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Fouling and slagging in combustion plant

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THE PREPARATION OF THIS DATA ITEM

The work on this particular Data Item was monitored and guided by the following Working Party on behalf of the Heat Transfer Steering Group:

Mr R. Ainsley	— BP International plc
Dr A. Anjum	— Foster Wheeler Power Products Ltd
Dr W.H. Gibb	— PowerGen plc
Dr J.D. Isdale	— National Engineering Laboratory
Dr A. Sanyal	— Babcock Energy Ltd
Dr J. Williamson	— Imperial College of Science, Technology and Medicine.

The Heat Transfer Steering Group first met in 1966 and now has the following membership:

Chairman	
Eur.Ing. D. Butterworth	— HTFS, Atomic Energy Authority, Harwell
Vice-Chairman	
Dr R. Cheesewright	— Brunel University
Members	
Mr R.J. Allam	— Air Products Ltd
Dr T.R. Bott	— Birmingham University
Prof. P.J. Heggs	— Bradford University
Eur.Ing. T.J. Loraine	— Stone and Webster Engineering Ltd
Dr A.C. Pauls*	— Monsanto Company, USA
Prof. R.H. Sabersky*	— California Institute of Technology, USA
Mr E.A.D. Saunders	— Independent
Dr J. Taborek*	— Independent
Eur.Ing. M.A. Taylor	— Independent
Mr G.H. Walter	— Independent
Dr D. Wilkie	— Independent
Eur.Ing. D.A. Winkworth	— Foster Wheeler Energy Ltd.

* Corresponding Member

The technical work involved in the assessment of the available information and the construction and subsequent development of the Data Item was undertaken (under contract to ESDU) by

Dr T.R.Bott — Birmingham University.

The person with overall responsibility for the work in this subject area is Mr S.J. Pugh, Head of Thermofluids Group.

FOULING AND SLAGGING IN COMBUSTION PLANT

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FOULING AND SLAGGING IN COMBUSTION PLANT

1. PURPOSE AND SCOPE OF THIS ITEM

This Data Item, ESDU 92012, is one in a group on the fouling of heat exchanger surfaces^{42, 53, 66, 67, 68} and deals particularly with flue gas streams.

Conditions in combustion equipment vary widely from relatively low temperatures at the stack to over 1500°C in the radiant sections of the boiler and over 1800°C in the flame. The size of solid particles carried in the flue gases may vary from sub-micron to a few millimetres in diameter. The shape and consistency of particles varies throughout the equipment, as well as between different fuels and equipment designs, ranging from near spherical to grossly irregular shapes and from the solid to the molten state.

Sketch 2.1 presents a simplified guide to the Data Item, and it is intended to illustrate the logical steps from an assessment of the potential problems to the possible solutions and the cleaning of equipment.

The introduction to the Item (Section 3) includes definitions of fouling and slagging and discusses the effects of methods of combustion on the potential for deposition. The consequences of deposition on efficiency are discussed.

Mechanisms by which surfaces become contaminated with particles and deposits which result from chemical reactions and corrosion are outlined in Section 4.

In Section 5 the principles of combustion are discussed in some detail in relation to different fuels, for example, coal, oil, natural gas and waste products, and with particular reference to heat transfer surface contamination. The chemical reactions that are responsible for deposit formation are outlined for the different fuels. Section 6 provides techniques, which are largely empirical, for the assessment of fouling and slagging propensity.

Based on an appreciation of mechanisms of fouling and slagging, techniques are presented in Section 7 for the limitation of these problems in combustion systems. These include blending, combustion conditions and the use of additives.

Section 8 provides a discussion of cleaning techniques that might be applied during operation (on-line) or after shutdown (off-load).

Section 9 discusses the implication of fouling and slagging for the design of combustion equipment with tentative recommendations on good design practice.

