MODELLING ALKALI SALT VAPOUR DEPOSITION IN THE BRITISH COAL TOPPING CYCLE SYSTEM.

John E Fackrell Richard J Tabberer
Power Technology Centre
PowerGen plc
Ratcliffe-on-Soar
Nottingham
United Kingdom

John B Young
Whittle Laboratory
Engineering Dept.
Cambridge University
Cambridge
United Kingdom

Ian R Fantom
Coal Research Establishment
British Coal Corporation
Stoke Orchard
Cheltenham
United Kingdom

ABSTRACT

The British Coal Topping Cycle is a proposed advanced coal-fired power generation system in which gases derived from the coal and containing low levels of alkali vapours are passed to a gas turbine. The deposition of these vapours onto the turbine blades needs to be assessed because deposited alkali salts may accelerate corrosion and hence reduce blade lifetimes.

A model for the thermochemical behaviour was derived by assuming frozen chemistry in the external and boundary layer flows, but equilibrium at the surface and within the deposit, including an allowance for non-ideal behaviour in the deposit. The model is currently formulated for sodium and potassium chlorides and sulphates in the deposit and can deal with deposition to either a solid or liquid deposit. The boundary layer mass transfer has been calculated by both a simple heat transfer analogy model and a numerical solution of the two-dimensional diffusion equation within the boundary layer.

Some examples of general results obtained with the model are described, including a comparison of the effects of different deposit phase, non-ideal behaviour and film cooling. Some predictions are compared with measurements of alkali salt deposition obtained in experiments simulating the conditions expected in a Topping Cycle system.

NOMENCLATURE

- D: molecular diffusion coefficient
- D_e: eddy diffusion coefficient
- m: mass fraction
- T: gas temperature
- u,v: velocity components along and normal to surface
- x,y: coordinates along and normal to surface
- δ: thermal (Soret) diffusion factor
- ρ: gas density

INTRODUCTION

The British Coal Topping Cycle is a coal–gasification combined-cycle power generation system in which part of the power is provided by burning gases derived from the coal in a topping combustor and passing the resultant hot gases through the expander section of a gas turbine (Minchener et al, 1991).

Figure 1 is a schematic of the gas turbine circuit of the Topping Cycle system. (To avoid complication, the steam turbine circuit is not shown, since only the gas circuit is relevant to this paper). The gases coming from the gasifier are cleaned by being first cooled and then passed through a ceramic filter, before being burnt in the topping combustor and then expanded through the gas turbine. This cleaning process is very effective in removing contaminants, but still leaves a low level of alkali (sodium and potassium) salt vapours in the gases going to the turbine. The alkali salt vapours may condense out on cooled turbine blade surfaces and cause accelerated corrosion of the blades, greatly reducing blade lifetimes. It is important to be able to estimate these effects as part of the technical and economic assessment of the system.

The Grimethorpe Topping Cycle Project was set up with the aim of obtaining estimates of deposition and corrosion in a Topping Cycle gas turbine and hence deducing blade cleaning and replacement intervals, (for details see Clark et al, 1991). The strategy of the project was to perform an experiment in the existing large PFBC rig at Grimethorpe in which turbine blade materials would be exposed to a contaminated gas flow roughly similar to that which would occur in a Topping Cycle system. The experiment provided a test case to refine and validate a modelling programme, before the models were used to provide predictions for a utility Topping Cycle turbine.

In the experiment, gases from the PFBC combustor were first cleaned in a high temperature ceramic filter unit, before going to a topping combustor and then through a single stage turbine. In addition, in order to extend the range of exposure conditions,
cooled cylindrical materials probes were mounted in the ductwork of the rig, upstream and downstream of the turbine. An initial period was devoted to commissioning the rig and characterising the gas component concentrations and contaminant levels. Turbine blades and probes were then replaced and the experiment run at nominally constant conditions with the turbine on-line for about 530 hours. An extensive post-test analysis exercise was then undertaken on all blades and probes to establish the deposition and corrosion suffered. This could then be compared to the model predictions.

