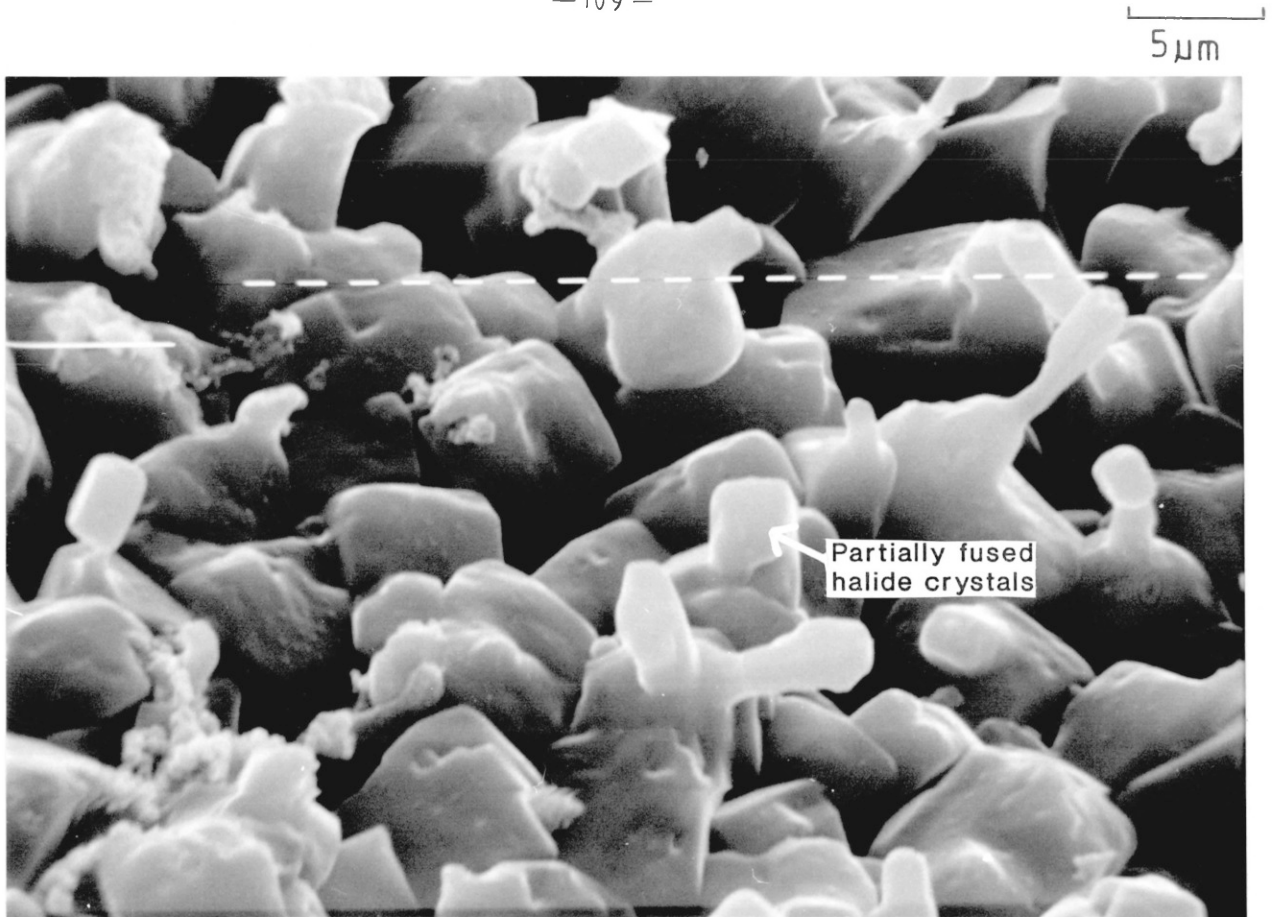


Figure 35. Electron Micrograph of Deposit from Coal 1 showing predominantly Cubic Crystals of NaCl and KCl.

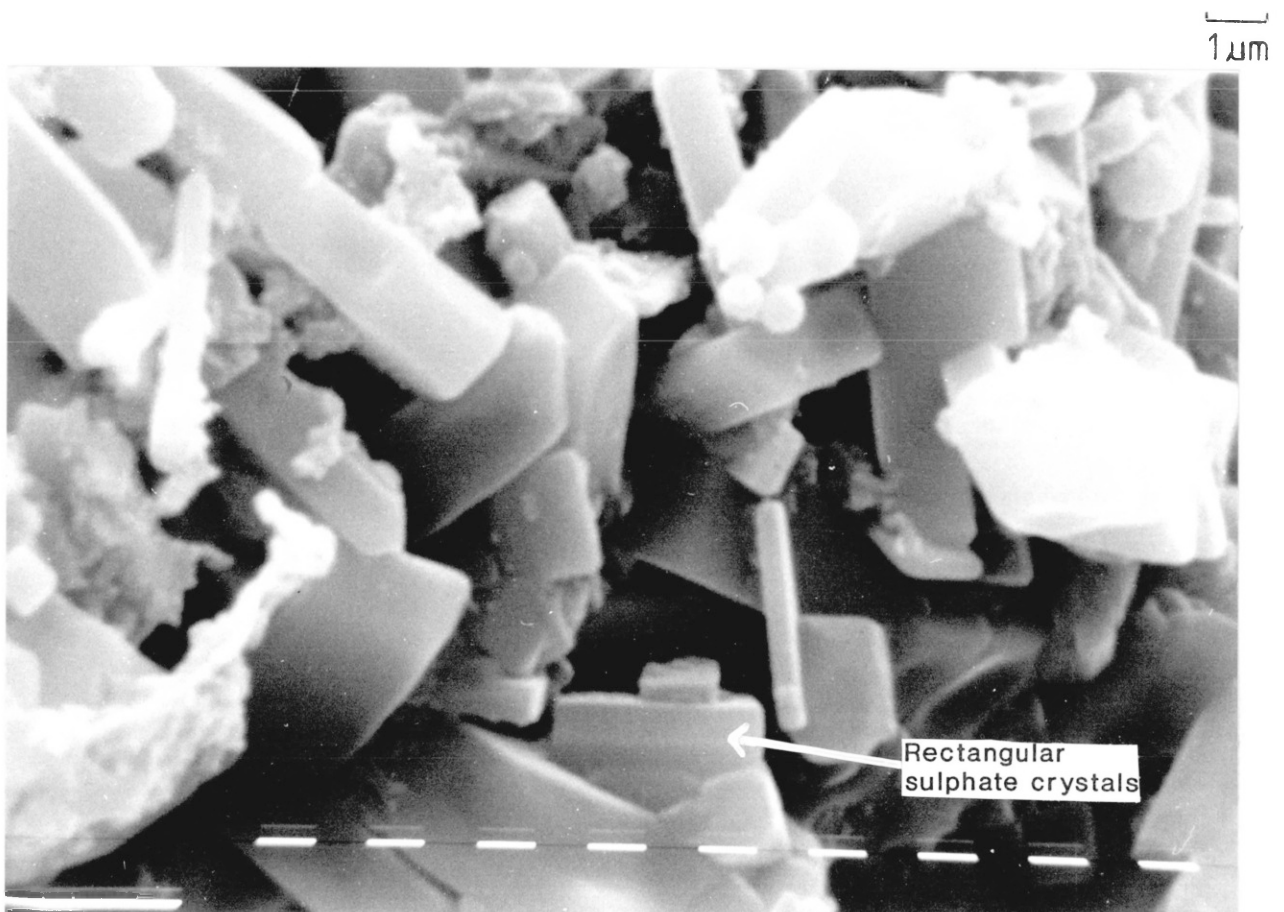


Figure 36. Electron Micrograph of Deposit from Coal 1 showing "Rectangular" Sulphate Crystals.

10µm

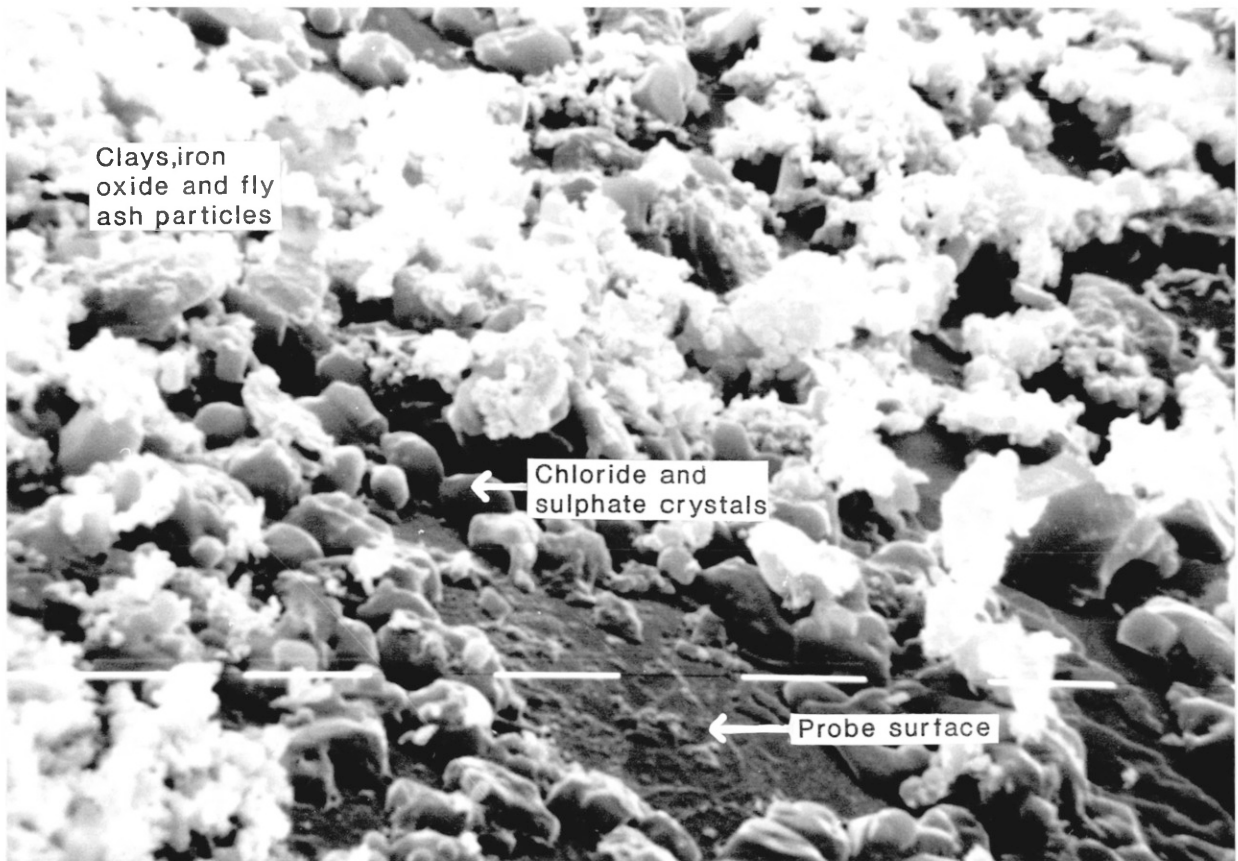


Figure 37. Electron Micrograph of Deposit from Coal 1 showing deposit build up on the probe surface.

10µm

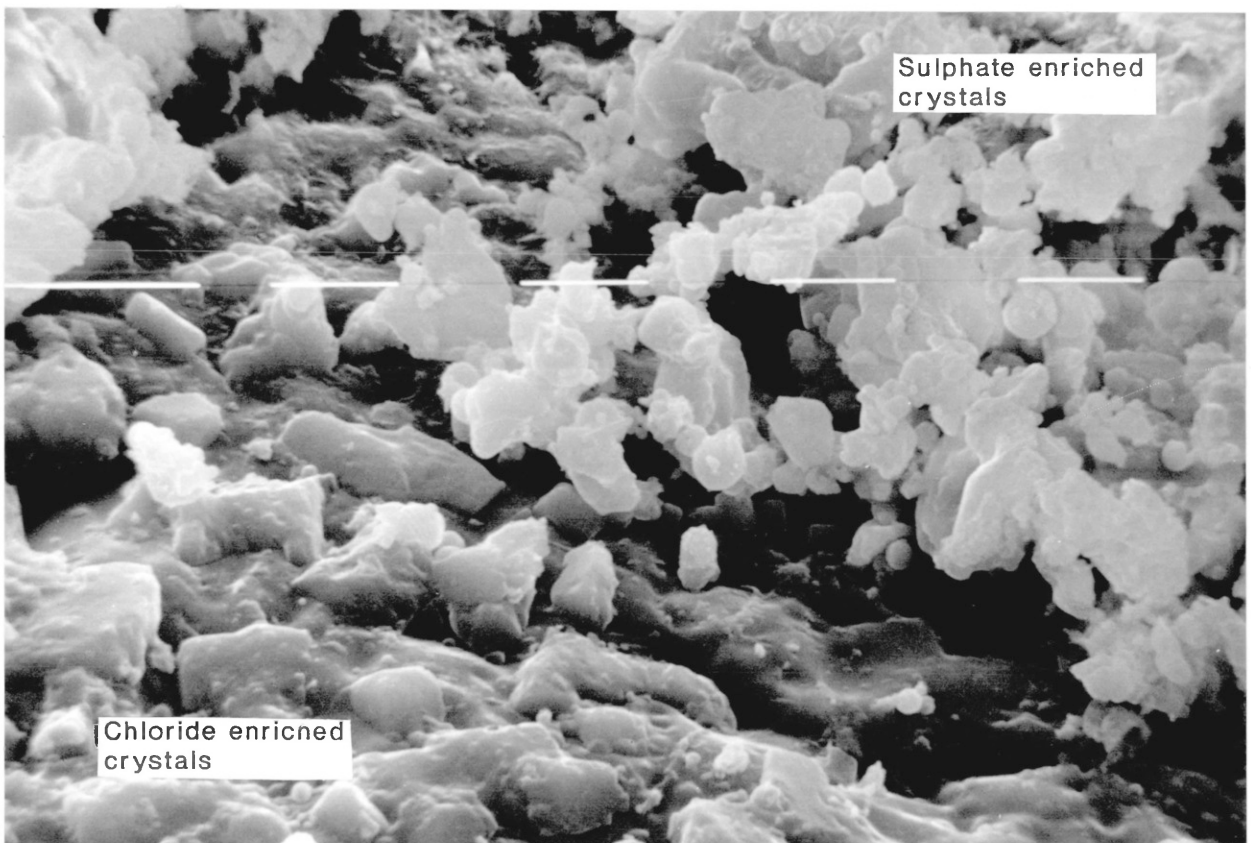


Figure 38. Electron Micrograph of Semi-Fused Deposit from Coal 1.

sulphate crystals play in forming an initial sticky deposit which provides a surface on which gas borne particulates, such as clays and iron oxides, can adhere. In contrast, the lighter deposits from Coals 2 and 3 (Figures 39 and 40) lacked crystallinity and consisted typically of friable, loosely adhering particles of dehydrated clays, iron oxides and fly ash.

These results suggest that reactions occur between the alkali-containing coal minerals and gaseous combustion products during combustion of the higher chlorine, sodium and calcium content coal, Coal 1, to form volatile salts. These salts, and possibly low melting point eutectics, can condense in the cooler regions of the combustor and act as an adhesive layer for impinging gas borne particulates, causing the build-up of deposits.

Sodium is largely present in Coal 1 as ions associated with the coal matrix, potassium predominantly in association with the insoluble micaceous clays and calcium and magnesium as carbonates. Hydrogen chloride, evolved during combustion, can react with these compounds or their decomposition products to form volatile chlorides (Section 2.5.1). The volatile chlorides can themselves undergo chemical reactions with gaseous sulphur oxides to form sulphates. Such changes can occur by gaseous reactions in the freeboard or at convenient surfaces e.g. probes, fly ash particles.

Keairns et al (115) reported that 10 to 50% of the total sodium present in coal can be released into the gaseous phase during FBC. This would correspond to sodium chloride vapour concentrations of between 20 and 90 ppm for Coal 1. Assuming the extent of conversion to sulphate, at 850°C, is more than 90% (Figure 6) the corresponding vapour concentration of gaseous sodium sulphate would be 20 to 100 ppm. These levels are well above the estimated vapour saturation concentrations of sodium sulphate (0.05 ppm, Section 2.5), suggesting that sodium occurring as sulphate, will be present predominantly as a condensed species.

The perfect form of the 'rectangular' sulphate crystals (Figure 36) collected on probes suggest such gaseous phase reactions, with subsequent direct condensation of the crystals

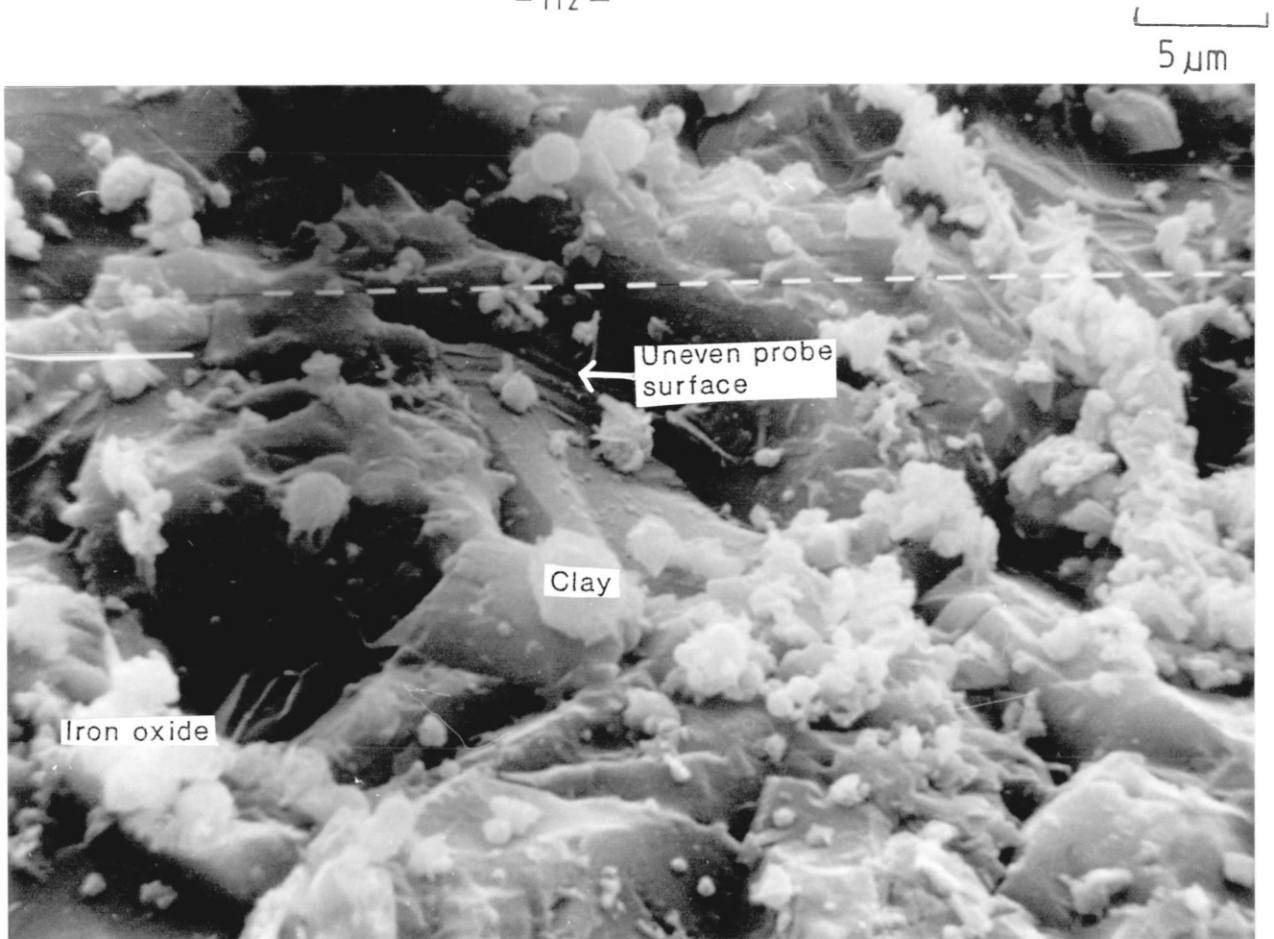


Figure 39. Electron Micrograph of Typical Deposit from Coal 2 showing particles of clays, iron oxide and flyash loosely adhered to the surface.

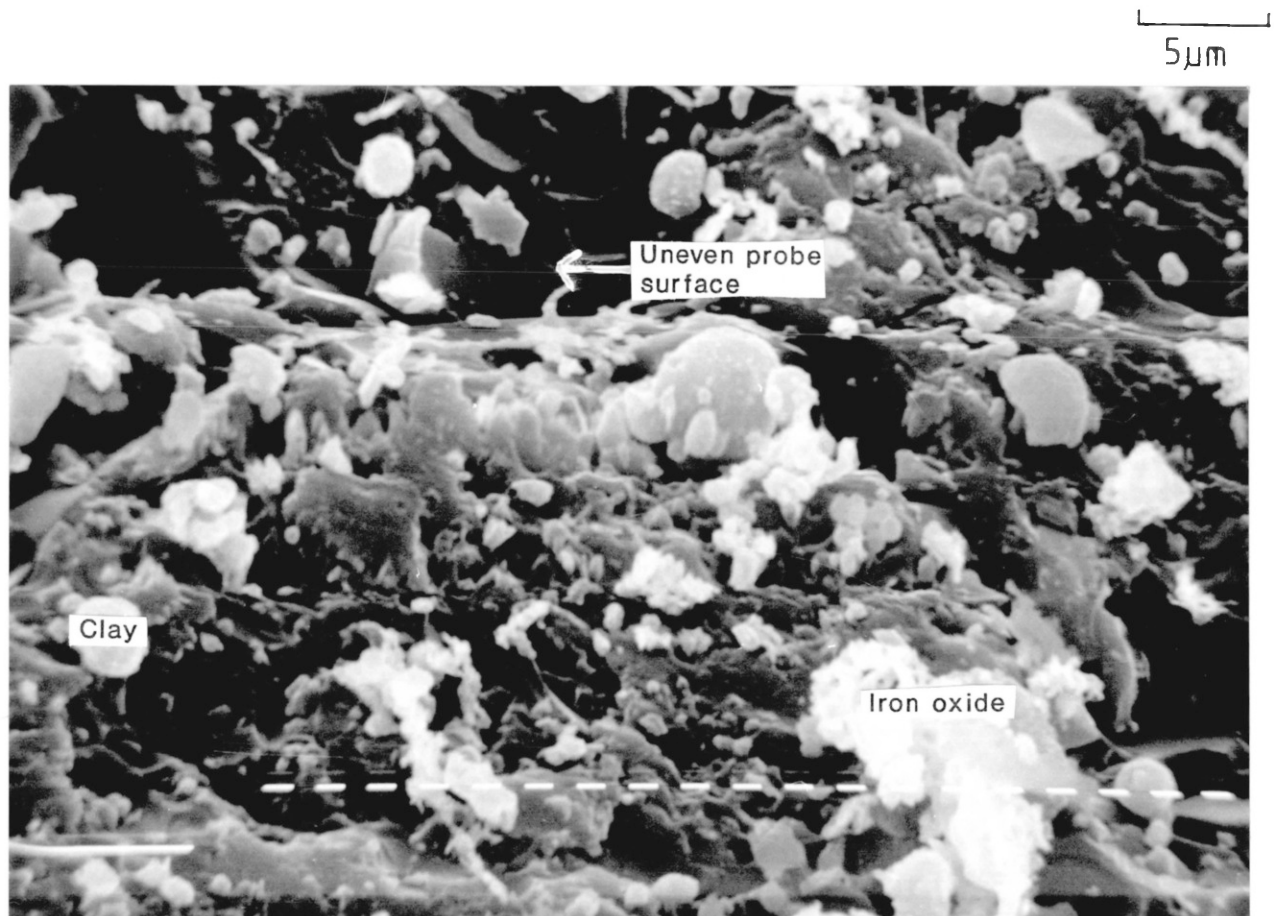
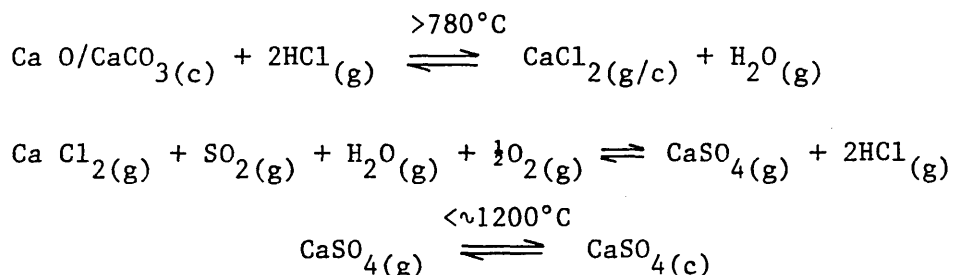


Figure 40. Electron Micrograph of Typical Deposit from Coal 3 showing particles of clays, iron oxide and flyash loosely adhered to the surface.

from the gas phase onto the cooled probes, may be a major reaction mechanism.



g = gas phase
c = condensed phase

Condensation from the vapour to a solid or liquid phase is dependent on deposition, bed and nucleation threshold temperatures and on the melting points of the condensing species (180). As the deposition temperatures (450 to 750°C) are lower than the melting points of the majority of alkali chlorides and sulphates, direct condensation to a solid would be expected.

Phase diagrams for systems containing NaCl, KCl, CaCl₂, Na₂SO₄, K₂SO₄, CaSO₄ (Figure 41) (181), however, indicate that eutectic mixtures of chlorides can occur with liquids present as low as 500°C, e.g. system NaCl - KCl - CaCl₂. Melting in sulphate-chloride mixtures occurs at higher temperatures, >520°C. This presumably accounts for the partially fused form of the halide crystals and for the slightly higher maximum deposition temperatures for sulphate (Figure 32).

The condensation mechanism can involve (a) nucleation of minute crystals of alkali salts on the probe surface with subsequent growth directly from the gas phase and/or (b) solidification of the volatile salts in the flue gases approaching cooler zones in the combustor. Deposition by the latter mechanism would be dependent on the melting point of the condensing species, the probe temperature and on the presence of an initial, partially fused, adhesive layer.

The extent of crystal growth for the two mechanisms will differ. Microscopic observations indicate that the majority of alkali chloride and sulphate crystals lie in the range <1 to 10 μm, however some calcium sulphate crystals >20 μm diameter were also

KCl-NaCl-CaCl₂

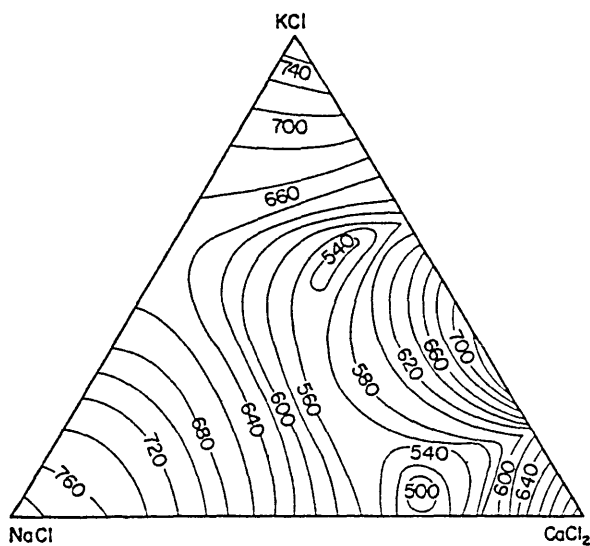


FIG. 1410.—System KCl-NaCl-CaCl₂.

F. C. A. H. Lantsberry and R. A. Page, *J. Soc. Chem. Ind.*, 39, 40T (1920).

KCl-NaCl-CaSO₄

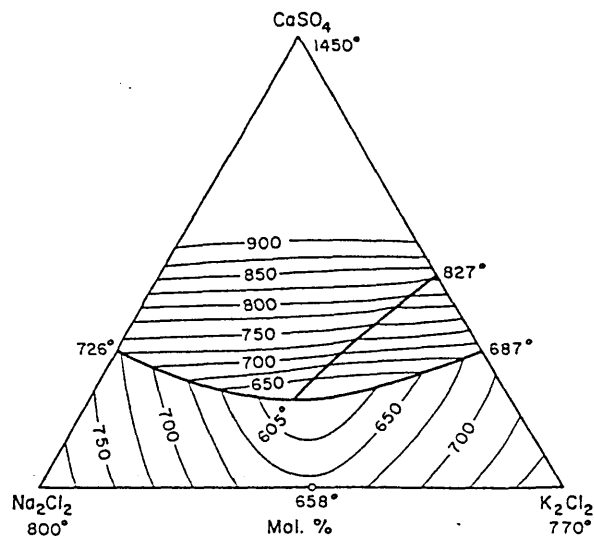


FIG. 1779.—System KCl-NaCl-CaSO₄.

V. V. Rubleva and A. G. Bergman, *Zhur. Obshchei Khim.*, 26, 654 (1956).

KCl-NaCl-K₂SO₄-Na₂SO₄

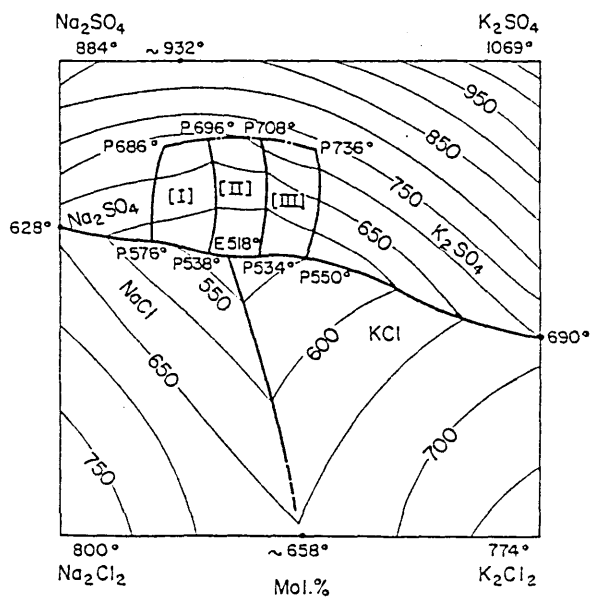


FIG. 1789.—System KCl-K₂SO₄-NaCl-Na₂SO₄. [I], [II], and [III] are unknown interior phases.

E. K. Akopov and A. G. Bergman, *Zhur. Neorg. Khim.*, 4 [7] 1655 (1959).

KCl-CaCl₂-K₂SO₄-CaSO₄

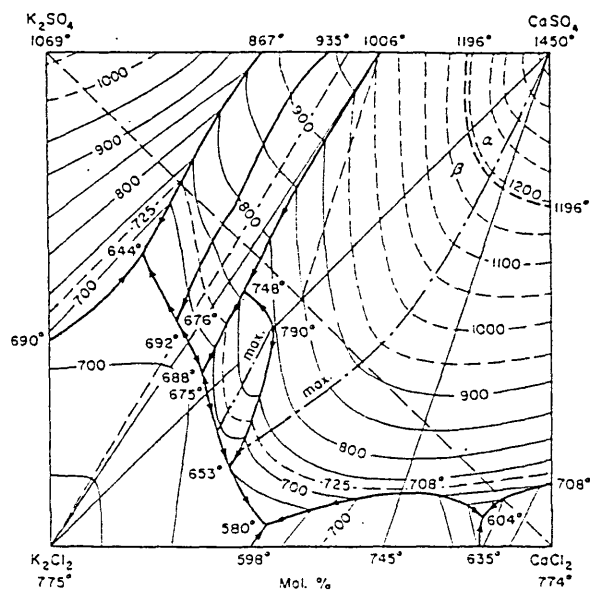


FIG. 1790.—System KCl-K₂SO₄-CaCl₂-CaSO₄; reciprocal.

M. S. Golubeva and A. G. Bergman, *Zhur. Obshchei Khim.*, 26, 330 (1956).

FIGURE 41. PHASE DIAGRAMS FOR NaCl, KCl, CaCl₂, Na₂SO₄, K₂SO₄, CaSO₄ SYSTEMS.

present. This suggests that both condensation mechanisms probably occur and will be dependent on concentrations, temperatures, favourable nucleation sites/orientation for growth and the presence of an initial sticky deposit. The higher melting point sulphate crystals appear to favour the former condensation mechanism whilst alkali halides mainly seem to deposit as small (1-10 μm), partially fused, crystals.

Deposition appears to be highly temperature dependent (Figures 32 to 34). At lower deposition temperatures, $<400^{\circ}\text{C}$, the salts presumably will not be semi-molten, whilst at higher temperatures, $>800^{\circ}\text{C}$, differences between bed and deposition temperatures may be insufficient for significant condensation to occur.

The observations that the majority of calcium in the deposit is present as sulphate is consistent with the thermodynamic data obtained for the reactions between gaseous alkali chlorides and sulphur dioxide (Section 2.5.2, Figure 7). Calcium sulphate formation is the more favourable, with changes in free energy values for the reaction becoming increasingly more negative at lower temperatures.

The proportion of potassium deposited from Coal 1 is much higher than from Coals 2 or 3 which contain higher initial concentrations of this element (Table 19 and Figures 32 to 34). Potassium associated with insoluble micaceous clays is normally considered to be non-volatile at combustion temperatures of up to 850°C . The results suggest that the high concentration of sodium (and chlorine) in Coal 1 may influence the release of potassium, possibly by interstitial exchange reactions within the dehydrated clay structure. Further studies were carried out, using a bomb calorimeter, to investigate the behaviour of these alkalis during combustion (Section 5.4).

The initial salt rich deposits did not appear to have been formed to any significant extent in the case of the lower chlorine, sodium and calcium content coals, 2 and 3. The release and deposition of sodium and calcium may be influenced by the relatively higher concentrations of sulphur and clay minerals present in Coals 2 and 3, possibly being retained in the bed

incorporated within clay structures or as less volatile sulphates. The effect of varying combustion parameters on the nature (chemical composition) and extent of initial deposit formation has therefore been concentrated on the use of Coal 1.

5.1.2 Bed temperature

Deposition concentrations of soluble sodium, potassium, calcium, magnesium, chloride and sulphate from Coal 1 are reported in Table 28 and illustrated graphically in Figure 42a to d. Chemical and microscopic analyses (Figure 43) showed the nature of the deposits obtained from the combustion of Coal 1 at temperatures of 850°C or above were similar. Calcium, sodium and potassium chlorides and sulphates were the major species present with smaller amounts of iron oxides and clays. The abundance of Na^+ , Ca^{2+} , Mg^{2+} and SO_4^{2-} (in particular Ca^{2+} and Mg^{2+}) in the deposits collected at the highest bed temperature of 925°C was noticeably increased (Figures 42a to d).

The temperatures of the individual char particles containing the alkalis will exceed the bed temperature by several hundreds of degrees. Vapour pressure data (Section 2.5.1) indicates that significant concentrations of these salts will be volatile at these temperatures ($\sim 1 \times 10^{-2}$ atms. at 1000°C for NaCl and KCl); their volatility increasing at higher combustion temperatures. Deposition of K^+ and Cl^- did not appear to be significantly affected by an increase in bed temperature.

The insignificant increase in chloride species detected at the higher bed temperatures may be due to the position of the probes in the freeboard with the gaseous alkali chlorides having a greater opportunity to react with the gaseous sulphur oxides.

Although potassium probably volatilises as its chloride, the mechanism of release of potassium from the micaceous clays, possibly by alkali exchange reactions, may not be significantly affected by increases in combustion temperatures of the order used, i.e. 850°C - 925°C.

5.1.3 Coal feed rate

Operation at the higher feed rates produced dirty (high carbon content fly ash) and less stable combustion conditions. Carbon dioxide contents of the flue gases rose from ~8% to ~11.5% with a subsequent lowering of oxygen levels from ~9% to ~3.5%.

Table 28 Deposition of Soluble Sodium, Potassium, Calcium, Magnesium, Chloride and Sulphate from Coal 1
Combusted at Bed Temperatures of 875°C, 900°C and 925°C

Deposition Temperature, °C	DEPOSIT CONTENT, gm ⁻² x 10 ⁻²					
	Na	K	Ca	Mg	Cl	SO ₄
<u>Red Temperature, 875°C</u>						
440	45	30	110	<10	85	220
500	100	85	365	15	190	460
520	200	170	580	45	290	895
570	290	145	760	70	280	1,070
605	330	110	910	80	200	1,850
630	435	150	950	110	215	2,030
685	345	60	520	30	45	1,220
725	195	<10	60	<10	<10	540
<u>Bed Temperature, 900°C</u>						
430	90	120	390	35	295	330
455	140	80	160	<10	265	150
500	280	180	265	30	390	300
525	410	205	400	50	720	475
570	470	140	540	65	700	700
590	450	115	1,110	185	415	1,295
605	350	110	1,250	195	320	1,800
645	390	110	860	190	290	1,955
710	230	30	410	30	15	905
750	200	<10	110	<10	<10	440
<u>Bed Temperature, 925°C</u>						
450	100	55	200	35	210	265
500	160	50	460	50	210	570
520	200	70	580	85	265	820
550	210	100	640	70	210	1,050
590	370	120	1,200	165	520	2,230
620	550	140	2,200	345	580	2,205
665	330	70	1,020	125	130	1,850
705	200	15	750	85	105	1,170
740	240	<10	210	20	10	645

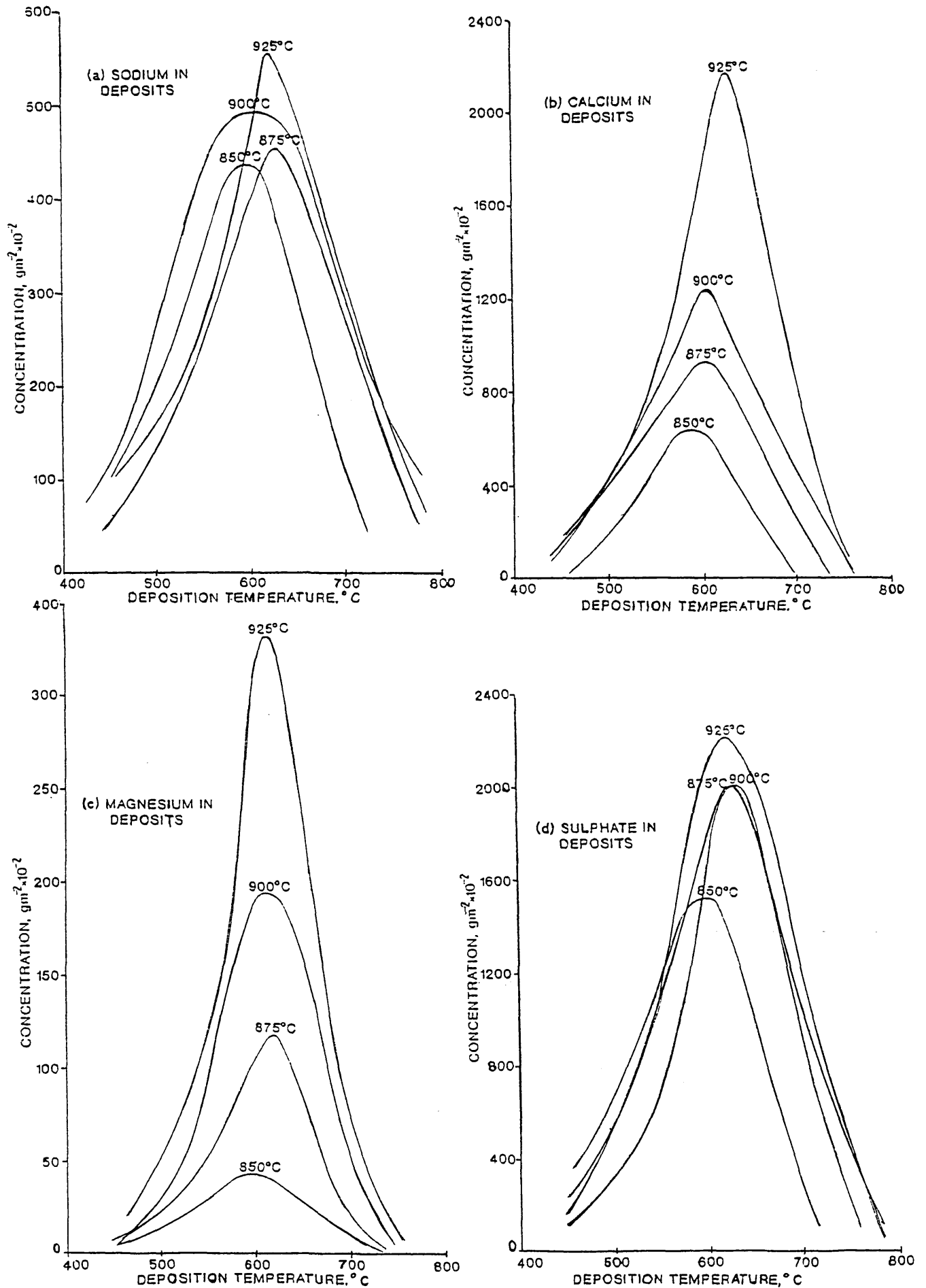


FIGURE 42a to d. DEPOSITION OF SOLUBLE SODIUM, CALCIUM, MAGNESIUM AND SULPHATE AT VARIOUS BED TEMPERATURES.