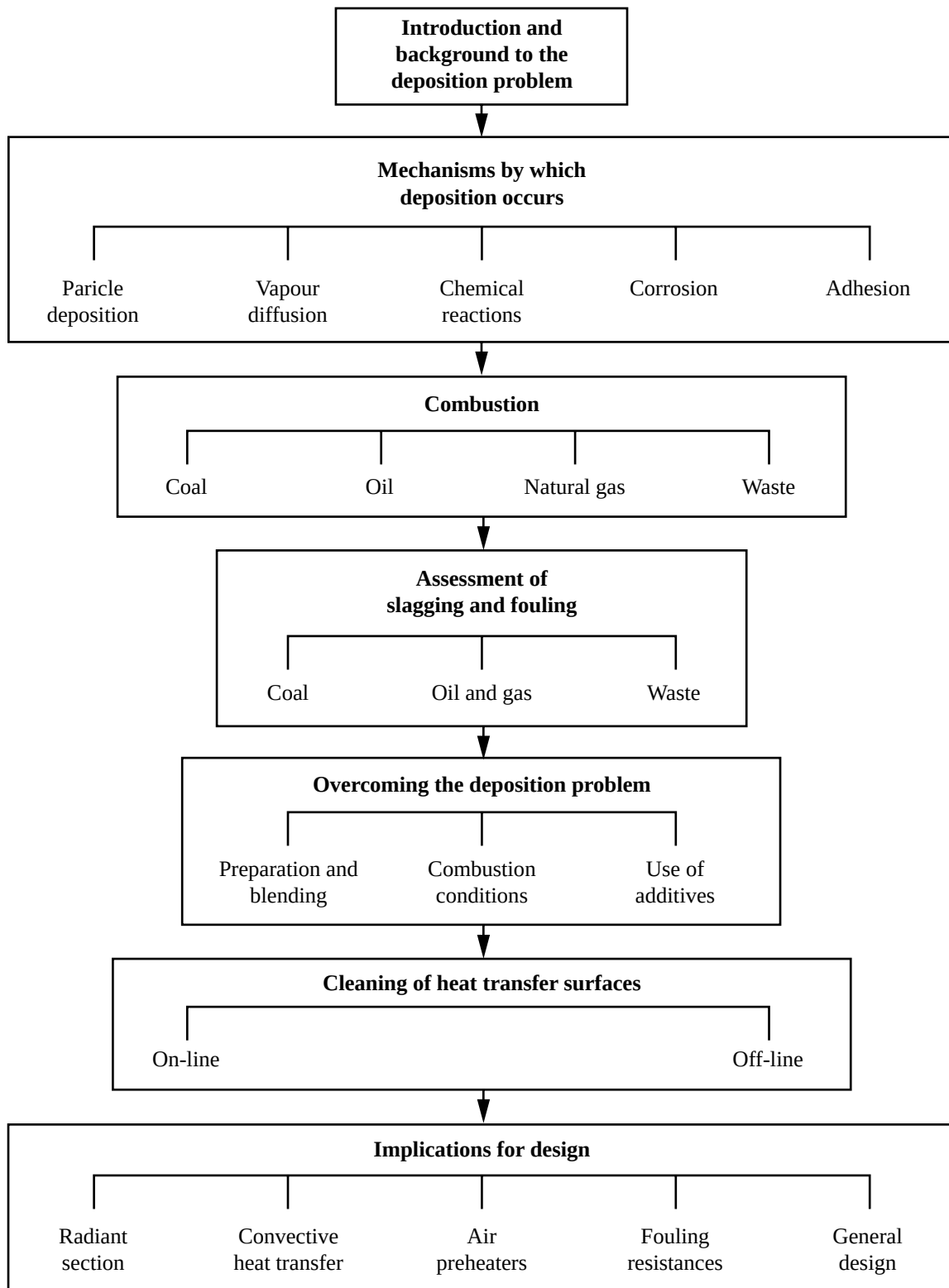
2. NOTATION AND UNITS

		Units
Ar	aromatic content, expressed as a percentage	—
CCR	Conradson carbon residue	—
CT	caking temperature	°C or K
D_c	composition of ash deposits on surface (see Section 5.1.1)	—
DT	deformation temperature	°C or K
d_p	particle diameter	m
f_s	severity factor	—
FS	slagging index	°C or K
FT	fluid temperature	°C or K
HT	hemisphere temperature	°C or K
IDT	initial deformation temperature	°C or K
k	thermal conductivity	W/m K
K	constant	—
l	thickness or length	m
M_{ox}	metal oxide composition	—
$\dot{Q}_c$	convective heat flux	W/m ²
$\dot{Q}_r$	radiation heat flux	W/m ²
R	electrical resistivity	ohm
$R_{b/a}$	base to acid ratio	—
R_c	rate of corrosion	mg/s
R_d	residue, expressed as a percentage	—
R_f	fouling factor or resistance	m ² K/W
R_s	resin content, expressed as a percentage	—
R_s	product of base to acid ratio and total sulphur content	—
R_{TS}	slagging index	—

SR	silica ratio	—
ST	softening or fusion temperature	°C or K
t	time	s
T_{cv}	temperature of critical viscosity	°C or K
T	temperature	°C or K
T_e	exposure temperature	°C or K
T_r	temperature of radiant source	K
T_R	absolute temperature at which electrical resistivity is measured	K
T_s	temperature of surface	°C or K
T_{v6}	temperature at which slag viscosity is 10^6 N s/m ²	°C or K
T_x	temperature at depth x	°C or K
$T_{25}, T_{200}, T_{1000}$	temperatures at which the ash viscosities are 25, 200 and 1000 N s/m ² respectively	°C or K
U	overall heat transfer coefficient	W/m ² K
V	flow velocity	m/s
X	some function of depth	—
α	heat transfer coefficient	W/m ² K
ε	emissivity	—
λ	thermal conductivity	W/m K
ϕ	Stefan Boltzmann constant	W/m ² K ⁴
η	viscosity	N s/m ²
ρ	density	kg/m ³

Subscripts

f	deposit
g	gas
m	metal
o	metal oxide
p	particle
w	cold fluid or wall



Sketch 2.1 Guide to the use of this Item

3. INTRODUCTION

Gas-side fouling of heat exchanger surfaces is manifest in a wide range of industries. Wherever there is heat recovery from gas streams that contain particulate matter, or corrosive or reacting components, the accumulation of deposits on all receptive surfaces, not just heat exchangers, can be a problem. As a result, accumulations of unwanted solids can occur in transfer lines and valves, in equipment such as dryers and reactors, and in combustion spaces and stacks. The extent of the detrimental effects will depend upon many factors. Temperature of operation, fluid velocities, particle size and concentration of any solid material carried in the stream, and the chemical composition of the components of mixtures are all likely to affect the fouling.

The presence of deposits on heat exchanger surfaces will generally impede efficient heat transfer with resultant effects on the thermal efficiency of the plant. In addition, the accumulation of unwanted material on the structure can cause mechanical damage that may result in enforced shut down (outage) with attendant loss of production and maintenance costs. Because the accumulation of deposits on heat transfer surfaces often encourages corrosion it is not usually easy to differentiate between the direct effects of deposited material and the degradation of the metal surface of the heat exchanger which also constitutes a heat transfer resistance.

The source of the fuel constituent that results in fouling conditions may be continuous or intermittent but, to a lesser or greater extent, the overall result is the same, namely a reduction in efficiency and an increase in fuel usage. In combustion systems, for instance, the existence of continuous fouling conditions depends on the quality and chemical composition of the fuel, whereas intermittent deposition may originate from poor combustion control and periods of incomplete combustion.

In many systems, the deposition can be directly related to particulate matter in the gas stream. Inorganic substances, together with possibly carbonaceous particles, are common foulants in combustion systems burning traditional fuels like oil and coal. Fouling also occurs with the incineration of waste, for example domestic refuse and industrial waste, wood, straw or biomass.

Each system will have its own characteristics but the general principles of the fouling process will be the same, as described in earlier Data Items^{42, 53}. In essence the process involves:

- (i) transport of particles or chemically reacting components to the surface,
- (ii) adhesion of particles (or agglomerates) to the surface either by physical processes or chemical reaction,
- (iii) possible transport of some material away from the surface.

The result of this process is the net accumulation of solids on a surface from a balance between deposition and removal, the latter being very much dependent upon the nature of the deposit in terms of its cohesiveness and adhesion to the surface.

Any attempt to mitigate the problem of gas-side fouling must take into account all the factors that influence the overall fouling process.

It also has to be appreciated that as the fouling process continues the thermal and hydrodynamic conditions within the equipment change. Initially a clean metal surface is in contact with the hot gas but, as deposition is initiated and develops, the outer layers of the deposit constitute the interface between the gas and the solid surface. The situation is not one of steady state. There are two principal effects.