The modelling programme had a suite of interacting models for flow, thermochemistry, deposition and corrosion. This paper concentrates on the modelling of the alkali vapour deposition that was undertaken for the project. Whilst some of the detailed chemistry in this model is fairly specific to the Topping Cycle system, the overall approach adopted to the vapour deposition modelling is quite generally applicable to any system undergoing deposition.

THE VAPOUR DEPOSITION MODEL

Input Information Required

The basic input required for the deposition modelling process is information on the alkali levels entering the turbine. The model considers only the chlorides, sulphates and hydroxides of sodium and potassium, since these are the dominant salts in the Topping Cycle turbine gas stream. The distribution into these individual salt vapours is calculated by assuming thermo-chemical equilibrium at the topping combustor exit. The chemistry is then assumed to be frozen in the time it takes the vapours to traverse a turbine, so these mainstream salt concentrations are only changed by dilutions due to any cooling flows. In the Grimethorpe experiment, the levels of sodium and potassium were obtained directly from measurements in the gas stream. For a proposed utility Topping Cycle system, the input levels must be estimated from a combination of theoretical models (e.g. thermo-chemical equilibrium, kinetics and nucleation models) and available empirical information (e.g. on filter performance, the amount of alkali in the coal and ash, etc.).

The flow and heat transfer behaviour within a turbine is also required for the deposition modelling. In the Grimethorpe project, the three dimensional turbine flow field was calculated by the European Gas Turbine division of GEC-Alsthom using an enhanced version of a program described by Dawes (1992). The heat transfer within the turbine was also calculated by European Gas Turbines using their ESATAN code, to enable the blade surface temperatures to be defined. When extra detail was necessary for modelling diffusive deposition through the blade boundary layers, a specific boundary layer flow code was used, (STANCOOL, described by Crawford et al, 1976 and 1980), with the main flow calculation providing the external boundary conditions to this code. Calculations of deposition were also required for the cylindrical probes used at Grimethorpe and heat transfer coefficients for these were obtained directly from published empirical information. In all the cases which were considered, the alkali concentrations were so low that there was no interactive effect of the deposition on the flow or heat transfer, so only one initial calculation of these was needed to provide an input to the deposition modelling.
Boundary Layer Mass Transfer Models

With the flow variables known, the rate of the mass transfer can be found by solving a time-mean turbulent diffusion equation of the form:

$$\frac{\partial}{\partial x}[p \overline{u} \frac{\partial \overline{m}}{\partial x}] + \frac{\partial}{\partial y}[p \overline{v} \frac{\partial \overline{m}}{\partial y}] = \frac{\partial}{\partial y} \left[ \rho \left( \overline{D} \overline{D} + \overline{D} \frac{\partial T}{\partial y} \right) \right]$$

(1)

The overbars here indicate time-mean values of the variables. The equation has been derived by using an eddy diffusivity to model the turbulent eddy transport. The terms on the left hand side of this equation represent convection of the vapour by the mean flow in the boundary layer. The first term on the right hand side represents diffusive transport of the vapour by both molecular (D) and turbulent (D) means. The last term on the right hand side represents transport down temperature gradients by thermal (Soret) diffusion. In a turbulent boundary layer, the turbulent diffusion term dominates the right hand side, except very near the wall where D tends to zero. This near wall region is known as the laminar sublayer and provides the main resistance to mass transfer in a turbulent layer. In a laminar boundary layer, the turbulent diffusion term is absent (D is zero everywhere).

For use in the above equation, the molecular diffusion coefficients of the alkali salt species have been obtained from their molecular properties as in Reid and Sherwood (1966). Thermal diffusion coefficients of the salt species were obtained as in Rosner (1980). The eddy diffusion coefficients are derived directly from the eddy viscosity values given by the boundary layer flow code.

A computer program was written which uses a finite volume discretisation on a variable grid to solve this equation, starting from an initial concentration profile at the first x station and proceeding stepwise in the x direction. The approach used is similar to the Keller Box Method described by Cebeci and Smith (1974). The initial profile can be specified as input or can be generated within the program from a self-similar solution of the laminar boundary layer diffusion equation.