10 μ m

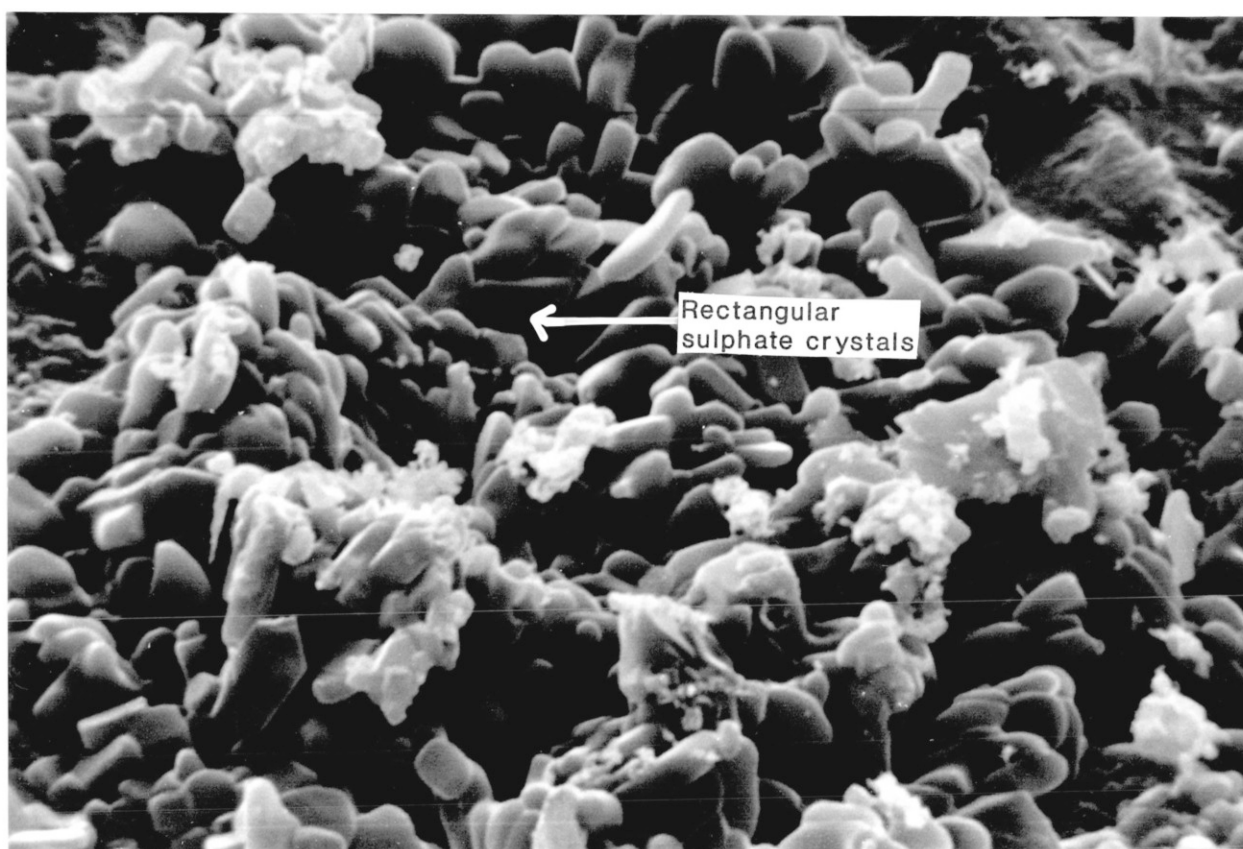


Figure 43. Electron Micrograph of Deposit Formed from the Combustion of Coal 1 at 925°C showing the abundance of Calcium Sulphate crystals.

Chemical and microscopic analyses of the deposits formed from the combustion of Coal 1 showed that an increase in feed rate did not appear to significantly affect the nature or extent of deposition for given amounts of coal. (Table 29 and Figure 44a to d).

5.1.4 Combustion atmosphere

Operation at the lower oxygen concentrations of 10% and 15% resulted in flue gases low in oxygen (2 to 6%), carbon dioxide (4 to 7%) and carbon monoxide (<0.5%) content. Enhanced local reducing environments surrounding the burning coal particles could be expected.

Chemical and microscopic analyses of the initial deposits formed from the combustion of Coal 1 (Table 30 and Figure 45a to f) showed that the release of the monitored cations Na^+ and K^+ had not been significantly affected by the lower partial pressures of oxygen whilst deposition of Ca^{2+} and possible Mg^{2+} had increased slightly. For the anions however, the lower oxygen fluidising atmospheres seemed to favour the deposition of chlorides as opposed to sulphates. This is almost certainly due to suppression of reactions in the freeboard of the type:

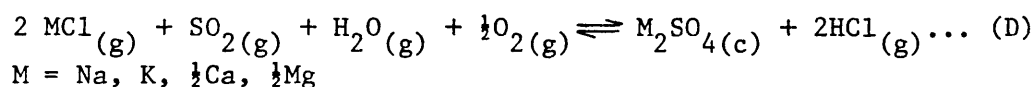


Figure 46 shows the abundance of sodium and potassium chloride crystals deposited in the lower (10%) oxygen fluidising atmosphere.

Alkali chlorides form lower melting point eutectics (from 500°C) than their sulphate forms, thus increasing their adhesive properties. Ensuing deposition in lower oxygen combustion atmospheres may become enhanced, as indicated by the small increase in deposition of Ca^{2+} .

5.1.5 Fluidising gas velocity

The fluidising gas velocities of 0.17, 0.13 and 0.09 msec^{-1} were equivalent to factors of ~ 2.7 , 2.0 and 1.3 times the minimum fluidising gas velocity, U_{mf} .

Reducing the fluidising gas velocity from 0.17 to 0.13 msec^{-1} did not appear to significantly affect the deposition of Na^+ , K^+ , Ca^{2+} and Mg^{2+} (Table 31 and Figure 47a-d). For the anions however, the lower gas velocity did appear to marginally favour

Table 29 Deposition of Soluble Sodium, Potassium, Calcium, Magnesium, Chloride and Sulphate from Coal ₁ Combusted at Feed Rates of 130 and 160 ghr

Deposition Temperature, °C	DEPOSIT CONTENT, gm ⁻² x 10 ⁻²					
	Na	K	Ca	Mg	Cl	SO ₄
<u>Coal Feed Rate,</u> <u>130 ghr</u>						
440	140	140	300	15	370	250
490	205	205	110	<10	450	250
535	395	200	790	110	660	850
580	370	205	920	100	610	1,300
615	450	135	1,060	105	550	1,765
640	210	100	650	75	150	930
715	<10	<10	90	<10	90	235
<u>Coal Feed Rate,</u> <u>160 ghr</u>						
485	110	90	95	<10	290	140
500	315	95	260	15	470	275
520	305	230	300	30	600	440
540	490	230	310	40	740	1,090
585	425	135	1,110	130	730	1,500
600	340	115	1,060	125	695	1,795
650	440	115	620	55	620	1,845
690	15	<10	350	15	25	400

Table 30 Deposition of Soluble Sodium, Potassium, Calcium, Magnesium, Chloride and Sulphate from Coal 1 Combusted in an Atmosphere of 15% and 10% Oxygen

Deposition Temperature, °C	DEPOSIT CONTENT, $\text{gm}^{-2} \times 10^{-2}$					
	Na	K	Ca	Mg	Cl	SO ₄
<u>15% Oxygen</u>						
500	235	85	300	20	340	460
520	300	95	510	55	610	680
530	465	170	660	65	890	915
550	480	125	760	70	845	1,110
580	475	100	980	105	700	1,430
600	460	60	955	90	480	1,480
630	360	30	770	65	280	1,430
655	250	15	505	45	120	925
685	145	<10	175	<10	10	440
<u>10% Oxygen</u>						
465	80	80	<10	<10	695	40
510	220	110	<10	<10	500	210
535	360	155	220	50	965	295
575	455	95	640	95	655	600
590	470	95	1,020	80	615	1,020
600	425	80	1,005	80	535	1,070
635	395	40	720	50	420	1,025
670	120	10	550	30	100	820

Table 31 Deposition of Soluble Sodium, Potassium, Calcium, Magnesium, Chloride and Sulphate from Coal 1
Combusted in Fluidising Gas Velocities of 0.13 and 0.09 m sec⁻¹

Deposition Temperature, °C	DEPOSIT CONTENT, gm ⁻² x 10 ⁻²					
	Na	K	Ca	Mg	Cl	SO ₄
<u>Fluidising Gas</u> <u>Velocity, 0.13 m sec⁻¹</u>						
485	80	45	95	<10	45	230
525	265	125	595	30	190	860
540	280	110	550	10	170	970
550	300	140	690	30	235	1,155
575	340	140	595	10	285	1,415
600	375	140	660	30	130	1,780
625	360	140	775	<10	85	1,970
665	315	95	520	<10	30	1,205
700	100	20	20	<10	<10	250
<u>Fluidising Gas</u> <u>Velocity, 0.09 m sec⁻¹</u>						
500	95	95	65	<10	190	70
515	110	110	95	<10	155	165
550	200	120	340	<10	60	870
585	160	65	175	<10	90	450
600	170	100	360	<10	120	795
640	160	80	395	<10	35	905
660	120	50	240	<10	20	460
685	90	45	205	<10	<10	300

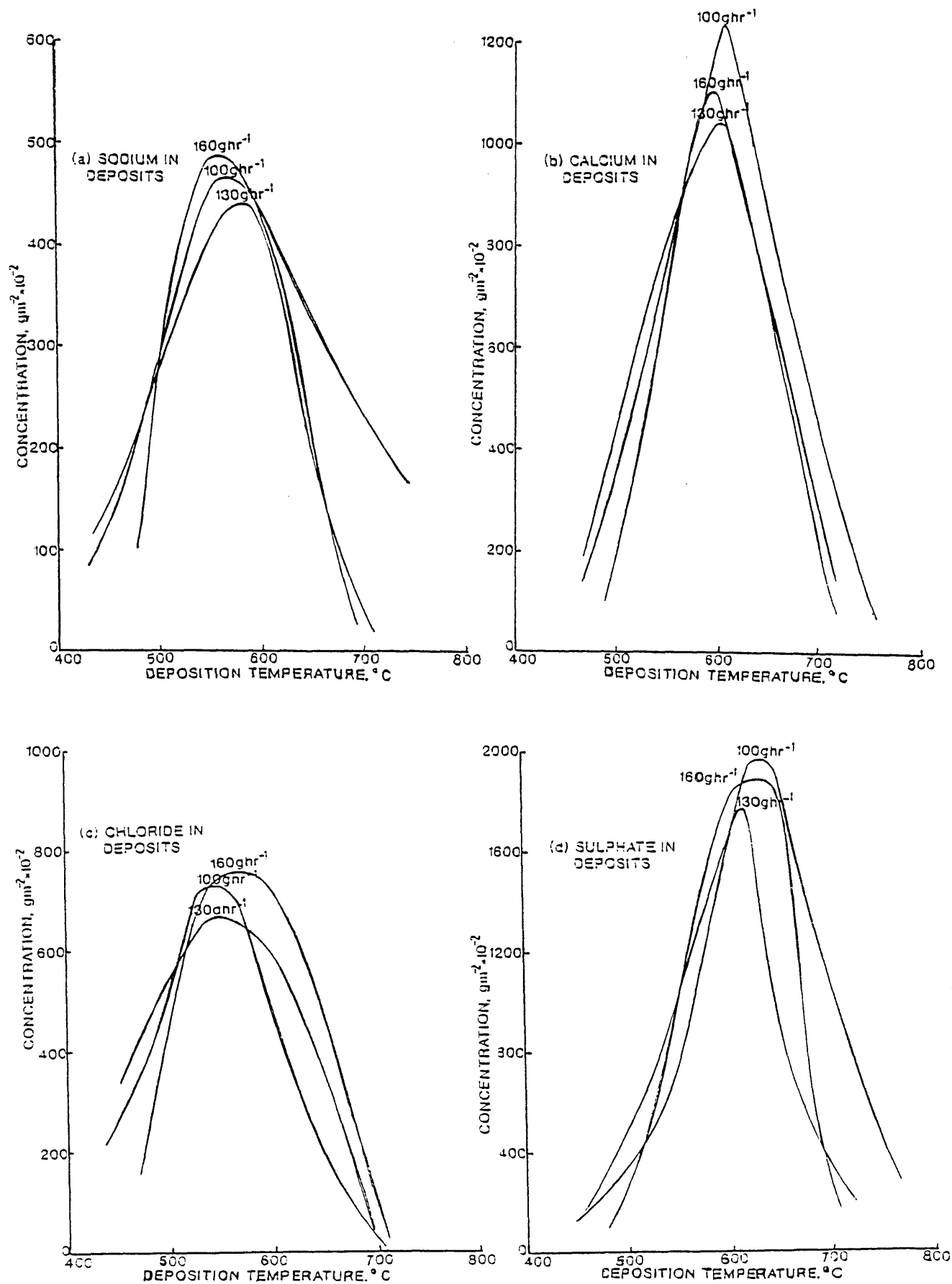


FIGURE 44a to d. THE EFFECT OF INCREASING THE COAL FEED RATE ON THE DEPOSITION OF SOLUBLE SODIUM, CALCIUM, CHLORIDE AND SULPHATE DURING THE COMBUSTION OF COAL 1.

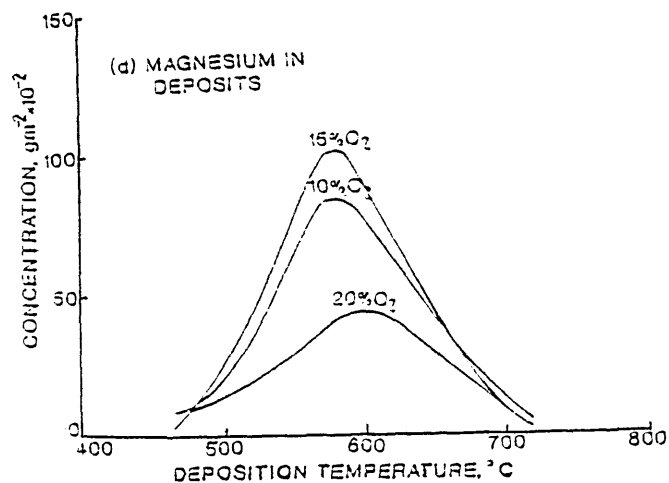
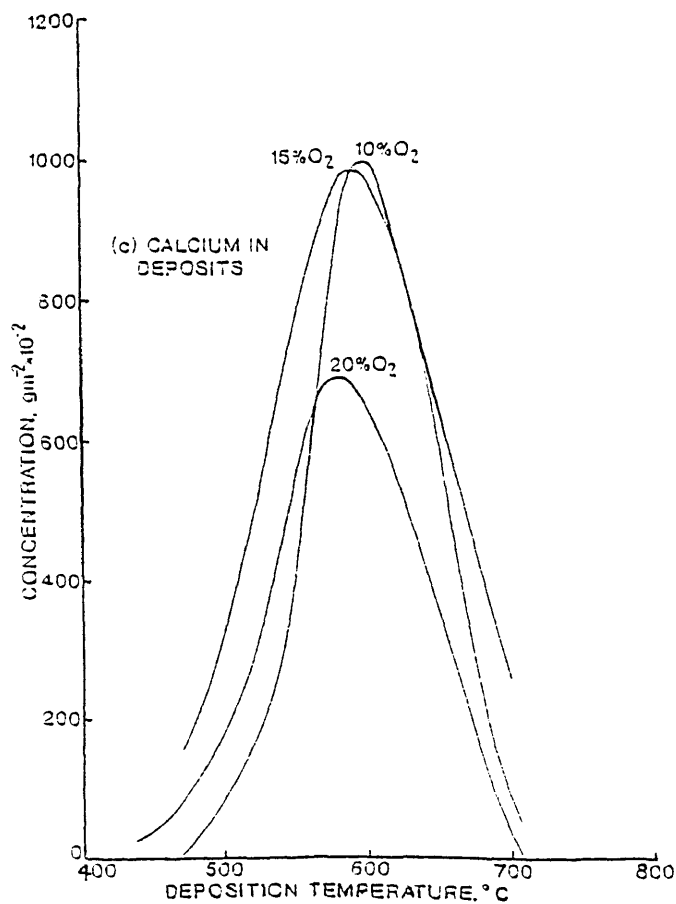
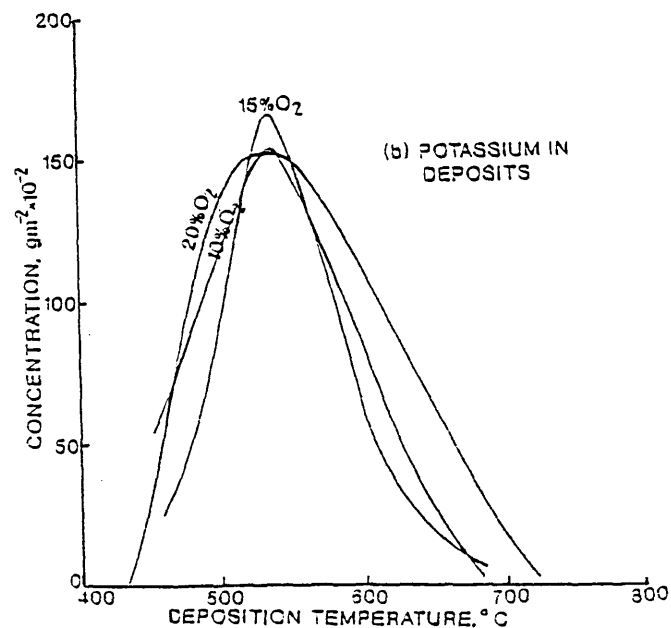
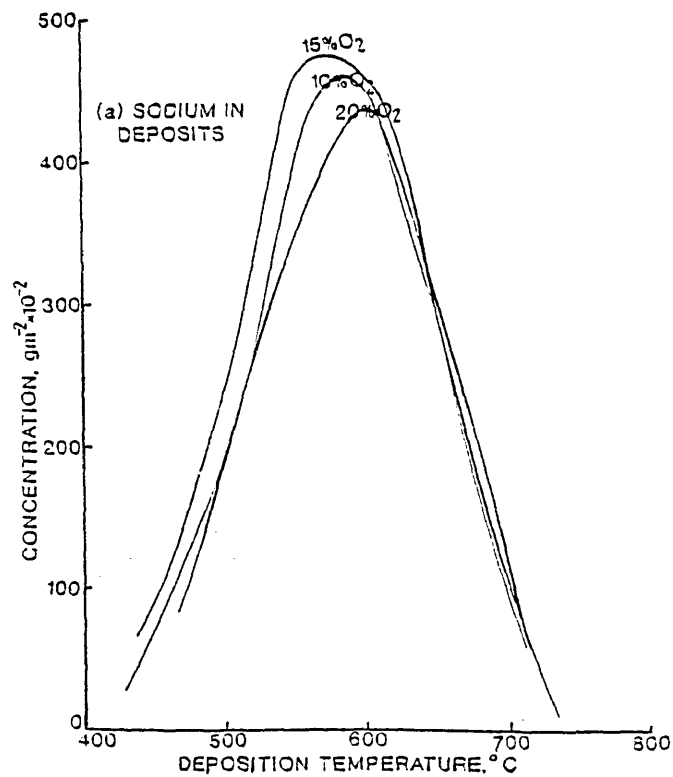


FIGURE 45a to d. THE EFFECT OF REDUCING THE PARTIAL PRESSURE OF P_{O_2} IN THE FLUIDISING ATMOSPHERE ON SOLUBLE SODIUM, POTASSIUM, CALCIUM AND MAGNESIUM DEPOSITION - COAL 1

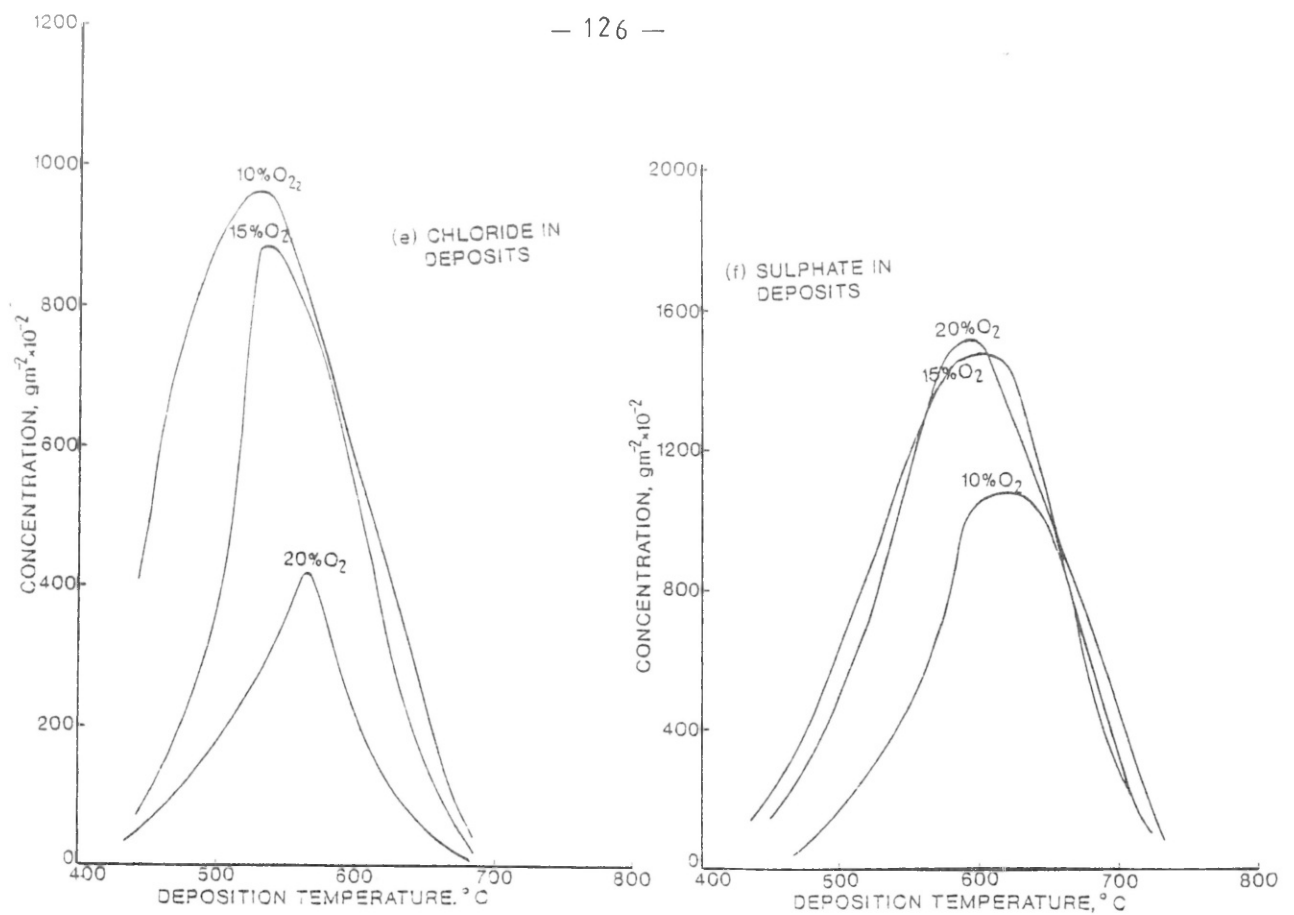


FIGURE 45e and f. THE EFFECT OF REDUCING THE PARTIAL PRESSURE OF P_{O_2} IN THE FLUIDISING ATMOSPHERE ON SOLUBLE CHLORIDE AND SULPHATE DEPOSITION - COAL 1

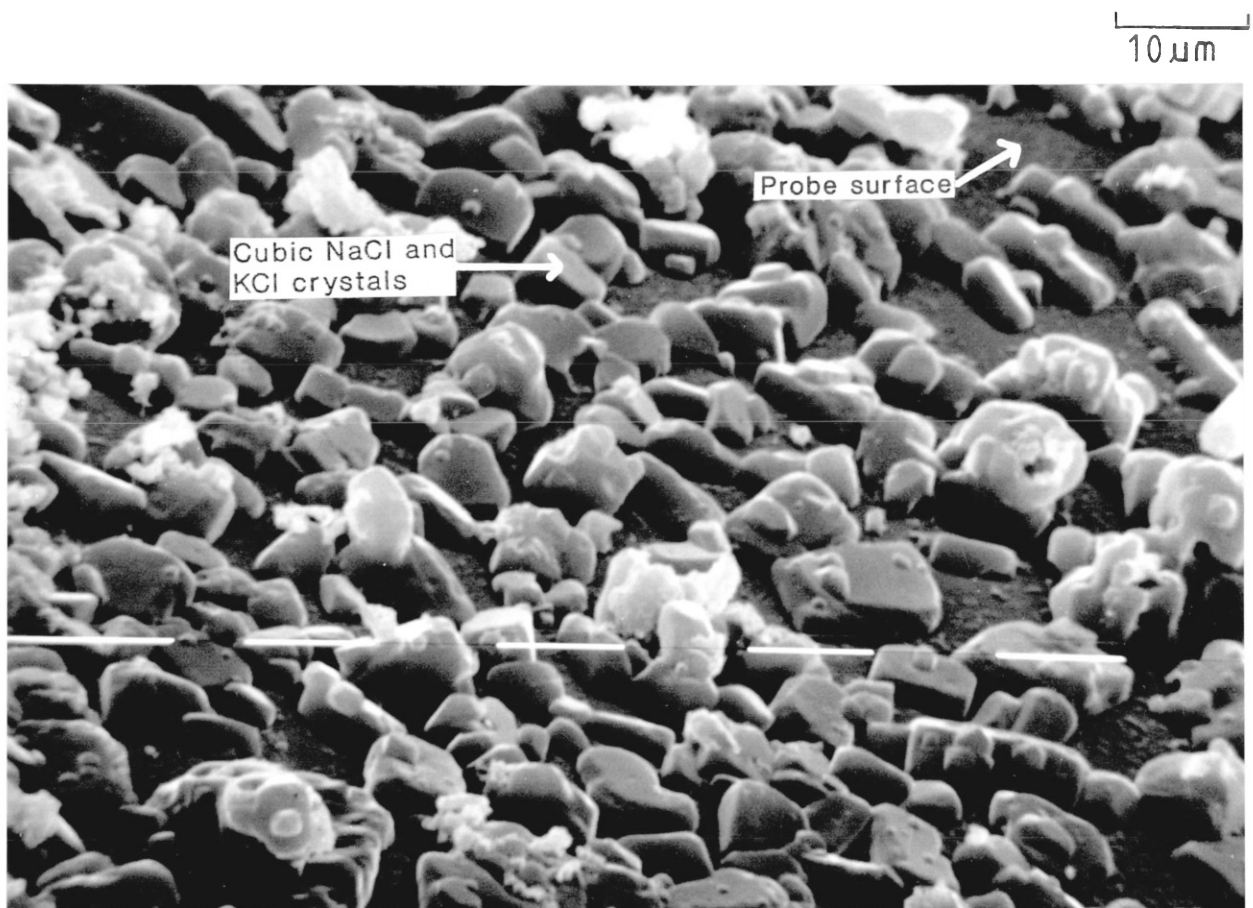


Figure 46. Electron Micrograph of Deposit from Coal 1 Combusted in an Atmosphere of 10% Oxygen, showing abundance of cubic Sodium and Potassium Chloride crystals. Some rectangular Calcium Sulphate crystals are also present.

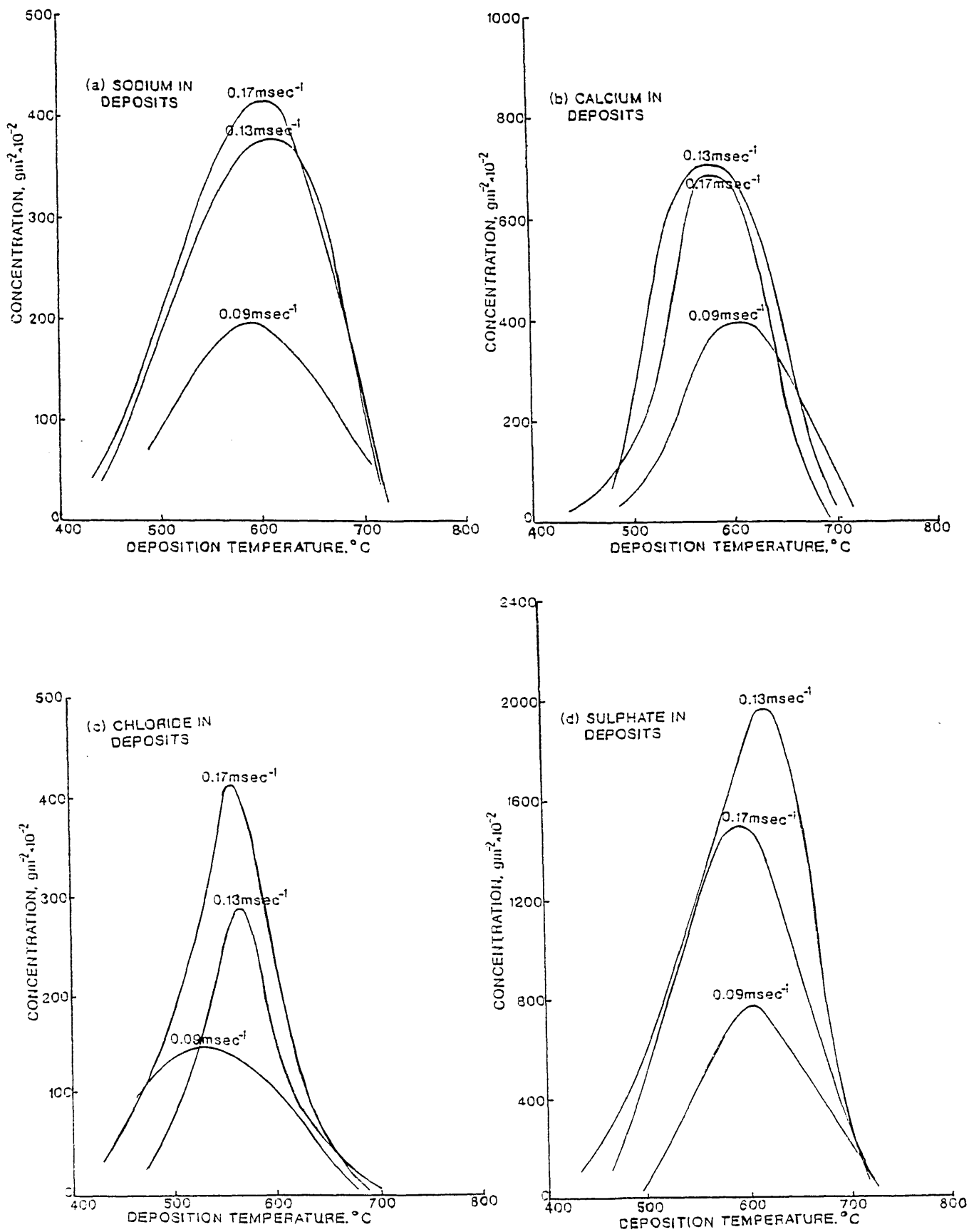


FIGURE 47a to d. THE EFFECT OF REDUCING THE FLUIDISING GAS VELOCITY ON THE DEPOSITION OF SOLUBLE SODIUM, CALCIUM, CHLORIDE AND SULPHATE - COAL 1

deposition of sulphates as opposed to chlorides (Figures 47c and d and 48). Presumably the longer residence times of the volatile alkali chlorides at the lower gas velocity increases the opportunity for reactions with gaseous sulphur dioxide to occur. At even lower fluidising gas velocities, 0.09 msec^{-1} , transportation of the volatile inorganic species appears to be affected. Lower concentrations of all the monitored cations and anions were deposited (Figure 49).

5.1.6 Rate of deposition; including bed ash and deposit nature.

(a) Rate of deposition: As anticipated, amounts of the monitored ions deposited on three probes with surface temperatures of 515°C , 565°C and 620°C , increased with time. Table 32 gives the soluble ion content deposited as the weight of coal combusted was increased to 700 g. Figure 50, a to e, shows the variation in the rate of increase for Na^{+} , Ca^{2+} , Mg^{2+} , Cl^{-} and SO_4^{2-} and illustrates the significance of the formation of the initial semi-molten alkali chloride layer which acts as an adhesive layer for impinging gas borne particulates. Microscopic analysis of a deposit formed by Coal 1, at 620°C , (Figure 51), shows the presence of an initial crystalline layer and subsequent accumulation of gas borne particulates.

The deposition of sodium showed a steady increase with time for all three surface temperatures and presumably is lower for the probe at 515°C due to the reduction in semi-molten adhesive properties of the halide.

Deposition of calcium and sulphate (Figure 50b and e) shows an initial steady growth which increases rapidly after 2 hours. Microscopic studies (Section 5.1.1) have indicated that deposition of calcium sulphate probably occurs by condensation, either by nucleation and growth from the gas phase or as small deposited crystals. In the latter instance initial deposition of calcium sulphate (m.pt $\sim 1450^{\circ}\text{C}$) is at least partially dependent on the formation of the semi-molten alkali chloride layer, which may account for deposit growth as illustrated in Figures 50b and e. In addition an increase in calcium sulphate content in the initial layer will raise the melting point of the $\text{NaCl} - \text{KCl}$ -

Table 32 Deposition of Soluble Sodium, Potassium, Calcium, Magnesium, Chloride and Sulphate from Coal 1 at Three Surface Temperatures

Deposition Temperature, °C	Weight of Coal Combusted, g	DEPOSIT CONTENT, gm ⁻² x 10 ⁻²					
		Na	K	Ca	Mg	Cl	SO ₄
515	100	360	185	345	20	395	950
	200	775	320	795	60	50	2,425
	300	1,665	45	1,825	95	855	4,230
	400	2,045	170	4,400	520	1,105	10,125
	500	2,670	110	4,875	505	1,320	11,930
	600	4,150	125	5,500	375	1,520	15,720
	700	3,490	175	5,660	330	1,730	17,605
565	100	1,135	200	845	100	535	1,690
	200	1,155	315	915	<10	340	2,905
	300	3,300	55	3,980	280	210	11,480
	400	4,180	205	2,585	180	305	12,730
	500	4,775	160	5,100	555	460	14,395
	600	6,505	140	6,465	480	475	22,680
	700	8,755	300	9,790	620	1,155	23,360
620	100	1,055	110	695	110	175	1,520
	200	1,095	260	505	<10	195	2,685
	300	3,080	80	1,995	110	220	6,710
	400	2,670	220	2,045	125	265	8,410
	500	4,400	125	3,615	300	250	14,620
	600	5,975	110	5,690	380	280	21,220
	700	8,095	250	6,760	505	410	26,815

5 μ m



Figure 48. Electron Micrograph of Deposit from Coal 1
Combusted in a Lower Fluidising Gas Velocity (0.13 m sec⁻¹)
showing abundance of Calcium and Sodium Sulphate crystals.

10 μ m

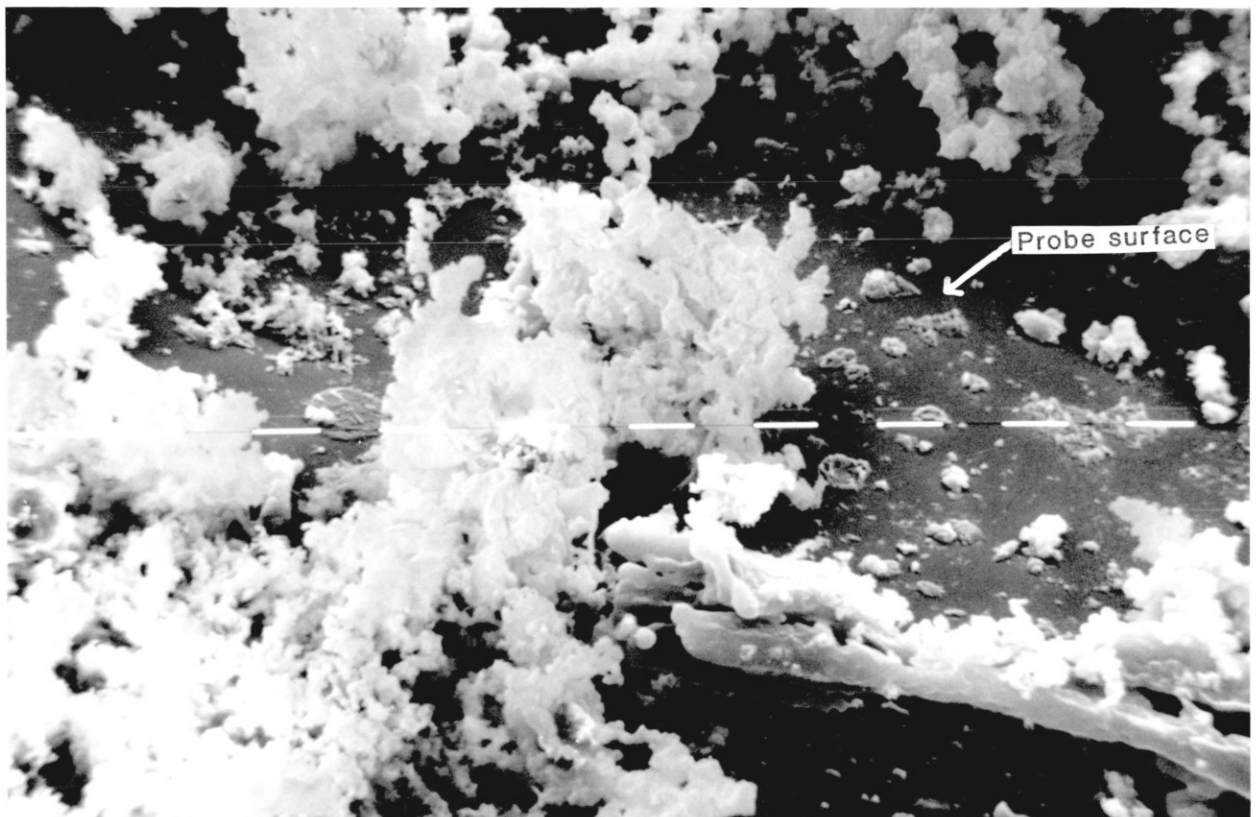


Figure 49. Electron Micrograph of Deposit from Coal 1,
Combusted in a Fluidising Gas Velocity of 0.09 m sec⁻¹,
showing reduced deposition.

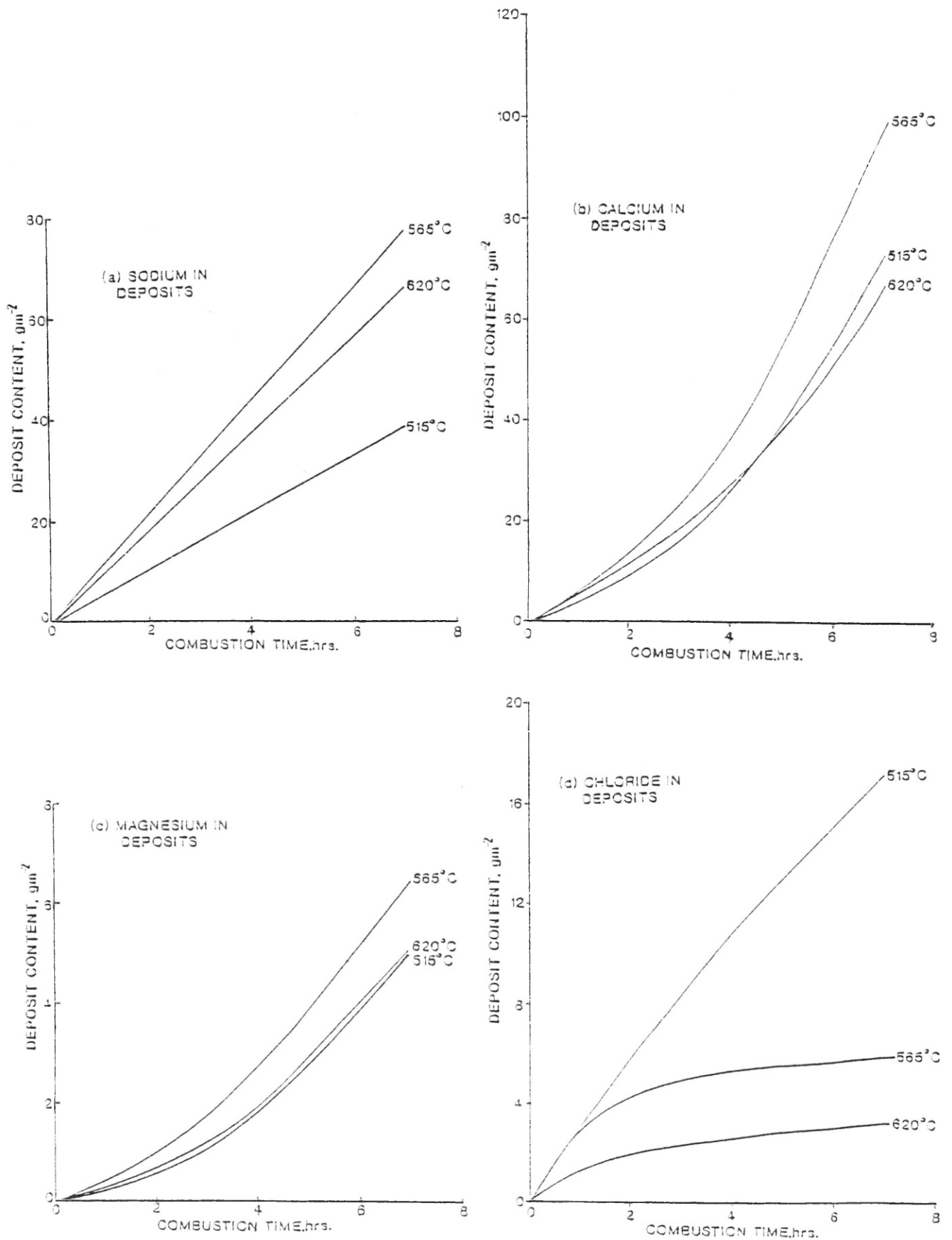


FIGURE 50a to d. RATE OF DEPOSITION OF SOLUBLE SODIUM, CALCIUM, MAGNESIUM AND CHLORIDE FROM COAL 1 AT THREE SURFACE TEMPERATURES.