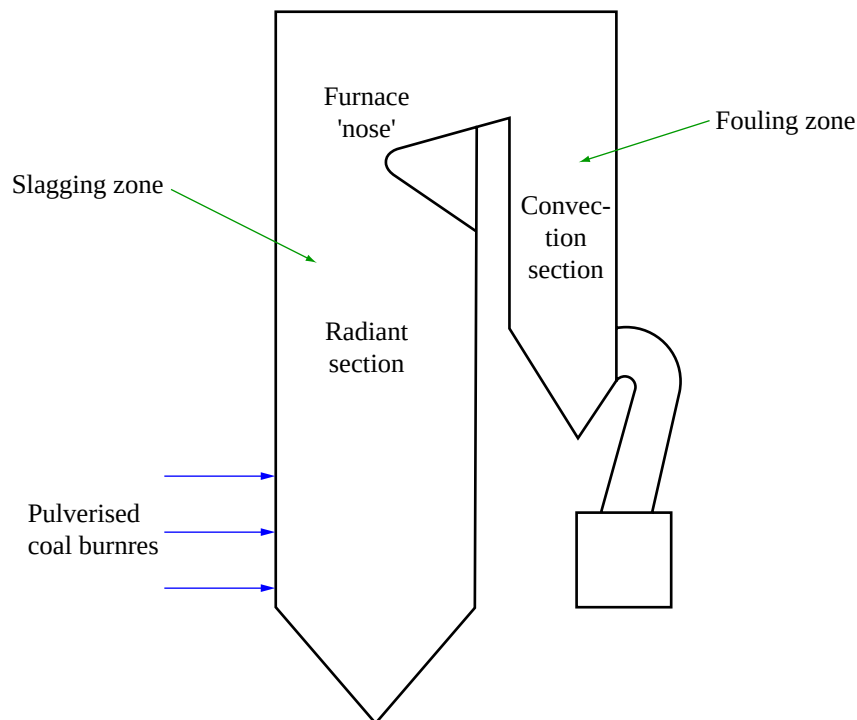
- (1) The deposit on, say, the outside of a heat exchanger tube containing boiling water acts as a thermal insulator, restricting heat transfer. In the presence of the deposit the tube outer skin temperature is reduced. It is the outer surface of the deposit that is now near the local gas temperature.

As the deposit grows on either side of the metal wall, the overall temperature distribution between the boiling water temperature and the flue gas temperature is affected. Not only may this affect the chemical character of the deposit because different chemical reactions may take place within the deposit at different temperatures, but the deposition rate may also be affected (see Section 4).

- (2) If substantial deposits are laid down, restrictions are imposed on the flow of combustion gases due to the narrowing of the flow areas. Apart from increasing the pressure drop across the combustion system, there will be effects on the deposition mechanism.

As the deposits build up within the equipment, and on the heat transfer surfaces in particular, the efficiency of heat removal is lowered so that the exit flue gas temperatures are higher than originally anticipated. In turn this may give rise to enhanced deposition in the cooler parts of the plant due to thermophoresis (see Section 4.1).

Many of the data reported in the literature are concerned with large scale boilers and this is reflected in this Data Item.



Sketch 3.1 Location of slagging and fouling zones in a pulverised coal steam generator

3.1 Definitions of Slagging and Fouling

In heat transfer technology the term fouling is usually attributed to any accumulation of deposit on heat transfer surfaces that impedes the efficient operation of the equipment. In furnace and boiler technology, however, the term “fouling” has a more specialised meaning. The following are general definitions of slagging and fouling.

- (1) **Slagging** may be defined as the formation of fused or sintered deposits usually in the radiant zone

of a boiler (the location of the highest temperatures), that is, the furnace walls, ash hopper and radiant superheater.

- (2) **Fouling** may be defined as the formation of loose, discrete particles or loosely sintered deposits usually in the convection zone of the boiler, for example, in the secondary superheater pendants.

Although there has been an attempt here to differentiate between slagging and fouling, there are locations in a furnace where it is difficult to allocate the observed deposition entirely to one form.

Sketch 3.1 shows the position of slagging and fouling zones in a conventional pulverised coal steam generator.

3.2 Method of Firing

The types of fuel and the way in which fuels are burnt will affect the deposition potential. This is discussed below.

3.2.1 Coal fired combustion plant

The two major types of coal combustion plant are chain grate stokers and pulverised fuel burners. The residence time of the fuel in the combustion chamber of each type of plant is very different and leads to different characteristic fouling potentials even from coal of similar composition.

On a chain grate stoker the fuel and residues remain in the high temperature region for up to 30 or 40 minutes. The majority of the ash (up to 80%) remains on the grate with only the least dense ash particles blown off the grate and carried forward in the flue gas. This is the origin of the term “fly ash”, to describe the mineral matter transported by the flue gases. In addition carbonisation and distillation of organic compounds takes place on the grate. Under poor combustion conditions the residue can retain a relatively high carbon content (up to 20%).

In a pulverised fuel operation the fuel and residues remain in the high temperature region for only 1 to 2 seconds. The majority of the ash (at least 80%) passes through the flue gas system for removal in the precipitators. The remainder of the ash goes out of the bottom of the pulverised fuel boiler. Evolution of organic volatile compounds into the gas stream is minimised due to the short residence time of the fuel and residues.

A modification of the pulverised coal plant has a combustion chamber in the form of a cyclone. Molten slag is collected on the walls of the chamber and flows downwards and out of the bottom through a specially designed port. The design is generally known as a “slagging combustor”.

3.2.2 Oil and gas combustion plant

The principle of oil and gas combustion is very similar to that of pulverised coal firing, *i.e.* the fuel is mixed with air in a specially designed burner. There is no equivalent to a chain grate stoker so that the differences and the consequences discussed in Section 3.2.1 do not apply to liquid and gaseous fuels. Any mineral material in the fuel passes through the system with the flue gases.

3.3 The Consequences of Deposition

The results of deposition are as follows.

- (i) There is a reduction in heat transfer efficiency that will increase operating costs.

- (ii) The presence of deposits in the radiant section reduces the emissivity of the surfaces thereby reducing the radiant heat transfer and adversely affecting the evaporation/superheat ratio.
- (iii) There is a risk of outage (the need to shut down the plant for maintenance) with the attendant costs in terms of lost production and labour for cleaning and repair.
- (iv) There is a risk that large pieces of dislodged deposits may fall into the plant causing broken membrane tubes and ash hopper bridging.
- (v) The presence of deposits on metal surfaces can promote corrosion.
- (vi) Exit flue gas temperatures are raised with the risk of overheating in air preheaters and consequent damage to the equipment.