The individual salt vapour concentrations at the outer edge of the boundary layer and at the blade surface are also required as boundary conditions. The outer concentration is set by the combustor equilibrium values and is taken to be constant along the blade. The inner concentration is set by a thermo-chemical model of the deposit, as described below.

In addition to the above approach, a much simpler model for boundary layer mass transfer has also been used in some cases, when only limited flow information was available. This model uses the standard analogy between heat and mass transfer to derive a mass transfer coefficient from a known heat transfer coefficient for the same flow situation. The heat transfer coefficient can come from experiment or previous heat transfer calculations. An estimate for thermal diffusion effects on this mass transfer coefficient was obtained from factors given by Gokoglu and Rosner (1984).

Surface Thermochemistry Model

To complete the calculation of vapour deposition, an inner (surface) concentration for each alkali salt must be supplied and these are obtained from the surface thermochemistry model. The model used is similar in principle to that of Rosner et al. (1979) but with extensions to allow for non-ideal behaviour in the deposit and for different deposit phases. Because of this extra complexity, the model is currently formulated only for cases with sodium and potassium chlorides and sulphates in the deposit, although in principle the model could be extended to other systems. The case of deposition to a single liquid phase is described here, but a similar model has also been developed for a solid sulphate deposit and for a two-phase solid-liquid deposit. Even for the single phase deposit, the model leads to many simultaneous equations (mostly non-linear), so only a brief outline of the approach can be given here.

The calculation of the deposit composition (i.e. the relative amounts of sodium and potassium cations, and of chloride and sulphate anions) and of the deposition rate is complex, due to the highly coupled nature of the phenomena involved. It is assumed that the sodium and potassium species (NaCl, Na2SO4, KCl and K2SO4) immediately above the deposit at the inner edge of the boundary layer are in chemical equilibrium with the HCl and sulphur oxides at this point. For example:

$$2 \text{NaCl} \rightarrow \text{SO}_3 + \text{H}_2\text{O} = 2 \text{HCl} + \text{Na}_2\text{SO}_4$$

(2)

These equilibria fix the ratio of chloride to sulphate in the deposit. The ratio of potassium to sodium in the deposit (the cationic composition) is fixed by the relative rate of deposition of sodium and potassium species, which is in turn determined by the difference in partial pressures of the salts across the boundary layer. The partial pressures of the four salt species above the deposit are determined by the saturated vapour pressures of each salt at that temperature and the activity of each salt in the deposit. Activities are calculated by thermodynamically modelling the deposit as a reciprocal ternary system (Na+, K+, Cl-, SO4-) with empirically derived interaction parameters to allow for the non-ideality of the system (see Pelton and Inouye, 1983, for a description of this type of modelling). The system is formally a ternary system because only three composition parameters can be independently varied, as there is a condition that overall the deposit must be electrically neutral. These assumptions lead to a set of simultaneous equations which must be solved by iteration. This can include the recalculation of the mass transfer, if thermal diffusion is important. The model assumes that the vapour deposition is not affected by any simultaneous particle deposition.

EXAMPLES OF DEPOSITION PREDICTIONS

As an example of the model predictions, the deposition behaviour was estimated for the stagnation region of a first stage nozzle of a utility turbine. The simple heat transfer analogy model was invoked to obtain the mass transfer, with the heat transfer coefficient coming from expressions given by Rubesin and Inouye.
(1973) for compressible flow to the stagnation line of a cylinder. For this example, an arbitrary contaminant level of 100 parts per billion by weight of both sodium and potassium was chosen. Chemical equilibrium at the combustor outlet suggested that the dominant salt vapours in the main gas stream would be the chlorides, with hydroxides about an order of magnitude lower and sulphates several orders of magnitude lower. The gas temperature was taken as 1375°C, a typical value at inlet to the first stage stator on the latest utility turbines. A range of surface temperatures from 600 to 900°C was considered. Figure 2 gives the deposition flux rates for the individual salt vapours plotted against blade surface temperature. (Arbitrary units are used for flux rates in all these examples, since it is the comparative behaviour that we wish to illustrate). The flux rates of chlorides dominate, with that of sodium chloride being greatest. The hydroxide vapours make a small contribution, but the sulphate flux rates are negligible. At the lowest surface temperatures, the flux rates are almost constant, but, as the temperatures increase, the flux rates decrease and at some temperature the nett flux rate passes through zero and becomes negative (i.e. away from the surface). This negative result is because the model assumes that a deposit is always present on the surface. We have therefore taken the point of zero nett flux rate to be a definition of the dewpoint temperature.