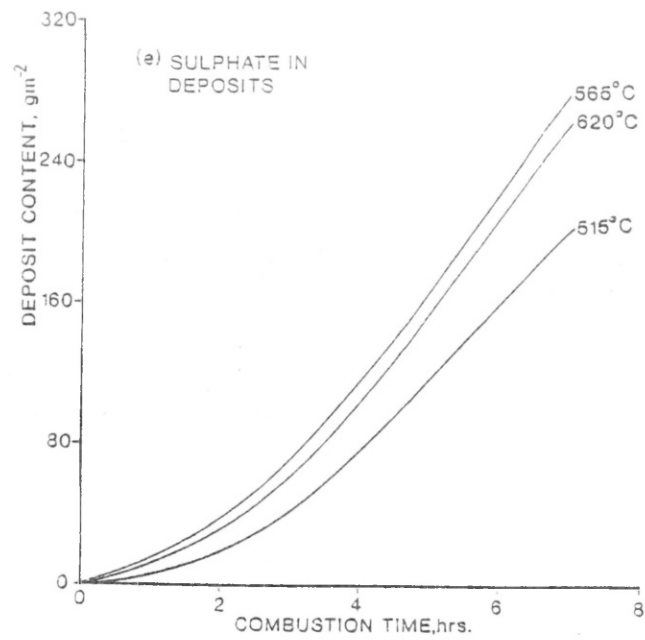


FIGURE 50e. RATE OF DEPOSITION OF SOLUBLE SULPHATE FROM COAL 1 AT THREE SURFACE TEMPERATURES.

10 μ m

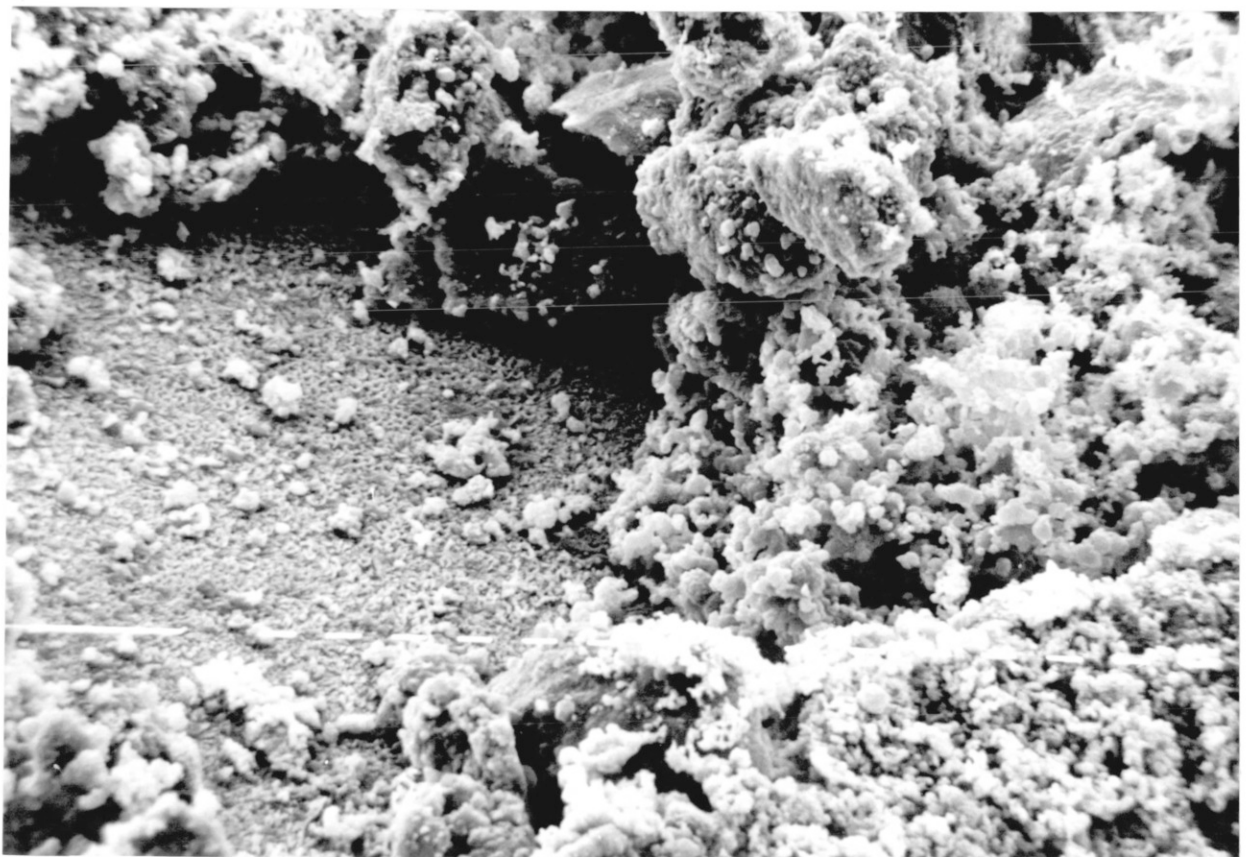


Figure 51. Electron Micrograph of a Deposit from Coal 1 showing Deposit Accumulation.

CaSO₄ mixture (Figure 41). As the thickness of the deposit increases, however, temperature gradients between inner and outer probe surfaces will become significant and the temperature of the outer target surface will rise. Subsequently deposition of calcium sulphate will become increasingly favoured. Similar mechanisms may be applicable for magnesium deposition.

Conversely the rate of chloride deposition decreases (Figure 50d), presumably after the initial layer of alkali chlorides has been established. This decrease in deposition rate is more apparent on surfaces of probes at the higher temperature of 565°C and 620°C and may be attributable to reactions between alkali chlorides and gaseous sulphur oxides occurring on, or near, the probe surface, (see Reaction D). Sodium, potassium, calcium and magnesium sulphates are thermally more stable than their respective chlorides in combustion atmospheres. At the lower surface temperature of 515°C, the equilibrium between volatilising and condensing alkali chlorides existing at the probe surface, would favour the condensed phase and presumably Reaction D would be suppressed.

The results obtained for potassium deposition are inconclusive. As the run progressed sand elutriated from the fluidising bed adhered to the probe and became incorporated in the deposit. Unfortunately the K⁺ content of the sand is relatively high, 0.6% w/w compared to <0.06% for Na⁺, Ca²⁺ and Mg²⁺. This may account for the fluctuating potassium deposition concentrations. Some increase in potassium content of the deposit with time would be expected.

The rate of total alkalis (Na + K) deposited during the combustion of Coal 1 in the laboratory FBC, on surfaces of 565° and 620°C is ~12 gm⁻² hr⁻¹. These levels suggest that some corrosion of tube metal, at these surface temperatures, would be likely to occur (147).

b) Nature of bed ash and deposits: The major phases identified by XRD in the -106 µm fraction of deposits and bed ash samples collected from an extended 20 hour run, in which 2 kg of Coal 1 was combusted, are reported in Table 33. Chemical analysis of the bed ash is given in Table 34. Corrections were made for the

Table 33 X-Ray Diffraction Analysis of Bed Ash and Deposit from the Combustion of Coal 1

SAMPLE	MAJOR PHASES DETECTED		
BED ASH	(SiO ₂ , CaSO ₄ , Fe ₂ O ₃ , (C CaCO ₃ , Na ₂ SO ₄ , Ca ₂ Al ₂ SiO ₇ , and other aluminosilicates)	Quartz Anhydrite Haematite Carbon) Calcite Sodium Sulphate Gehlenite) - minor	- major - major - major - minor
DEPOSIT	(SiO ₂ , CaSO ₄ , Na ₂ SO ₄ , NaCl, Fe ₂ O ₃ , CaCl ₂ , K ₂ SO ₄ , KCl,	Quartz Anhydrite Sodium Sulphate Sodium Chloride Haematite Calcium Chloride Potassium Sulphate Potassium Chloride	- major - major - major - minor - minor - minor

Listed in order of intensity

Table 34 Analysis of Coal 1 Bed Ash (ex laboratory FBC)

ELEMENT	Wt.% on Ash*		
	COAL 1	BED ASH,	-106 µm
Na		5.2	
K		1.2	
Ca		10.2	
Mg		1.2	
Fe		11.1	
Al		9.8	
Si		9.8	
S (retained as SO ₄)		8.1	

* Results have been corrected for the presence of bed material (silica sand).

presence of bed material (silica sand) by assuming the Al to Si ratio in the HTA and bed ash to be similar. Electron micrographs illustrating the morphology of typical bed ash particles are shown in Figure 52a and b.

Table 33 confirms that the major coal derived phases present in the deposits are calcium sulphate, sodium salts and ferric oxide, with smaller amounts of calcium chloride and potassium salts also detected.

Calcium and sodium sulphates and ferric oxide were also identified in the bed ash samples, along with calcium carbonate and various aluminosilicates. Comparison of Tables 19 and 34 indicates that calcium, magnesium and possibly sodium are the cations most likely to be released during combustion, whilst proportions of silicon, aluminium and iron are enhanced in the bed ash.

The bed ash material consisted largely of slightly sintered, nonspherical particles ~5 to 120 μm in diameter. The mean particle diameter of the bed material, however, will be dependent on the size of coal feed and for industrial FBC plants is usually $\ll 0.5$ mm.

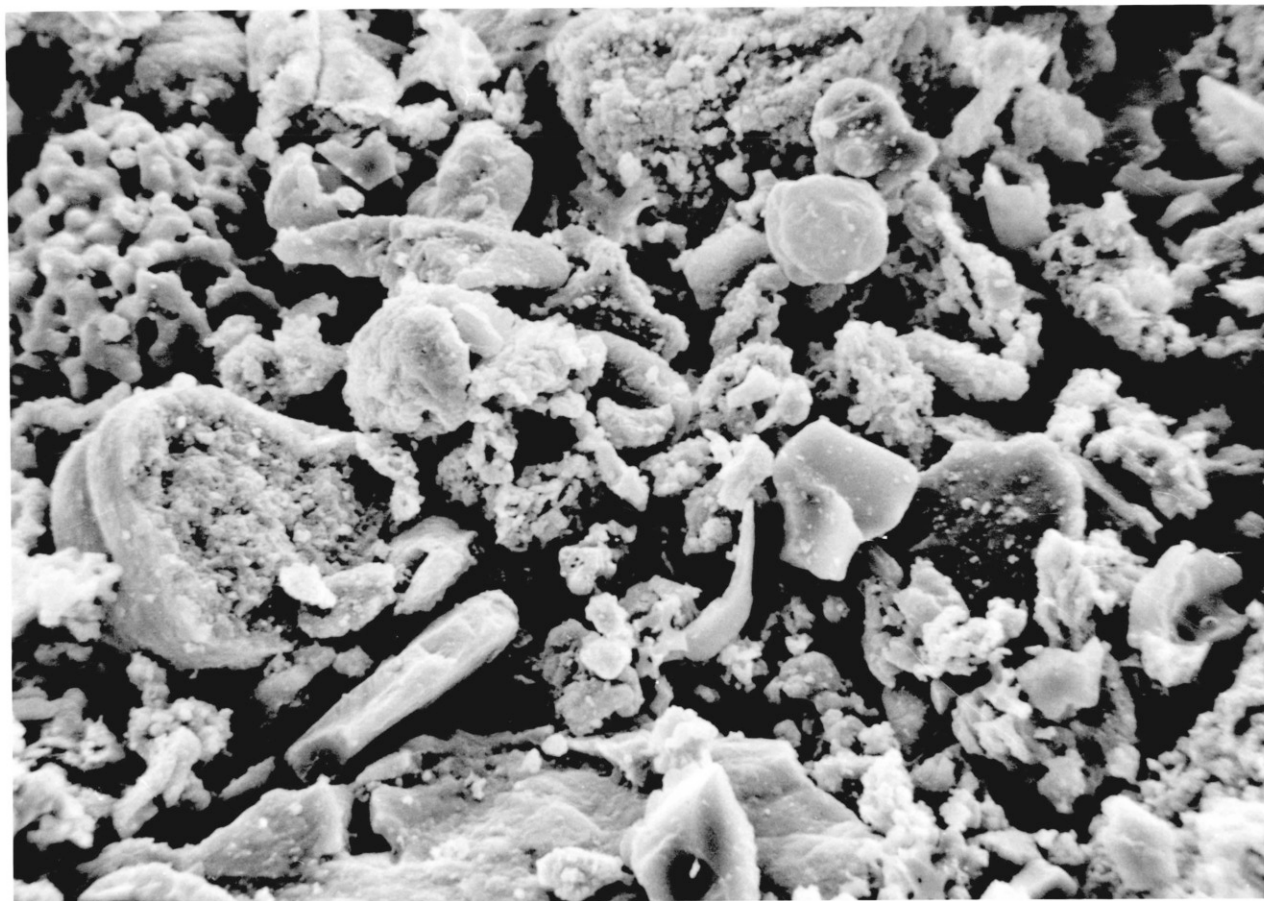
5.1.7 Deposit surface position

The influence of deposit surface position on the nature and extent of deposition was studied using a gas cooled probe. For a given surface temperature a cooled probe will be closer to the fluidising bed than an uncooled probe.

The monitored temperatures of outer and inner cooled probe surface differed linearly by 70° to 110°C in the range 705° to 445°C (outer surface temperature) respectively. This temperature difference is probably largely attributable to heat transferred by radiation in the very small air gap which unavoidably exists between the thermocouples and probe surfaces. At higher temperatures radiant heat transfer increases and temperature differences between inner and outer (cooled) probe surfaces will decrease. Deposition temperatures reported are those of the outer surface.

The influence of deposit surface position in the reactor on the initial deposition of acid soluble Na^+ , K^+ , Ca^{2+} , Mg^{2+} , Cl^- and

(a)



10 μ m

(b)

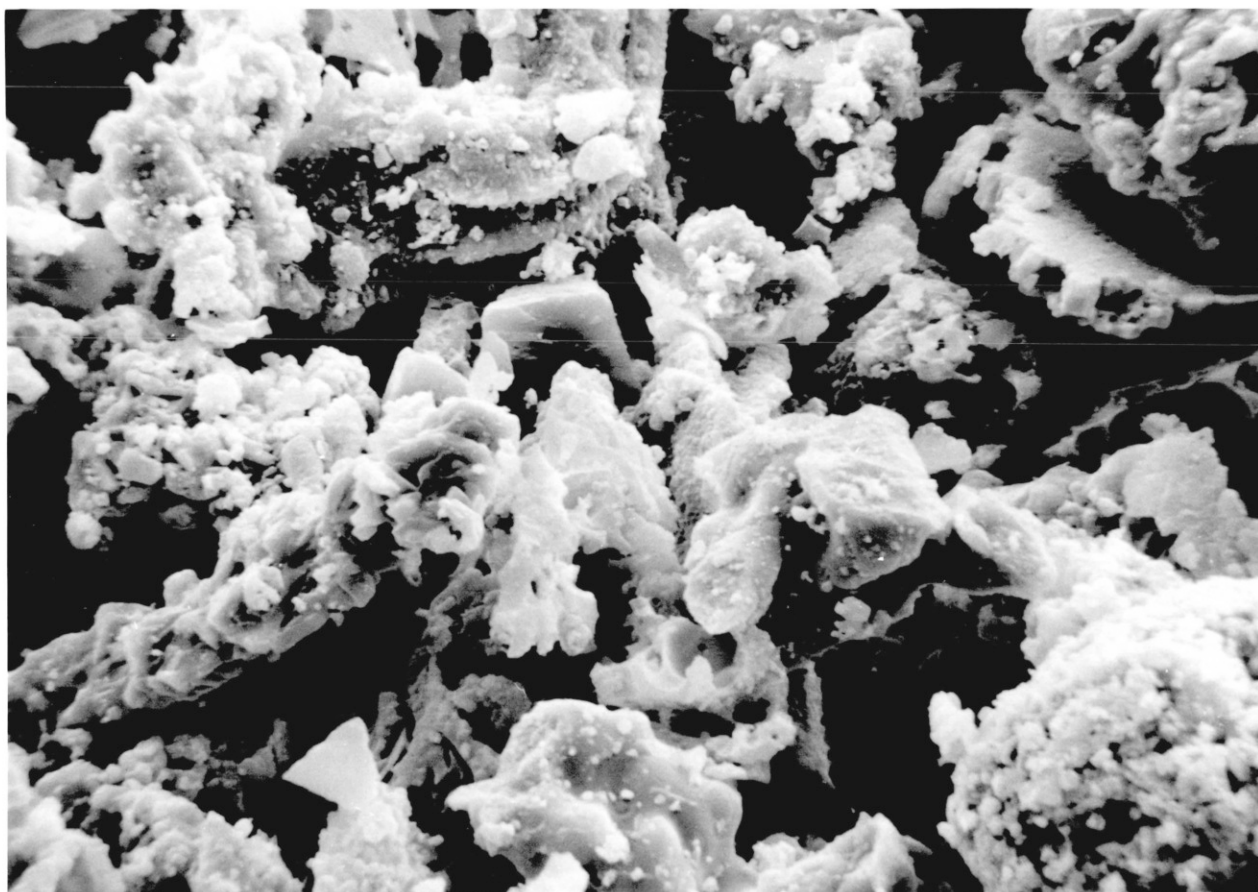


Figure 52a and b. Electron Micrographs of Bed Ash ($\sim 106 \mu$ m) from Coal 1 Combusted in the Laboratory FBC, showing predominantly slightly sintered, non-spherical particles.

SO_4^{2-} is reported in Table 35 and shown graphically in Figure 53, a to d. The results indicate that for Coal 1 deposition of the cations Na^+ and K^+ has not been significantly affected by the relatively small (~ 40 mm) change in location of the deposit collecting surface, for a given temperature. However Ca^{2+} , Mg^{2+} and SO_4^{2-} deposition had markedly reduced and the Cl^- content of the deposits increased.

Due to the closer proximity of a cooled probe to the fluidising bed, deposition of chlorides was favoured in preference to sulphates as the reaction between volatile alkali chlorides and sulphur dioxide would be reduced. In addition the combustion gas temperature in close proximity to the cooled probe will be comparatively higher and reactions between alkali chlorides and sulphur dioxide are less favourable at higher temperatures.

The unexpected decrease in calcium and magnesium deposition may be attributable to differences in saturation vapour pressures for the chlorides which, although low, increase at a comparatively greater rate for these elements between 600° and 800°C , than for sodium and potassium (Section 2.5.1, Figure 4). Consequently relatively high proportions of calcium and magnesium chlorides would remain gaseous.

5.1.8 Deposit surface material

Alumina and stainless steel (type 321) were chosen as alternative probe materials. Concentrations of the dilute acid soluble ions, Na^+ , K^+ , Ca^{2+} , Mg^{2+} , Cl^- and SO_4^{2-} , deposited on the alumina and stainless steel surfaces during the combustion of Coal 1 and given in Table 36 and illustrated graphically in Figure 54, a to d. Electron micrographs illustrating the morphology of the deposits collected on these surfaces at $\sim 600^\circ\text{C}$, are shown in Figures 55 and 56.

Temperature differences between inner and outer alumina and stainless steel probe surfaces varied between 40 and 120°C in the temperature range 780 to 450°C respectively. This is partially due to an increase in the radiant heat transferred, in the small air gap which unavoidably exists between the thermocouples and probe surfaces, at higher temperatures. In addition thermal

Table 35 Deposition of Soluble Sodium, Potassium, Calcium, Magnesium, Chloride and Sulphate from Coal 1 on Nitrogen-Cooled Probe

Outer Cooled Probe Surface Temperature, °C	DEPOSIT CONTENT, $\text{gm}^{-2} \times 10^{-2}$					
	Na	K	Ca	Mg	Cl	SO ₄
395	125	30	10	<10	75	210
445	205	30	10	<10	140	210
460	175	30	20	<10	160	220
470	205	30	20	<10	190	370
480	205	50	80	<10	190	335
495	265	140	80	<10	445	350
500	400	175	95	<10	560	330
530	395	140	125	<10	550	550
545	395	125	160	<10	530	580
560	330	110	95	<10	420	390
575	370	95	95	<10	390	380
590	425	95	100	<10	460	420
600	395	95	95	<10	340	420
625	125	45	15	<10	150	275
640	110	15	<10	<10	65	300
655	15	<10	<10	<10	30	65

Table 36 Deposition of Soluble Sodium, Potassium, Calcium, Magnesium, Chloride and Sulphate from Coal 1 on Alumina and Stainless Steel Probes

Deposition Temperature °C	DEPOSIT CONTENT, $\text{gm}^{-2} \times 10^{-2}$					
	Na	K	Ca	Mg	Cl	SO ₄
<u>ALUMINA</u>						
515	285	35	175	<15	25	260
555	420	70	315	<15	80	640
590	460	105	415	50	55	680
615	530	70	495	40	35	1280
630	480	70	440	50	20	1550
645	490	35	390	<15	20	1535
655	520	35	355	<15	15	1380
665	490	35	250	<15	10	1120
690	420	35	155	<15	10	795
765	240	35	70	<15	<10	150
<u>STAINLESS STEEL</u>						
510	140	110	120	<10	40	430
525	280	250	150	<10	90	890
555	700	215	170	<10	115	1065
575	865	200	245	10	200	1395
595	835	245	250	10	150	1650
625	910	220	355	40	65	1905
650	1280	300	440	50	110	2200
680	1355	280	475	50	90	2920
700	1125	270	490	20	35	2645
760	710	175	270	<10	10	1995

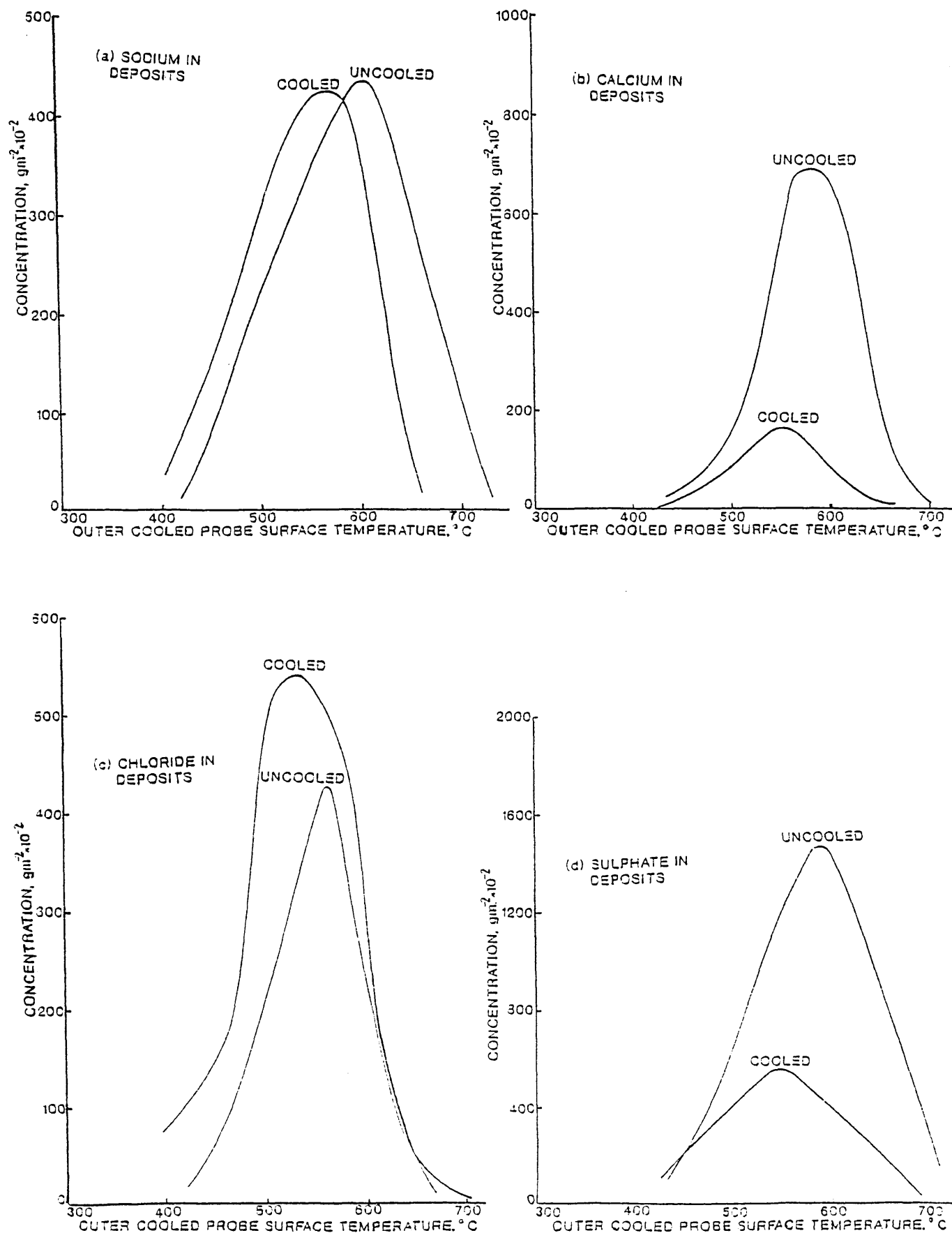


FIGURE 53a to d. THE EFFECT OF PROBE SURFACE POSITION ON THE DEPOSITION OF SOLUBLE SODIUM, CALCIUM, CHLORIDE AND SULPHATE FROM COAL 1 USING A NITROGEN-COOLED PROBE.

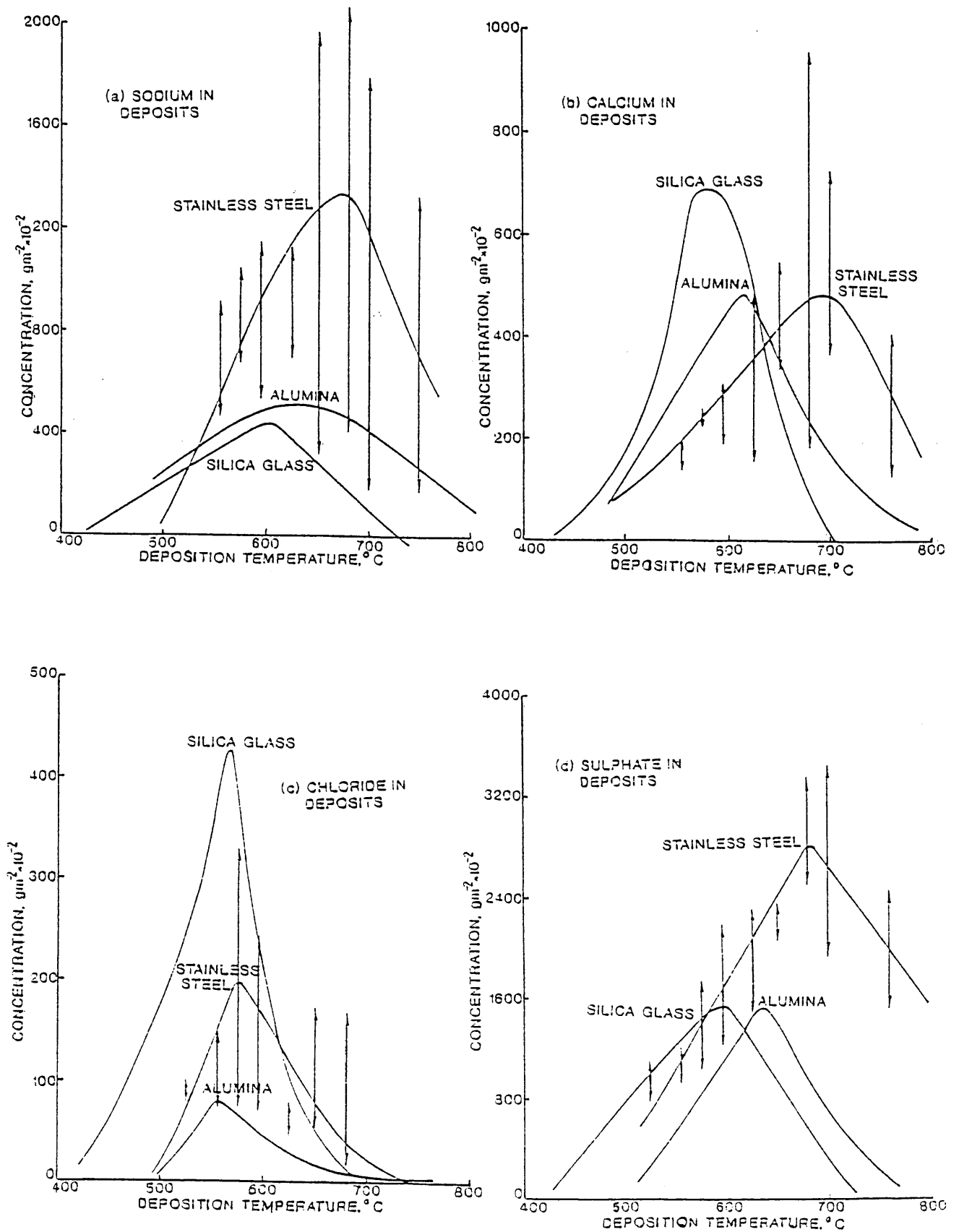


FIGURE 54a to d. DEPOSITION OF SOLUBLE SODIUM, CALCIUM, CHLORIDE AND SULPHATE FROM COAL 1 ON ALUMINA, STAINLESS STEEL AND SILICA GLASS PROBES.

5 μ m

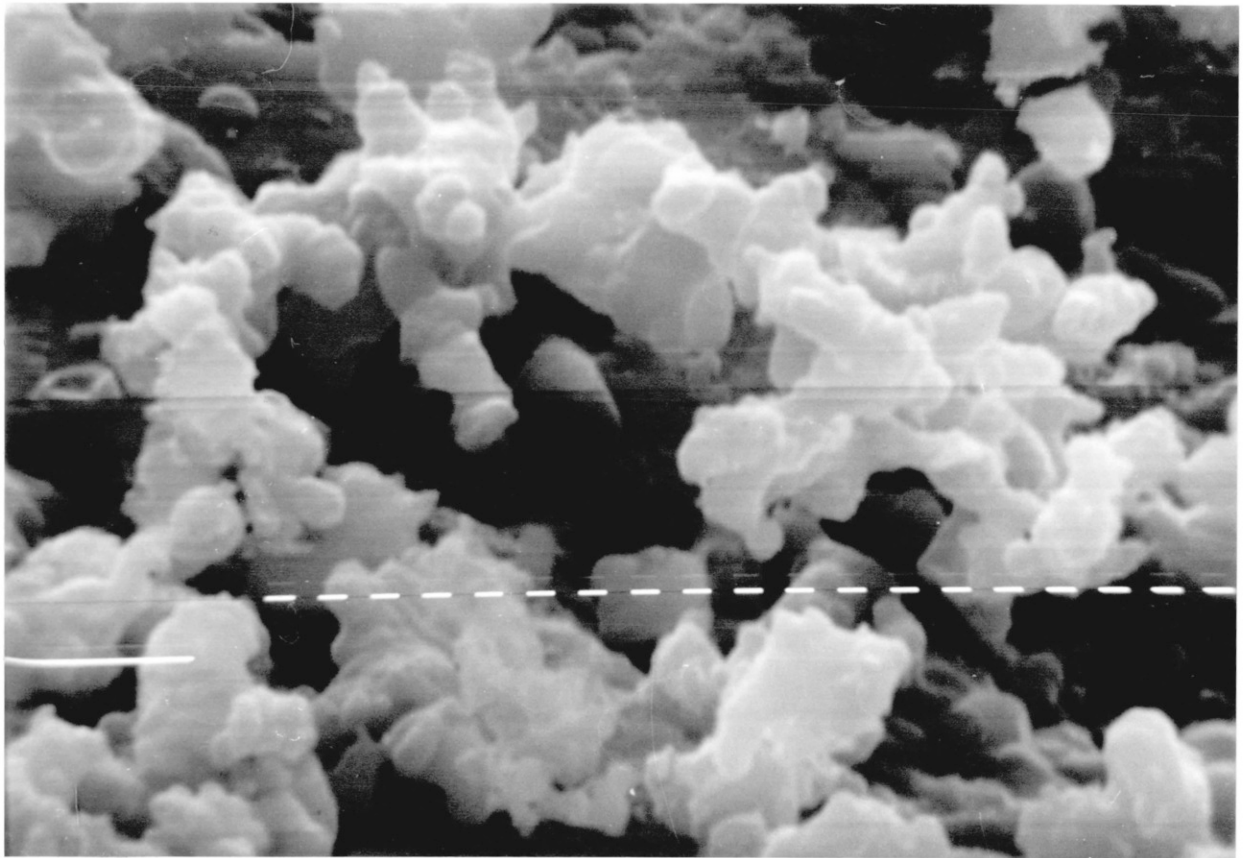


Figure 55. Electron Micrograph of Deposit from Coal 1 on an Alumina Probe, showing partially fused Sodium and Calcium Sulphate crystals.

10 μ m

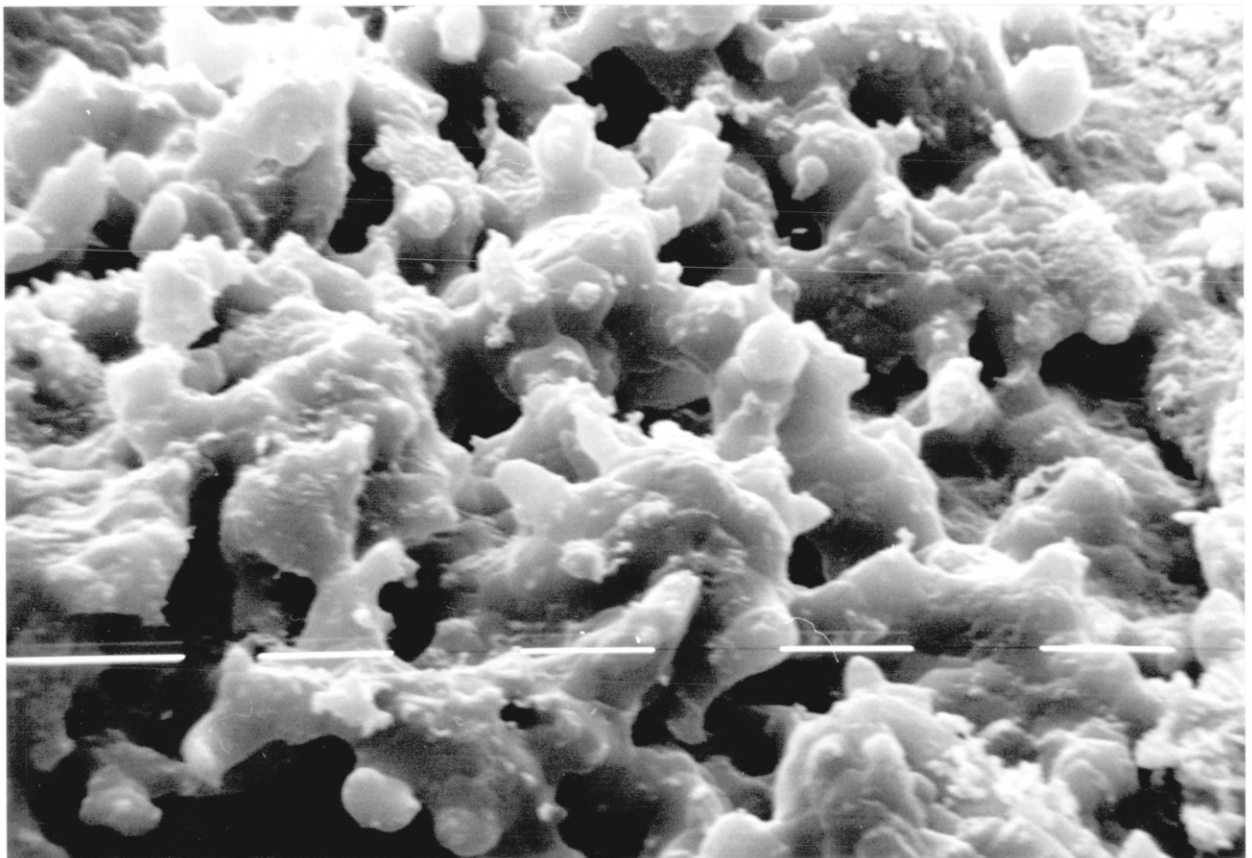


Figure 56. Electron Micrograph of Deposit from Coal 1 on a Stainless Steel Probe, showing partially fused Sodium and Calcium Sulphate crystals.

conductivities of stainless steel and alumina (both $\sim 20 \text{ Wm}^{-1} \text{ K}^{-1}$ @ 50°C) are higher than that of silica glass ($1.5 \text{ Wm}^{-1} \text{ K}^{-1}$). The temperatures reported are those of the outer contact surface. For Coal 1 deposition of the monitored ions, Na^+ , K^+ , Ca^{2+} , Mg^{2+} , Cl^- and SO_4^{2-} on alumina surfaces did not appear to be affected. Both silica glass and alumina are considered to be 'inert' at temperatures between 400 and 800°C ; silica glass being an amorphous material while alumina is crystalline. Similar adhesion properties of the semi-molten halides would be expected on both materials, however the rate of nucleation may be affected.

The mechanisms of high-temperature (400 - 800°C) chemical corrosion of metal surface in a combustor are complex and this study has concentrated on investigating the influence of deposit surface materials on the nature and extent of initial deposits formed during combustion.

Stainless steel 321 is a high chromium austenitic steel (17-19% Cr, 9-12% Ni) and will develop a protective chromium rich oxide scale when exposed to an oxidising atmosphere at metal temperatures above 600°C . The gaseous combustion environment above the fluidised bed is, however, potentially corrosive and can attack metal surfaces of high temperatures ($>550^\circ\text{C}$). In FBC the major forms of attack of above-bed surfaces are sulphidation-oxidation (69) and hot salt (2) corrosion. Deposited molten alkali sulphates containing sulphur or sulphur trioxide can dissolve metal protective oxide coatings to form iron and chromium based sulphides and sulphates. This will diminish the protectiveness of the scale layer and increase the rate of corrosion.

Large variations in deposit concentrations from duplicate runs on stainless steel surfaces were recorded (denoted by error bars in Figure 54, a to d) possibly due to corrosion/acid leaching effects. Consequently the results only indicate trends in initial deposition behaviour.

Deposition of Na^+ , K^+ and SO_4^{2-} appeared to have increased (Figure 54, a to d, and Table 36), whilst Ca^{2+} , Mg^{2+} and Cl^- concentrations remained similar to those found on silica glass.

These results are consistent with the theory that sodium and potassium sulphates can readily diffuse through the molten deposit and attack the chromium rich scale. Ensuing deposition of sodium and potassium sulphates from the combustion gases will subsequently increase in order to maintain the equilibrium between condensing and volatilising halides and sulphates at the deposit-combustion gas interface. Calcium and magnesium sulphates are less thermally stable than sodium and potassium sulphates and are therefore not as likely to migrate. Figures 55 and 56 show the morphology of the deposits formed on alumina and stainless steel surfaces to be similar to those found on silica glass; the major features being partially fused, sodium and calcium chloride and sulphate crystals with overlying clays, iron oxide and fly ash particles.

5.1.9 Sulphur sorbent bed material

The influences of sulphur sorbent bed material (limestone and dolomite) on the nature and extent of initial deposit formation was investigated. Coals 1 and 3 were combusted in a limestone bed and Coal 1 in the dolomite bed. The results are reported in Tables 37 and 38 and illustrated graphically in Figures 57 and 58. Electron micrographs showing the morphology of deposits collected on surfaces at $\sim 600^{\circ}\text{C}$, are shown in Figures 59 to 66. The sulphur retention capacity of the carbonate rock bed materials from the combustion of Coal 1 (Figure 67) show the sulphur retention efficiency of both carbonate rock bed materials is $>90\%$.

Figures 57a, 57e, 58a and 58c, indicate that a marked increase in deposition of Na^{+} and Cl^{-} could be expected when coals are burnt in sulphur retaining carbonate rock bed materials. Interestingly the SO_4^{2-} content of deposits formed from the combustion of Coal 3 in a limestone bed had increased (Figure 58d) whilst only relatively small increases in the K^{+} content of deposits from Coal 1 were observed (Figure 57b).

Higher deposition concentrations of Ca^{2+} and, for Coal 1 combusted in a dolomite bed, of Mg^{2+} , were apparent. Ion mass balances for these deposits, however, showed an excess of cations (a typical imbalance of +30 to +60%), indicating that bed material had adhered to the initial halide deposit on the probe surface.