It is for the reasons listed above that designers and operators of boiler and similar plant seek to mitigate the effects of slagging and fouling.

3.4 Corrosion

In a pure oxidising atmosphere the establishment of an oxide on the surface of metals is often employed as it provides a protective layer that limits the rate of metal attack. Most fuels contain chemical compounds or impurities that, during combustion, give rise to corrosive agents. In the presence of deposits and in combination with particular constituents of the flue gases, for example chlorine and sulphur compounds, the corrosion effects can be much greater than in the presence of a pure oxidising atmosphere. Under such conditions the protective oxide layer becomes involved with the chemical reactions and is destroyed or severely damaged.

The presence of oxides of sulphur in the flue gases may give rise to further problems. In addition to oxides of sulphur and other chemical compounds, flue gases contain water vapour from the combustion of material containing hydrogen and moisture originally in the fuel. As the flue gas temperature is progressively lowered by the transfer of heat, condensation will occur at some specific temperature. The resulting condensate is acidic in character and will be highly corrosive. The temperature at which condensate appears is usually termed the acid dew point and is generally around 120°C although its particular value will depend upon the fuel burnt.

4. MECHANISMS BY WHICH DEPOSITS ACCUMULATE ON SURFACES IN COMBUSTION SYSTEMS

In attempting to understand the effects of different variables on deposition in a combustion system, it is useful to have a general conception of the mechanisms involved so that the needs and requirements for good design and operation of equipment may be appreciated.

The mechanisms involved will differ depending on whether particulate deposition, vapour diffusion or chemical reaction is involved. It is convenient to discuss these mechanisms separately although they will rarely occur in isolation, and some interactions are, to a lesser or greater extent, more likely under industrial conditions.

4.1 Particulate Deposition

Particle deposition from a flowing stream has been studied extensively, generally under ideal experimental conditions where the system is well defined. Such work does give an indication of the effects of the variables even though its direct application to complex combustion systems is not possible.

Some of the early work ignored the presence of a boundary layer close to a solid surface over which a gas is flowing. The presence of the boundary layer will have a major influence not only on the deposition of particles, but also on their removal, if transfer back to the fluid stream is feasible.

Transport of particles to the solid surface may be visualised as occurring in two stages.

- (1) Transport through the bulk gas stream to the boundary region.
- (2) Transport through the boundary region to the solid surface.

The major mechanisms include the following.

- (1) Convective diffusion which results from concentration gradients and turbulence. The number of particles contained in unit volume of the gas space and, to some extent, their size, will be a direct consequence of the quality of the fuel and the combustion conditions. The level of turbulence for a given flow system geometry is generally related to the gas velocity in that region.
- (2) Diffusion which results from temperature gradients. Where considerable temperature gradients exist there is a tendency for small particles to move from the hot to the colder region. This physical process is usually referred to as thermophoresis. Such an effect may be quite pronounced in combustion systems because the temperature of the flue gases is very much higher than the cooler heat exchange surface in boiler plant. The movement arises from the difference in agitation of the molecules and particles at different temperatures. In a temperature gradient any one particle will have a slightly greater degree of agitation on its warmer side compared with its cooler side. The effect is a "thermal pressure" on the particle along the gradient.

In general it is the smaller particles that are subject to these mechanisms, that is particles of less than 1 μm size.

Using the theoretical work of Owen² as a basis, Glen⁵⁸ has plotted the collection efficiency for 0.2 μm diameter particles contained in a gas of temperature 700°C with different surface temperatures. The collection efficiency is the percentage of particles collected compared with the particles available in the system for given conditions. The results are shown on Sketch 4.1 and the increased deposition at the higher temperature differences is demonstrated. The approach to an

asymptotic collection efficiency (rather than a straight line relationship) at temperature differences of the order of 400°C or 500°C is attributed to the relatively changing thermal properties of the solid and gas. Some experimental data are given on Sketch 4.2³³. The break point at a temperature difference of approximately 250°C gives a surface temperature in the region of 150 to 160°C. The change in collection efficiency at this point is considered to be due to a dew point effect of the particular fuel studied (not necessarily an acid dew point, as discussed in Section 3.4, but one related to hydrocarbon condensation) that enhances the collection efficiency through the retention of particles by the wet surface. (In practical thermophoretic systems not all the particles that move to the surface actually stay on the surface; a proportion move away from the surface and back again into the bulk gas flow.)

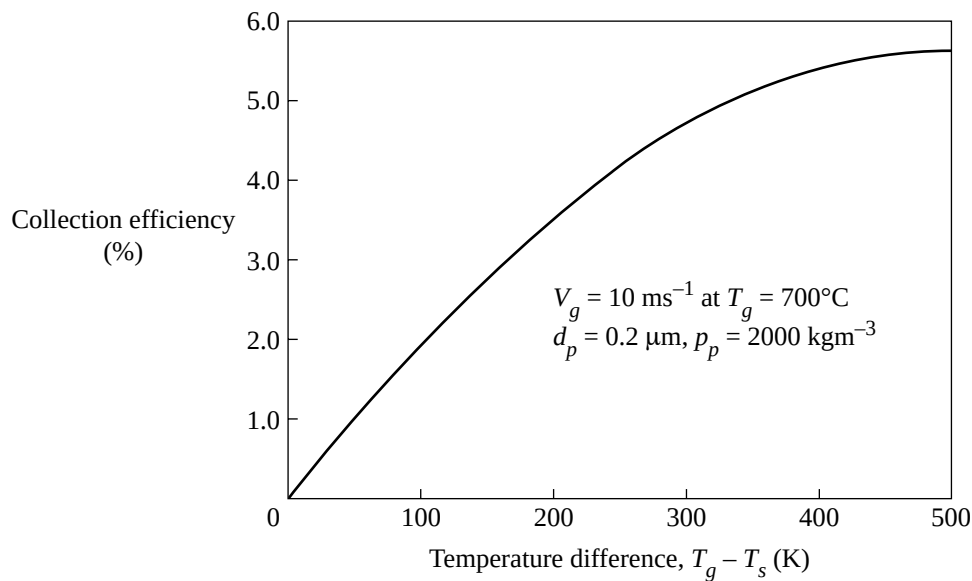
- (3) Inertial transport which is important only for the larger particles. Under conditions in the combustion space, the momentum of the larger particles may be sufficiently high for them to deviate from the gas streamlines. They may then follow trajectories that will carry them through the bulk fluid and across the boundary layer to the surface. The process is sometimes referred to as inertial impaction.