In Figure 3, the rate of salt accumulation within the surface deposit is given for the same case as Figure 2. The chemical composition of the deposit formed on the blade surface by the vapour fluxes is determined by the equilibrium which is assumed there, between the deposited salts and between the salts and their vapours immediately above. In this case, the equilibrium at the surface temperature leads to the sulphates being by far the dominant salts in the deposits, with just traces of chlorides, despite the low concentration of sulphates in the external flow and their low vapour flux rates.

The above predictions were calculated for a solid phase deposit with non–ideal activity coefficients. Figure 4 gives predictions of total deposition rate for two alkali levels differing by a factor of four, with a comparison for both solid and liquid phase deposits and for ideal and non–ideal liquid deposits. The change from a solid to a liquid deposit, illustrated by the lower alkali result, produces very little difference in the predicted deposition rates. This insensitivity to the phase of the deposit is fairly typical of the model predictions. The difference between non–ideal and ideal (unity) activity coefficients is illustrated by the higher alkali result. The difference is not large, with the ideal result being slightly greater than the non–ideal one. In some of our calculations somewhat larger differences have been found.

When the mainstream alkali level is changed by a factor of 4, the total deposition rate in the almost constant 'plateau' region at lower surface temperatures changes in direct proportion. This is not surprising since at these temperatures the inner concentration (determined by the local saturated vapour pressure) is so much lower than the outer, that it is negligible, and the concentration difference driving the mass transfer across the boundary layer is just determined by the external concentration (or external partial pressure). This also means that flux rates in this region do not depend to any great extent on the deposit chemistry, which is why...
they are almost constant and independent of assumptions about deposit phase or ideality. As the surface temperature increases, the deposition rate for the lower alkali level falls to zero at a lower temperature than with the higher level (about 45°C lower). Having a lower dewpoint temperature could be important in practice, since it might mean that no alkali deposition would occur on a particular blade.

Figure 5 presents similar results for the stagnation regions of all blade rows in a three stage turbine. The main effect on the deposition as the gases pass through the machine is that the absolute molar density of the contaminants decreases, in line with the drop in overall gas density. This reduces the absolute level of the difference driving the mass transfer and hence 'plateau' deposition levels tend to be lower in later blade rows. The only exception to this in the figure is in the first stage, where the rotor blade has a higher 'plateau' level than the stator blade. This is because the relative onset velocity to the first rotor row is much higher than that to the first stator row in this example, hence the stagnation mass transfer coefficient is much higher for the rotor, which in this case more than compensates for the reduction in pressure. Dewpoint temperatures also reduce through the machine because of the reduction in gas density. However, this does not reduce the risk of deposition in later stages, since blade temperatures may decrease by a greater extent than the dewpoint temperatures. A second effect reducing deposition in passing down the machine is due to the dilution produced by cooling air from blades and rotor discs being added to the mainstream flow, although this tends to be a smaller effect than the reduction in density. Of course, the mainstream gas temperature also drops through the turbine, but this tends to have only a small direct effect on the vapour deposition. It reduces any thermal diffusion effect, but this has been found to be fairly small in our calculations, increasing flux rates by no more than a few per cent. Also, for the low contamination levels considered, any nucleation in the gas stream itself (even heterogeneous nucleation on particles) is very unlikely to occur.