Table 37 Deposition of Soluble Sodium, Potassium, Calcium, Magnesium, Chloride and Sulphate from Coal 1 Combusted in Limestone and Dolomite Beds

Deposition Temperature °C	DEPOSIT CONTENT, gm ⁻² x 10 ⁻²					
	Na	K	Ca	Mg	Cl	SO ₄
<u>LIMESTONE BED</u>						
425	705	135	845	<10	410	250
530	1975	330	2690	<10	1645	180
540	2735	300	3045	<10	3195	310
555	3225	325	3950	<10	3725	640
590	5385	230	3565	<10	4340	780
600	5165	310	3130	<10	5315	735
615	4845	275	2975	<10	5550	600
625	4730	160	3095	<10	3725	450
645	3365	225	2250	<10	3970	830
650	3385	195	2250	<10	3630	920
665	2845	75	1780	<10	3245	585
695	2100	55	1050	<10	2250	480
725	1780	30	635	<10	1780	455
<u>DOLOMITE BED</u>						
430	185	15	550	210	290	125
470	440	30	1770	705	730	500
495	580	175	1770	805	1115	550
525	1040	180	1850	1075	1705	735
560	1090	225	1980	1130	1730	685
575	1205	140	2130	990	1855	595
600	935	125	1710	725	1400	565
620	910	50	2090	710	1280	550
630	895	40	1885	615	1215	575
640	730	30	1450	630	900	560
650	535	30	1390	455	885	535
665	350	15	1070	265	560	475
680	80	<10	880	190	180	460
690	50	<10	600	135	50	325
710	30	<10	490	45	15	225
730	15	<10	280	30	15	85
755	15	<10	60	<10	10	15

Table 38 Deposition of Soluble Sodium, Potassium, Calcium, Magnesium, Chloride and Sulphate from Coal 3 Combusted in a Limestone Bed

Deposition Temperature °C	DEPOSIT CONTENT, gm ⁻² x 10 ⁻²					
	Na	K	Ca	Mg	Cl	SO ₄
410	80	10	15	<10	80	40
460	200	10	180	<10	165	120
510	300	10	385	<10	150	225
535	410	30	680	<10	490	450
555	470	30	810	<10	430	430
600	440	30	990	<10	505	670
610	450	15	935	<10	260	720
620	365	20	820	<10	85	645
630	285	15	1000	<10	60	665
640	235	15	700	<10	40	510
655	260	30	430	<10	35	365
665	205	15	280	<10	25	360
680	205	15	380	<10	10	360
705	175	<10	220	<10	<10	300
745	80	<10	310	<10	10	130

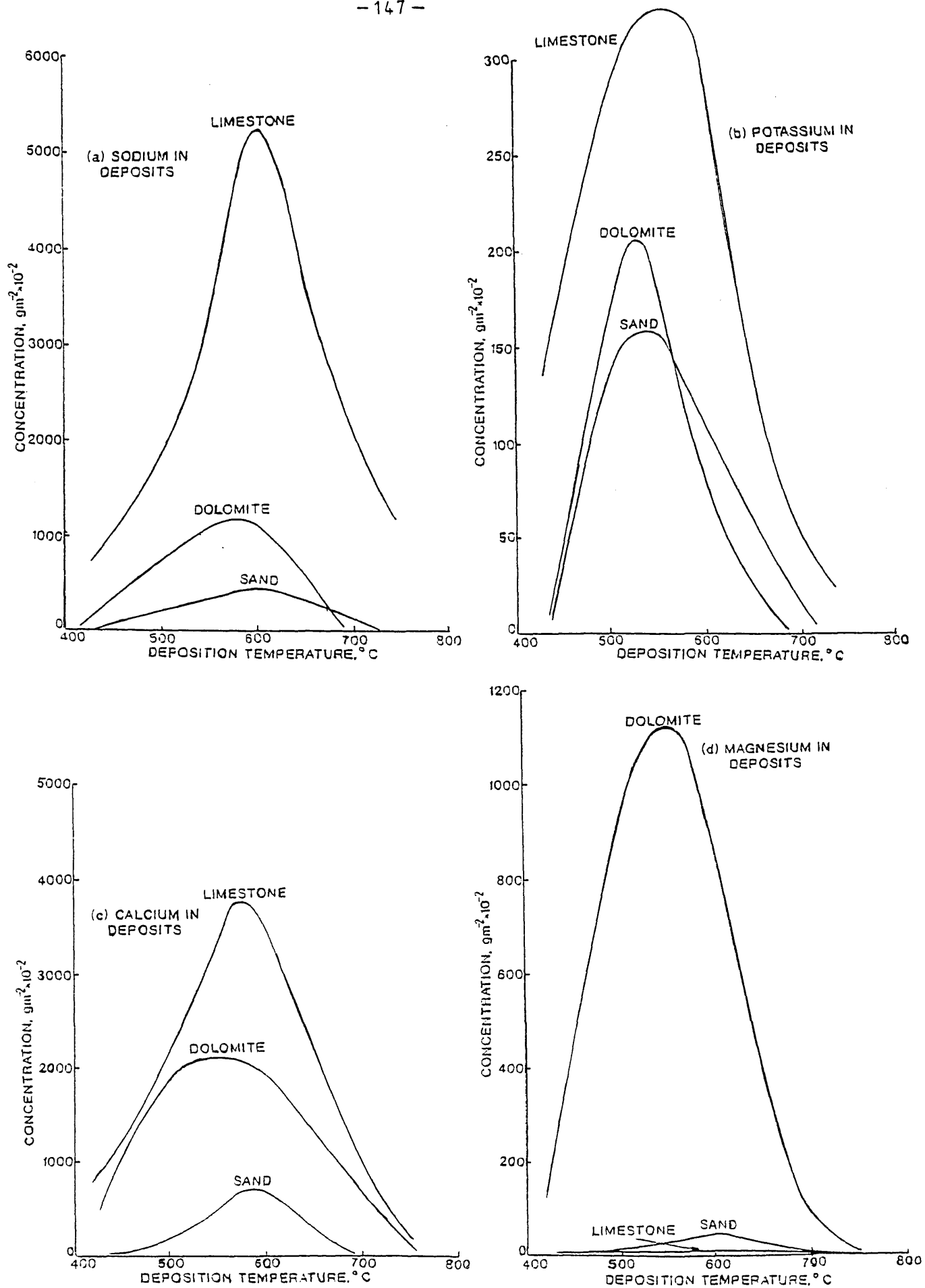


FIGURE 57a to d. THE EFFECT OF BED MATERIAL ON THE DEPOSITION OF SOLUBLE SODIUM, POTASSIUM, CALCIUM AND MAGNESIUM - COAL 1

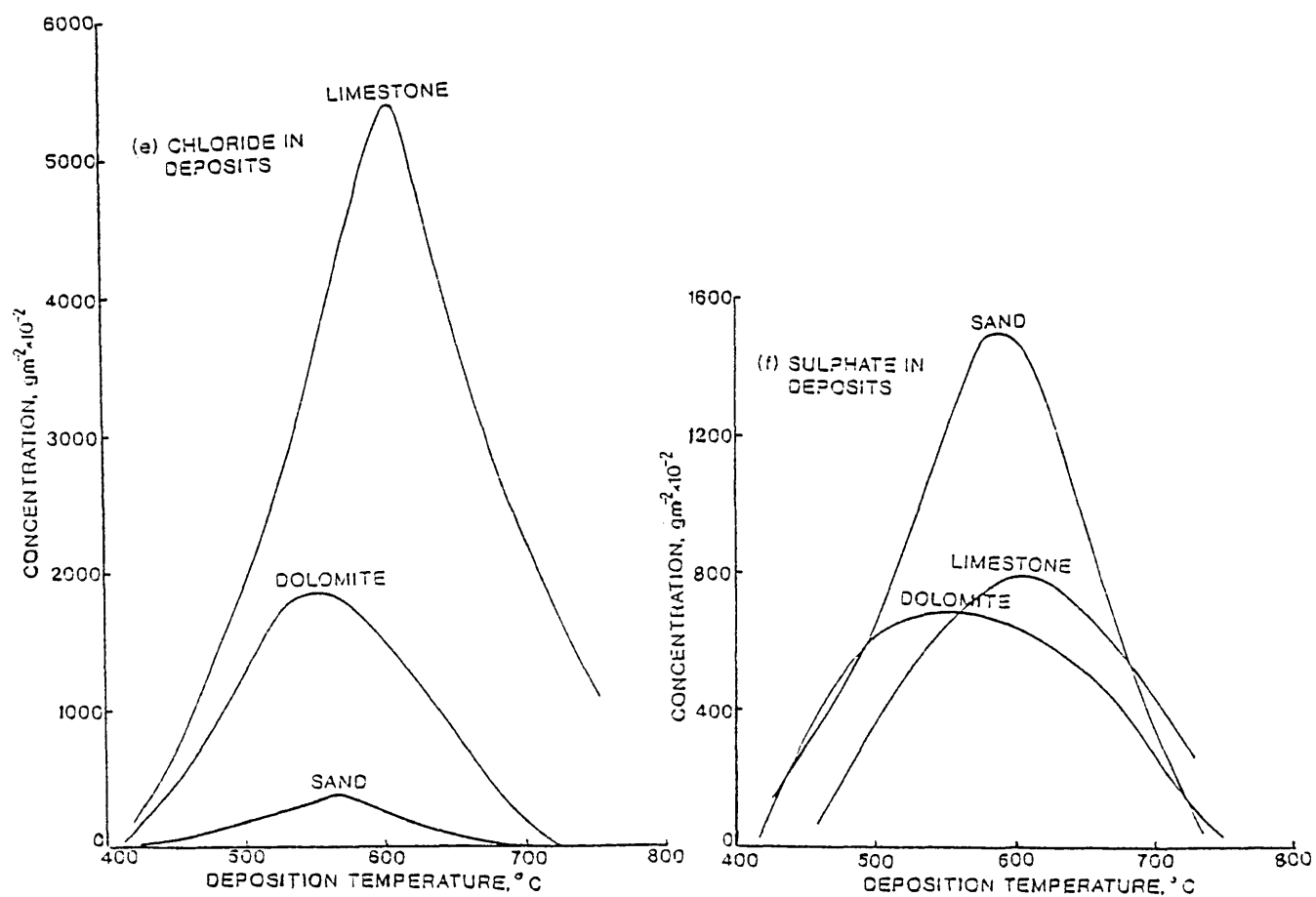


FIGURE 57e and f. THE EFFECT OF BED MATERIAL ON THE DEPOSITION OF SOLUBLE CHLORIDE AND SULPHATE - COAL 1

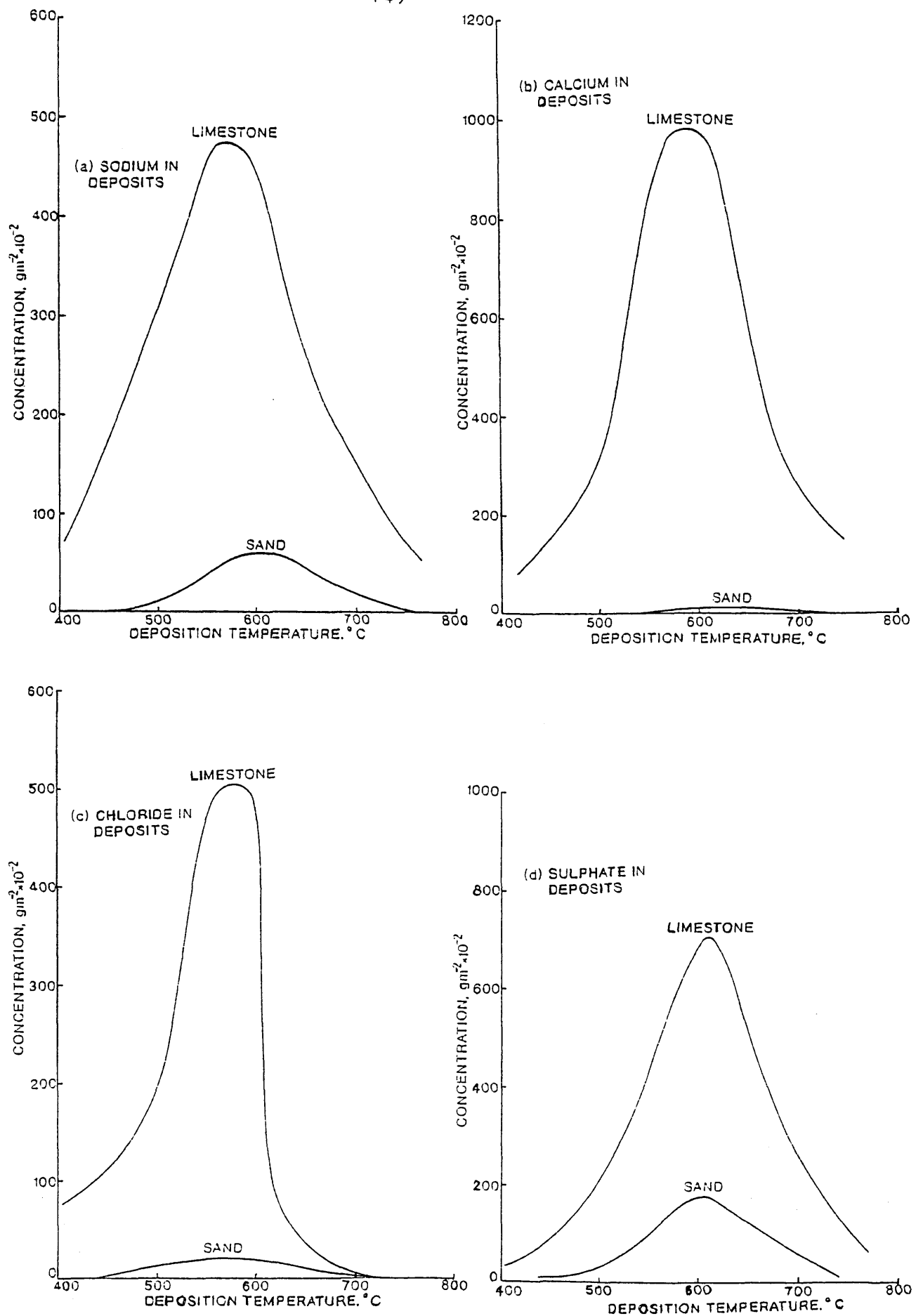


FIGURE 58a to d. THE EFFECT OF BED MATERIAL ON THE DEPOSITION OF SOLUBLE SODIUM, CALCIUM, CHLORIDE AND SULPHATE - COAL 3

5 μ m

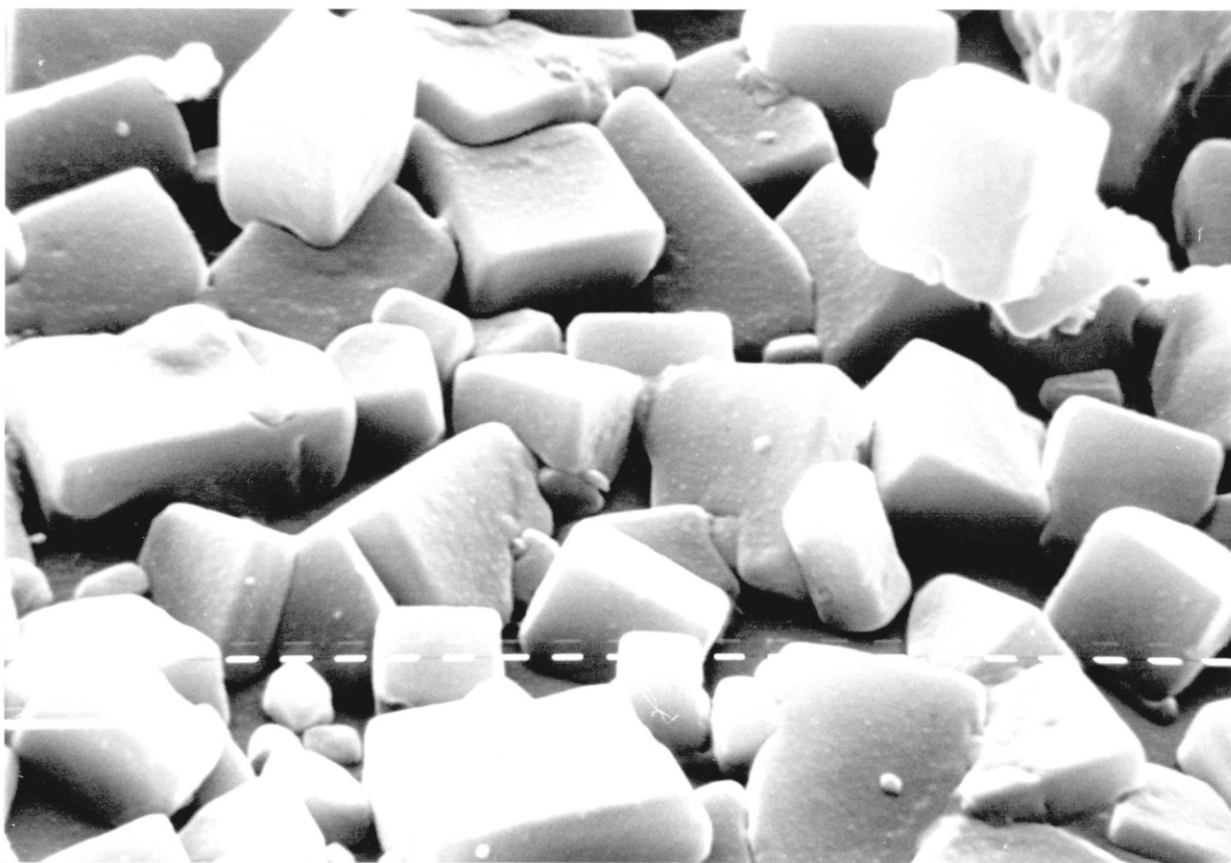


Figure 59. Electron Micrograph of Deposit from Coal 1 Combusted in a Limestone Bed, showing abundance of cubic halide crystals.

5 μ m

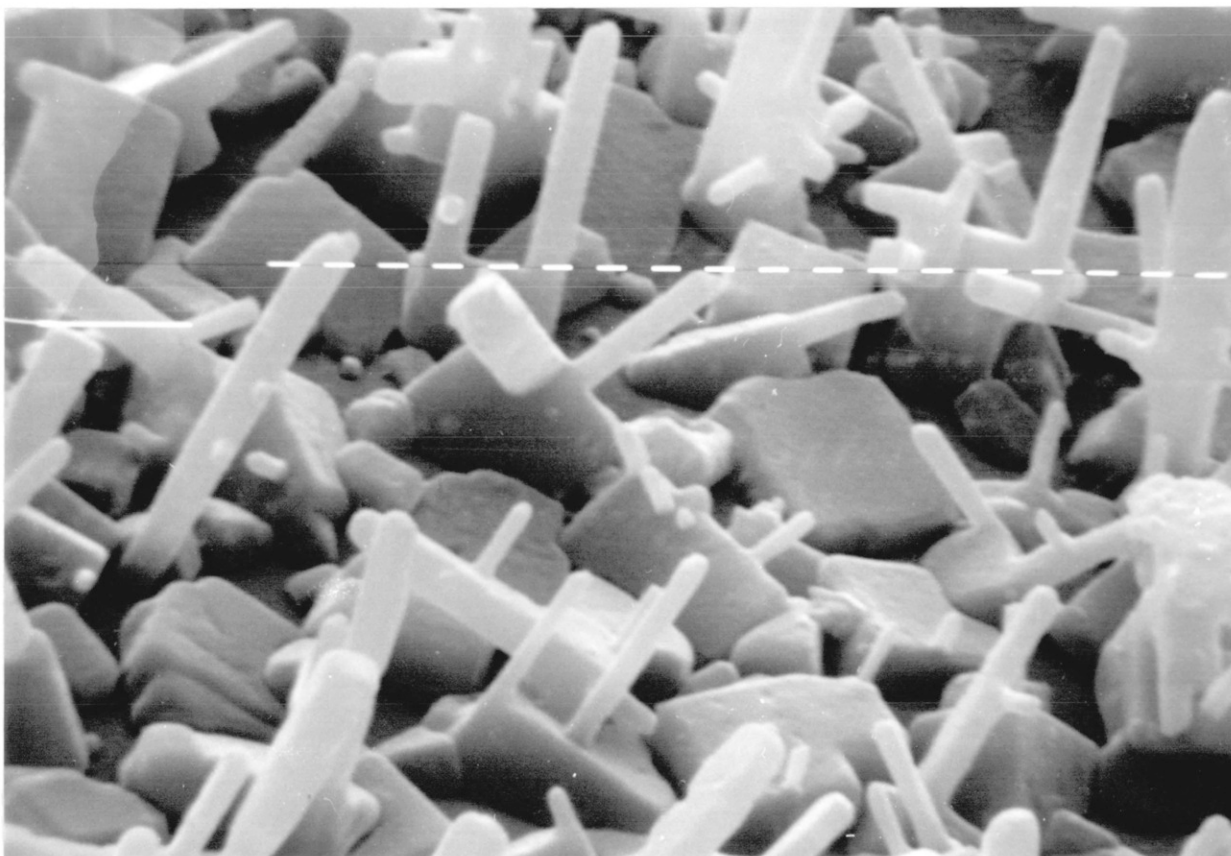
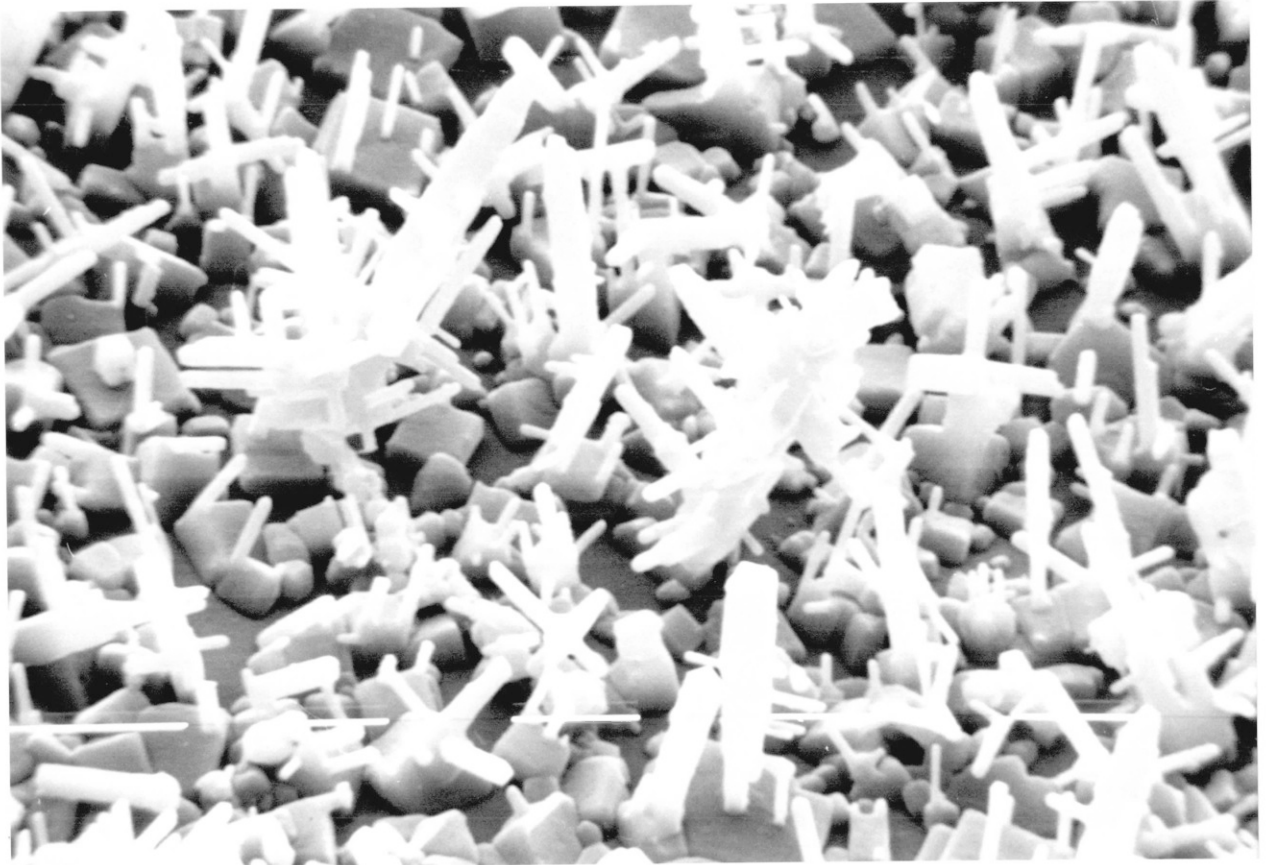


Figure 60a. Electron Micrograph of Deposit from Coal 1 Combusted in a Limestone Bed, showing needle-like growth on cubic crystals.

(b)



10 μm

(c)

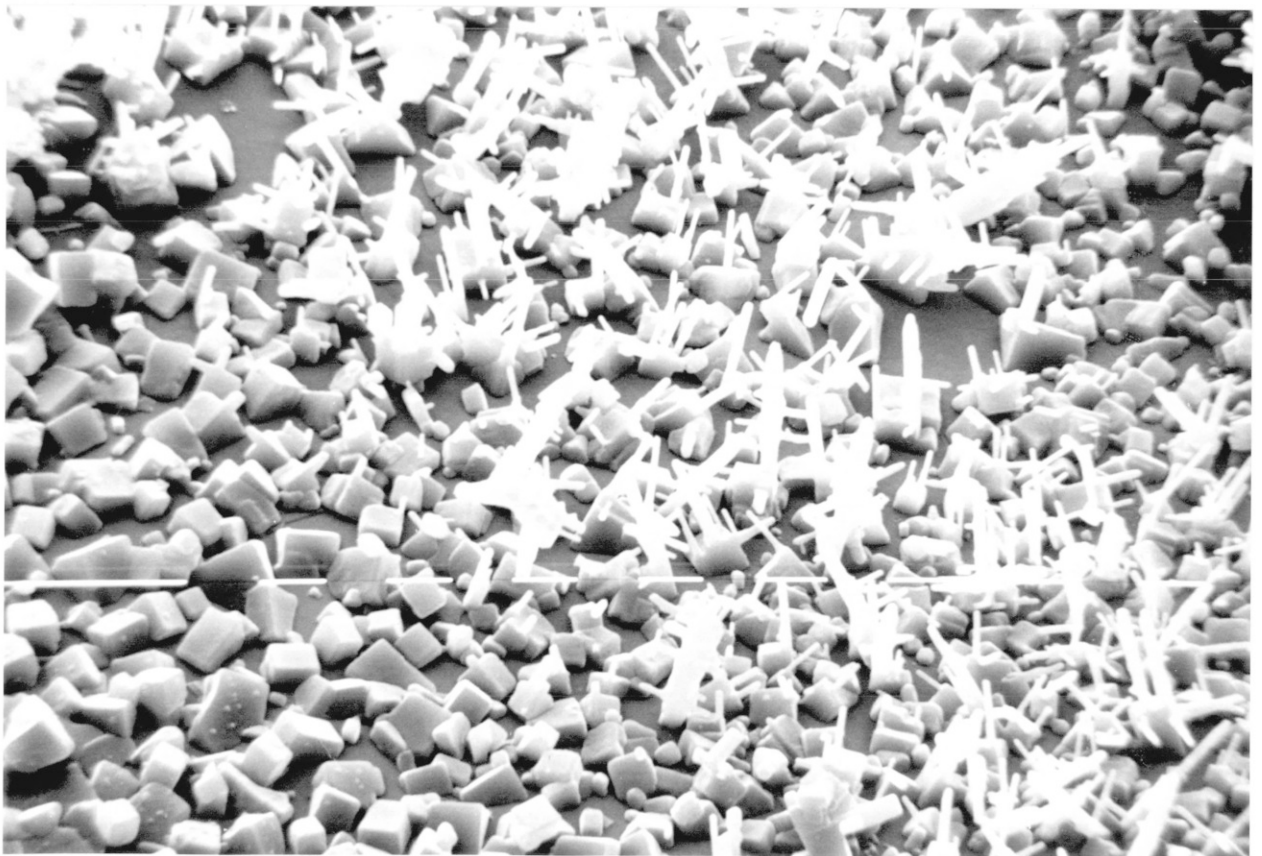


Figure 60b and c. Electron Micrographs of Deposit from Coal 1 Combusted in a Limestone Bed, showing needle-like growth on cubic crystals.



Figure 61. Electron Micrograph of Deposit from Coal 1 Combusted in a Limestone Bed, showing cubic and partially fused halide crystals.

10μm

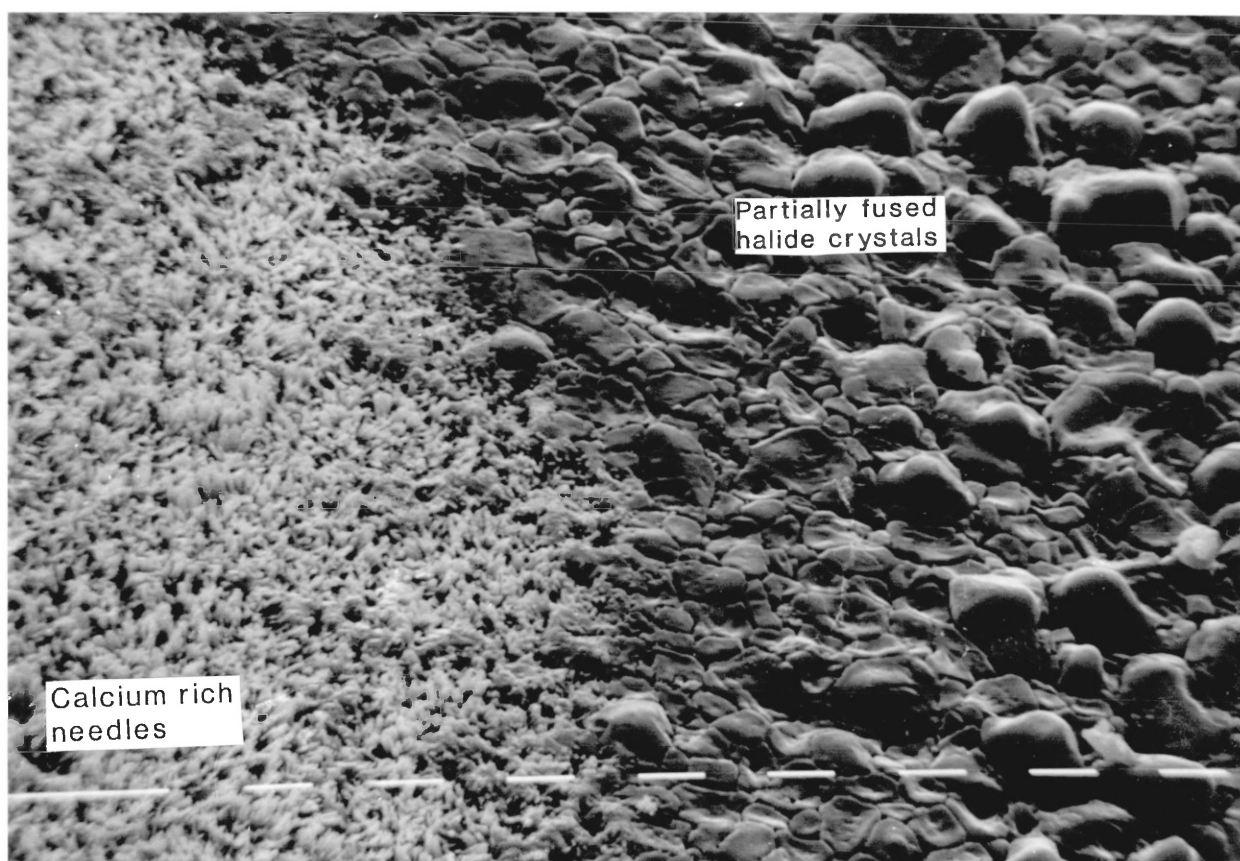


Figure 62. Electron Micrograph of Deposit from Coal 1 Combusted in a Limestone Bed, showing partially fused halide crystals and calcium rich needles.

5 μ m

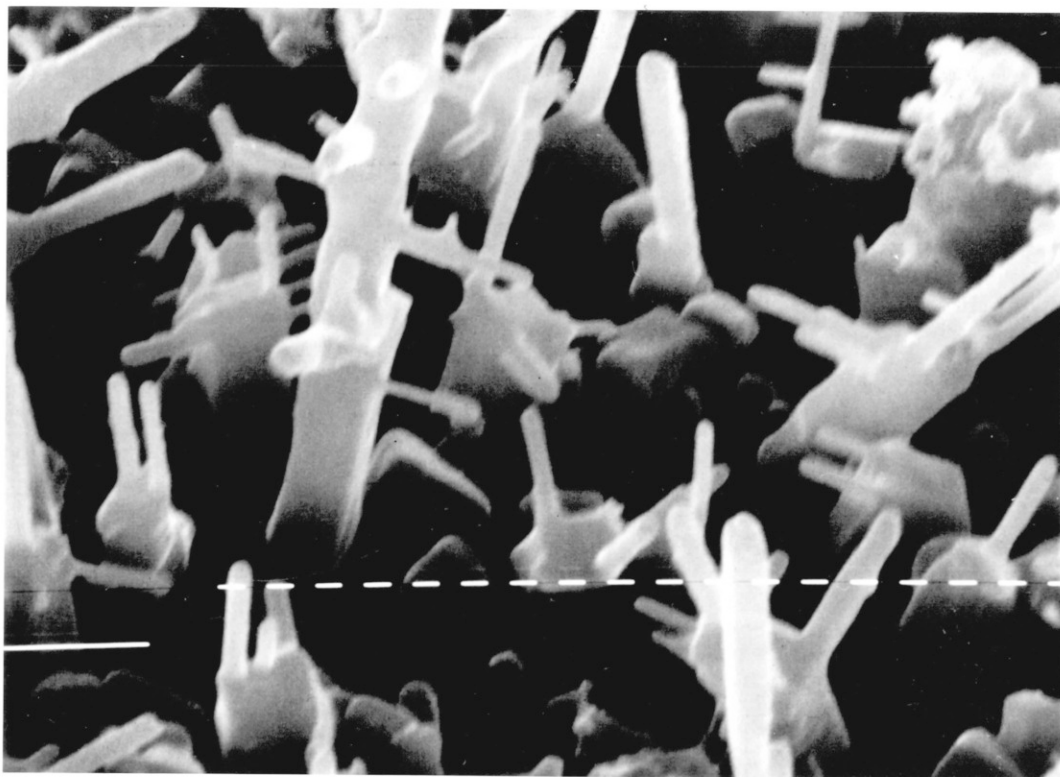


Figure 63a. Electron Micrograph of Deposit from Coal 1 Combusted in a Limestone Bed showing needle-like growth from cubic crystals.

5 μ m

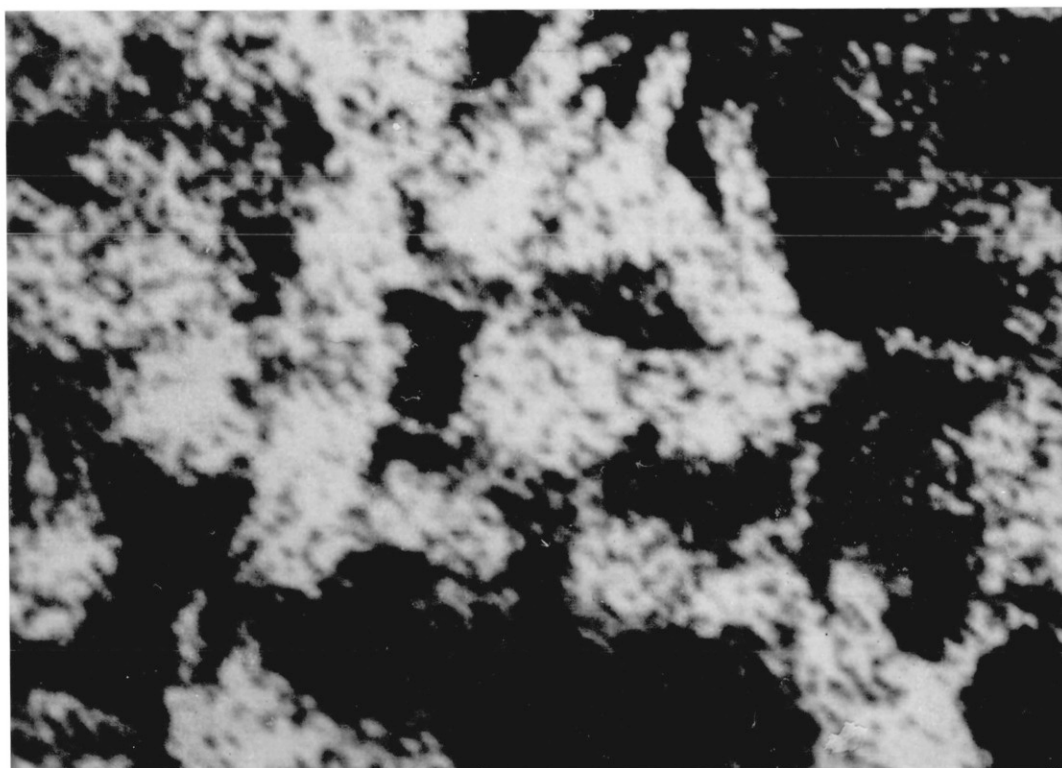
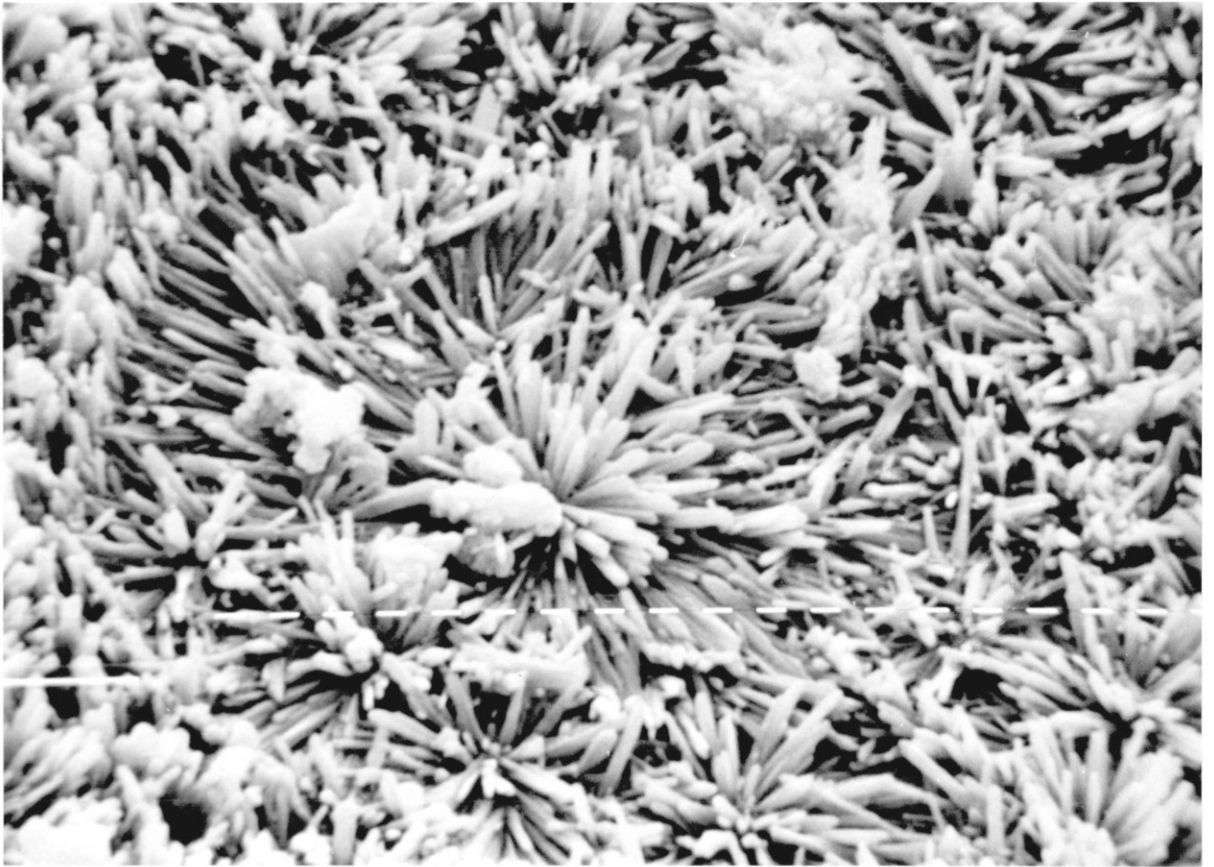


Figure 63b. Chlorine Digimap of Figure 63a showing Chlorine enriched areas. The dark background in both micrographs is the probe surface.

(a)



(b)



Figures 64a and b. Electron Micrographs of Deposit from Coal 1 Combusted in a Dolomite Bed, showing Calcium rich needle-like growths.



Figure 65. Electron Micrograph of Deposit from Coal 1 Combusted in a Dolomite Bed, showing deposit build-up.



Figure 66. Electron Micrograph of Deposit from Coal 3 Combusted in a Limestone Bed.