Under such conditions collision between particles is possible, leading to agglomeration facilitated by soft or sticky particles present in the high temperature region.

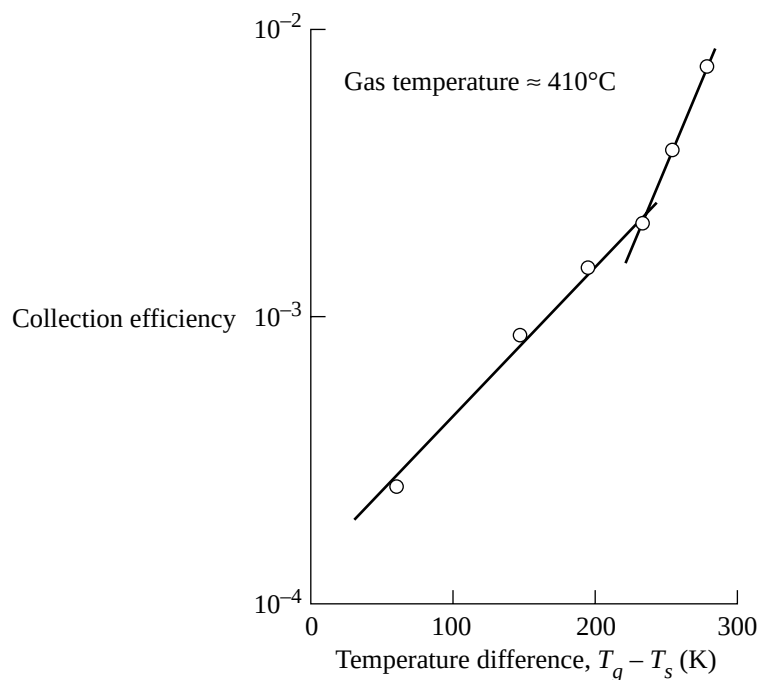
- (4) Gravitational effects, depending upon density differences between particles and flue gas, may also cause fouling, particularly where gas velocities are low and the suspension of particles in the gas is difficult to sustain.

In combustion systems the dominance generally of any of these mechanisms of particle transport in a particular situation or locality will depend very much on the conditions. With clean tubes containing boiling water adjacent to high gas temperatures (that is, large temperature differences) with a preponderance of fine particles, thermophoresis could well be the dominant deposition mechanism. On the other hand where gas velocities and particle size are relatively large, inertial transport could be the principal deposition process responsible for surface accumulations.

It is also true to say that, as conditions change along the gas path, the deposition mechanism is likely to change. Thermophoresis near the point of combustion could give way to convective diffusion in the cooler parts of the equipment. The agglomeration of the smaller particles, or chemical reactions between the solid and flue gas components during passage through the equipment, may result in a general increase in particle size that may change the dominant mechanism of deposition.



Sketch 4.1 Theoretical collection efficiency for thermophoresis



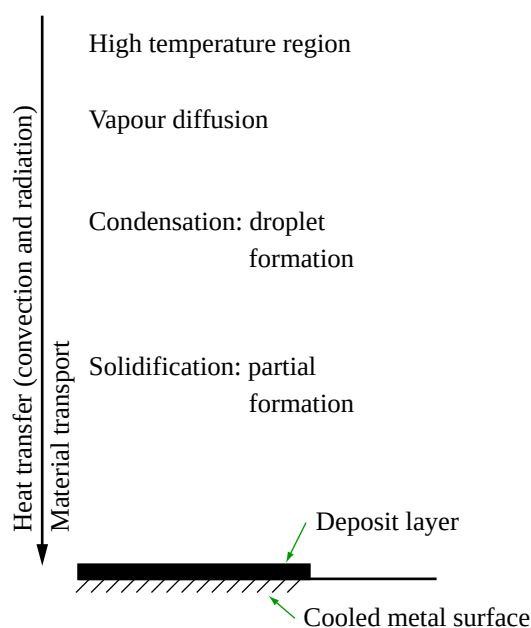
Sketch 4.2 Experimental determination of collection efficiency with temperature driving force

The passage of time is also likely to affect the dominance of particular mechanisms. For instance, as a clean surface gradually becomes covered with deposit the temperature difference in that region of the combustor, between the hot gas and the gas/solid interface, will decline. The opportunity for thermophoresis to occur will be reduced. As the flow area for the flue gas diminishes, for a given combustion rate, the flue gas velocity will increase; such a change may increase the possibility of convection deposition or inertial transport.

It is for these reasons that no general advice on likely mechanisms can be given.

4.2 Vapour Diffusion

The transport of material towards the cooler surfaces in a combustion system may result from the vaporisation of inorganic ash components and their subsequent diffusion to the cooler surfaces of the equipment. Flame volatilisation of inorganic material is the usual origin of these vapours. In general the principles of diffusion (except inertial impaction) discussed in Section 4.1 will apply to these molecules of vapour, but some marked consequences may result from the temperature gradients existing in the equipment. As the vapour diffuses from the hot zone towards the cooler regions it may change in stages, from a vapour to a liquid droplet and ultimately to a solid particle. The conditions are illustrated in Sketch 4.3.



Sketch 4.3 Phase changes along a temperature gradient in a combustion chamber

The location of the different zones, as loosely defined on Sketch 4.3, will be under constant change due to the changing temperature distribution as the deposit thickness increases. Due to these spatial changes in temperature, the vapour and droplet zones will move towards the fouling (cooler) surface, which after the accumulation process has begun will be the outer layers of the deposit. In the limit, if the deposition was due solely to vapour diffusion, the thickness of the deposit would become asymptotic with respect to time because the outer layer would ultimately be above the dew point of the condensing vapour. The changes in phase of the diffusing species may give rise to other enhancement effects including:

- (i) droplet coalescence,
- (ii) agglomeration of particles during transport by cementing due to their sticky or molten state,
- (iii) condensation of vapour either onto the cooler surfaces of equipment or onto particles in cooler regions.

4.3 Chemical Reactions

Bearing in mind the complex chemical nature of most fuels, for example the fossil fuels oil and coal, or less conventional sources of energy such as domestic refuse or biomass incineration, the opportunities for chemical reaction are very great. It is not relevant here to discuss a wide range of possible chemical reactions. It is useful, however, to identify some of the conditions found in combustion systems that will influence

the kind of chemical reactions that are possible. They are discussed in Sections 5.1 to 5.5 according to the fuel used.

4.4 Corrosion

The presence of impurities in the fuel, notably the constituents that give rise to acid gases such as SO_2 and SO_3 , in conjunction with deposits susceptible to further chemical reaction, can give rise to corrosion of the metallic surfaces on which the deposits reside. The extent of the corrosion may be severe and lead to a rapid deterioration of the metal integrity unless steps are taken to reduce the risks.

An extensive discussion of corrosion is outside the scope of this Data Item, but some discussion of the potential corrosion reactions associated with different fuels will be presented as appropriate in Sections 5.1.1 and 5.2.2.

4.5 Adhesion

The previous discussion reveals a complex reacting chemical and physical environment within the combustion space. Depending on the fuel a range of droplets through sticky to solid particles will be present in the combustion gases as they transfer heat to the cooler surfaces in the equipment. For this reason the particles arriving at heat exchanger surfaces may be present in a number of physical conditions that will have a marked influence on the deposition process. Molten or sticky particles are likely to be more firmly attached than solid particles and may be cemented within the deposit matrix.

The availability of mechanical keying locations, for example struts and hangers, will also influence the adhesion of the deposits. Reduction in deposit accumulation may be achieved by attention to the design of these details.

5. COMBUSTION

During the burning of a fuel, oxidising or reducing conditions may prevail either locally or throughout the system, depending upon the way the equipment is operated. Large percentages of excess air will generally ensure oxidising conditions, whereas oxygen levels near stoichiometric values may mean that some locations will experience reducing conditions. With poor control of the burners and associated equipment, unintentional reducing conditions may be created within the system. The nature of the conditions, either oxidising or reducing, will affect the chemistry of the deposit-forming compounds present in the flue gas either in suspension or on the surfaces exposed to the deposits.

In addition, the quality of combustion as exemplified by oxidising or reducing conditions will affect the efficiency of the fuel conversion. Under reducing conditions, for instance, it is likely that some fuel will pass through the system in the unburnt condition. Carbonaceous material is then likely to be a constituent of the deposit, either physically or through chemical combination thereby changing its character. The presence of soot (that is unburnt carbon) on heat transfer surfaces gave rise to the development of "soot blowers" for the removal of the carbon deposits (see Section 8.1.1).

Most fuels in general contain certain impurities or chemical compounds that contribute to the deposits residing on heat transfer surfaces. These compounds themselves may constitute the deposit layers, or during the combustion process they may be chemically changed either through the effects of the high temperatures, or through chemical reactions, particularly those associated with gaseous products of combustion such as CO (when combustion is incomplete), CO_2 , SO_2 , SO_3 or volatile chlorine compounds. Chemical reaction with the metal surfaces (corrosion) in the equipment is also a distinct possibility. The extent and pathways of the chemical reactions will be dependent on whether or not oxidising or reducing conditions are present.

Since all fuels vary in character, including the potential for deposit formation, it is useful to discuss the principal fuels separately and in some detail.

5.1 Coal Combustion

The spectrum of the mineral deposits in coal depends on the geology of the site where the coal is located, its depth in the ground and the age of the deposits. The elements contained in the mineral matter are diverse and can include metals such as Fe, Al, Ca, Na, K, Ti and Mg; non metals include O, Cl, S, P and Si. There are considerable differences between the mineral contents of coals from different mines. In turn this produces different slagging and fouling characteristics when coal from different sources is burnt in an identical combustor. The physical and chemical changes that these materials experience when they are rapidly heated in a flame have a direct bearing on the deposition process. An extensive review of the mineral content of various coals is given by Raask³⁸.

The mineral matter contained in coal may be broadly classified into two categories.

- (1) Inherent mineral components that are in intimate contact with the coal substance or even chemically bonded with it and finely distributed throughout the dense phase.
- (2) Adventitious mineral matter loosely attached to the coal substance or mixed with the coal during the mining process.

Mineral compounds found in coal include alumino-silicate (or clay) material, along with quartz (SiO_2), and together these impurities represent 60 to 90% of the total mineral matter in coal substance³⁸. Potassium, sodium and calcium alumino-silicates are common, but clays containing iron and magnesium are also found in coal. Anions usually associated with metals such as iron, magnesium, potassium, calcium and possibly copper and zinc include Cl, CO_3 and SO_4 .

The sodium and chlorine ions tend to be associated with the coal substance whereas the alumino-silicate material (associated with clays) tends to be found mainly in the adventitious matter. In many coals sodium and chloride ions are evenly distributed throughout the coal mass but not necessarily combined as the salt NaCl. Indeed the ratio of Na: Cl may be different from 1:1.

The inherent mineral matter is intimately associated with the coal particles and so it usually attains a higher temperature during combustion than the surrounding flue gases. Under such conditions, fusion and chemical reaction are likely to occur. Conditions near the flame will probably cause the particles to experience a reducing environment for relatively long periods that will also influence the character of the chemical reactions, particularly those involving the variable oxidation states of iron.

Adventitious matter, as distinct from inherent mineral components, will tend to behave as isolated particles and may experience either oxidising or reducing conditions.

The method of firing (that is stoker, pulverised fuel, or slagging combustor) will also affect the extent of particular chemical reactions because each of these techniques will have different temperature/time characteristics.

Changes in the shape of the silicate particles that depend upon the surface tension and the viscosity of the ash at the particular temperature are likely to occur as a result of heating. The originally irregular sharp-edged particles are likely to assume a more rounded or even spherical form. The water loss and transformation reactions may not have gone to completion by the time these deformations have occurred.

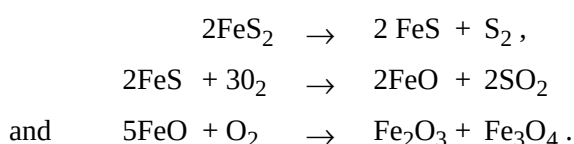
The temperatures encountered in normal combustion conditions are generally not high enough to volatilise any silica, but it is possible that where higher temperatures do exist a small degree of silica vaporisation could occur, via the reduction of silica with carbon to SiO which later reoxidises to SiO₂, creating a fume.

Bearing these observations in mind it is likely that the smallest quartz particles will fuse and become spherical in the flame and, at temperatures of 1500° C and above, will react with the other ash-forming particles.

Sulphur is present in coal either organically bound or as part of some inorganic species, usually as pyrite (FeS₂). In general, inorganic sulphur content is usually higher than that associated with the organic molecules but the organic sulphur content of British coals is likely to represent of the order of 50% of the total sulphur.