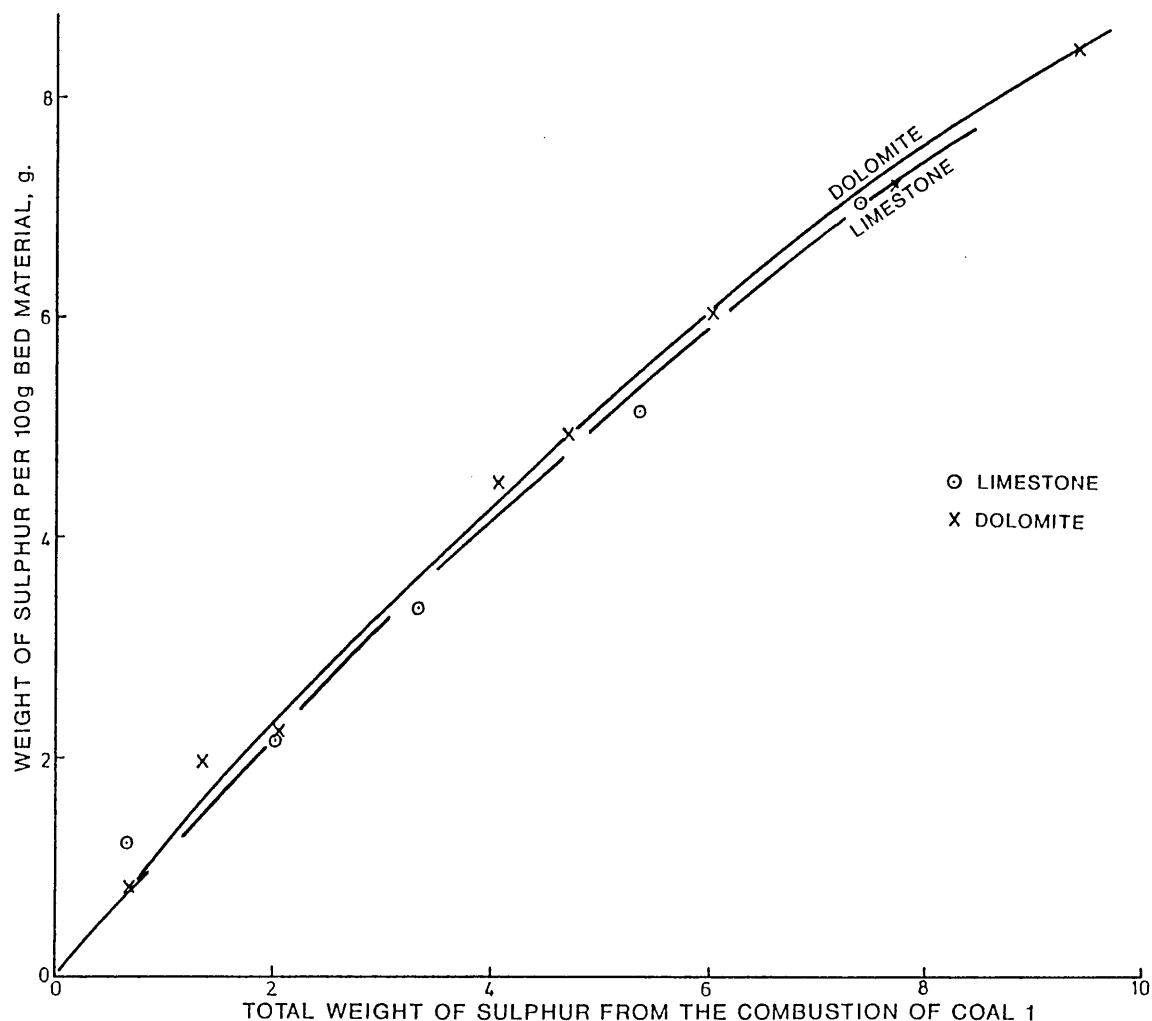


Figure 67. Sulphur Retention in Limestone and Dolomite Beds during the Combustion of Coal 1.

Adhesion of bed material to 'clean' probe surfaces during blank runs, in which no coal was combusted, was not significant.

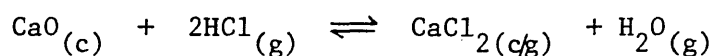
Due to the high sulphur retention efficiency of the sorbent (>90%), partial pressure of sulphur dioxide in the freeboard will be significantly lower and gas phase reactions with alkali chlorides to form alkali sulphates reduced. Increased proportions of gaseous alkalis as their chlorides will enhance initial and ensuing deposition.

The results are particularly significant for Coal 3 whose high sulphur content may previously have acted as an alkali sorbent during FBC in a sand bed, fixing Na^+ and Ca^{2+} as their sulphates. The increase in SO_4^{2-} deposited may be partially attributable to the higher proportion of cations released.

Concentration levels of Na^+ and Cl^- deposited during combustion of Coal 1 in a limestone bed are particularly high. In addition, morphological evidence for the vapour-solid condensation mechanism, by nucleation and growth at a site on the probe surface, is shown in Figures 59 and 60, and appears to become an increasingly important mechanism for higher particle pressures of gaseous sodium chloride. Figures 61 and 62 show both unfused and partially fused alkali chloride crystals adhering to the probe surface. An additional feature of the cubic crystals were the needles growing at right angles to the crystal face, frequently adjacent to a crystal edge (Figure 60). The digimap of the probe surface, illustrated in Figure 63a, highlights chloride enriched areas (Figure 63b) and confirms the needle-like growths are also halides. The dark background in both photomicrographs is the probe surface. The needle-like type of crystal growth may partially be attributable to stress dislocations (surface tension or thermal). In addition ion impurities or poisoning of areas of the cubic crystal surface (by elutriated bed material) could leave remaining sites to grow rapidly by faults and screw dislocations. A number of these needle-like crystals exhibited 'dendritic-like' growths, which consisted of perpendicular branches.

This type of crystal growth was less apparent in deposits formed from Coal 1 combusted in a dolomite bed, possibly due to the additional presence of fine MgO particles inhibiting halide crystal growth further, and would account for the lower concentrations of Na^+ and Cl^- in Figure 57a and e. An interesting feature of the deposits were calcium rich needle-like crystals which appeared to have nucleated and grown from the vapour phase from a particular site on the probe/deposit surface (Figure 64). This type of elongated single crystal growth can occur under conditions in which only a slight supersaturation of the gaseous phase is experienced. Calcium enriched needles of similar morphology were present in deposits formed from Coal 1 combusted in a limestone bed (Figure 62) and at low oxygen partial pressures (Section 5.1.4). The needle-like crystals illustrated in Figures 62 and 64 may have originated from the

carbonate rock bed material following attack by hydrogen chloride. Thermochemical data, obtained from NPL, of standard free energy changes for the chlorination of calcium oxide at elevated temperatures, indicate that the following reaction is favourable at FBC temperatures.



$$\Delta G^{1100} = -96.7 \text{ kJ mol}^{-1}$$

At 830°C the vapour pressure of calcium chloride is significant and concentrations will be at least partially dependent on the partial pressure of hydrogen chloride i.e. the chlorine content of the coal. Volatile calcium chloride will preferentially react with the lower partial pressure of sulphur dioxide present, to form calcium sulphate (Section 2.5.2). The needles, which are low in chlorine, are however, significantly smaller than the calcium sulphate crystals deposited during the combustion of Coal 1 in a sand bed (Figure 36).

The small increase in K^+ deposition for Coal 1 may be attributable to the reduction in sulphonation reactions and subsequent enhanced adhesion properties of the depositing potassium species as chlorides.

Figure 65 illustrates deposit build-up for Coal 1 combusted in a dolomite bed. In contrast, deposition from Coal 3 combusted in a limestone bed, was lighter and less crystalline (Figure 66), the major features being unfused iron oxide, dehydrated clays and calcium enriched crystals (probably CaSO_4).

5.2 Coal Pretreatments

5.2.1 Coal blends

The alkali, alkaline earth, chlorine and sulphur analyses for the two coals and their three blends are given in Table 39, together with their alkali/alkaline earth to chlorine and sulphur ratios. The results of deposition concentrations from the three blends of coals are listed in Table 40 whilst Figures 68 to 70 compare theoretical deposition concentrations (Tables 25 and 27) with those found in practice.

Table 39 Elemental Analysis of Blends of Coals 1 and 3

ELEMENTS	% m/m db in Coal				
	COAL 1	COAL 3	COAL 1:COAL 3 2:1	COAL 1:COAL 3 1:1	COAL 1:COAL 3 1:2
Na	0.18	0.11	0.16	0.145	0.13
K	0.01	0.10	0.04	0.055	0.07
Ca	0.47	0.13	0.36	0.3	0.24
Mg	0.08	0.04	0.07	0.06	0.05
Cl	0.8	0.3	0.63	0.55	0.47
S	0.84	1.65	1.11	1.245	1.38

ELEMENTAL RATIOS

Na/Cl	0.225	0.37	0.25	0.26	0.28
Na/S	0.21	0.07	0.14	0.12	0.09
K/Cl	0.01	0.33	0.06	0.1	0.15
K/S	0.01	0.08	0.04	0.045	0.05
Ca/Cl	0.59	0.43	0.57	0.545	0.51
Ca/S	0.56	0.13	0.32	0.24	0.17

Table 40 Deposition of Soluble Sodium, Potassium, Calcium, Magnesium, Chloride and Sulphate from Blends of Coals 1 and 3

Deposition Temperature °C	DEPOSIT CONTENT, gm ⁻² x 10 ⁻²					
	Na	K	Ca	Mg	Cl	SO ₄
<u>2:1 Blend of Coal 1 : Coal 3</u>						
405	40	10	15	<10	<10	150
475	90	50	40	<10	<10	320
515	135	75	130	<10	10	460
540	145	65	160	<10	15	560
560	205	75	180	<10	20	620
575	255	75	290	10	20	790
590	265	90	300	10	15	790
600	310	95	250	10	20	795
610	305	100	230	15	10	750
630	275	95	200	15	15	680
640	270	80	150	10	10	640
650	255	75	135	10	10	580
680	175	60	110	<10	10	535
745	150	30	60	<10	10	340
<u>1:1 Blend of Coal 1 : Coal 3</u>						
475	15	25	<10	<10	10	60
500	55	40	30	<10	15	180
520	75	50	40	<10	15	220
555	115	65	50	<10	15	300
565	140	85	85	<10	20	430
580	155	100	100	<10	15	485
590	170	80	100	<10	15	475
600	195	90	90	<10	15	515
615	195	75	140	<10	15	515
620	175	75	110	<10	15	510
630	160	75	90	<10	15	470
655	155	65	50	<10	15	390
695	50	40	25	<10	<10	150
<u>1:2 Blend of Coal 1 : Coal 3</u>						
475	25	25	<10	<10	10	80
505	60	25	10	<10	15	165
525	80	30	15	<10	15	265
545	115	40	35	<10	10	280
560	125	60	55	<10	20	330
580	150	70	55	<10	15	405
590	170	70	55	<10	15	475
605	180	65	50	<10	15	470
615	145	60	50	<10	15	390
630	135	60	45	<10	15	355
670	120	45	40	<10	15	300
690	100	25	25	<10	10	220

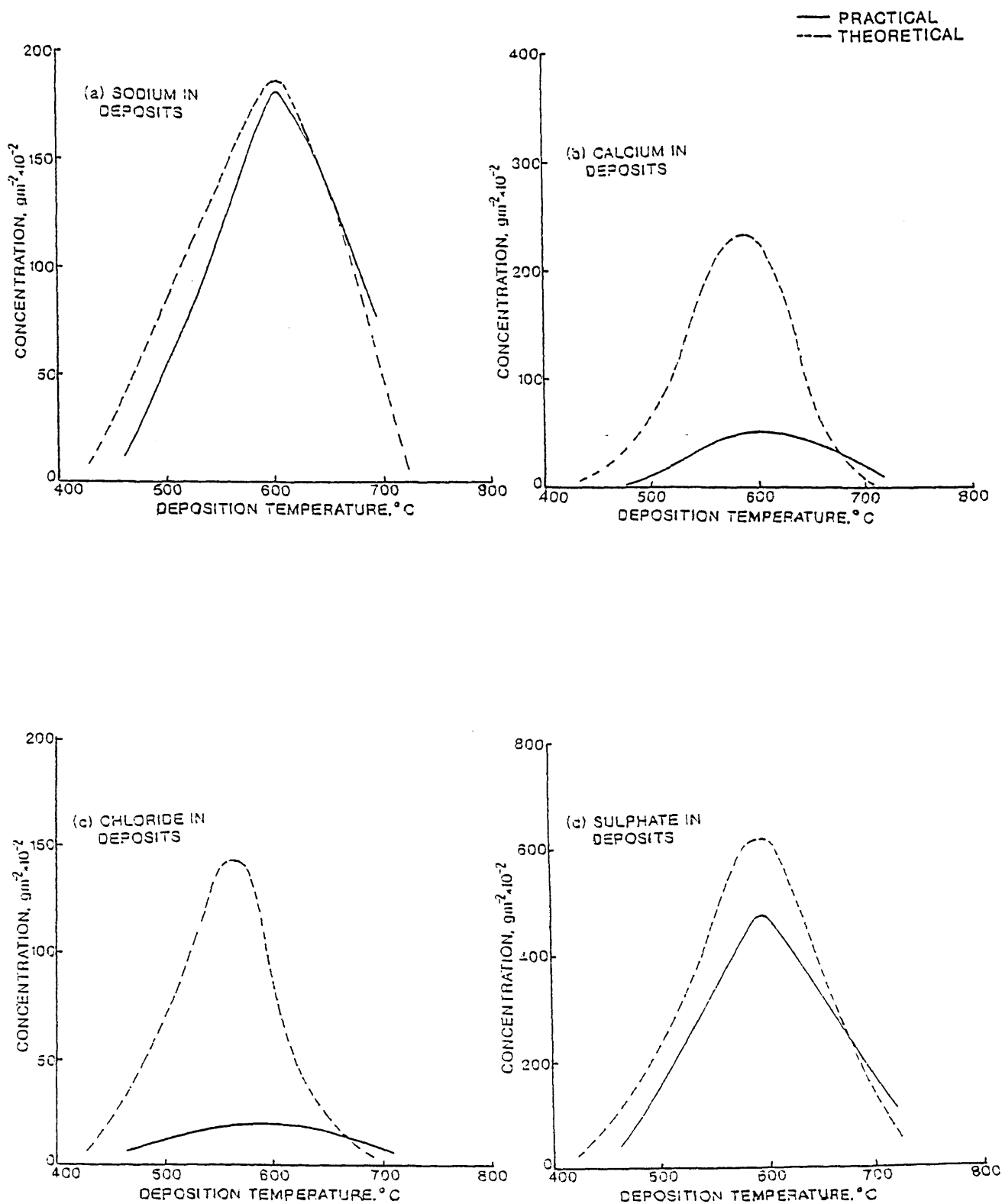


FIGURE 68a to d. DEPOSITION OF SOLUBLE SODIUM, CALCIUM, CHLORIDE AND SULPHATE FROM A 1:2 BLEND OF COALS 1 AND 3.

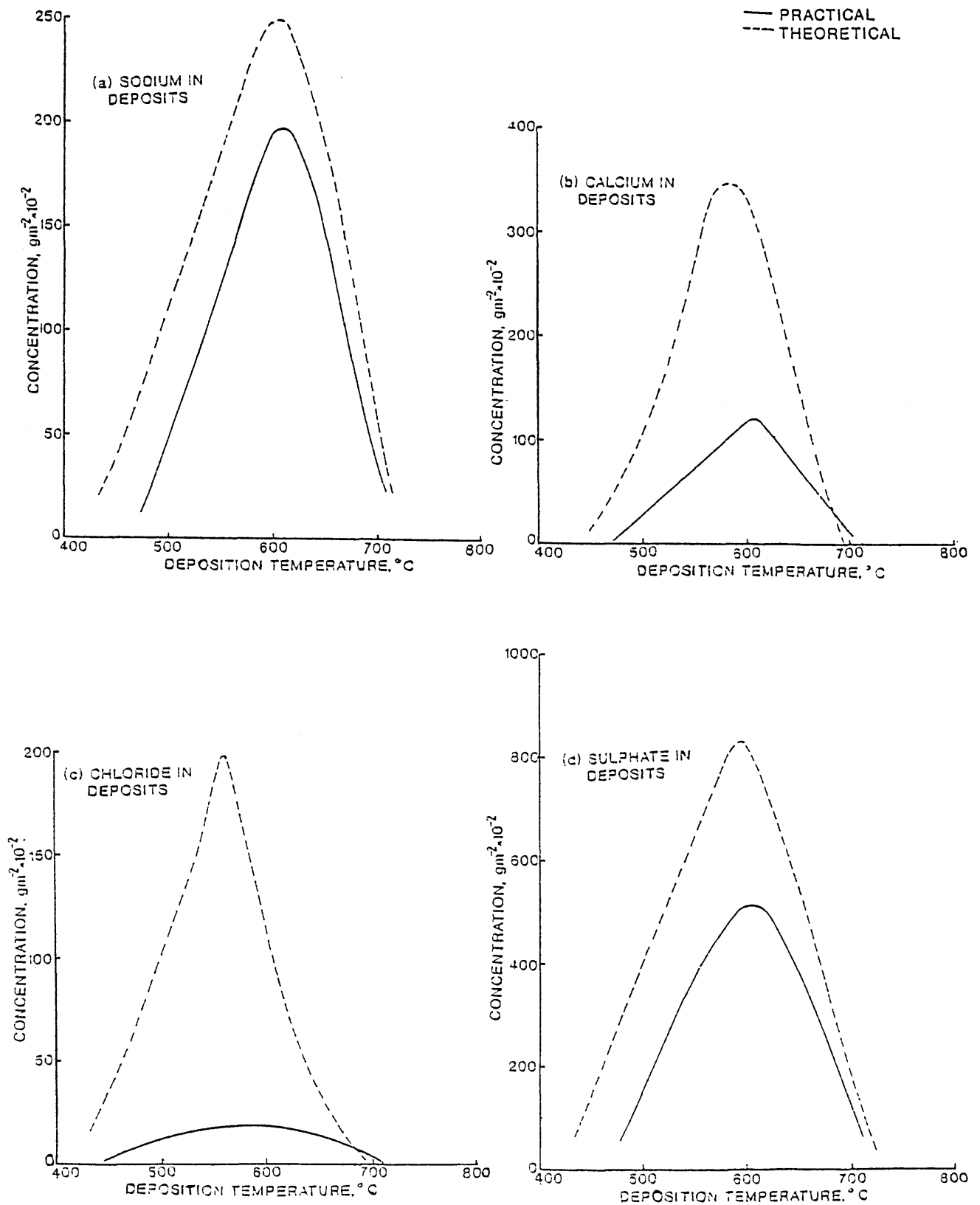


FIGURE 69a to d. DEPOSITION OF SOLUBLE SODIUM, CALCIUM, CHLORIDE AND SULPHATE FROM A 1:1 BLEND OF COALS 1 AND 3.

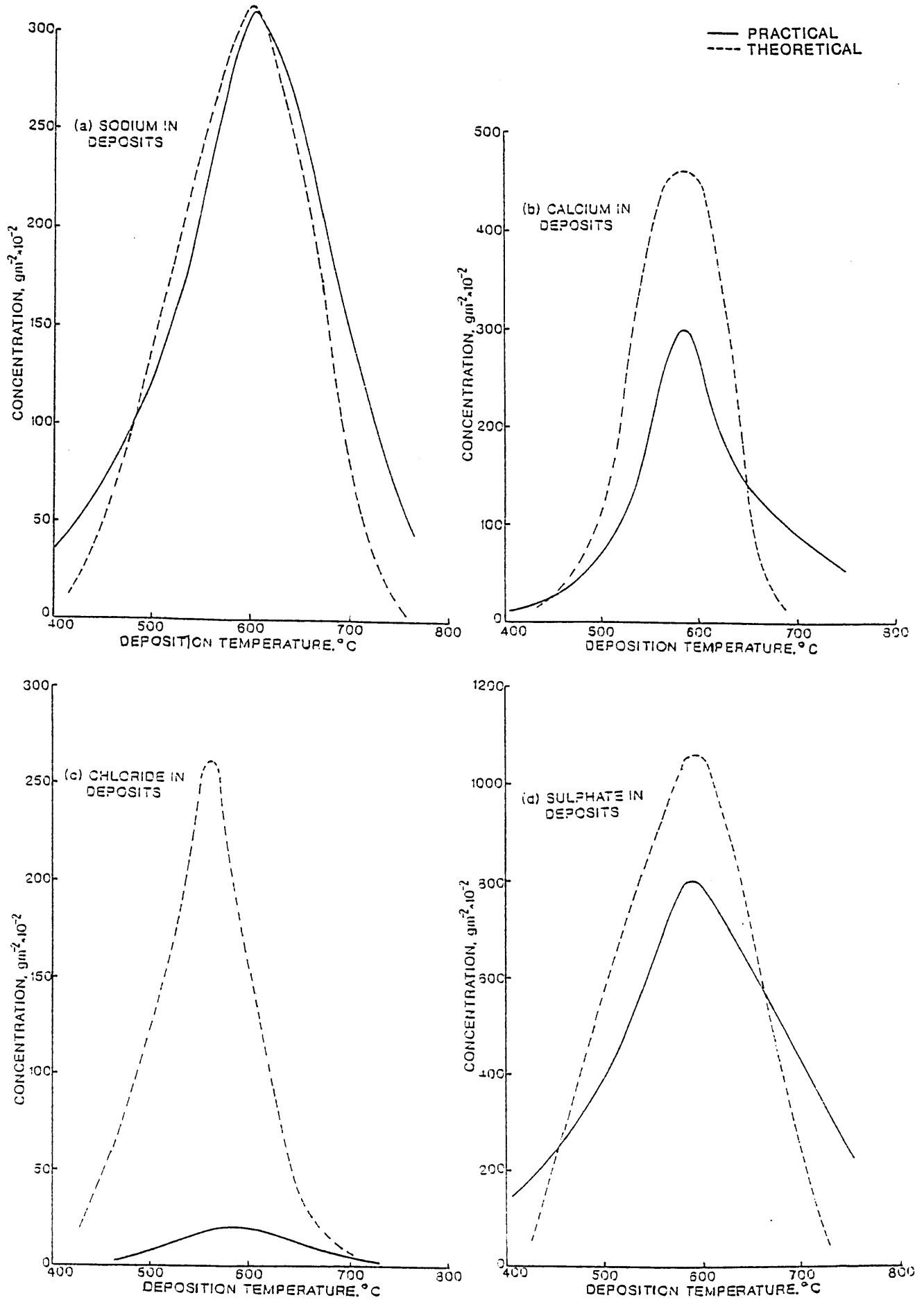


FIGURE 70a to d. DEPOSITION OF SOLUBLE SODIUM, CALCIUM, CHLORIDE AND SULPHATE FROM A 2:1 BLEND OF COALS 1 AND 3.

Differences between theoretical and practical deposition concentrations can be assumed to be due to reactions/interactions occurring between minerals from the two coals.

The release of sodium as sodium chloride is unlikely to be influenced by physical blending of the two coals due to the close proximity of Na^+ and Cl^- ions in the coal pore. The comparative increase in sulphur of the blended coals, as the proportion of Coal 3 increases, will however, enhance reactions between volatile sodium chloride and sulphur dioxide to form sodium sulphate; sodium sulphate being more thermally stable in the combustion atmosphere. Melting points of sodium chloride and sulphate are similar (800 and 884°C respectively) and deposition of Na^+ does not appear to be significantly affected (Figures 68a, 69a and 70a).

Earlier work has indicated that the release of potassium from the micaceous clay minerals may be particularly dependent on alkali exchange mechanisms and to a lesser extent on the volatility of potassium chloride. Blending the coals does not appear to significantly affect the release or deposition of K^+ , although it should be noted that the concentration of K^+ in the deposits is low and susceptible to analytical errors.

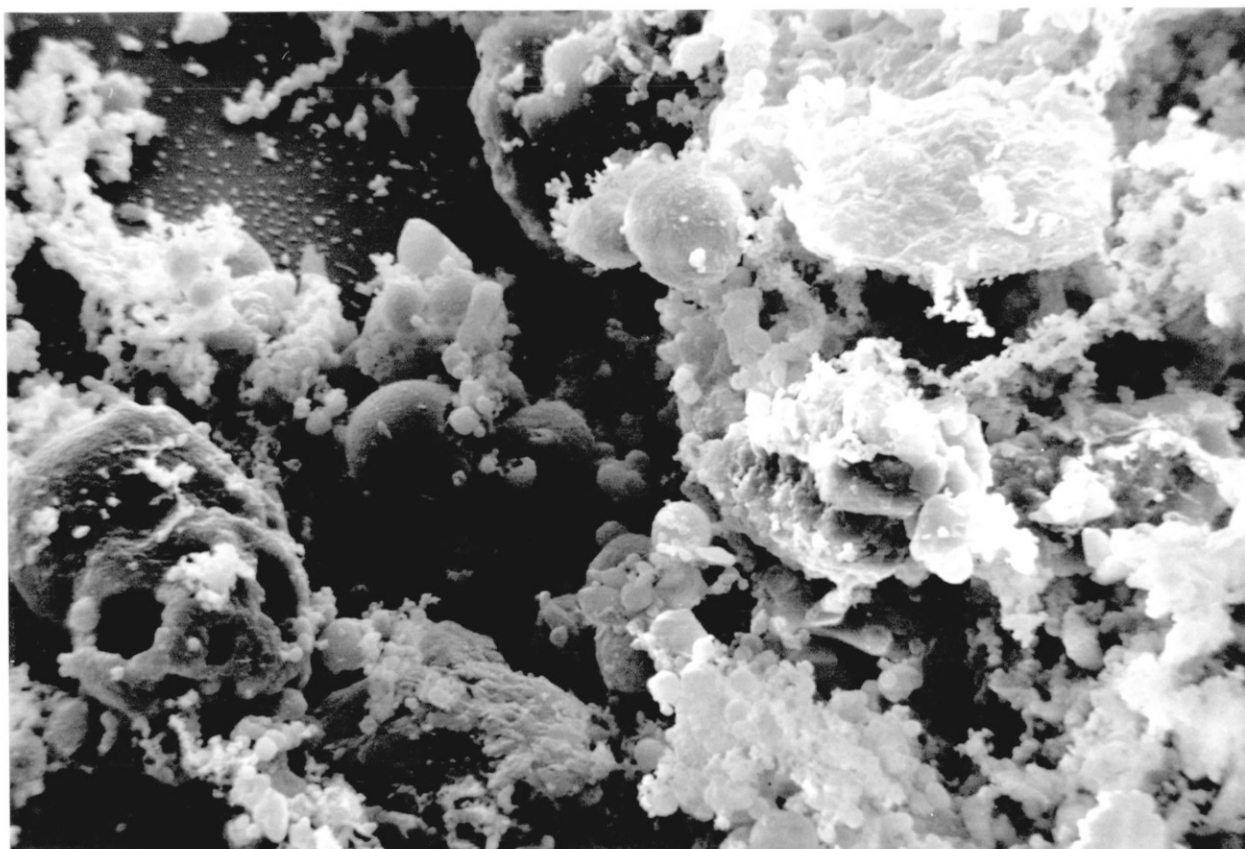
Interestingly, Figures 68b, 69b and 70b show a steady decrease in observed calcium concentration of the deposit as the proportion of Coal 3 increases. This may be due to the sorbent effect of blending a relatively high calcium coal with a high sulphur coal, fixing both as calcium sulphate in the bed.

The significant reduction in Cl^- deposited from the combustion of the blended coals, compared to theoretical data, is probably due to enhancement of reactions between volatile alkali chlorides and sulphur dioxide, and the small decrease in SO_4^{2-} deposition to lower levels of Ca^{2+} volatilised.

Electron micrographs of deposits formed from the combustion of the blended coals (Figures 71 to 73) show an increase in abundance of non-crystalline species, compared to those from the combustion of Coal 1 alone.

Deposition across the probe surface was variable, with dehydrated clays, iron oxides and other fly ash particles adhering to the

(a)



10 μm

(b)

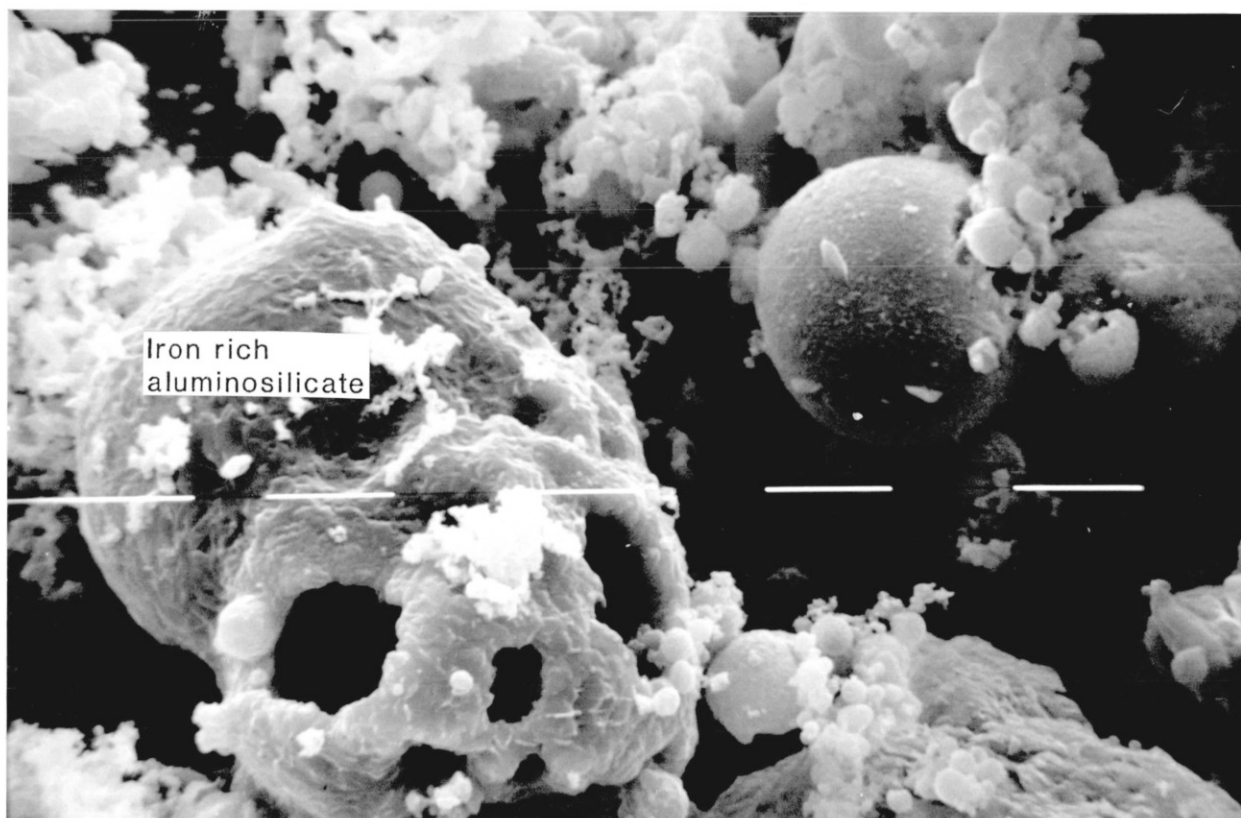


Figure 71 a and b. Electron Micrographs of Deposit formed from the Combustion of a 1:1 Blend of Coals 1 and 3, showing the presence of non-crystalline particles.

10 μm



Figure 72. Electron Micrograph of Deposit formed from the Combustion of a 2:1 Blend of Coals 1 and 3, showing the presence of non-crystalline particles.

10 μm

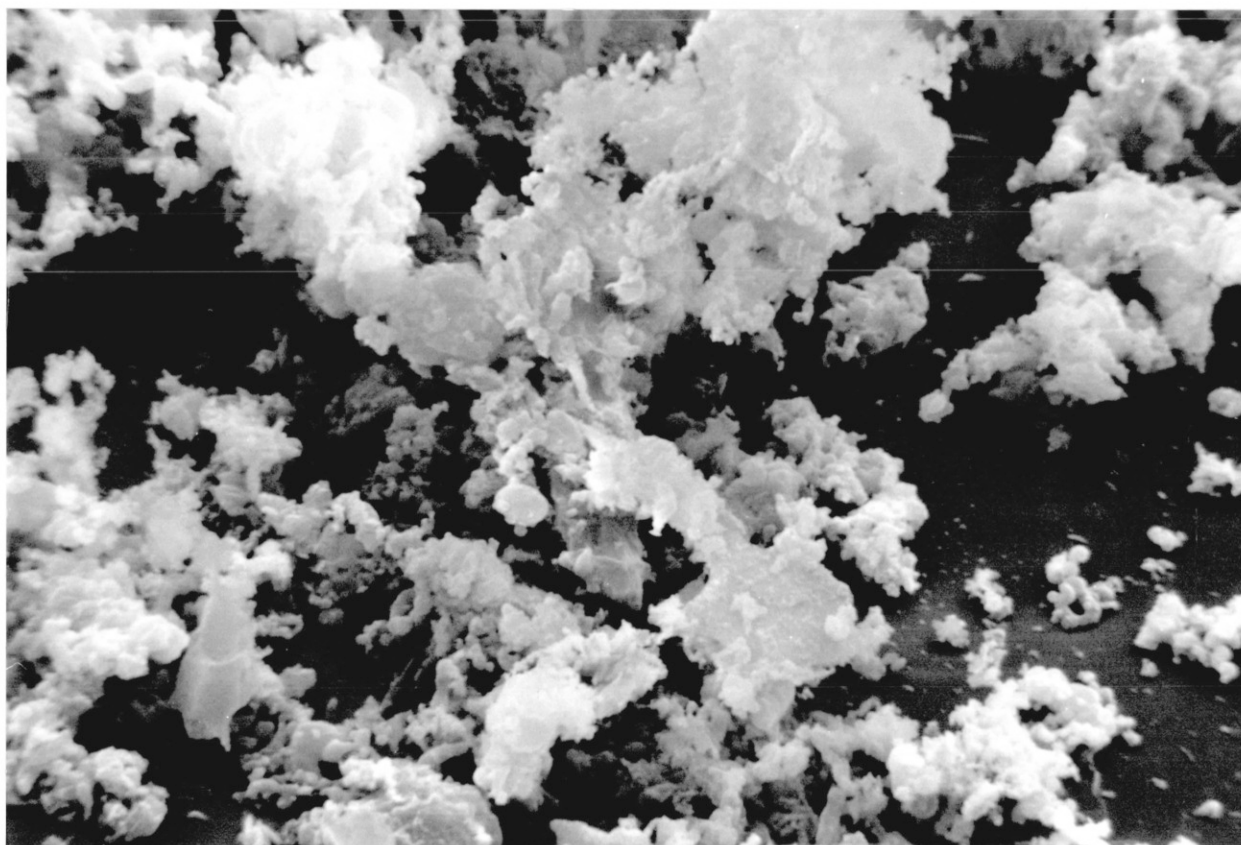


Figure 73. Electron Micrograph of Deposit formed from the Combustion of a 1:2 Blend of Coals 1 and 3, showing the presence of non-crystalline particles.

areas of crystalline deposit. The fused agglomerate in Figure 71a, shown in more detail in Figure 71b, was an iron rich aluminosilicate, the holes presumably being formed from the release of coal volatiles during combustion.

5.2.2 Coal chlorine content

Concentrations of the major dilute acid soluble cations and anions deposited during the combustion of chlorine reduced and enhanced Coal 1 are listed in Table 41 and illustrated graphically in Figure 74 a to f. Table 42 lists the moisture, ash, chlorine, total sulphur and carbon dioxide contents of the treated coals.

Thermal transformation reactions, for the majority of coal minerals, occurred by heating coal in nitrogen at 300°C for 48 hrs, to reduce the chlorine content of the coal, are minimal. The clay minerals and gypsum may dehydrate; the clays only losing surface adsorbed and interlattice water and probably rehydrating when allowed to equilibrate with the atmosphere.

Some of the chlorine (~0.23%) introduced into coal during pretreatment via gaseous hydrogen chloride has probably dissolved in water trapped in coal pores. The reduction in carbon dioxide content of the chlorinated coal, however, indicates that significant decomposition of the carbonate minerals has occurred (~90%) resulting in their presence as more volatile chloride species of calcium, magnesium and iron. Solid-state ^{23}Na NMR indicated that the occurrence of sodium in Coal 1 was not significantly affected by either coal pretreatments.