Some minerals display a different behaviour from those containing silicon in the combustion process, and undergo thermal fracture and decomposition as well as some fusion. For instance the pyrite (FeS₂) undergoes decomposition to FeS and sulphur. The FeS and elemental sulphur under the combustion conditions rapidly oxidise to FeO with the release of SO₂.

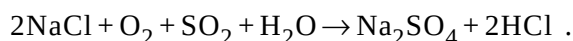
The reactions involved are:



The evolution of the reactive acid gas SO₂ from the sequence of reactions, and the oxidation of organically bound sulphur, has implications for further reactions, for example to produce SO₃ and subsequent corrosion of metal surfaces.

Minerals containing carbonate, for example calcite, dolomite and siderite, will fragment and decompose under the effects of temperature, giving rise to oxides such as CaO and MgO that are themselves susceptible to further chemical reaction, particularly from acidic reagents such as SO₂ and SO₃, to form sulphates.

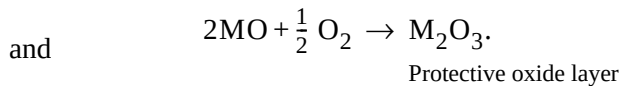
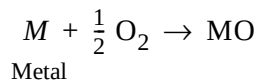
The volatilisation of the Na⁺ and Cl⁻ ions probably occurs almost instantaneously in the flame. In the presence of SO₂ derived from chemical reactions and oxidation as explained earlier, water vapour and oxygen and some of the salt that may be present, will be converted to sulphate according to the reaction:



From this brief review of the chemical reactions the particles (some of which may relatively be quite large) carried forward in the high temperature gas stream, comprise a complex mixture. Melting silicates and sulphides, oxidising sulphides, vaporising sodium chloride, fragmenting and decomposing carbonates, and an oxide “fume” all undergo reaction with sulphur dioxide and, in various combinations, with burning carbonaceous particles. The mineral particles embedded in the carbon will involve extensive coalescence and chemical interaction. It is the fate of this high temperature cloud of particles that will decide the extent and nature of the deposits on heat exchange surfaces and on the equipment. During the passage through the plant, extensive fusion and coalescence of the flame borne alumino-silicates and their reaction with other minerals produce a relatively small number of particles compared with the potential number contained in the fuel. However, these particles and any subsequent chemical reactions are responsible for deposition problems.

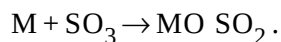
5.1.1 Corrosion resulting from coal combustion

The rate of corrosion of metals in contact with the combustion gases depends to a large extent on the integrity of the surface oxide layer. The basic chemical reactions are:



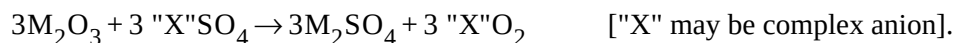
In the presence of the corrosive agents in the flue gases, and in the deposits on the surfaces, principally sulphur and chlorine compounds, the rate of metal wastage can be very much higher than that under contact with gaseous oxidising agents. Typical of the reactions that are possible are³⁸ the following.

Enhanced oxidation,



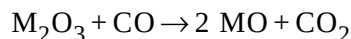
Reaction with the protective oxide layer and hence its total or partial destruction,

(a) with molten sulphate deposit,



or

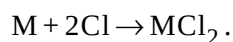
(b) with reducing atmospheres,



In the presence of sulphur or sulphur bearing compounds sulphidation reactions are possible to give, for example, the sulphide,



In the presence of chlorine or chlorine compounds chloridation is possible to give, for example, the chloride,



A large temperature difference usually occurs across the protective oxide layer, the size and range of which may influence the effectiveness of the layer in resisting further corrosion. For instance it could increase the porosity of the layer and reduce the integrity of the bond between the metal oxide and the metal surface. Under these conditions it is possible to obtain enhanced diffusion of potentially corrosive agents towards the metal oxide/metal interface. Raask³⁸ concludes that there are four important variables in this respect.

- (1) The composition of the protective metal oxide, M_{ox} .
- (2) The metal temperature, T_g .

- (3) The exposure temperature (flame or flue gas temperature in the proximity of the metal), T_e .
- (4) The composition of the ash deposits residing on the surface, D_c .

The rate of corrosion, R_c , can therefore be expressed in terms of these four variables,

$$R_c = f(M_{ox}, T_m, T_e, D_c).$$

The exact relationship will involve a complex interaction between all four variables.

5.2 Oil Combustion

Light oils may be troublesome in some respects, but attention to combustion conditions can usually relieve any problems associated with deposition. In general oil for large scale combustion purposes, such as steam raising, is highly viscous at ambient temperatures and for this reason is often referred to as heavy fuel oil or residual fuel oil (because it is the residue from the refining operations). It is with this fuel that deposit formation on heat exchangers is likely to be most pronounced.

The particulate matter formed consists of two discrete fractions⁵² arising from separate sources.

- (1) The inorganic content of the fuel that may have been in the crude oil from which the fuel was derived or in material "picked up" during the oil processing operations.
- (2) Carbonaceous material due to the incomplete combustion of all the combustible material in the oil.

The ash constituents of oil differ greatly from those associated with coal. Table 5.1 provides an indication of the metallic elements found in UK residual fuel oil⁴⁶. The wide range of values for each of the constituents reflects the different sources of crude oil processed in the UK.

TABLE 5.1 Major metallic components in UK residual fuel-oils*

Vanadium (ppm)	10 – 500
Sodium (ppm)	10 – 150
Nickel (ppm)	5 – 100
Iron (ppm)	5 – 60
Silicon (ppm)	10 – 80
Aluminium (ppm)	5 – 50
Calcium (ppm)	5 – 50

* weight basis.

Much higher proportions of sodium are encountered in fuel-oils than coal and there are very high levels of vanadium, an element that is virtually never present in coal. The total mineral content of oil is likely to be as low as 0.1% of the oil substance whereas the mineral content can be as high as 50% in some poor quality coal.

The vanadium, nickel and iron content of the oil are indigenous to the oil whereas the sodium occurs in a brine phase and silicon and aluminium result from processing the oil. It would appear that the vanadium is closely linked to the asphaltenes present in the fuel oil. Organically bound sulphur is also present in most fuel oils in varying amounts depending on the origin of the crude oil. The presence of these elements can give rise to a range of chemical compounds that constitute the deposits in oil fired equipment.

The combustion process for fuel oil involves a sequence of events³². When residual fuel oils are atomised by the burner to a fine droplet spray and ignited, a spray diffusion flame results. The chemical reactions occurring within an oil particle subject to oxidising and high temperature conditions are extremely complex. The reactions will depend not only on the chemical nature of the fuel but also on the droplet size. In simple terms the following process takes place:

- (1) The volatile content of the fuel is lost from the droplets, probably burning outside them. The result is generally a heavier fuel within the remainder of the droplet.
- (2) Pyrolysis reactions occur within the droplet giving rise to cracked and gaseous products that burn outside the fuel particles and porous petroleum coke particles.
- (3) Combustion of the coke particles will usually occur near the flame region. The combustion process depends on the size and porosity of the particles which affect reactivity with the oxidising species present.

It is likely that the large drops of oil contain the mineral matter since the volatiles will burn off rapidly. It is also likely that the burning process will not be complete if burner atomisation is poor, so that particles of carbon (coke) containing the mineral matter originally contained in the fuel will go forward into the convection section of the combustion equipment. The porosity and pore structure of the coke particles is likely to be influenced by the initial evolution of volatile material and cracked products. In addition, naturally occurring metals in the fuel oil may catalyse associated chemical reactions. A paper by Kelly *et al*⁵² suggested that in the combustion of a Visbreaker tar, particulate formation is affected by the amount of excess air present. Minimum particulate formation occurred at an excess air level of the order 30 to 35%.

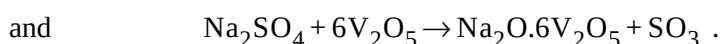
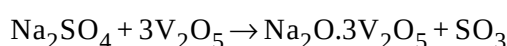
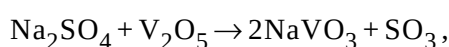
The particulate matter going forward to heat transfer regions of the equipment is likely to consist of reacting and burning droplets that gradually solidify and continue to burn. The particulate matter that can accumulate on the heat transfer surfaces will consist of the inorganic and metallic residues together with unburnt carbon.

An important development in oil combustion equipment is the relatively new technique of emulsion combustion which reduces the production of particulate material. The process employs a stable emulsion of oil droplets (5 to 10 μm diameter) in water using an emulsifying agent.

5.2.1 Sodium - vanadium - sulphur reactions

It is the sodium-vanadium-sulphur system that gives rise to deposition (and corrosion) problems in oil combustion equipment. The vanadium in the fuel oil is generally associated with organic material. As a result, during the combustion process the elemental vanadium will be subject to extremely high temperatures, since it will be precisely where the exothermic chemical reactions are taking place. Under these conditions the vanadium will be converted to the oxide V_2O_5 . The sodium compounds in the flue gas, probably in the form of vapour, are likely to be NaOH or Na_2SO_4 ¹⁸. In the presence of relatively high sulphur contents there is likely to be a relatively high proportion of the sulphate. In particular the reactions between Na_2SO_4 and V_2O_5 will be important.

Niles and Sanders³ have confirmed that only three sodium-vanadium compounds can form in reactions of Na_2SO_4 and V_2O_5 :



The extent of these reactions will depend upon the relative amounts of the Na_2SO_4 and V_2O_5 present in the gas. Niles and Sanders³ suggest that mixtures of vanadates are produced according to the molar ratio $\text{V}_2\text{O}_5/\text{Na}_2\text{SO}_4$, but it is recognised that these basic chemical reactions may only exist when the ash contains relatively large proportions of sodium and vanadium along with the sulphur.

Tipler⁴ has investigated the sodium-vanadium-sulphur system and concluded that a sodium/vanadium molar ratio of 1:6 is critical. A lowering of the sodium/vanadium ratio to 1:6, by water washing for instance, should be advantageous. Reduction below this ratio would ensure that no Na_2SO_4 appears in the deposit (it is replaced by V_2O_5).

In addition to the Na-V-S reactions a number of other possible constituents of deposits are formed. Table 5.2 gives a list of some possible constituents in oil combustion deposits (together with their melting points) derived from chemical reactions based on data of Tipler⁴ and Kirk Othmer⁶⁴.

TABLE 5.2 Melting points of some deposit compounds in fuel oil combustion⁽⁴⁾

Compound	Chemical formula	Melting point °C
Aluminium oxide	Al_2O_3	2049
Calcium sulphate	CaSO_4	1450
Ferric oxide	Fe_2O_3	1566
Magnesium sulphate	MgSO_4	MgO at 1124
Nickel sulphate	NiSO_4	NiO at 840
Potassium sulphate	K_2SO_4	1069
Potassium pyrosulphate	$\text{K}_2\text{S}_2\text{O}_7$	300
Silicon oxide	SiO_2	1721
Sodium sulphate	Na_2SO_4	882
Sodium pyrosulphate	$\text{Na}_2\text{S}_2\text{O}_7$	401
Sodium ferric sulphate	$\text{Na}_3\text{Fe}(\text{SO}_4)_3$	540
Sodium metavanadate	NaVO_3	630
Sodium orthovanadate	Na_3VO_4	856
Sodium pyrovanadate	$\text{Na}_4\text{V}_2\text{O}_7$	632-654
Sodium vanadyl vanadates	various	535-625
Vanadium pentoxide	V_2O_5	690

5.2.2 Corrosion associated with deposits

It is generally known that some heavy fuel oils cause more severe corrosion than others. The corrosion is attributed to the presence of the vanadium compounds. In most cases the higher corrosion rates have been considered to be the result of either ash content or a less favourable ratio of vanadium to sodium in the ash.

In binary mixtures of Na_2SO_4 and V_2O_5 corrosion of a stainless steel at temperatures above about 790°C increased markedly when the V_2O_5 content was above 66% by weight³. Below 50% by weight the V_2O_5 mixture was only slightly corrosive. Corrosion is very much a function of temperature. Naturally occurring contaminants other than sodium and vanadium present in the ash of heavy fuel oil tend to act as corrosion inhibitors by shifting the reaction toward the formation of the relatively non-corrosive NaVO_3 (the metavanadate)³.

The low melting points of V_2O_5 and the various vanadates enhance the corrosion effects.

The presence of V_2O_5 in the outer layers of a deposit can catalyse the oxidation of SO_2 to SO_3 . This reaction has implications for the allowable flue gas exit temperature as it affects the acid dew point in the cooler regions of the plant.