Table 41 and Figure 74, a to f, show that lower concentrations of all the monitored ions were deposited on the probes during the combustion of the lower chlorine content coal; the temperature at which maximum depositions occurred being 50-90°C higher for the majority of these ions. Earlier work (Section 5.1.1) has suggested that sodium, potassium, calcium and magnesium are mainly released from UK coals, during FBC, as their chlorides. The reduction in coal chlorine content will presumably affect the volatilisation of these cations, fixing them in the bed as less volatile species, such as oxides or sulphates. Studies (30) of low chlorine, sub-bituminous, US coals have suggested that sodium

Table 41 Deposition of Soluble Sodium, Potassium, Calcium, Magnesium, Chloride and Sulphate from Chlorine Reduced and Enhanced Coal 1

Deposition Temperature °C	DEPOSIT CONTENT, $\text{gm}^{-2} \times 10^{-2}$					
	Na	K	Ca	Mg	Cl	SO ₄
<u>Chlorine Reduced Coal 1</u>						
465	25	30	10	<10	<10	120
515	50	10	10	<10	10	180
530	70	10	10	<10	10	225
550	85	45	30	<10	15	325
555	85	55	30	<10	20	360
565	90	55	40	<10	20	345
575	110	65	55	<10	20	355
575	145	70	60	<10	20	430
605	150	75	65	<10	20	460
620	165	70	60	<10	20	425
630	140	50	70	<10	15	430
640	140	55	60	<10	10	450
665	180	45	110	<10	<10	490
675	200	45	110	<10	<10	610
680	195	45	115	<10	10	620
700	160	30	105	<10	<10	640
720	175	15	125	<10	<10	560
725	175	10	110	<10	<10	470
730	155	15	140	<10	<10	400
750	125	10	50	<10	<10	150
785	125	10	45	<10	<10	130
<u>Chlorine Enhanced Coal 1</u>						
475	105	60	95	<10	125	110
520	95	65	215	<10	170	545
550	170	100	625	25	340	895
555	220	125	640	10	340	900
575	400	100	535	15	300	1335
595	625	90	1200	90	420	1470
600	630	90	1350	80	410	1965
605	630	80	1360	65	270	1925
620	630	70	1460	80	270	2120
630	580	65	1320	50	250	1265
650	395	45	460	30	145	1025
660	395	40	470	15	140	940
685	280	25	425	<10	85	810
730	80	15	95	<10	<10	110

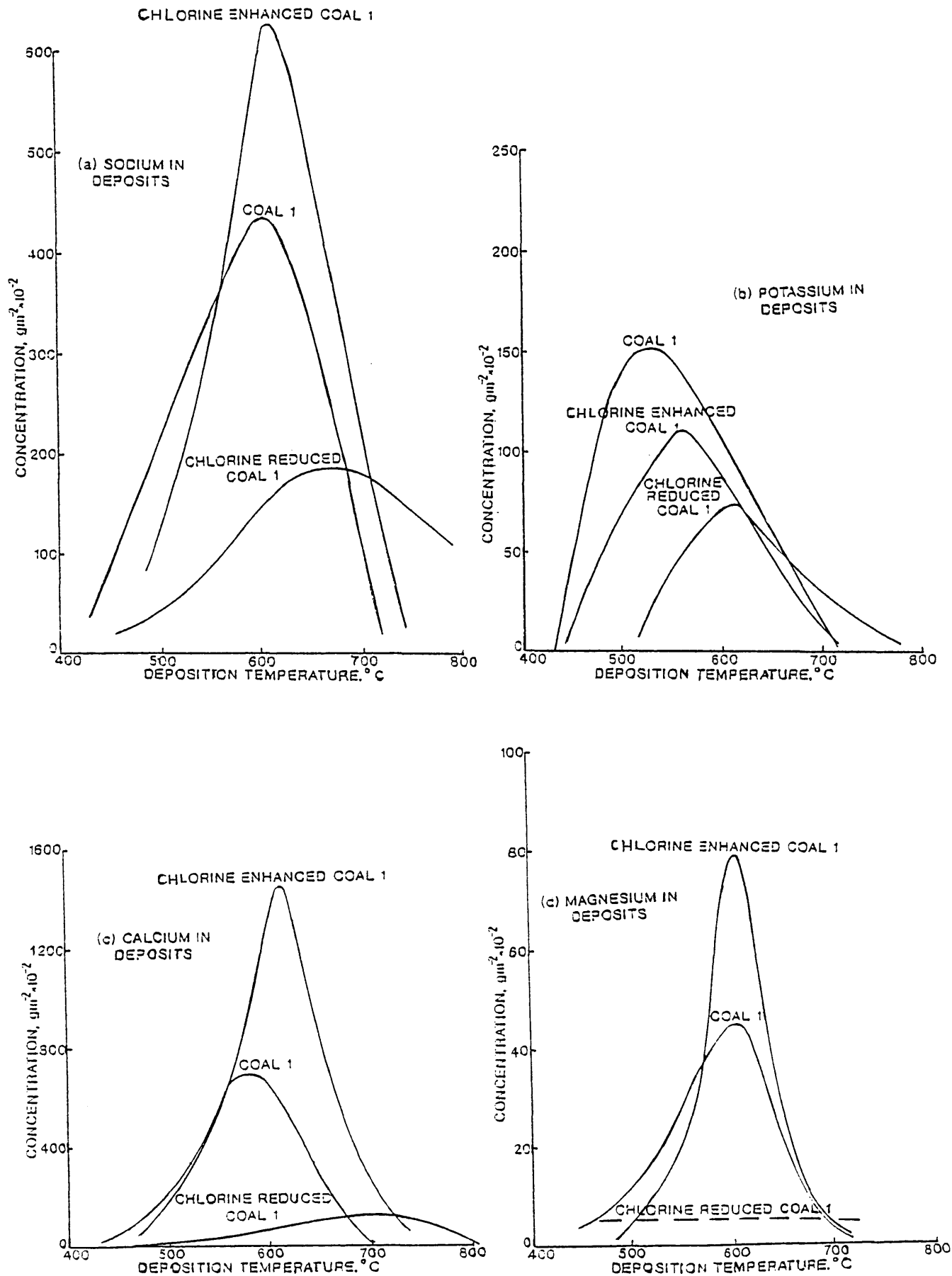


FIGURE 74a to d. THE EFFECT OF COAL CHLORINE CONTENT ON THE DEPOSITION OF SOLUBLE SODIUM, POTASSIUM, CALCIUM AND MAGNESIUM - COAL 1

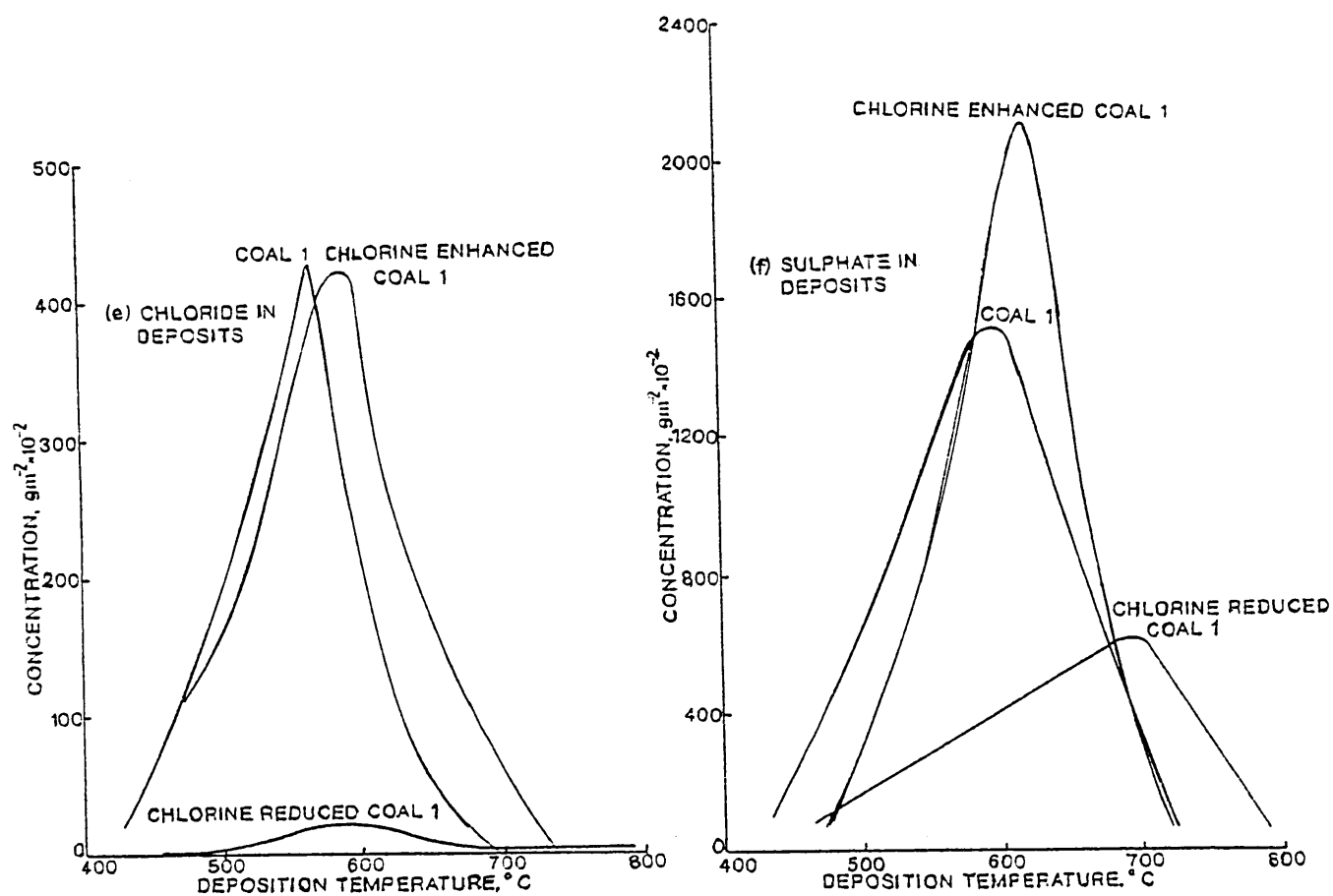


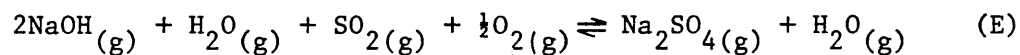
FIGURE 74e and f. THE EFFECT OF COAL CHLORINE CONTENT ON THE DEPOSITION OF SOLUBLE CHLORIDE AND SULPHATE - COAL 1

Table 42 Analysis of Chlorine Reduced and Enhanced Coal 1

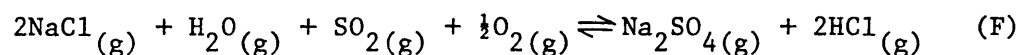
		Chlorine Reduced Coal 1	Coal 1	Chlorine Enhanced Coal 1
Moisture,	aa	5.4	8.0	8.1
Ash,	aa	3.2	3.1	3.0
Total Sulphur,	db	0.78	0.84	0.80
Chlorine,	db	0.18	0.8	1.43
CO ₂	db	ND	0.5	0.05

ND = not determined

and potassium may also be released as their hydroxides. Vapour pressure data for NaCl and NaOH and for KCl and KOH at 850°C, are similar (Figure 4). However vapour pressures of CaO and MgO at 850°C are very low which could account for the significantly lower calcium content of the deposits. Reactions between sodium and potassium hydroxides and sulphur dioxide are highly favourable at temperatures in the range 400 to 800°C (Figure 7) e.g.



$$\Delta G^{873} = -3.52 \times 10^2 \text{ kJ mol}^{-1}$$



$$\Delta G^{873} = -2.43 \times 10^2 \text{ kJ mol}^{-1}$$

and sodium volatilised as sodium hydroxide will probably be present as sodium sulphate on the probe surface. In addition, lower levels of HCl_(g) in the combustion atmosphere will favour deposition of alkali sulphates (Reaction F). Consequently the

melting point of the initial deposit will rise as the proportion of alkali sulphates increases (Figure 41), as will the maximum deposition temperature of the probes. This further reduces ensuing calcium and magnesium deposition at lower probe temperatures.

Micrographs of deposits collected during the combustion of chlorine reduced Coal 1 (Figure 75, a and b) show the partially fused cubic crystals of sodium and potassium sulphates adhered to the probe surface and illustrate that ensuing deposition is lower and largely consists of non-crystalline fly ash particles.

Analyses of deposits formed from the combustion of chlorine enhanced Coal 1 (Table 41 and Figure 74, a to f) also suggest that chlorine affects the release/deposition of the ionisable salt minerals during combustion. Enhanced deposition of Na^+ is partially due to chlorine promoting the release of the alkali metals from the mineral matter (Section 2.6.1). In addition, slightly higher partial pressures of gaseous hydrogen chloride will suppress the formation of sodium sulphate in Reaction F. This will also affect ensuing deposition.

The increase in Ca^{2+} and Mg^{2+} deposition is largely attributable to the decomposition of the carbonate minerals during coal preparation. Work by Ruch et al (111) and earlier work on deposition trends of the three coals of varying calcium, magnesium and chloride contents (Section 5.1.1), however, indicates that the chlorine content of a coal may influence the release of Ca^+ and Mg^+ from the carbonate minerals during combustion.

The increase in SO_4^{2-} content of the deposit could be partially attributable to enhanced sulphonation of equilibrating $\text{MCl}_{(g)} \rightleftharpoons \text{MCl}_{(c)}$ at the probe surface, (where $\text{M} = \text{Na}, \text{K}, \frac{1}{2}\text{Ca}$ and $\frac{1}{2}\text{Mg}$), as the halide content of the initial deposit increases.

The K^+ content of the deposit appears to be largely independent of an increase in chlorine concentration. This suggests that the release of K^+ from the micaceous clay minerals, by some form of cation exchange mechanism is the major rate governing factor for potassium deposition. The role of Cl^- is to promote its volatilisation as potassium chloride following release.

5 μm

(a)



10 μm

(b)

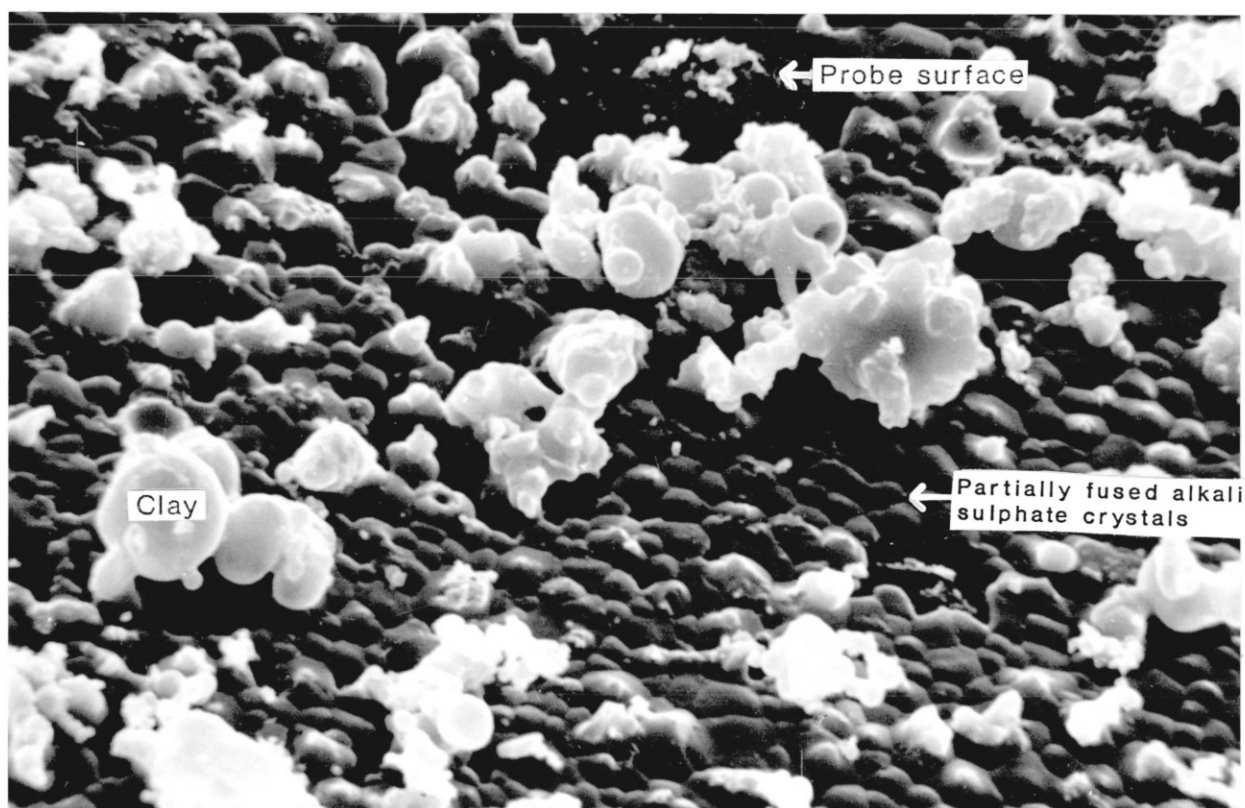


Figure 75a and b. Electron Micrograph of Deposit formed from the Combustion of Chlorine Reduced Coal 1, showing the partially fused cubic crystals of sodium and potassium sulphates.

Figure 76, a and b are micrographs of deposits collected during the combustion of chlorine enhanced Coal 1 and show the predominance of calcium sulphate crystals and deposit build up.

5.3 Encomech Pilot Plant Trials

The Encomech is a 0.2 MW FBC sited at CRE and used for pilot plant trials. It is designed on the 2.5 MW Peabody Encomech FBC which supplies clean hot air to Bass Maltings, Burton, Staffordshire (182).

Coals 1 and 3 were burned as washed singles under the test conditions given in Table 43. Moisture, ash, carbon, chloride and ash analyses/fusion data for the two coals and their associated fly and bed ashes (+2 mm) are given in Table 44. Weights of deposit found on a typical in-bed and above-bed 310 stainless steel heat exchanger tube following both plant trials are listed in Table 45 and their chemical analyses in Table 46.

Table 43 Pilot Plant Test Conditions

Time	100 hours
Bed temperature	900°C
Coal feed rate	~40 kg hr ⁻¹
Fluidising air velocity	1.2 m s ⁻¹
Excess oxygen	8.5%
Total coal burnt	4 tonnes
Bed material	Sand

The melting behaviour of the deposits, fly ashes and LTA, determined by high-temperature microscopy is reported in Table 47. Major phases detected by XRD in above-bed and in-bed deposits are given in Table 48. Figure 77 shows the morphology of the above-bed deposit formed during combustion of Coal 1 whilst Figure 78 graphically illustrates the variations of elemental concentrations (of Na, Ca, Al, Si, S and Cl) of a 0.2 by 0.2 mm area across the deposits' cross sectional surface.

Table 44 Coal, Fly and Bed Ash Analyses

		Coal 1			Coal 3		
		Coal	Fly ash	Bed ash +2 mm	Coal	Fly ash	Bed ash + 2 mm
Moisture	aa %	10.1	2.0	1.0	6.3	1.0	0.4
Ash	aa %	2.8	51.0	83.8	5.8	60.4	93.9
Carbon	db %	79.9	47.2	11.5	79.2	38.9	3.8
Chlorine	db %	0.8	1.6	0.4	0.4	0.03	0.05
Ash fusion							
- reducing atmosphere							
Deformation	°C	1090	1120	1060	1170	1180	1200
Hemisphere	°C	1130	1140	1130	1240	1230	1350
Flow	°C	1250	1170	1180	1290	1290	1390
<u>% on ash</u>							
Na ₂ O		7.6	4.4	6.2	2.7	2.4	2.0
MgO		3.6	4.2	1.1	1.2	0.5	1.4
Al ₂ O ₃		14.2	21.4	14.9	28.3	27.9	23.1
SiO ₂		17.0	30.4	46.8	42.9	45.6	59.0
P ₂ O ₅		0.9	0.9	0.4	0.2	0.2	0.4
SO ₃		23.2	5.8	7.0	2.3	1.4	1.7
K ₂ O		0.1	<0.2	0.9	1.7	2.0	2.8
CaO		19.2	19.7	4.0	3.2	2.7	1.9
TiO ₂		0.65	0.6	0.6	1.1	0.7	1.1
Mn ₃ O ₄		0.2	0.2	0.2	0.1	0.03	0.1
Fe ₂ O ₃		11.6	12.3	18.0	16.4	16.5	6.4

aa - as analysed
db - dry basis

Table 45 Pilot Plant Deposit Weights

Coal	Tube location	Deposit wt, g	
		On tube	Total
1	In-bed	46.7	126.2
	Above-bed	79.5	
3	In-bed	8.2	52.7
	Above-bed	44.5	

Table 46 Chemical Analyses of Furnace Deposits

%	Coal 1		Coal 3	
	In-bed	Above-bed	In-bed	Above-bed
Carbon	0.1	<0.1	<0.1	<0.1
Na ₂ O	24.1	23.5	6.7	9.8
MgO	0.7	1.9	0.4	0.8
Al ₂ O ₃	2.3	7.8	12.5	23.2
SiO ₂	11.6	11.1	60.0	33.1
P ₂ O ₅	0.5	0.9	0.2	0.5
SO ₃	1.3	36.7	6.9	10.8
Cl	31.7	0.35	0.02	<0.1
K ₂ O	0.1	0.3	1.0	3.3
CaO	2.8	9.6	2.3	1.7
TiO ₂	0.3	0.5	1.0	1.5
Cr ₂ O ₃	5.1	<0.1	1.1	0.2
Mn ₃ O ₄	0.5	0.1	0.1	0.1
Fe ₂ O ₃	17.0	5.9	7.3	14.2
NiO	2.1	0.1	0.2	0.2
Total	100.1	98.8	99.7	99.5

Table 47 High-Temperature Microscopic Analysis

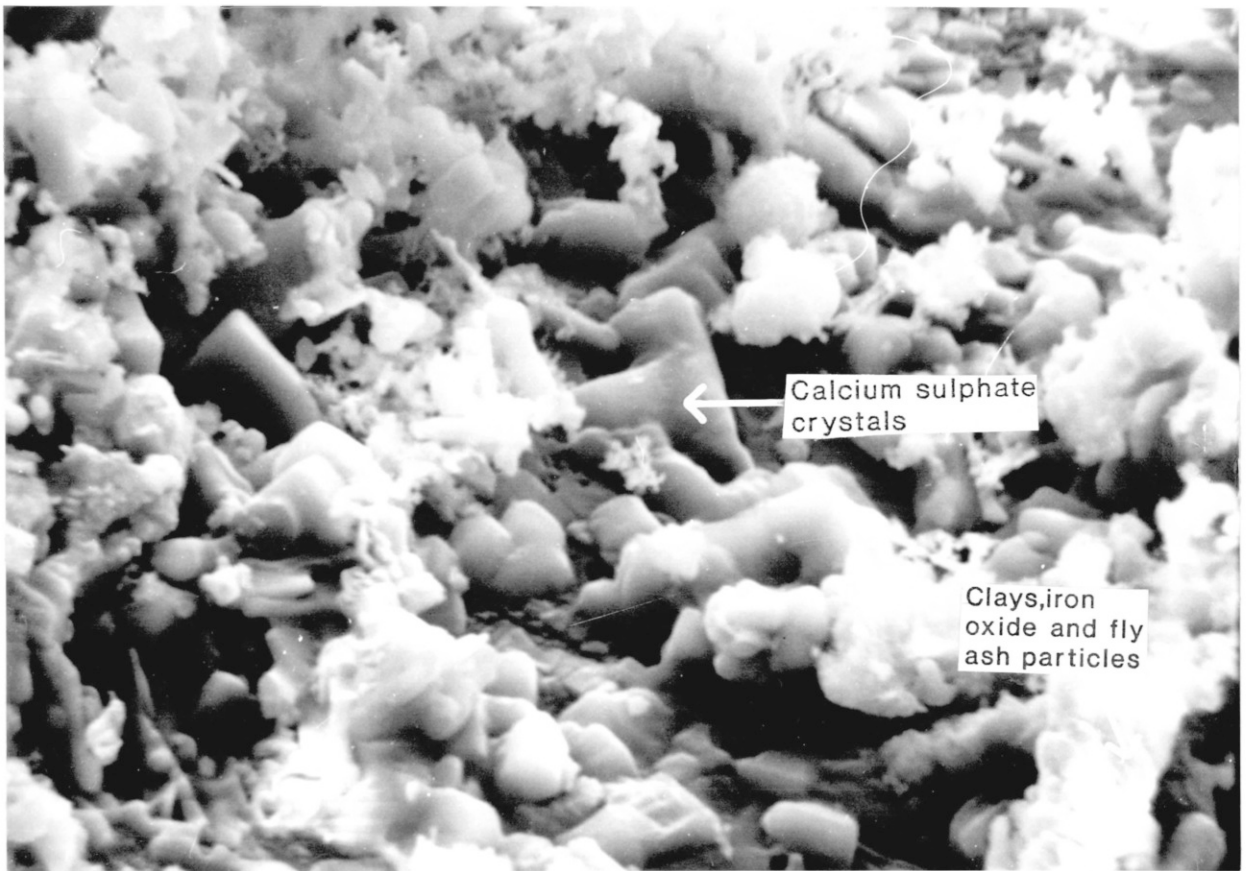
	Temperature °C	
	Solidus	Liquidus
<u>Coal 1</u>		
In-bed deposit	790	1260
Above-bed deposit	720	1250
Fly ash	1070	1270
LTA	1040	1260
<u>Coal 3</u>		
Above-bed deposit	840	1250
Fly ash	1090	1310
LTA	1120	1280

Table 48 X-Ray Diffraction Analysis of Deposits
Collected from the Pilot Plant Trials

Coal	Tube location	Major phases detected in deposit
1	Above bed	Fe ₂ O ₃ , CaSO ₄ , Na ₂ SO ₄ , NaCl, sand (SiO ₂), Cr ₂ O ₃ . Minor - Fe ₃ O ₄ and KCl
1	In bed	NaCl and sand (SiO ₂) Minor Fe ₂ O ₃ , Fe ₃ O ₄ and Na ₂ SO ₄
3	Above bed	Fe ₂ O ₃ and sand (SiO ₂)

10 μ m

(a)



10 μ m

(b)



Figure 76a and b. Electron Micrographs of Deposit formed from the Combustion of Chlorine Enhanced Coal 1, showing the predominance of Calcium Sulphate crystals.

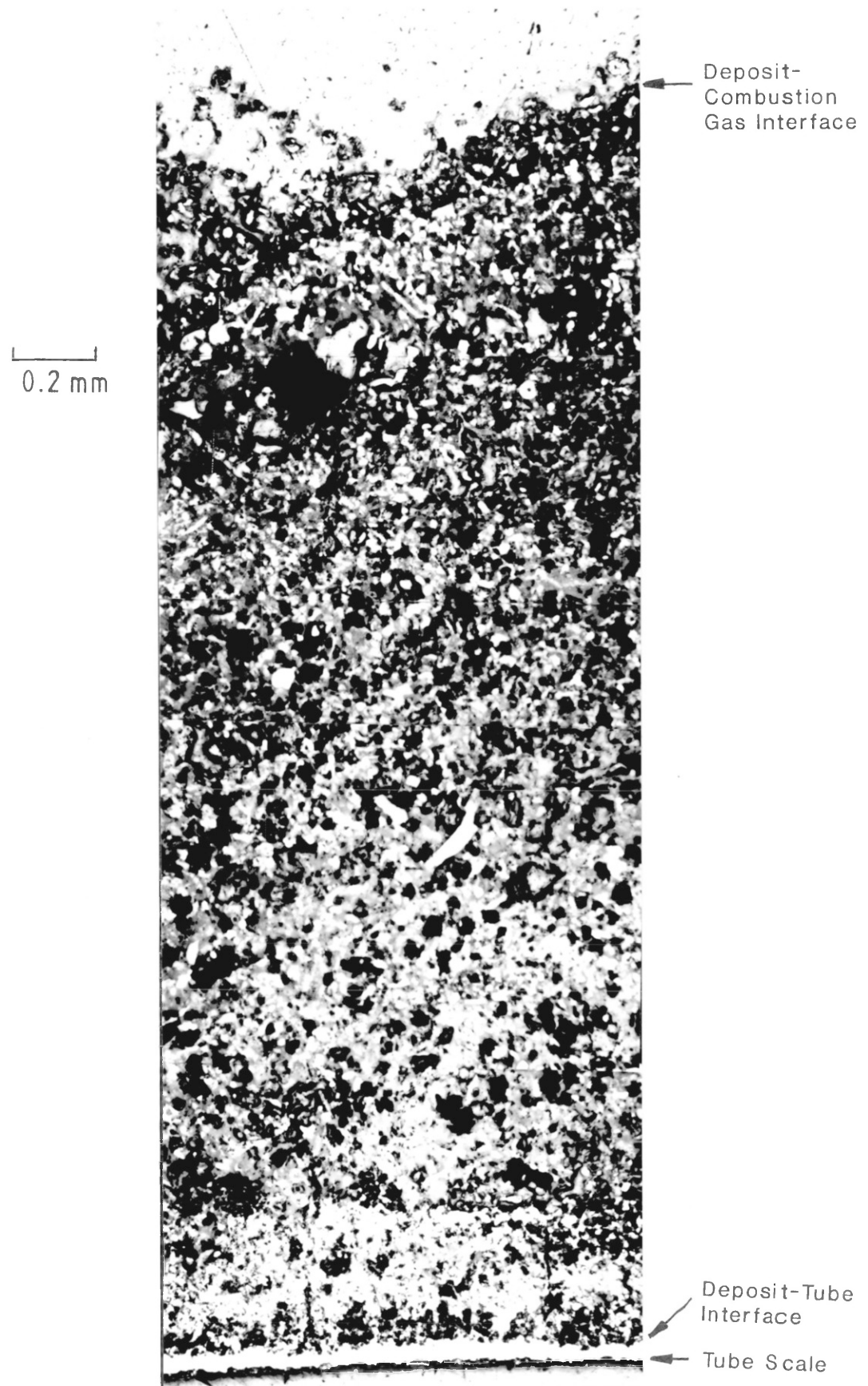


Figure 77. Deposit Formed on Above-Bed Tubes during Combustion of Coal 1 in Pilot Plant FBC, showing porous sintered matrix.

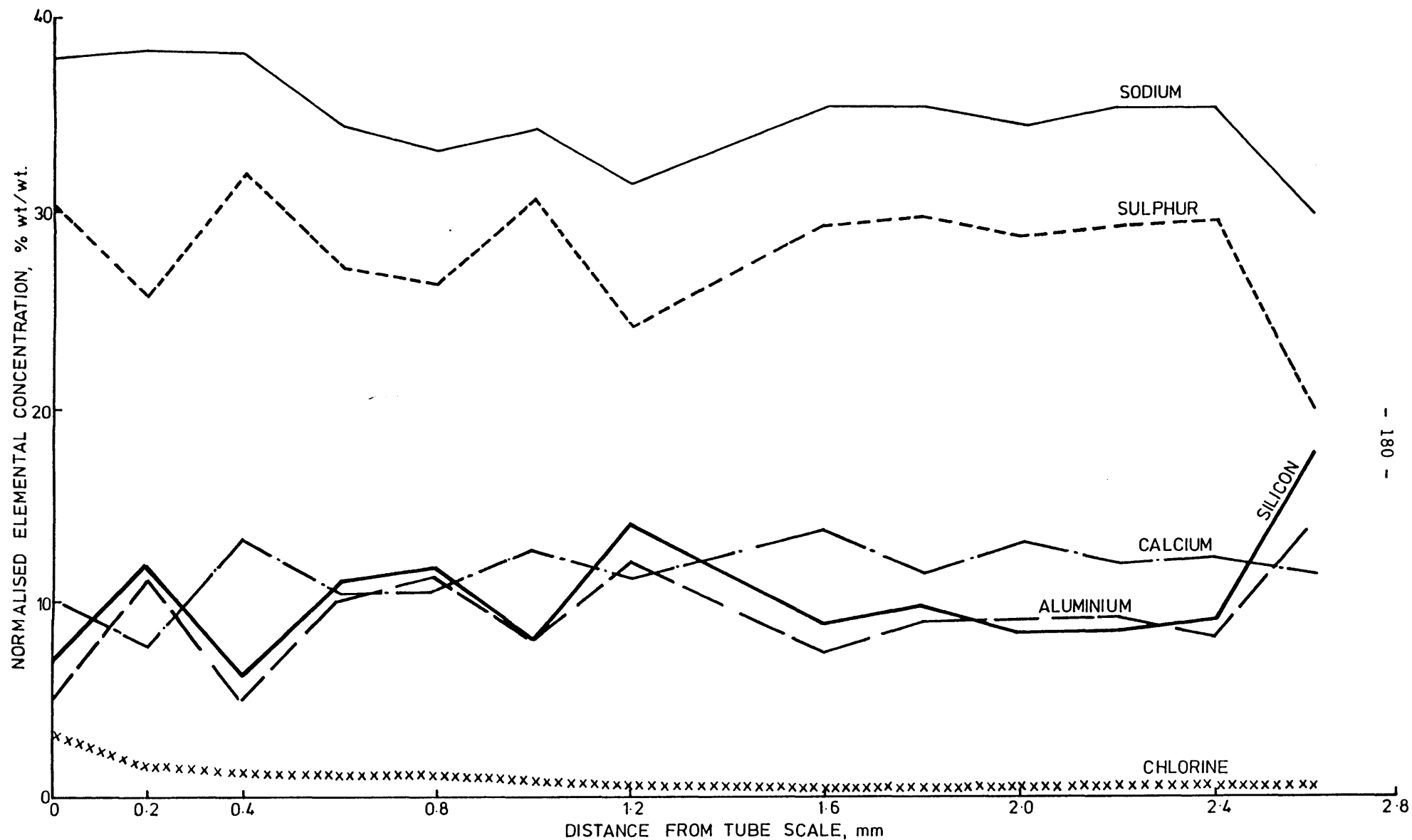


FIGURE 78. ELECTRON PROBE MICROANALYSIS OF ABOVE BED DEPOSITS COLLECTED AFTER THE COMBUSTION OF COAL 1 IN THE ENCOMECH PLANT TRIALS.

Iron, chromium and oxide concentrations have been excluded from the graph and concentrations of the remaining elements, Na, K, Ca, Mg, Al, Si, Ti, S, Cl and P have been normalised. Table 46, however, has not been corrected for contributions from the tube scale; this is particularly relevant for the in-bed deposits. The high SiO_2 content of +2 mm bed ash in Table 44 is attributable to the presence of bed material.

The ash analyses in Table 44 suggest that the fate of the individual elements varies depending upon the coal mineralogy. For Coal 1 the proportion of iron remaining in the bed ash had increased and for Coal 3 decreased, compared to their coal/HTA analyses. These results were reflected in their observed ash fusion temperatures; the bed ash from Coal 3 melting at higher temperatures than its HTA. Lower concentrations of calcium and to a lesser degree sodium in the bed ashes indicate that these elements are more likely to be volatilised during combustion. Smaller variations between coal and bed ash for the higher sulphur content coal, Coal 3, may be attributable to enhanced retention of these elements as their sulphates in the bed. Diversities in retention of iron in the bed ash may be attributable to the mode of occurrence of pyrite in the two coals. In Coal 3 pyrite is more abundant and mainly occurs as fine multiple agglomerations (framboids) whereas a higher proportion of pyrite in Coal 1 is present as larger crystals. During combustion, the larger fragments of pyrite will have a greater tendency to fuse and remain in the bed; whereas the lighter fine particles may be elutriated from the bed with the fly ash. The proportion of Fe_2O_3 in the above-bed deposits had increased for Coal 3 and decreased for Coal 1.

A surprisingly high proportion of alkalis in the fly and bed ashes from Coal 1 are present as their chlorides (Table 44). Conversely the chloride content of ashes from the high sulphur, low alkali content coal, Coal 3, is low.

The amount of carbon present in fly ash from the laboratory FBC is typically ~50%, compared to ~39-47% in Table 44. The lower degree of coal burnout will largely be attributable to the shorter residence time of the coal particles in the freeboard of the laboratory combustor.

Tables 45 and 47 confirm that Coal 1 has the greater tendency to form more abundant, lower melting deposits during combustion. Coatings removed from the in-bed tubes from Coal 3 consisted largely of scale. Deposits collected on above-bed tubes from Coal 3 were friable and loosely adhered.

The major coal derived component identified on the in-bed tubes from Coal 1 is sodium chloride. The above-bed tubes were rich in sodium sulphate, calcium sulphate and haematite, with lower concentrations of sodium chloride, potassium chloride, magnetite and aluminosilicates. Haematite and tentative identifications of sodium sulphate and aluminosilicate phases were also present in the above-bed tubes from Coal 3. Very small concentrations of sodium sulphate were detected, in the mainly scale deposit, found on the in-bed tubes from Coal 3. These results are consistent with the laboratory FBC studies (Section 5.1.6).

Figure 78 confirms that sodium and sulphur are the major elements present in the above-bed deposits from Coal 1 and indicates that the concentrations of all the monitored six elements remain relatively constant across the deposit matrix. Small variations were only apparent in the deposit layer adjacent to the cooler tube scale, which was slightly richer in sodium and chlorine, and in the outermost layers exposed to the hotter combustion gases, where the proportion of aluminium and silicon had increased and that of sulphur decreased.

Sintered ash deposits formed on boiler tubes usually have a layered structure. This is mainly attributable to the diffusion of alkali sulphates (Na, K) through the porous matrix of silicate ash deposit and their condensation on the cooled surfaces (30). The formation of the layer-structured deposit is enhanced as a result of high porosity of the sintered matrix and the temperature gradient across the ash material on the cooled tubes. Figure 77 illustrates that the sintered matrix of the deposit is highly porous. The porosity of the deposit appears to increase outwards, away from the tube-deposit interface, in keeping with the reduced sintering times.

5.4 Bomb Combustion Studies

Two of the coals studied, Coals 1 and 3, were chosen to further investigate the release of the alkali species during combustion. The coals and their blends were separately fired in a bomb calorimeter, charged with oxygen and the water soluble constituents of the residue analysed in an attempt to investigate any possible reactions between the minerals of the different coals. Coal 1 with a reduced chlorine content was also fired to determine the influence of chlorine on the release of the alkali species. The mineral constituents of coal released during combustion are assumed to be those which are water soluble (30,172) and sodium and chlorine in the coal may by some mechanism promote the release of naturally involatile potassium from the clay minerals during combustion (30).

The major salt mineral elements found, together with their concentrations in the coals and their blends are given in Table 49. This table included total mineral matter and ionisable salt contents for the coal: total sulphur and sulphate contents are also listed.

Extraction data for the removal of water soluble salts, before and after combustion in the bomb calorimeter, are recorded in Tables 50 and 51. Table 51 also includes theoretical extraction data for the three coal blends after combustion calculated from data given in Table 50. Comparative extraction data before and after bomb combustion for the coals and for Coal 1 with reduced chlorine content are illustrated as a histogram in Figure 79. The histogram shown in Figure 80 compares theoretical extraction data with that found in practice for the three coal blends.

Sulphate concentrations of the aqueous extracts after combustion are high due to sulphur oxidation and its fixation as alkali sulphates. These results have been excluded from Figures 79 and 80 together with those for the low concentration and less important element magnesium.

Electron micrographs of ash from the combustion of Coals 1 and 3 (Figures 81 and 82) show the morphology of the ash particles.

5.4.1 Coals

The major water soluble components of Coals 1 and 3 are the anions Cl^- and SO_4^{2-} , the alkali metal cations Na^+ and K^+ and the

Table 49 Analysis of Coal Blends

	Coal 1	Coal 3	2:1 Blend Coal 1:3	1:1 Blend Coal 1:3	1:2 Blend Coal 1:3
<u>% m/m db</u>					
Na	0.25 ^a	0.11	0.20	0.18	0.16
K	0.01	0.10	0.04	0.05	0.07
Ca	0.47	0.13	0.36	0.30	0.24
Mg	0.08	0.04	0.07	0.06	0.05
Cl	0.91 ^a	0.34	0.72	0.62	0.53
S _(total)	0.84	1.65	1.11	1.24	1.38
S _(as SO₄)	0.02	0.03	0.02	0.02	0.03
% Mineral Matter (m/m ad) (Parr)	4.1	6.8	5.0	5.4	5.9
% Ionisable Salts ^a (m/m ad)	1.4	0.7	1.2	1.05	0.9

^a From aqueous extraction study (Section 4.1.7)

ad air dried basis

db dry basis

Table 50 Aqueous Extraction Data for Coals 1 and 3

%	Coal 1						Coal 3						Coal 1 Reduced Chlorine Content					
	Na	K	Ca	Mg	Cl	SO ₄	Na	K	Ca	Mg	Cl	SO ₄	Na	K	Ca	Mg	Cl	SO ₄
Concentration of Water Soluble Constituents in Dry Coal (A)	0.25	0.003	0.21	0.04	0.91	0.02	0.11	0.016	0.08	0.005	0.29	0.235	0.25	0.003	0.05	0.02	0.24	NA
Concentration of Water Soluble Constituents After Combustion (B)	0.19	0.006	0.175	0.03	0.74	1.87	0.05	0.035	0.05	0.005	0.25	3.12	0.07	0.006	0.11	0.01	0.25	NA
Element Extracted Before Combustion	100	30	45	50	100	NA	100	15	60	15	85	NA	100	30	10	25	100	NA
Element Extracted After Combustion	75	60	35	40	80	NA	45	35	40	10	75	NA	30	60	25	10	100	NA

NA Not Applicable

Table 51 Aqueous Extraction Data for Blends of Coals 1 and 3

%	2:1						Blends of Coals 1 and 3 1:1						1:2					
	Na	K	Ca	Mg	Cl	SO ₄	Na	K	Ca	Mg	Cl	SO ₄	Na	K	Ca	Mg	Cl	SO ₄
Concentration of Water Soluble Constituents in Dry Coal (from A)	0.20	0.01	0.17	0.03	0.71	0.09	0.18	0.01	0.14	0.025	0.60	0.13	0.16	0.01	0.12	0.02	0.50	0.16
Concentration of Water Soluble Constituents After Combustion (in theory from B)	0.14	0.015	0.13	0.02	0.58	2.29	0.12	0.02	0.11	0.02	0.50	2.49	0.10	0.025	0.09	0.01	0.41	2.70
Concentration of Water Soluble Constituents After Combustion (in practice)	0.07	0.012	0.16	0.01	0.67	2.38	0.09	0.025	0.10	0.02	0.50	2.33	0.06	0.025	0.11	0.01	0.53	2.99
Element Extracted Before Combustion (from A)	100	15	45	45	100	NA	100	15	40	40	95	NA	100	15	50	35	95	NA
Element Extracted After Combustion (in theory from B)	70	40	40	30	80	NA	65	35	35	30	80	NA	60	35	40	20	80	NA
Element Extracted After Combustion (in practice)	35	30	45	15	95	NA	50	45	35	30	80	NA	35	35	45	15	100	NA

NA Not Applicable

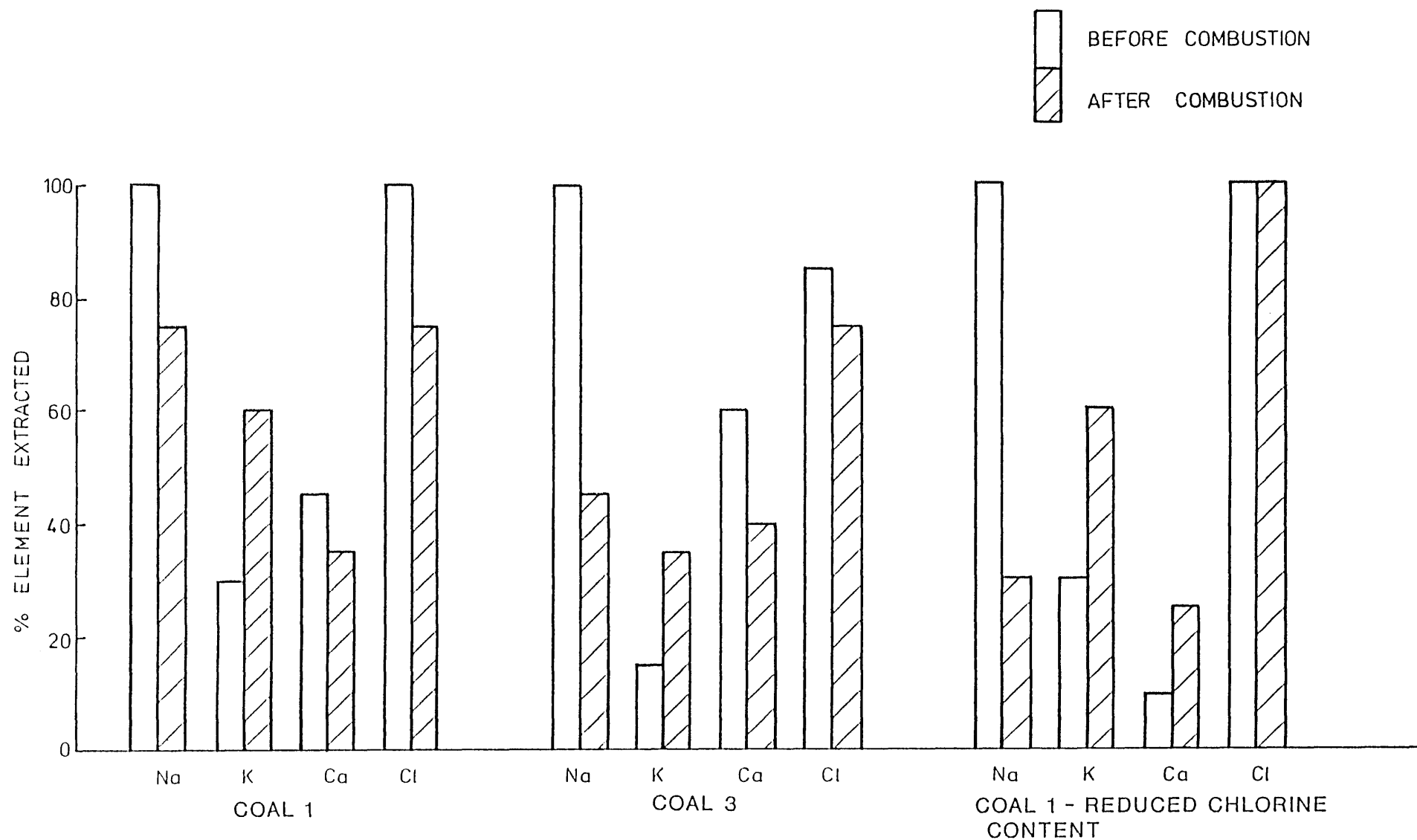


FIGURE 79. HISTOGRAM OF EXTRACTION DATA BEFORE AND AFTER COMBUSTION FOR COALS 1 AND 3.

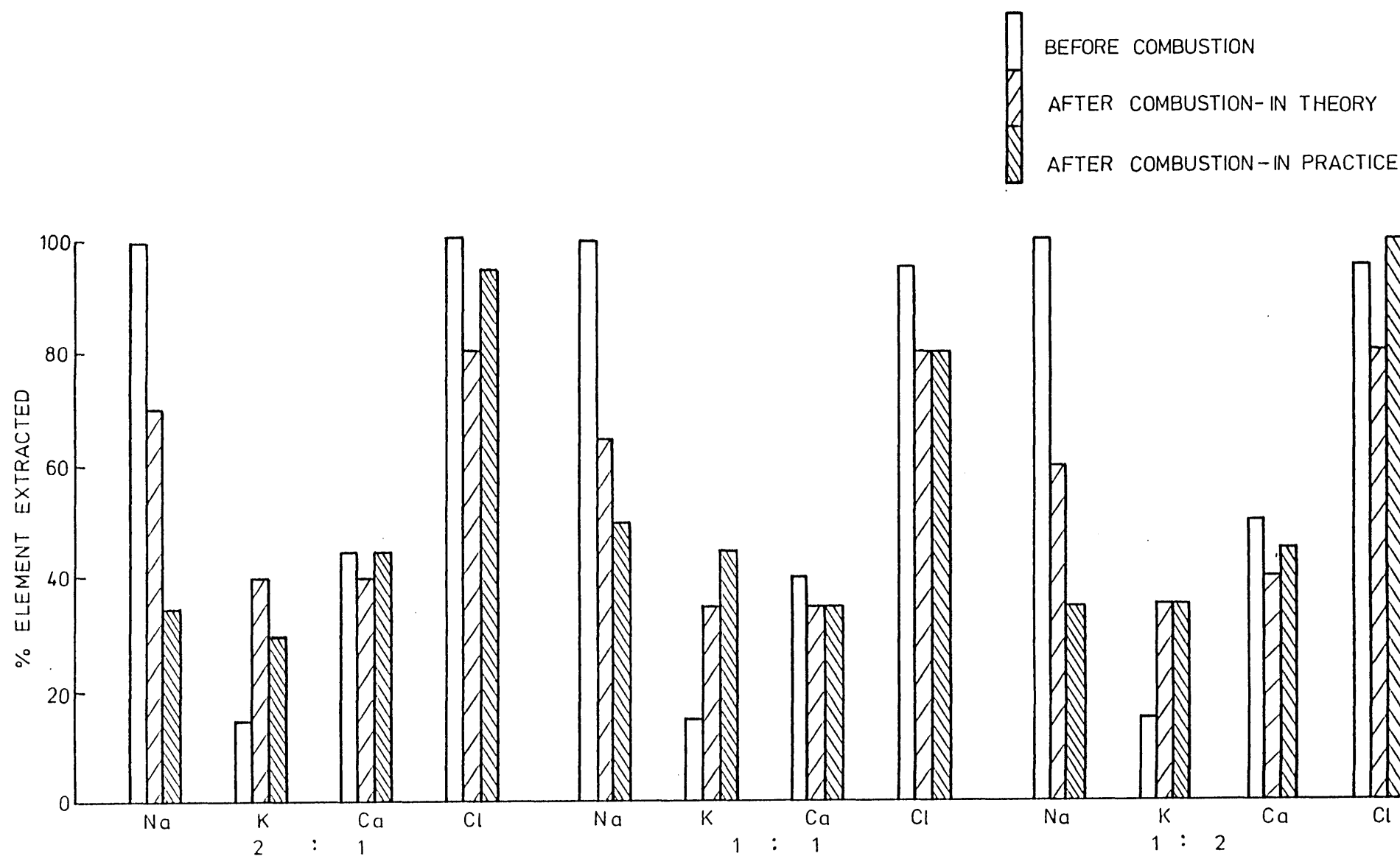


FIGURE 80. HISTOGRAM OF EXTRACTION DATA BEFORE AND AFTER COMBUSTION FOR BLENDS OF COALS 1 AND 3.

10 μ m



Figure 81. Electron Micrograph of Ash from Coal 1 after Bomb Combustion, showing crystalline and fused particles.

10 μ m

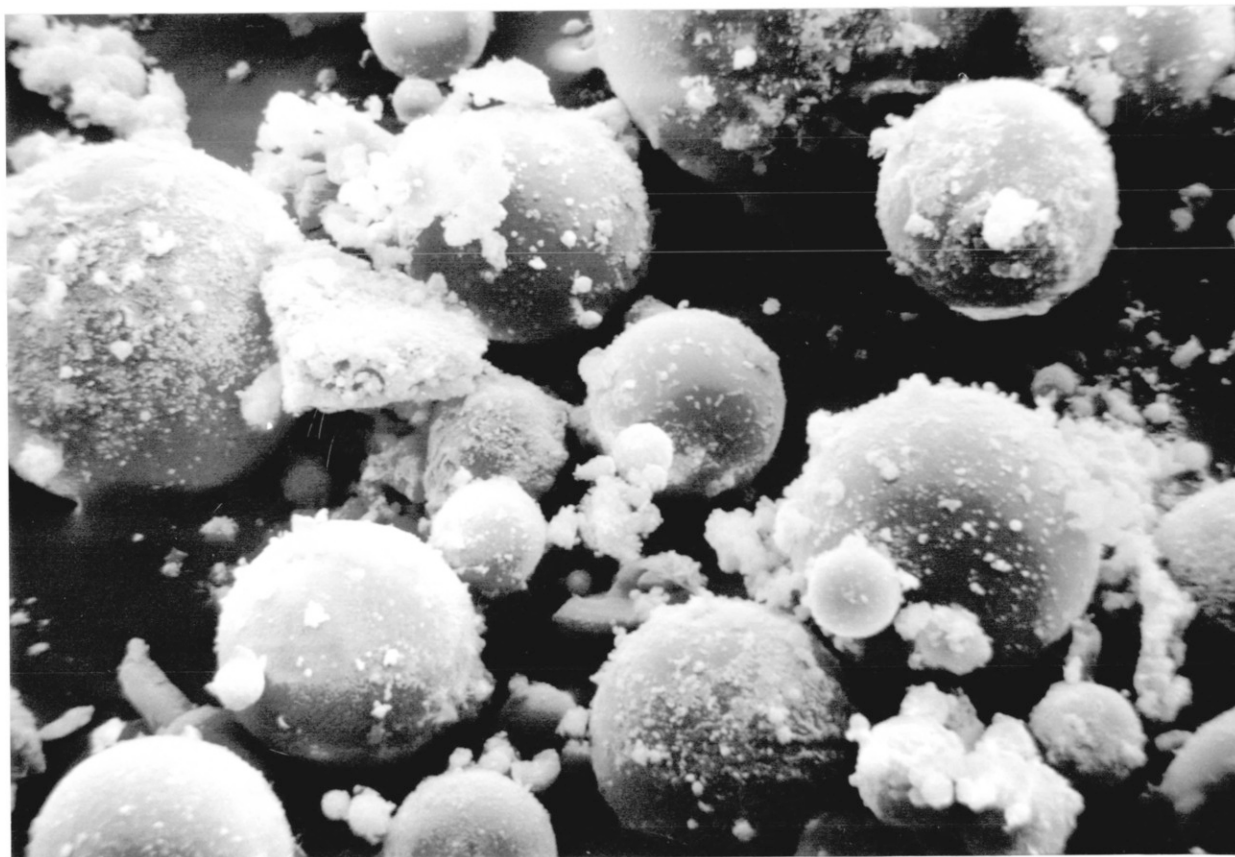


Figure 82. Electron Micrograph of Ash from Coal 3 after Bomb Combustion, showing abundance of fused, spherical particles.

alkali earth cations Ca^{2+} and Mg^{2+} . The histogram in Figure 79 and Tables 49 and 50 confirm that virtually all of the sodium and chlorine can be washed from the ground coals whilst significant proportions of the potassium, calcium and magnesium appear to be fixed in the insoluble mineral/coal matrix.

Table 50 and Figure 79 show that, after combustion in the bomb calorimeter, concentrations of water soluble sodium, calcium, magnesium and chlorine have decreased whilst potassium has increased.

The decrease in water soluble sodium after combustion may be attributable to alkali exchange reactions within the dehydrated clay mineral structures and/or by dissolution in the silica melt. At bomb combustion temperatures the latter mechanism is more likely.

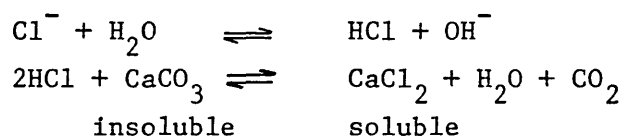
The solubility of alkali metals in silicate slags is highly dependent on the basicity of the ash. The higher ash content coal, Coal 3, has a more acidic ash than Coal 1 and will have a greater affinity for the alkali metals. This is apparent in Figure 79, where a greater proportion of the sodium in Coal 3 compared to Coal 1 has been retained as insoluble species after combustion.

Potassium is incorporated mainly in the silicate fraction of the coal ash and can be relatively mobile in basic melts (3). In addition, potassium forms comparatively volatile chlorides and hydroxides. Consequently potassium will be more mobile in the basic ash of Coal 1 and hence more readily released as volatile chlorides. Figure 79 shows an increase in extractability of potassium from both combusted coals. Due to the low concentrations of water soluble potassium present, however, quantitative comparisons are impracticable.

Gibb and Angus (3) have shown that the release of potassium is dependent on the chlorine and ash contents of the coal, the K_2O content of the ash and the ash basicity. They also noted that water soluble sodium concentration of the coal did not appear to be a major factor of potassium release for this reaction mechanism.

The greater proportion of water soluble potassium inherent in Coal 1 may be due to the presence of small concentrations of potassium ions associated with the organic coal matrix. During combustion chlorine is released as a volatile chloride, presumably hydrogen chloride, which can react with some coal minerals to form relatively volatile alkali chlorides. The major alkali chlorides are water soluble and the decrease in chlorine after combustion probably results from the loss of hydrogen chloride during extraction.

A significant proportion of the insoluble calcium and magnesium containing carbonate minerals, calcite, dolomite and ankerite, appear to have decomposed during aqueous extraction forming water soluble species. This has probably resulted from the formation of hydrochloric acid during extraction, e.g.



The decrease in calcium concentration after combustion probably results from reactions occurring with sulphur oxides or from dissolution in the silicate melts.

Microscopic examination of the residual ashes from the combusted coals (Figures 81 and 82) showed them to be largely composed of fused and partially fused spheres of iron and calcium enriched aluminosilicates. Crystalline and unfused ash particles were also present. These and other smaller fused spheres were often found adhered to the surface of the large aluminosilicate spheres. The abundance of crystalline ash particles appeared to be greater in the higher sodium, calcium and chlorine content coal, Coal 1.

Incomplete fusion of the coal minerals may be attributable to combustion conditions in the bomb calorimeter. Coal particles in the bomb calorimeter are subjected to an explosive combustion and rapid cooling regime compared to the longer high temperature resident time and relatively slow cooling of particles experienced in industrial combustors. Additionally, coal and char particles in industrial combustors can experience local reducing environments and temperature variations which could

promote ion-exchange type interactions. Without further work, such differences in combustion conditions make direct comparisons with the likely effects in industrial combustion plant difficult to predict.

5.4.2 Coal blends

Aqueous extraction data for the three coal blends (2:1, 1:1 and 1:2) given in Table 51 and illustrated in the histogram (Figure 80) show some differences between theoretical extraction data (obtained from Table 50) and that found in practice. These differences may be due to reactions occurring between minerals from the two coals. Figure 80 indicates this to be particularly relevant for sodium.

By blending Coal 3 with Coal 1, the acidity of the blended ash increases thus enhancing the affinity of the melt for alkali ion capture. This trend however is not apparent from the results presented possibly due to difficulties in accurately determining the small changes in elemental concentrations. The results do suggest that the basicity of a coal ash is an important factor to be considered when blending coal to maximise sodium capture in the ash.

5.4.3 Chlorine reduced coal

The influence of chlorine on the release of the alkalis during bomb combustion was investigated from additional experiments using Coal 1 with a reduced chlorine content. Thermal treatment had reduced the chlorine content from 0.91 to 0.24%.

Aqueous extraction data for the reduced chlorine coal, before combustion (Table 50 and Figure 79) showed that extractions of water soluble sodium, potassium and chlorine were unaffected, whilst those for calcium and magnesium had decreased markedly. These observations are consistent with the theory that insoluble calcium and magnesium carbonate minerals are reacting with hydrogen chloride during aqueous extraction to form soluble calcium and magnesium chlorides (Section 4.1).

Extractions of sodium, magnesium and to a lesser extent, calcium, from the reduced chlorine content coal have decreased after combustion, suggesting that the chlorine content of the coal can

affect the solubilisation and hence release these elements. The reduction in chlorine presumably suppresses the reaction between sodium ions in the coal matrix, and calcium and magnesium carbonates with hydrogen chloride gas to form volatile/water soluble sodium, calcium and magnesium chlorides.

Potassium extractions do not appear to have been significantly affected by the chlorine content of the coal. It should be noted, however, that the concentration of water soluble potassium is low, and that although ~70% of the chlorine has been removed from the coal, the reduced chlorine content (0.24%) is significantly in excess of the low concentration of potassium present (0.01%).

6. DISCUSSION

6.1 Characterisation of Minerals present in UK Bituminous Coals

The three UK bituminous coals were selected for study on account of their varying ionisable salt content and their respective poor to good behaviour when burned in industrial boiler plant.

The mineral matter, ionisable salts and ash were separated from the coals by four techniques prior to characterisation.

The low-temperature ashing procedure was considered to be the best method available for obtaining the mineral matter from the coal. During this procedure the carbonaceous constituents of the pulverised coal are oxidised at comparatively low temperatures ($<150^{\circ}\text{C}$) and consequently the effect of the oxidising gas stream upon the minerals in bituminous coals and anthracites is relatively small, although some changes to the mineral matter do occur. All organically associated elements, such as chlorine, sulphur, and sodium were affected. The major portions of chlorine and organic sulphur were lost as gaseous hydrogen chloride and sulphur dioxide, whereas organically associated cations were retained in the ash mainly as their sulphates. Some of the inorganic minerals were also altered; gypsum dehydrated to bassenite ($\text{CaSO}_4 \cdot \frac{1}{2}\text{H}_2\text{O}$) and anhydrite (CaSO_4) and $\sim 10\%$ of the pyrite oxidised to haematite (Fe_2O_3). The LTA were used in the mineral characterisation studies (allowances being made for these mineralogical changes) and as material for coal ash melting studies.

The water soluble (ionisable) salt minerals were removed from the three coals by two aqueous extraction procedures. Extraction data provided information on the coals' ionisable salt content and both elucidated and confirmed the mode of occurrence of the minerals.

Ash is produced by the British Standard method of high-temperature (815°C) oxidation of coal and its composition is very different from the constituent coal minerals. The ashing procedure resulted in a series of reactions with all the mineral components, with the exception of quartz. Pyrite and the carbonate minerals evolve sulphur dioxide and carbon dioxide, and

the clay minerals lose their water of hydration. Some of the sulphur dioxide may remain in the ash, mainly in combination with calcium, but much is lost. During the ashing procedure, the coal was slowly raised in temperature, to 815°C, and all the chlorine volatilised as hydrogen chloride; the majority before the organic matrix began to oxidise (52). Consequently all the inorganic cations remained in the ash as involatile oxides, sulphates and aluminosilicates. The HTA were used to determine the chemical composition of each coal ash and as a material for ash melting studies. In addition, HTA was used to estimate the mineral matter content of coal by applying various calculation procedures to the proximate, ultimate and ash analysis.

An alternative method of measuring the mineral matter content of coal is by acid demineralisation. This procedure, however, proved to be time consuming although it provided samples of essentially clean (mineral free) coals which were used for FT-IR characterisation studies.

The ionisable salt contents of the three coals (washed singles) decreased from Coal 1 to 3 (1.4 to 0.7% wt.), as do their ash fouling/corrosion propensities, whereas their mineral matter contents increased (4.1 to 6.8% wt.), as illustrated in Figure 83a. The more reactive elements e.g. Na, Cl and Ca, are concentrated in Coal 1. Coal 3 contained higher proportions of Al, Si, Fe, K and S.

The three coals were characterised by a number of analytical techniques. The most specific method used for identifying minerals by their structures, is XRD.

The XRD procedure devised for quantifying the mineralogical composition of the three coals used the pyrite already present in the LTA as an internal standard. Pyrite gave several strong diffraction peaks which did not overlap those from other minerals. The concentration of pyrite in the three LTA studied ranged from 6.8 to 15.6% wt., making it suitable for use as an internal standard. Calcite, dolomite, ankerite, siderite and quartz were successfully identified and quantified. Analysis of the clay minerals was somewhat limited, however, largely due to preferred orientation effects and the selection of appropriate

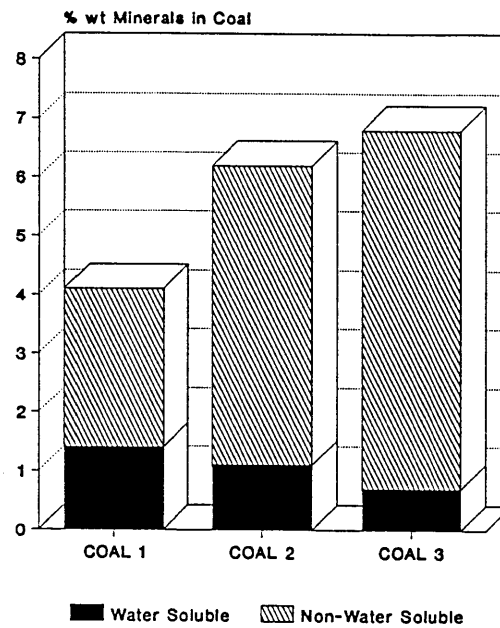


Figure 83a. Mineral Contents of Coals 1,2 and 3.

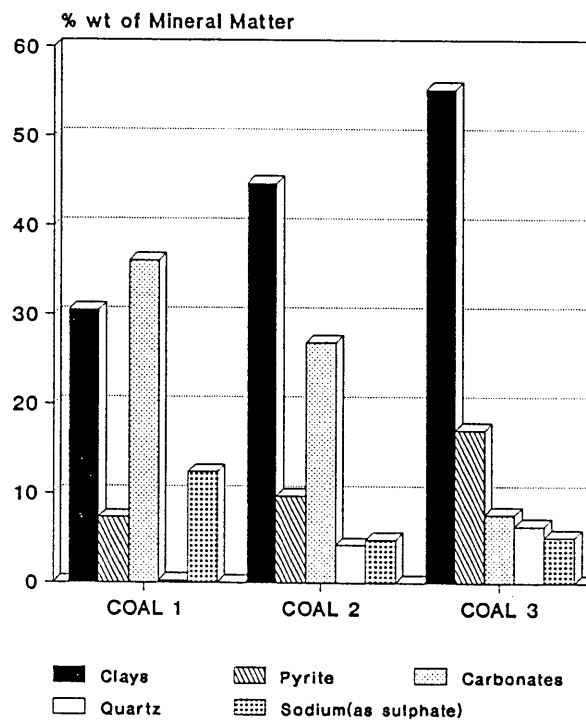


Figure 83b. Proportions of Minerals in Coals 1,2 and 3.

mineral standards (i.e. clays can vary both in the degree of crystallinity and chemical composition). Consequently, identification of the mica minerals in particular was difficult, and concentration levels for the aluminosilicate minerals were underestimated. Although the broad reflections in the diffractograms obtained from the LTA correspond with those for muscovite, the potassium aluminosilicate mineral, illite (for which no standard was available), is more common in UK bituminous coals. Illite is structurally similar to muscovite with less substitution of Al^{3+} for Si^{4+} . This leads to the presence of less interlayer potassium holding the units together and therefore less well ordered units. Careful interpretation of LTA diffraction patterns was required as certain species present in the LTA were artifacts of the ashing procedure eg. Na_2SO_4 , CaSO_4 and Fe_2O_3 (Appendix I).

Quantification of the minerals was supplemented by normative analysis. For this procedure it is important to first identify the mineral components of the coal including the occurrence and concentrations of organically associated elements. However, although normative analysis proved to be successful for the mineralogical quantification of the three coals studied, it can only be considered as yielding hypothetical mineralogical compositions as it is often difficult to ascribe entirely certain elements to specific minerals. This procedure is unable to account for substitution and solid solutions unless additional information, e.g. EPMA of individual mineral particles, is available.

Thermal analysis was used for confirmational mineral identification. Comprehensive identifications and quantitative measurements of complex mineral mixtures by thermal analytical techniques was difficult mainly due to peak superposition and non-thermally active components. Thermal analysis was used most effectively for following changes with thermal treatment, including reactions between evolved gases and residual minerals. FT-IR studies have provided information on the abundance of minerals and on the changes which can occur during low-temperature ashing. Comparison of difference spectra for

as-received and demineralised coals with their respective LTA spectra showed that organically associated cations, such as sodium, were probably being fixed in the ash as their sulphates. Mineral identification by FT-IR was limited due to the strong absorption bands exhibited by kaolinite. Minor variations in the mineral structure of kaolinite make the application of spectral subtraction difficult.

The three coals have essentially been shown to contain the same salts and minerals which differ in the relative proportions from one coal to another. The most abundant mineral components of the three coals were the kaolinite and mica groups of aluminosilicates, quartz, pyrite and the carbonates calcite, dolomite and ankerite. These and smaller concentrations of gypsum, rutile, apatite, siderite and sodium (as sodium sulphate) were quantified. Each method gave comparable results; the most comprehensive being the results of normative analysis. A number of trends for the mineral composition of the three coals were observed and illustrated as a histogram in Figure 83b. The relative proportions of kaolinite, mica (probably as illite), pyrite and quartz increased from Coal 1 to 3 whilst proportions of dolomite, ankerite, calcite, chlorine and sodium decreased from Coal 1 to 3.

The major ions which could be aqueously extracted from the coals were Na^+ , K^+ , Ca^{2+} , Mg^{2+} , Cl^- and SO_4^{2-} . These elements were the constituents of coal most likely to be released during combustion (30). Aqueous extraction and fine grinding resulted in ionisable salt removals of 1.4, 1.1 and 0.7% wt. for Coals 1, 2 and 3 respectively; representing reductions in overall mineral matter of 34, 18 and 10% wt. All the Na^+ and Cl^- could be leached from each coal, and a high proportion of Ca^{2+} could also be removed. Calcium and magnesium were mainly associated with the insoluble carbonate minerals. During aqueous extraction, reactions can occur with hydrochloric acid to form calcium and magnesium chlorides. Similar reactions between carbonates and gaseous hydrogen chloride might be expected during combustion.

Potassium was present predominantly associated with insoluble micaceous clays. The low levels of leachable potassium may be

attributable to the presence of organically associated potassium or to ion exchange reactions. Coal 1 had the highest proportion of water soluble potassium.

²³Na MAS-NMR spectroscopy indicated that sodium was present in an ionic form, fully hydrated and attached to an organic functional group on the pore structure. The majority of sodium in coal originates from sea water and presumably chlorine also exists in an ionic form held separately on the coal substance. The higher porosity shown by Coal 1 would enhance the ability to adsorb Na⁺ and Cl⁻, which can be correlated to the potential volatility of these elements during combustion and to their fouling tendencies. Sulphur exists in coal in three forms, namely sulphate, sulphide and organically bound sulphur compounds. The sulphur content of the three coals ranged from 0.84 to 1.65 % wt., of which 20 to 40% was present as sulphide (pyrite), ~2% as sulphate and the remainder as organically associated sulphur. The majority of pyrite in the three washed coals was intimately associated with the coal macerals (syngenetic) and cannot easily be removed. Pyrite was most abundant in Coals 2 and 3, appearing as multiple fine agglomerations; whereas a higher proportion of pyrite in Coal 1 was present as larger crystals.

The total alkali contents of the coals could be correlated with the physical behaviour of the ash during heating. The ashes from Coals 1 and 2 contained higher proportions of basic ash constituents (Na₂O, CaO and MgO), which act as strong fluxing agents, and were shown to fuse and flow at lower temperatures than the ash from Coal 3.

The alkali content of coal is also used as an index for measuring potential boiler fouling. During combustion, however, the fouling reactions may be influenced as much by the nature of the alkali as by the amount of the alkali in the coal. The water soluble mineral constituents of coal are thought to be those which are released during combustion (30,172) and consequently the ionisable salt content of coal would provide a more accurate guide to the fouling propensity of a given coal. Coal 1, containing the higher ionisable salt content, shows the higher fouling potential.

The fouling and slagging parameters were determined from the ash composition and sulphur content of the coals to give a broad ranking of coal ash performance. The results were consistent with their observed fouling and slagging trends, with Coal 1 exhibiting the highest fouling and slagging tendencies. Coal 3 was considered to be a relatively non-problem coal when burnt in industrial boiler plant. The predicted extent of fouling for this coal, as indicated by the fouling factor, R_f , however, was high. The mineral matter content of a given coal will vary and the ash content of the coals used for study appear to be low (<5.2%) compared to industrial grade coals. Coal washing can remove a large proportion of the aluminosilicates, i.e. the acidic ash components, and thus concentrate the minerals which are associated with the coal matrix, the predominantly basic ash components. This would increase the value of the fouling factor, R_f and the fouling propensity. It should be noted that the fouling factor, R_f , is probably more appropriate for pf boilers operating at higher combustion temperatures (>1200°C). At FBC temperatures, where little of the potassium is released, the factor R_f' , based solely on Na_2O content and applicable to lignitic type ash, may be more appropriate.

6.2 The Laboratory Fluidised Bed Combustor

The laboratory-scale fluidised bed combustor was designed to study the nature and abundance of deposits formed during combustion from minerals inherent in coal. Due to the enormous difference in scale between the laboratory combustor and an industrial fired plant, however, the temperature gradients in the respective freeboards are bound to differ and the probes used here to simulate heat exchange surfaces are relatively close to the fluidising bed. The effect of deposit surface position (gas cooled probe, Section 5.1.7) was shown to influence the ratio of chloride to sulphate content of the deposit. Deposition of chlorides as opposed to sulphates was favoured. Additionally, the extent of deposition may be affected by the close proximity of the fluidising bed, the sand causing mechanical attrition of deposits. The laboratory combustor does appear to have provided

a clean and rapid method of assessing the characteristics of each coal, as well as providing information on the chemistry of deposit formation under strictly controlled conditions. The effect of varying controlled and monitored combustion parameters on the nature and relative abundance of deposits was thus studied.

Repeatable results were obtained for the concentrations of the major elements in a deposit, allowing variances in deposition behaviour to be monitored.

6.3 Release of the Ionisable Salt Minerals during Fluidised Bed Combustion

The behaviour of the ionisable salt minerals during FBC under given conditions will be dependent on the chemical state of the ions, the distribution of the minerals in the coal and on the relative rates of each thermodynamically favourable reaction.

When coal is fed to the fluidised bed the particles are heated rapidly. Typically the residence time of a coal particle in the laboratory combustor is several seconds. The moisture is removed first and further heating releases the volatile matter from the coal. The volatile matter and char burn in the air used to fluidise the bed, releasing gaseous combustion products of CO_2 , H_2O , NO_x , SO_2 and HCl . It has been estimated that the temperatures of the individual char particles containing the minerals may exceed the bed temperature by several hundred degrees (104). At these temperatures hydrogen chloride can attack sodium, potassium, calcium and magnesium containing compounds to form volatile chlorides (68,113). Vapour pressure data indicates that sodium and potassium may also be released as their hydroxides (Section 2.5.1).

Sodium and chlorine are probably in close proximity on the surface of the coal pore. As the coal matrix burns away, sodium and chlorine may either initially be released separately as Na^+ and Cl^- ions and immediately react to form sodium chloride, or the Cl^- ions may directly attack the sodium-coal bond. Vapour pressure data show that a significant proportion of sodium chloride is gaseous at FBC temperatures and 10 to 50% of

the total sodium present in coal can be released into the gaseous phase during combustion (115). This would correspond to sodium chloride vapour concentrations of between 20 and 90 ppm for Coal 1.

Potassium appears to be released from the micaceous clay minerals by interstitial cationic exchange reactions, possibly with sodium, within the dehydrated clay structure. The role of chlorine is to promote the volatilisation of potassium as potassium chloride following its release (Section 5.2.2). Consequently some of the volatilised sodium will be captured by the involatile clay minerals. The extent of the reactions will be at least partially dependent on the proportions of Na^+ , Cl^- and clay mineral species present and on combustion temperatures. These observations were supported by the higher concentrations of potassium found in the initial deposit formed on surfaces at 450° to 650°C, during the combustion of Coal 1 (the high Na^+ and Cl^- , and low K^+ content coal).

The study has shown that calcium and magnesium associated with carbonate minerals, mainly volatilise as chlorides following reactions with hydrogen chloride. Some calcium oxide may be elutriated from the bed during the decomposition of the carbonate minerals, however the majority of calcium species found in the initial deposit resulted from gas-solid condensation mechanisms. Similar reactions are thought to occur for magnesium.

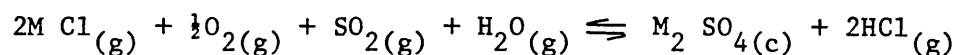
These findings are in agreement with thermodynamic calculations made by Scandrett and Clift (68,113) to predict the behaviour of sodium and potassium during PFBC. Alkali salts in the combustion gases can damage gas turbomachinery and hence efforts have been made to lower the concentration of these species in the gas. Combustion temperatures found in FBC are lower than those found in pf plant and this should reduce the problems associated with the volatilization of the mineral species. Consequently few studies have been reported for atmospheric FBC systems on the mechanisms of the release and the deposition (above-bed) of the alkali salts.

The proposed mechanism for the release of the majority of ionisable salt minerals during FBC is illustrated schematically

in Figure 84. This presents a simplified version, since the heterogeneous nature of coal and the interactions/reactions which occur between the minerals and combustion products can be very complex. The mode of occurrence, size and distribution of minerals in coal will all affect their fate during combustion, as will combustion conditions and the presence of other mineral species. Alkali and alkaline earth elements bound within clay structures will be released less readily than those bound to the coal matrix. In addition, minerals more closely associated with the organic coal structure will be subjected to higher combustion temperatures. Larger crystals of pyrite will have a greater tendency to fuse and remain in the bed ash, whereas lighter fine particles (framboids) may be elutriated from the bed with the fly ash. Coals with high sulphur or clay contents may, however, have the natural ability to retain alkalis in the bed as alkali sulphates or aluminosilicate complexes. The release of alkalis from coal minerals can be correlated with the chlorine content of the coal and is not necessarily proportional to the total alkali content (111).

6.4 Deposition of the Ionisable Salt Minerals during Fluidised Bed Combustion

The volatilised inorganic species are transported via the mechanism of vapour diffusion and can condense on cooler surfaces in the combustor (<800°C), on gas borne particulates or undergo chemical reactions with gaseous sulphur oxides to form sulphates. Volatilised alkali chlorides are thermodynamically less stable in combustion atmospheres, at FBC temperatures, than alkali sulphates (30). The most likely reaction for the sulphonation of alkali chlorides is:



Where M = Na, K, $\frac{1}{2}$ Ca, $\frac{1}{2}$ Mg,

g = gaseous phase

c = condensed phase

Thermodynamic data (Figure 7) has shown that conversion of alkali chlorides to sulphates is most favourable for calcium and free

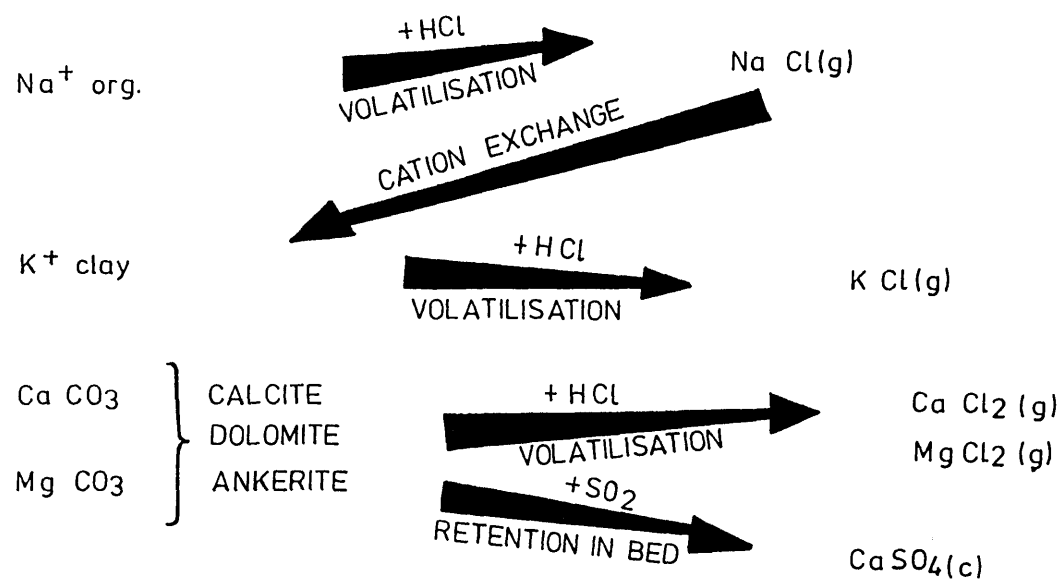


FIGURE 84. PROPOSED MECHANISM FOR THE RELEASE / RETENTION OF IONISABLE SALT MINERALS IN UK COALS DURING FLUIDISED BED COMBUSTION.

energy values for the reactions above become increasingly negative at lower temperatures. These reactions appear to be very important in regulating vapour phase alkali content and equilibrium proportions of chlorides and sulphates, and are dependent on temperature, pressure and gas composition.

Assuming that 10 to 50% of the total sodium present in Coal 1 is released into the gaseous phase as sodium chloride during FBC (115) and the extent of conversion to sulphate, at 850°C, is more than 90% (Figure 6), the corresponding vapour concentration of gaseous sodium sulphate would be 20 to 100 ppm.

Estimated saturated vapour concentrations of sodium and potassium sulphates (0.05 and 0.3 ppm respectively at 1 atm. and 850°C) are well below estimated total alkali concentrations suggesting that if the alkalis are present as sulphates, they will be present predominantly as a condensed species.

Two deposition mechanisms appear to exist. In the first mechanism the volatile alkali chlorides and sulphates can condense homogeneously in the combustion gases forming partially molten or solid crystals which can subsequently adhere to cooler surfaces. The second mechanism involves nucleation of minute crystals of the alkali chloride or sulphate on the deposition surface with subsequent growth directly from the vapour phase. Growth time for the two mechanisms may differ, possibly being shorter for the former. Microscopic observations indicate that both partially molten and perfectly formed crystals are present in the deposits, with particles ranging in size from <1 to >20 μm . This suggests that both mechanisms probably occur and will be dependent on concentration, temperature, melting points of condensed alkali phases and availability of suitable nucleation sites (substrate).

SEM/EDX examination of the deposits showed that crystals at the probe surface-deposit interface were rich in Na^+ , K^+ (with some Ca^{2+}) and Cl^- . Under the laboratory combustion conditions the lower melting alkali chlorides appeared to be partially molten (Figure 35) and favour the former deposition mechanism. In addition, halides can form low melting point eutectic mixtures (above 500°C) which can enhance subsequent deposition.

Calcium was shown to be predominantly associated with sulphate in the initial deposits. This is consistent with thermodynamic data for the free energy change associated with the sulphonation of the alkali chlorides. The melting point of calcium sulphate (1450°C) is significantly higher than those of the alkali chlorides (typically 712 to 800°C). Consequently calcium sulphate crystals are less likely to adhere directly onto a clean cooler surface. The abundance of perfectly shaped monoclinic calcium (and sodium) sulphate crystals in the initial deposits suggests that the predominant deposition mechanism for the higher melting point alkali sulphates involves either nucleation and growth at a site on the probe surface, or condensation in the combustion gases and subsequent adhesion to the initial partially molten halide layer. Both mechanisms will be influenced by the formation of the halide layer and the nature of the substrate, and these alkali sulphates appear to be largely present as secondary deposits. At higher surface temperatures and longer residence times, sulphate deposition could similarly form the initial deposit and enhance deposit build up.

The magnesium content of the deposits is small. Thermodynamic data show that although magnesium chloride is less thermally stable than magnesium sulphate in combustion atmospheres, sulphonation reactions are less favourable than for calcium between 500° and 700°C . The melting point for magnesium chloride is relatively low (712°C) and presumably will exhibit similar deposition mechanisms to sodium and potassium chlorides. At lower temperatures, $<730^{\circ}\text{C}$, sulphonation of magnesium chloride is increasingly favoured and deposition of magnesium sulphate, which has a higher melting point, will be dependent on the formation of the initial adhesive layer or initiated by nucleation at a site on the probe surface. Analyses of deposits formed from the combustion of Coal 1 under various controlled combustion parameters, such as combustion atmosphere and deposit growth rate, indicated that the magnesium is mainly present as the sulphate.

The melting characteristics of the deposits will be dependent on the composition of the alkali chlorides and sulphates, deposit surface and combustion gas temperatures. As the proportion of

the thermodynamically more stable alkali sulphates increases, the melting point of the deposit will also increase. This was generally supported by the slightly lower maximum deposition temperatures observed for chloride ions as opposed to sulphates. Conversely, as the thickness of the deposit increases the temperature of the deposit at the combustion gas interface will rise, thus maintaining the partially molten 'sticky' surfaces of the deposit, providing a substrate on which other gas borne particulates, such as dehydrated clays and iron oxides, could adhere causing build up of the deposits.

The sodium, calcium, magnesium and chloride contents of the coals decrease from Coal 1 to 3 and relatively lower concentrations of these ionisable salt elements will be released from Coals 2 and 3 during combustion (111,115). In addition, their relatively high sulphur and clay contents will enhance reactions between volatile alkali chlorides and sulphur dioxide, retaining a higher proportion in the bed as alkali sulphates, or for the latter, as aluminosilicate material (30). Alkali sulphates which are released from the fluidised bed will favour the condensed phase (Figure 4) and deposition via adhesion to the probe surface will be reduced due to the lower levels of an initial, partially fused alkali salt layer. Consequently, lighter deposits from Coals 2 and 3 lacked the same degree of crystallinity and consisted typically of friable, loosely adhered particles of dehydrated clays, iron oxides and fly ash particles.

Suggested mechanisms for the deposition of the ionisable salt minerals in the three coals studied are set out diagrammatically in Figure 85.

6.5 Influence of Combustion Parameters on Deposition and Combustion Gas Composition

6.5.1 Deposition

The effect of independently varying nine combustion parameters on the formation of the initial deposit was investigated. The results aided elucidation and confirmation of the mechanisms of release and subsequent condensation of the ionisable mineral salts. The nature and extent of deposition of these salts

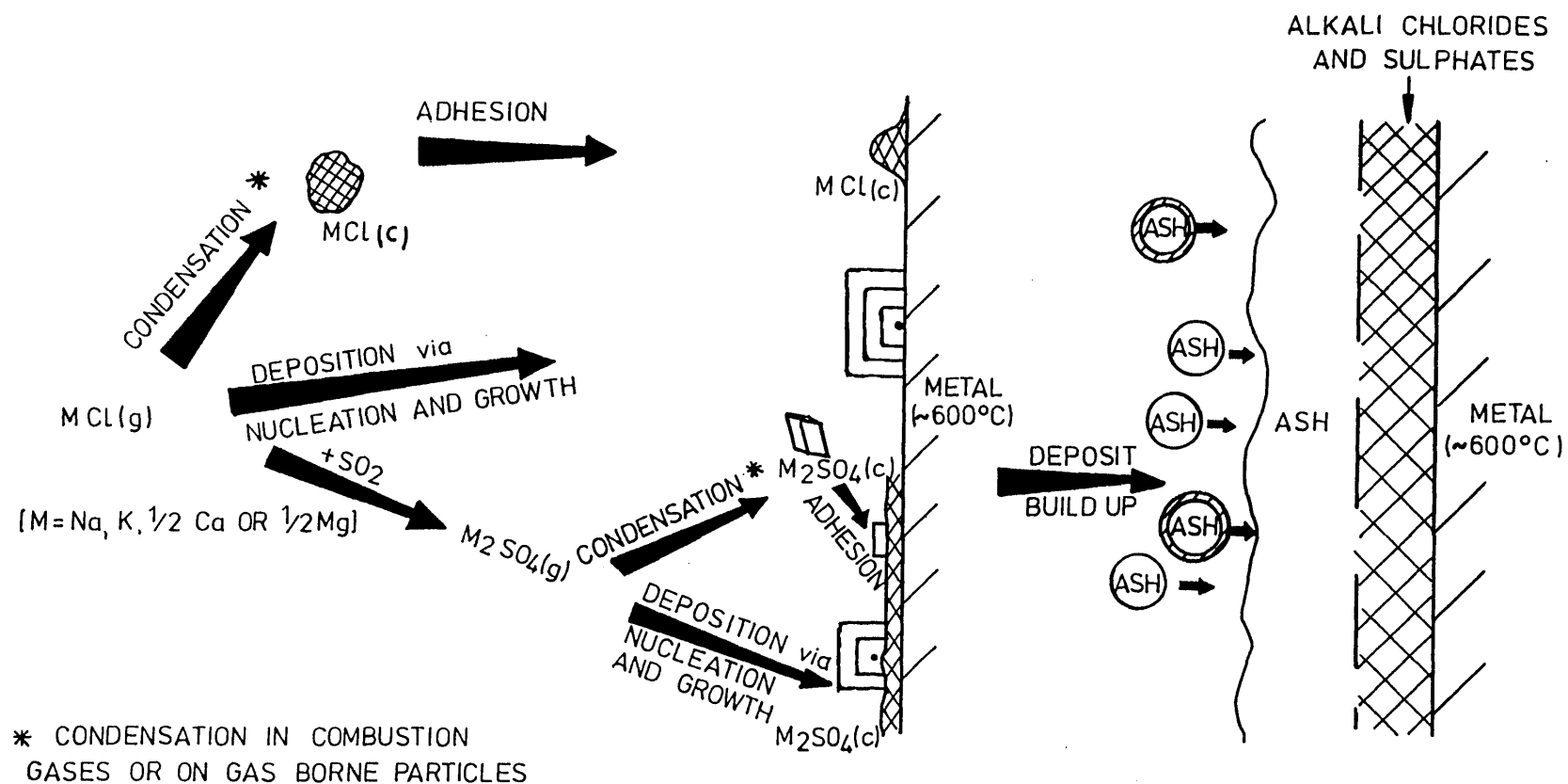


FIGURE 85. PROPOSED MECHANISM FOR THE DEPOSITION OF IONISABLE SALT MINERALS IN UK COALS DURING FLUIDISED BED COMBUSTION.

appears to be influenced in particular by combustion parameters of probe surface and bed temperatures, combustion atmosphere and time, deposit surface position and bed material.

i) Deposit surface temperature

Deposition appears to be highly temperature dependent, with maximum deposition occurring on probe surfaces between 500° and 700°C. This reflects the melting characteristics (and stabilities) of the composite alkali salts mixtures. At lower deposition temperatures <400°C, the condensing salts will ^{not} possess the partially molten adhesive property, whilst at higher temperatures >800°C, alkalis volatilised during combustion will remain gaseous.

Interestingly the characteristic bell shaped deposition curves are similar to curves for corrosion rate versus temperature reported by Laxton et al (2) (Figure 11), where the shape of the curve reflected the stability of the complex alkali sulphates. The temperature at which maximum rate of corrosion occurred was ~70°C lower for the laboratory FBC results. This may be attributable to the higher proportions of chlorides deposited in the laboratory FBC lowering the melting point of the initial layer.

ii) Bed temperature

Higher combustion temperatures will increase volatilisation of the alkali salts (115) and subsequently, enhanced deposition of Na^+ , Ca^{2+} , Mg^{2+} and SO_4^{2-} occur on cooler surfaces in the combustor. The smaller increase in chloride species detected at the higher bed temperatures may be due to the position of the probes in the freeboard, with the gaseous alkali chlorides having a greater opportunity to react with sulphur dioxide; a probe of a given temperature being further from the fluidising bed at the higher bed temperatures. The mechanism for the release of potassium from the micaceous clays did not appear to be influenced by an increase in combustion temperature from 850° to 925°C.

iii) Combustion atmosphere and deposit surface position

Lower partial pressures of oxygen (10 and 15 % wt.) and cooled surfaces closer to the fluidising bed favoured deposition of chlorides in preference to sulphates.

The formation of alkali sulphates is highly dependent on the fuel:air ratio i.e. available oxygen (183). At lower oxygen partial pressures reactions between gaseous alkali chlorides and sulphur dioxide would decrease (Reaction D). The lower melting points of the halides will enhance ensuing deposition, as indicated by the small increase in deposition of Ca^{2+} and Mg^{2+} . Consequently industrial fluidised bed plant operating at low partial pressures of oxygen (eg. fluidised bed gasification) may experience higher fouling tendencies.

To investigate the effect of deposit surface position, gas cooled probes were used. For a given temperature, a cooled probe will be closer to the fluidising bed than an uncooled probe. The shorter residence times prior to deposition will reduce the time available for reactions between volatile alkali chlorides and sulphur dioxide. In addition, the combustion gas temperature in close proximity to the cooled probe will be comparatively higher and reactions between alkali chlorides and sulphur dioxide are less favourable at higher temperatures. The unexpected decrease in calcium deposition may be attributable to differences in saturation vapour pressures for the chlorides which, although low for calcium chloride, increase at a comparatively greater rate between 600° and 800°C for sodium and potassium chlorides. The higher combustion gas temperatures surrounding the cooled probe will ensure that a comparatively higher proportion of calcium chloride will remain gaseous, thus reducing deposition.

(iv) Fluidising gas velocity

Decreasing the fluidising gas velocity from ~ 3 to $2 \times U_{mf}$, seemingly favoured the deposition of sulphates in preference to chlorides. The longer residence time of the volatile alkali chlorides at the lower gas velocities increases the opportunity for reactions with sulphur dioxide. At even lower fluidising gas velocities, $\sim 1.3 \times U_{mf}$, transportation of the volatile inorganic species appeared to be affected.

Industrial FBC normally operate over a wide range of gas velocities (3 to $7 \times U_{mf}$) and control of bed temperature is often achieved by adjustment of the fluidising gas velocity. As the gas velocity is increased, the bed height rises, increasing heat

transferred to partially submerged heat exchange tubes and so cooling the bed. Modifying the coal feed rate usually proves to be less responsive.

This study indicated that increasing the fluidising gas velocity would decrease residence times and increase deposition of the lower melting alkali chlorides as opposed to sulphates. In addition, higher fluidising gas velocities will increase erosion wear damage of the in-bed heat exchanger tube banks.

To simulate gas residence times comparable to industrial FBC, the laboratory FBC height to diameter ratio should be increased e.g. ~1 m height : 70 mm diameter. These dimensions would however encourage a slugging bed, where the bed surface fluctuates widely. Formation of deposits in higher fluidising gas velocities, $>0.17 \text{ m sec}^{-1}$ was not studied as the subsequent increase in bed height would have had a sand blasting action on the probe surface.

v) Deposit growth

The rate of deposition of the monitored ions was shown to vary and be partially dependent on the deposition surface temperature and on the formation of the initial semi-molten halide layer. Surface temperatures for optimum rate of deposition would be $\sim 600^\circ\text{C}$, corresponding to the apex in the deposition versus temperature curves. Lower deposition rates for Na^+ , Ca^{2+} , Mg^{2+} and SO_4^{2-} on the probe surfaces at 515°C are due to the reduced adhesive properties of the initial alkali chloride deposit.

The initial steady increase in the Ca^{2+} and SO_4^{2-} content of the deposit (present mainly as calcium sulphate, m.pt. 1450°C), rose rapidly after ~two hours, illustrating the importance of the initial adhesive layer. In addition calcium sulphate deposition will become increasingly favourable as the deposit grows and the temperature of the deposit-combustion gas interface increases.

Conversely, the rate of chloride deposition decreased after the initial halide layer had been established, presumably due to reactions with sulphur dioxide to form the more thermally stable alkali sulphates. At the lower surface temperature of 515°C , the saturation vapour pressures of alkali halides are reduced and a higher proportion will be present as condensed phases and subsequently reactions with sulphur dioxide will be suppressed.

The rate of deposition of sodium, presumably mainly as partially molten sodium chloride crystals, appeared to be largely independent of the physical characteristics of the deposition surface.

Potassium deposition did not show any conclusive trends, possibly due to contamination of the deposits by elutriated sand from the fluidising bed. Some increase in potassium content of the deposit with combustion time would be expected.

vi) Deposit surface material

In current operating practice high chromium stainless steels are extensively used to provide strong, corrosion and erosion resistant materials with high thermal conductivities, for heat exchange materials with metal temperatures between 400° and 800°C (148,149). The corrosion resistance of these alloys are enhanced by increased amounts of chromium, with the development of chromium-rich oxide layer on the parent metal. This constitutes a barrier which reduces diffusion of metal and corrodant species. In addition, chromium oxide has a lower rate of dissolution, than iron oxides, in molten sulphates.

The gaseous combustion environment above the fluidising bed is, however, potentially corrosive and can attack metal surfaces at temperatures >550°C. The mechanisms of high-temperature corrosion are complex and rates are highly dependent on the composition of the alloy, the metal and gas temperatures and the composition of the deposits (30). This study has looked at the role of probe surface materials on the initial deposition of the ionisable salts during combustion. Consequently an alternative non-reactive material, i.e. alumina, in addition to stainless steel, type 321, was used.

Both silica glass and alumina are considered to be inert at temperatures up to 800°C; silica glass being an amorphous and alumina a crystalline material. Deposition of the ionisable salts was shown to be similar on both materials suggesting that the crystalline nature of the deposit surface did not significantly affect adhesion properties nor rates of nucleation and growth of the condensing salts.

Deposit concentrations of the ionisable salts on stainless steel surfaces gave variable results. The general trends, however, indicated that the nature of the initial deposit does not appear to have been influenced by deposit surface material, although subsequent reactions between the molten salts and the chromium-rich oxide layer could enhance condensation of the more corrosive elements Na^+ , K^+ and SO_4^{2-} .

Deposited sodium and potassium sulphates can form low melting point eutectics at temperatures $>518^\circ\text{C}$. The molten alkali sulphates contain free sulphur trioxide which reacts with the protective oxide coating to form iron and chromium based sulphides and sulphates. This will diminish the protective nature of the oxide layer and increase the rate of corrosion. Sodium and potassium sulphates are thermally more stable than calcium and magnesium sulphates and can diffuse through the molten deposit more readily. EPMA of deposits formed on above-bed tubes in the pilot plant trials with Coal 1, confirmed that the innermost deposit layer at the metal-deposit interface, was slightly enriched in sodium, sulphur and chlorine. The stability of the corrosion products decreases with increasing temperature through the deposit, giving rise to a concentration gradient for the dissolved metal ions. This ensures that the dissolution is effectively a continuous process, with iron and chromium diffusing outward through the molten sulphate layer. Ensuing deposition of sodium and potassium sulphates from the combustion gases will subsequently increase in order to maintain the equilibrium between condensing and volatilising halides and sulphates at the deposit-combustion gas interface.

vii) Sulphur sorbent bed material

The most marked effect of any of the combustion parameters on deposit formation was the use of limestone or dolomite as a sulphur sorbent bed material. Sulphur dioxide formed from the oxidation of pyrite and organically bound sulphur, reacts with the calcined bed material to form calcium sulphate, the majority of which is retained in the bed (130). The lower partial pressure of sulphur dioxide in the combustion gases reduces alkali sulphate formation. The majority of alkalis will be

present as low melting point chlorides and consequently enhanced deposition via condensation in the combustion gases and subsequent adhesion to the probe surface would be expected.

Deposition of Na^+ from Coal 1 combusted in a limestone bed was, however, surprisingly high. The perfect morphology of the halide crystals present in the initial deposit indicated that deposition by nucleation and growth at a site on the probe surface may become an increasingly important condensation mechanism with higher partial pressures of gaseous sodium chloride; presumably as saturation vapour pressure is reached (Figure 4).

A number of the halide crystals exhibited needle-like and dendritic growths which may partially be attributable to stress dislocations (surface tension or thermal). In addition, ion impurities or poisoning of certain areas on the growing cubic halide crystal surface, could leave remaining sites to grow rapidly by faults and screw dislocations. The latter may be a consequence of elutriated calcium oxide, and for a dolomite bed, magnesium oxide, adhering to the initial deposit due to the relatively close proximity of the probe surfaces to the fluidising bed.

The small increase in K^+ deposition from Coal 1 may be attributable to the higher proportion of potassium condensing as partially molten chlorides as opposed to sulphates. The release of potassium from the insoluble micaceous clay minerals did not appear to be markedly affected by the bed material or sulphur retention.

Concentrations of Na^+ deposited during the combustion of Coal 1 in a dolomite bed had also increased, though not as dramatically as with a limestone bed. The needle-like crystal growth at the probe surface was less apparent, possibly due to the additional presence of fine elutriated magnesium oxide particles, which inhibited further crystal growth. Although deposition concentrations of Ca^{2+} and Mg^{2+} are not indicative of the alkaline earth behaviour of the coal during combustion, a higher proportion would be expected to adhere to the probe surface.

Deposits obtained from Coal 1 combusted in a dolomite bed contained calcium rich needle-like crystals (which were low in

chlorine) that must have originated from either the coal or bed material. Hydrogen chloride formed during coal combustion can also attack the limestone or dolomite bed to produce volatile chlorides. Gaseous calcium chloride may preferentially react with the lower partial pressure of sulphur dioxide present to form calcium sulphate. The needle-like crystals were observed to be nucleating and growing from sites on the probe/deposit surface. This type of elongated single crystal growth (Figure 60) can occur in conditions in which only a slight supersaturation of the gaseous phase is experienced.

Similar increases in deposition of Na^+ , Ca^{2+} , Mg^{2+} and Cl^- were observed for Coal 3 combusted in a limestone bed, indicating that the high sulphur content of Coal 3 may act as an alkali sorbent during FBC in a sand bed, fixing sodium, calcium and magnesium as their sulphates. Microscopic examination of the deposits revealed an abundance of unfused iron oxide, dehydrated clays and calcium enriched crystals, which were well adhered rather than loosely held to the probe surface by the underlying initial crystalline deposit.

On the industrial scale, adhesion of fine elutriated bed material should be less pronounced as the heat exchange surfaces will be relatively further from the ebulating bed. Combustion of high chlorine coals may, however, result in the release of bed material as calcium and magnesium chlorides.

This study has shown that the use of in-bed sulphur retention components may cause significantly enhanced deposition of alkali chlorides on surfaces between 500° and 700°C. Subsequent build up of fouling/corrosive deposits would be expected.

viii) Coal feed rate

Industrial fluidised bed combustors often operate at high coal feed rates with fly ash recycling to achieve higher combustion efficiencies. The results from the laboratory combustor suggest that higher feed rates should not present additional deposition problems, with the proviso that the additional carbonaceous matter may act as a binder for impinging fly ash particles (30).

6.5.2 Combustion gas composition

The oxygen and carbon dioxide contents of flue gases from the laboratory FBC were typically between 7 and 9% v/v. These levels are slightly lower than, but comparable with, industrial FBC exhaust gases with ~8 to 10% O₂ and 10 to 12% CO₂.

Operation at higher feed rates will increase the carbon to oxygen ratio, resulting in high carbon dioxide (~11.5%) and lower excess oxygen (~3.5%) levels in the laboratory FBC. Observations that higher feed rates produced a 'dirty burn' (ie. a higher proportion of unburnt carbon entrained in the flue gas) suggested that combustion efficiency had decreased.

Conversely increased fluidising gas velocities decrease carbon to oxygen ratios resulting in higher combustion efficiencies, with higher excess oxygen and lower carbon dioxide levels in the flue gas.

Lower oxygen levels in the fluidising gas may result in incomplete combustion of the coal particles, thus decreasing combustion efficiency and carbon dioxide levels.

6.6 Influence of Coal Pretreatments on Deposition

The effect of pretreating coals, by blending and varying the chlorine content, on the nature and extent of initial deposition, was also investigated.

1) Blending

Blending of high-ash and low-ash coals is widely practised by fuel suppliers such as British Coal. The main aim is to ensure that the ash content of the coal does not exceed an agreed limit and that the calorific value of the fuel remains constant. Sulphur and chlorine contents of coal can be reduced similarly.

Coals 1 and 3 were chosen for study on account of their differing mineral composition and were intimately blended in ratios of 1:2, 1:1 and 2:1 m/m. It should be noted that the blending procedures carried out by the fuel suppliers are less efficient than laboratory methods. Subsequent reactions/interactions occurring between minerals from the two coals would be observed as differences between theoretical and practical deposition concentrations.

The results showed the effect of blending a high sulphur coal (Coal 3) with a coal containing relatively high concentrations of sodium, calcium and chlorine (Coal 1). As the sulphur content of the blended coals increased, with higher proportions of Coal 3, enhanced reactions between the alkali chlorides and sulphur dioxide occurred forming the thermodynamically more stable alkali sulphates. This resulted in lower levels of chloride present in deposits from the blended coals compared to theoretical data.

The release of sodium as sodium chloride is unlikely to be influenced by physical blending due to the close proximity of sodium and chlorine in the coal pores. Reactions between sodium and sulphur dioxide are probably enhanced, as the increase in partial pressure of sulphur dioxide in the combustion gases is greater than the corresponding decrease in volatile sodium chloride for the blended coals (compared to Coal 1). The small difference between the melting points of sodium chloride and sulphate (84°C) did not appear to significantly affect sodium deposition.

The influence of blending Coals 1 and 3 was more significant for calcium deposition. Enhanced reactions between gaseous calcium chloride and sulphur dioxide resulted in a higher proportion of calcium sulphate being retained in the bed. The observed calcium content of the deposit showed a steady decrease from the theoretical deposition data as the proportion of Coal 3 increased.

Surprisingly, blending the coals did not appear to significantly affect the release or deposition of potassium. This is possibly due to the lower concentrations of potassium in the deposit and the susceptibility to contamination from elutriated sand. Previous results have suggested that a higher proportion of potassium may be released from a high sodium content coal (Sections 5.1.1 and 5.4.2).

The concept of blending low and high sulphur coals is therefore attractive for both the purpose of reducing gaseous sulphur oxide and alkali emissions and for decreasing corrosion/fouling tendencies.

ii) Coal chlorine content

The influence of the chlorine content of coal on the release and deposition of the ionisable salt minerals was also studied. The majority of chlorine in coal is water soluble and bound to the surface of the coal pores. Although the coals were originally supplied as washed singles, the residence time of coal in a conventional coal washing plant is too short to make a significant difference in the chlorine content of the coal. The major proportion of the chlorine can only be removed by fine grinding, followed by extraction with boiling water. This process would, however, also result in removal of the ionisable salt minerals.

Studies (52) have shown that a large proportion of the chlorine can be removed from coal by heating to 300°C in nitrogen. The latter method was chosen for study since both techniques are more of academic and economic interest. As previously discussed, blending may prove to be a successful and economic alternative.

During heat treatment, in which the chlorine content of the coal was reduced from 0.8 to 0.18% wt., the clay minerals and gypsum would partially dehydrate. This should not, however, affect the release/deposition of the ionisable salt minerals.

Chlorination of the pre-wetted coal with hydrogen chloride gas introduced ionically bonded chlorine into the porous coal structure. The impregnated chlorine will probably have dissolved in water trapped in the coal pores, thus being present in a similar mode to the inherent chlorine in coal. Unfortunately, enhancing the chlorine content of Coal 1 from 0.8 to 1.43% wt. resulted in a number of mineralogical changes. Reactions between hydrogen chloride and the carbonate minerals occurred, resulting in the formation of the potentially volatile chlorides of calcium, magnesium and iron. The occurrence of sodium in Coal 1 appears to be unaffected by either coal pretreatments.

The reduction in coal chlorine content appeared to affect the volatilisation of the monitored cations, Na^+ , K^+ , Ca^{2+} and Mg^{2+} during FBC, as their chlorides, fixing them in the bed as less volatile species eg. oxides or sulphates. Vapour pressure data

for the chlorides and hydroxides of sodium and potassium, at 850°C, are similar (Table 4), indicating that release as hydroxides is feasible. These concentrations are significantly higher than those of calcium and magnesium oxides. Consequently, lower concentrations of all monitored ions were deposited on the probes during the combustion of the lower chlorine coal; with the Ca^{2+} and Mg^{2+} contents of the deposits being particularly reduced. In addition, lower levels of hydrogen chloride in the combustion atmosphere will favour deposition of alkali sulphates (Reaction D). Consequently, the melting point of the initial deposit will rise as the proportion of alkali sulphates increases, as will the maximum deposition temperature of the probes. This further reduced ensuing deposition at lower probe surface temperatures.

Enhancing the chlorine content also affects the release/deposition of ionisable salt minerals. Higher levels of Na^+ were deposited during FBC, probably due to an increase in sodium volatilised and to higher partial pressures of gaseous hydrogen chloride suppressing the formation of sodium sulphate in Reaction D. The melting point of the deposit would be lowered, with enhanced adhesion properties. The increase in deposition of calcium and magnesium is largely attributable to the decomposition of the carbonate minerals during coal pretreatment, although some increase in deposition of Ca^{2+} and Mg^{2+} would be expected for a higher chlorine content coal. At the probe surface an equilibrium exists between condensing and vapour alkali chlorides and sulphates. The lower saturation vapour pressures of alkali sulphates at FBC temperatures will result in a comparatively higher rate of condensation. This will enhance reactions between gaseous alkali chlorides and sulphur dioxide, resulting in higher sulphate levels in the deposit. The K^+ content of the deposit appeared to be largely independent of the increase in chlorine concentration. This confirms that the role of chlorine is largely to promote the volatilisation of potassium as potassium chloride following release from the micaceous clay minerals. The release of potassium, possibly by some form of cation exchange mechanism with sodium, appears to be the major rate governing factor.

6.7 Pilot Plant Trials

The Encomech pilot plant trials enabled results obtained with the laboratory combustor investigations to be correlated with those from a 0.2 MW FBC. Coals 1 and 3 were selected for the test programme. The study confirmed observations that Coal 1 had the greater tendency to form more abundant, lower melting deposits on cooled surfaces (400° to 800°C) whilst deposits collected from the combustion of Coal 3 on above-bed surfaces were more friable and loosely adhered.

The major constituents present in the above-bed deposits, formed during the combustion of Coal 1 in both the laboratory and pilot plant combustion trials, were calcium and sodium sulphates, haematite and sodium chloride. Smaller amounts of calcium and potassium chlorides, potassium sulphate and aluminosilicates were also detected. The major coal-derived component identified on in-bed tubes with Coal 1, was sodium chloride. Haematite and tentative identifications of sodium sulphate and aluminosilicate phases were also present in above-bed tubes with Coal 3.

The pilot plant trials confirmed that a significant proportion of calcium and sodium are released from Coal 1 during combustion. For Coal 3, the high sulphur content coal, a higher proportion of these elements were retained in the bed ash as sulphates. Interesting observations were made regarding the fate of pyrite during combustion. Pyrite in Coal 3 is abundant and mainly occurs as fine multiple agglomerations, whereas a higher proportion of pyrite in Coal 1 is present as larger crystals. During combustion the larger fragments of pyrite will have a greater tendency to fuse and remain in the bed, whilst the lighter fine particles may be elutriated from the bed with the fly ash. Coal ashes of high iron content are often associated with slagging problems, whereas iron enriched deposits can cause fouling and corrosion of superheaters.

Bed ash from Coal 1 combusted in the laboratory FBC consisted mainly of unfused, non-spherical particles ~5 to 120 µm in diameter, of calcium and sodium sulphates, ferric oxide, calcium carbonate and aluminosilicates. In industrial fluidised bed boilers the mean particle diameter of the bed material is usually >0.5 mm, depending on the size of the coal feed (usually <6 mm).

The size of the bed material has a significant effect on the fluidising velocity and heat transfer efficiency to immersed tubes. At FBC temperatures fine particles of inherent ash do not tend to fuse as in higher temperature combustion regimes. Most of the clay particles (~50%) retain their original size and can be elutriated in the flue gas.

The sintered ash deposit formed on the above-bed tubes in the Encomech FBC during the combustion of Coal 1, has a layered structure which is slightly richer in sodium, sulphur and chlorine in the layer adjacent to the tube scale. This is mainly attributable to the diffusion of alkali sulphates (Na, K) through the porous matrix of silicate ash deposit. The formation of the layer-structured deposit is enhanced as a result of high porosity of the sintered matrix and the temperature gradient across the ash material on the cooled tubes. The porosity of the deposit increases outwards, away from the tube-deposit interface, in keeping with the reduced sintering times.

6.8 Bomb Combustion Studies on Coals

Coals 1 and 3 were also selected for further investigation of the release of the alkali species during combustion in a bomb calorimeter. The work was based on the assumption that the mineral constituents of coal released during combustion are those which are water soluble (30,172). Differences in concentration of water soluble constituents before and after bomb combustion would be due to reactions occurring between the minerals. Earlier studies from the laboratory FBC experiments had indicated that sodium and/or chlorine (and possibly calcium) in coal may, by some mechanism, promote or influence the release of naturally involatile potassium from the clay. The maximum temperatures reached in the explosive reaction in the bomb calorimeter are likely to be several hundreds of degrees higher than those experienced during FBC. The study has, however, indicated that exchange reactions can occur between potentially volatile alkali metal cations and those incorporated in aluminosilicate minerals. During bomb combustion some sodium became incorporated in the silica melt, whilst potassium was released, probably as water

soluble potassium chloride. The dissolution of alkali metals in a silicate slag is highly dependent on the basicity of the ash. Coal 3, with a higher silica and alumina content, has a more acidic ash than Coal 1 and this will have a greater affinity for the alkali metals. Consequently a greater proportion of the sodium in Coal 3 was retained as insoluble species after combustion compared to Coal 1.

Potassium is incorporated mainly in the insoluble silicate fraction of the coal ash and can be relatively mobile in basic melts. In addition, potassium forms comparatively volatile chlorides and hydroxides. Consequently, potassium will be more mobile in the basic ash of Coal 1 and hence more readily released as volatile chlorides. The major alkali chlorides are water soluble and the decrease in chlorine after combustion probably results from the loss of hydrogen chloride during extraction.

During aqueous extraction a significant proportion of the insoluble calcium and magnesium containing carbonate minerals, calcite, dolomite and ankerite, will have reacted with hydrochloric acid. The decrease in calcium concentration after combustion probably results from reactions occurring with sulphur oxides or from dissolution in the silicate melts.

At FBC temperatures the finely dispersed minerals inherent in coal are unlikely to agglomerate when burned (Figures 52 a and b illustrating fluidised bed ash verify this). At these temperatures, however, alkali exchange reactions can occur as the clay minerals dehydrate (from 400°C) and their structure collapses. At increasingly higher temperatures (>800°C) thermal expansion and reordering of the collapsed clay structures occurs resulting in interstitial in-filling by alkali cations within the dehydrated clay structure forming new aluminosilicate structures (102). The most likely cation to be exchanged with potassium is sodium, however, calcium and magnesium may also be involved. The role of chlorine is probably in the formation of a relatively volatile, water soluble species.

Three coal blends were also fired in the bomb calorimeter to study possible reactions occurring between minerals from differing coals. By blending Coal 3 with Coal 1, the acidity of

the blended ash increased thus enhancing the affinity of the melt for alkali ion capture. Although any changes in elemental concentrations were too small to be detected, results obtained from the bomb combustion of the individual coals suggest that the basicity of a coal ash is an important factor to be considered when blending coal to maximise sodium capture by the ash.

The influence of chlorine on the release of the alkalis during bomb combustion was investigated with additional experiments on Coal 1 with reduced chlorine content (0.24%). The decrease in sodium, magnesium and to a lesser extent, calcium, extracted after combustion suggested that the chlorine content of coal can affect solubilisation and hence release of these elements. The reduction in chlorine presumably suppressed the reaction between sodium ions in the coal matrix, and calcium and magnesium carbonates, with hydrogen chloride gas to form volatile/water soluble sodium, calcium and magnesium chlorides.

6.9 Implications for Industrial Fluidised Bed Combustion Plant

Coals of high ionisable salt (Na^+ , Ca^{2+} , Mg^{2+} and Cl^-) and low ash contents are more likely to initiate fouling problems during FBC than coals containing relatively high proportions of sulphur and aluminosilicate minerals.

Enhanced deposition may be experienced on above-bed cooled surfaces at temperatures in the range 450° to 700°C. Operation at higher bed temperatures, or with lower oxygen atmospheres and higher fluidising gas velocities may also increase deposition. The use of sulphur sorbent bed materials was shown to cause significant enhancement in deposition of both coal and bed derived constituents, particularly for coals of high chlorine content.

Blending coals of high aluminosilicate and sulphur contents with coals high in sodium, calcium and chlorine is attractive for reducing both gaseous sulphur oxide and alkali emissions, and for decreasing corrosion/fouling tendencies. Sodium and calcium may be retained in the bed as less volatile sulphates or aluminosilicate complexes.

Reducing the chlorine content of a high chlorine coal, possibly by enhanced washing or blending, may also alleviate fouling problems by reducing the release of the alkali metals as chlorides from the mineral matter.

7. CONCLUSIONS

Three coals, selected for their differing ionisable salt content, have been analysed and their minerals and salts separated, identified and estimated. The coals contain essentially the same salts and minerals but these vary in both abundance and relative proportions.

1. The most abundant minerals were the kaolin and mica groups of aluminosilicates, ankerite, dolomite, calcite, pyrite and quartz. The majority of sodium and chlorine appears to be organically associated. The relative proportions of kaolin, mica, pyrite and quartz increased from Coal 1 to 3, whilst those of dolomite, ankerite, calcium, sodium and chlorine decreased.
2. The ionisable salts appear to be present mainly as ions adsorbed on the coals surface and they may be substantially removed by aqueous leaching; the ease of leaching being controlled by the porous nature of the coal. Chloride, sodium and calcium are the predominant leachable ions.
3. Ash fusion and high-temperature microscopy data have shown that ashes from Coals 1 and 2 fuse and flow at lower temperatures than those for Coal 3. This is consistent with the ash analysis, the calculated fouling and slagging parameters, and observed fouling and slagging propensities when fired in industrial and pilot plant combustion boilers.
4. Improved fouling indices which were based on water soluble alkali metals could provide more reliable parameters for coal combustion than those currently based on total alkali metal content.
5. Use of a laboratory scale (70 mm) fluidised bed combustor suggests that this type of equipment provides a rapid and reproducible technique for studying the nature and extent of deposits formed from coals burned under a wide range of conditions.
6. Experiments with three coals of varying ionisable salt content have shown the importance of inherent salt minerals in the build-up of deposits. Condensing salts of predominantly sodium, potassium and calcium chlorides and

sulphates together with low melting point eutectic mixtures appear to provide an adhesive layer binding gas borne particulates and inducing deposit growth.

7. The mechanisms of release and deposition of the ionisable salts during FBC have been elucidated from studies on the nature and extent of deposits formed under different combustion conditions and coal pretreatments. The effect of varying probe and bed temperatures, coal feed rates, fluidising gas velocities, combustion atmospheres and time, selected deposit surface materials and position, bed material, coal blends and coal chlorine content have been evaluated.
8. The nature and extent of deposition of the inherent salt minerals appears to be influenced in particular by the surface deposition temperature and the use of sulphur sorbent bed materials.
9. Other combustion parameters which affect deposition are bed temperature, combustion atmosphere and time, deposit surface position and material.
10. Deposition of the ionisable salts, in the temperature range 400° to 800°C, has been shown to go through a maximum value, falling at higher temperatures, to give a bell-shaped curve. The shape of the curve reflects the melting characteristics (and stabilities) of the alkali salts.
11. Sulphur sorbent bed material, reducing combustion atmospheres and deposition surfaces near to the ebulating bed favoured deposition of the lower melting alkali chlorides as opposed to sulphates.
12. The release of sodium, calcium and magnesium chlorides is favoured with higher bed temperatures.
13. The rate of deposition of the higher melting salts and ensuing gas borne particulates is at least partially dependent on the formation of an initial partially molten crystalline deposit.
14. Enhancing the chlorine content of a coal has been shown to increase both the release and deposition of the ionisable salt minerals.

15. Reactions between minerals from intimately blended coals can occur during FBC. Blending a high alkali content coal with a coal of high sulphur content resulted in reducing gaseous sulphur dioxide and alkali emissions, fixing both as alkali sulphates.
16. The release of potassium from the aluminosilicate minerals during FBC appears to be mainly dependent on the chemical composition of the ash, in particular on the presence of sodium. Chlorine promotes the volatilisation of potassium as the chloride following release.
17. The extent of release of sodium and calcium from coals during fluidised bed and bomb combustion is variously governed by the chlorine and ash content of the coal, the sodium and calcium content of the ash, the mode of occurrence in the coal and combustion temperatures.

8. FURTHER WORK

The findings from this study have highlighted several areas of work where further knowledge would be of use in understanding and possibly overcoming deposition problems encountered during coal combustion.

An extension of the range of coals to provide a wider variation of ash composition and content, and studying deposit formation in the laboratory FBC, would supplement information on the influence of the ionisable salt minerals on the overall thermal behaviour of inorganic species in coal. Such knowledge may enable more reliable fouling indices, based on mineral composition, to be developed, which would be applicable to the performance of UK coals in FBC.

New EEC regulations may soon be enforced, which would require stringent control of emissions (such as SO_x and NO_x) from coal fired combustion plants. Implications that enhanced deposition may occur when using sulphur sorbent bed materials will therefore become increasingly important. The influence of a wider range of coals and bed materials on deposit formation and sulphur retention should be investigated, as should the effect of the various combustion parameters such as deposit surface position, bed temperature, combustion atmosphere etc. The possibility of high chlorine coals promoting the release of Ca^{2+} as calcium chloride from the bed material would also be of interest.

Further investigations, involving blending coals with a wide range of compositions and studying deposit formation when burned in industrial and laboratory scale combustion plants, may more readily provide information whereby problem coals could be suitably blended to optimise reduction of alkali and gaseous emissions.

Fuel additives also have the potential to reduce problems associated with fouling and gaseous pollutants, but their effectiveness is often dependent on the nature of the coal and combustion conditions. Information gained from the use of additives on deposit formation in the laboratory FBC may elucidate the nature of their reaction mechanisms and help to identify more effective additive formulations.

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APPENDIX I

Ashing Procedures

High-Temperature Ash

The high-temperature ash is the residual inorganic material when coal is raised to 815°C, in air (BS method (1)). However, high temperature ashing of coal results in a series of reactions, such as oxidation, dehydration, sulphur fixation, solid-state interactions or vaporisation, to all mineral components except for quartz (SiO_2). During the ashing procedure (oxidation of organic fraction), coal is heated relatively slowly and all the chlorine and the majority of sulphur are volatilised as hydrogen chloride and sulphur dioxide before minerals such as carbonates decompose. Some sulphur dioxide may remain in the ash in combination with calcium. All the clay minerals lose their water of hydration. Consequently the high-temperature ash consists mainly of oxides, sulphates and aluminosilicate complexes.

These changes to the mineral matter content in coal during ashing have been accounted for by applying various schemes. One of the earliest methods, and still most widely used, of estimating the mineral matter content of coals from the high-temperature ash analysis was developed by Parr (2), who considered only the total sulphur and ash contents in developing the conversion formula.

$$\text{M.M} = 1.08 \text{ ash} + 0.55 S_{\text{total}}$$

where

M.M = mineral matter on the air-dried basis

King, Maries and Crossley (3) modified the Parr formula by taking into account both the loss of CO_2 for carbonates and the decomposition of the chlorides. In the absence of sufficient analytical data to calculate mineral matter by their method, a slightly more accurate equation than the Parr formula is used (4):-

$$\text{M.M} = 1.10_{\text{ash}} + 0.53 S_{\text{total}} + 0.74 \text{CO}_2 - 0.36$$

Low-Temperature Ash

Low-temperature ashing was developed in 1962 by Gleit (5). Low pressure oxygen is activated by a radio-frequency (rf) discharge and the excited oxygen-containing atoms and free radicals oxidise the carbonaceous matter in the fine ground coal sample at comparatively low temperatures ($\sim 140^\circ\text{C}$).

The effects of the oxidising gas stream upon minerals in bituminous coals and anthracites is relatively small, although studies (6) have shown that some changes in mineralogical composition occur. Frazer and Belcher (7) reported that some pyrite (FeS_2) can be oxidised, gypsum ($\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$) is dehydrated to bassenite ($\text{CaSO}_4 \cdot \frac{1}{2}\text{H}_2\text{O}$), a major portion of chlorine is lost and that to some extent organic sulphur can be fixed as sulphates. The rates of these reactions are functions of operating conditions eg. rf power level and oxygen flow rate. Miller (6) found that the effect of fixation of organic sulphur as inorganic sulphates decreased with increase in rf power. Frazer and Belcher (7) also found, although some of the clay minerals may become partially dehydrated during low-temperature ashing, this process was reversed if the samples were allowed to equilibriate with the atmosphere after ashing.

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APPENDIX II

Normative Analysis Procedure and Assumptions

Normative analysis (1) was used to estimate the various amounts of each mineral in a coal and was based on the chemical analysis of its high-temperature ash. In this procedure the known concentrations of each analysed element in the ash (expressed as an oxide) have been ascribed to a mineral or minerals from stoichiometric relationships. For this procedure it was important to know qualitatively the mineralogical composition of the coal. This information was derived from X-ray diffraction of the low-temperature ashes, LTA.

The concentration of pyritic sulphur present was used to estimate the amount of pyrite, FeS_2 , in the coal. The amount of iron associated with the pyrite was then subtracted from the total iron content of the coal; the unaccounted iron was ascribed to other iron containing minerals. In a similar manner other elements were ascribed to various minerals.

The quartz content of the three coals was also determined from the Si to Al ratio of their HTA. The ratio of silica to alumina, for the majority of aluminosilicate minerals present in UK coals, is approximately one and the proportion of Si in excess of this can be attributed to quartz.

X-ray diffraction analysis of the LTA indicates that the principal carbonate minerals present were ankerite/dolomite, although it was not possible to readily distinguish between these two carbonate forms, and calcite. There was no evidence for the presence of significant concentrations of magnesite (MgCO_3), and siderite (FeCO_3) was only tentatively identified in Coal 2 ash. Similar observations on the composition of carbonate minerals in British coals have been reported by Dixon et al (2). Consequently, the normative procedure set out in Table 1 assumes that magnesium can be ascribed entirely to ankerite and dolomite and iron to ankerite and pyrite. For calculation purposes, the molar ratio of dolomite to ankerite for Coal 2 was assumed to be similar to that calculated for Coal 1.

One of the major assumptions made for these calculations was that all the potassium can be ascribed to muscovite mica (aqueous extraction data, Section 4.1.7). Another was the form of sodium as its sulphate in the LTA (FT-IR).

The scheme is detailed in Table 1 and it should be noted that the standard normative analysis method has been modified from a knowledge of minerals in the coals. The method is therefore applicable only to the three coals under investigation.

Table 1 Normative Analysis Method

The number of moles of each mineral is calculated from the number of moles of pyritic sulphur, sulphate sulphur, etc. using the following equations.

$$\text{Pyrite} = \frac{\text{Pyritic Sulphur}}{2}$$

$$\text{Gypsum} = \text{Sulphate Sulphur}$$

$$\text{Ankerite}^* = 2 \text{ Fe}_2\text{O}_3 - \text{Pyrite}$$

$$\text{Dolomite} = \text{MgO} - \text{Ankerite}$$

$$\text{Calcite} = \text{CaO} - 5 \text{ Apatite} - \text{Gypsum} - \text{Dolomite} - 2 \text{ Ankerite}$$

$$\text{Apatite} = \frac{2}{3} \text{ P}_2\text{O}_5$$

$$\text{Mica} = \text{K}_2\text{O}$$

$$\text{Kaolinite} = \text{Al}_2\text{O}_3 - 3 \text{ Mica}$$

$$\text{Quartz} = \text{SiO}_2 - 6 \text{ Mica} - 2 \text{ Kaolinite}$$

$$\text{Quartz} = \text{SiO}_2 - 2 \text{ Al}_2\text{O}_3$$

$$\text{Rutile} = \text{TiO}_2$$

$$* \text{ For Coal 2 Ankerite} = 2 \text{ Fe}_2\text{O}_3 - \text{Pyrite} - \text{Siderite.}$$

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APPENDIX III

Slagging and Fouling Factors

The most widely used parameters for judging the quality of coal, with respect to furnace fouling and slagging, are the slagging factor, R_s , and fouling factors, R_f and $R_f^{(1)}$.

i) Slagging Factor, R_s

The slagging factor, R_s , is a parameter empirically developed to relate ash analyses to fused slag deposits that form on furnace walls and other surfaces exposed predominantly to radiant heat and is defined as

$$Rs = (\text{Base/Acid}) \times \text{wt.}\% S_{(\text{total})} \text{ on dry coal}$$

where Base = wt.% ($\text{Fe}_2\text{O}_3 + \text{CaO} + \text{MgO} + \text{K}_2\text{O} + \text{Na}_2\text{O}$) on
 high-temperature ash (HTA)

Acid = wt.% ($\text{SiO}_2 + \text{Al}_2\text{O}_3 + \text{TiO}_2$) on HTA

This parameter is not applicable to lignitic type ash where $\Sigma \text{ wt.}\% \text{ CaO} + \text{MgO} > \text{wt.}\% \text{ Fe}_2\text{O}_3$. For bituminous type ash the $\Sigma \text{ wt.}\% \text{ CaO} + \text{MgO} < \text{wt.}\% \text{ Fe}_2\text{O}_3$.

% S gives an indication of the quantity of pyritic iron present which influences the state of oxidation of the iron in the slag and thus its plastic range. The parameter, R_s , has no theoretical basis but provides an indication of the melting point and viscosity of the slag.

ii) Fouling Factors, R_f and $R_{f'}$

The ash fouling factors, R_f and $R_{f'}$ are parameters empirically developed to relate ash analyses to the tendency of alkali bonded deposits to form on convection tube banks, especially superheaters and reheaters that are not exposed to radiant heat from the furnace.

These are mathematically defined as

$$Rf = (\text{Base/Acid}) \times \text{wt.\% Na}_2\text{O on HTA}$$

$$Rf' = \text{wt. \% Na}_2\text{O on HTA}$$

The ash fouling factor R_f is used to indicate the relative tendency of bituminous coals to cause low, medium, high or severe fouling of convection section surfaces and should not be applied to lignitic type ash. R_f' may be applicable for coal with lignitic type ash but insufficient experience is available to draw any firm conclusion.

The values of R_s , R_f and R_f' given by the original authors (2) correspond to the four slagging and fouling classifications given below.

Propensity for Slagging or Fouling	Slagging factor R_s	Fouling factors	
		R_f	R_f'
Low	<0.6	<0.2	<2.0
Medium	0.6 - 2.0	0.2 - 0.5	2.0 - 3.0
High	2.0 - 2.6	0.5 - 1.0	3.0 - 6.0
Severe	>2.6	>1.0	>6.0

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