As a final example, some effects of film cooling on the vapour deposition will be illustrated. In heat transfer calculations, the usual manner of dealing with film cooling is to specify a film cooling effectiveness, which is used to modify the actual external gas temperature (or the adiabatic wall temperature in compressible flow) to a reduced effective value. The effectiveness is usually an empirically derived function of hole size, spacing, downstream distance and relative coolant mass ejected. The same approach can be taken for the mass transfer, using the simple analogy model, with the external concentration being modified to a lower effective value, thus simulating the dilution effect of the film cooling. The other main effect of film cooling is to lower the blade surface temperature downstream of the holes. These two effects can have opposite influences on the vapour deposition. A rather extreme example of this behaviour is illustrated in Figure 6. The top graph is a plot of predicted surface temperature on a blade suction surface with two film cooling locations at about 12 mm and 40 mm, showing the sudden drops in temperature just downstream of these locations. (Temperature drops on real turbine blades would normally be much less than this). The bottom graph gives alkali deposition rates for two mainstream alkali levels differing by a factor of 10. These levels have been chosen so that,
with the highest alkali level, the blade surface temperature is always below the local dewpoint temperature, even upstream of the film cooling locations. There is therefore deposition to all the blade surface and in these circumstances the dilution effect of the film cooling reduces the deposition immediately downstream of the film cooling holes. However, with the lower alkali level, deposition only occurs in the lower temperature regions downstream of the holes. Thus, although the deposition rates are much lower, the effect of film cooling in this case is to increase (and indeed initiate) the deposition.

**COMPARISON WITH GRIMETHORPE EXPERIMENT**

The top graph in Figure 7 shows predicted temperatures on the suction surface of the internally cooled nozzles of the Grimethorpe turbine for two different cooling flow rates. Note that the lowest temperatures occur on the front part of the surface, around 5 to 35 mm from the leading edge. The bottom graph gives predictions of alkali deposition rates on the same blade surface, for the two cooling flows and for two different mainstream alkali levels differing by a factor of 4. The deposition was calculated by the full numerical solution of the diffusion equation. Only for the high cooling, high alkali case is vapour deposition predicted over the whole of the suction surface. The start of transition in the boundary layer is at about 20 mm and there is an increase in deposition rate after this, as the turbulence increases. This tends to be countered by the increase in surface temperature, which approaches quite close to the local dewpoint temperature, causing a reduction in deposition further downstream.

With the lower alkali level, but the same high cooling flow rate, deposition is predicted to occur only on the region of the blade where surface temperatures are lowest. With the lower cooling flow, hence higher blade temperatures, and the higher alkali level, similar limited deposition occurs. The case with low cooling, low alkali was also examined, but predicted that no deposition would occur.

Model predictions of the regions affected by alkali deposition, such as those illustrated in Figure 7, were found to agree well with the positions and surface temperatures at which alkali was observed on the blades in the Grimethorpe experiment. The predicted compositions of deposits on the surface were also well supported by the measurements.

Some of the cylindrical probes used in the Grimethorpe rig were designed to be retractable while the rig was running, so that they could be exposed for short periods only. These probes could therefore be used to characterise deposition rates without any corrosion or spalling complicating the results. For these probes, it proved possible, through some detailed post-test analysis of the deposits, to derive quantitative values for the amount of sodium and potassium deposited. The amount of sodium deposited was well predicted, but potassium tended to be underpredicted. This underprediction is believed to be mainly due to the fact that potassium was also brought to the surface inside ash particles, although measured levels of the potassium in the gas approaching the probe (which were very low) may also have been in error.
Because the cooling to these probes could be varied and their surface temperatures accurately deduced, they could be used to determine local dewpoint temperatures with some accuracy. It was found that the dewpoint temperatures predicted by the model gave a very good indication of the surface temperature at which alkali first appeared on the probes.

CONCLUSIONS
A vapour deposition model has been developed to predict the rate of alkali salt deposition in a turbine in an advanced coal system. The model has been applied to a utility turbine configuration to illustrate a number of aspects of the deposition behaviour. Model predictions have been compared with deposition behaviour observed on both cylindrical probes and turbine blades in an experiment at conditions representative of the real system. Many of the observed deposition features were well reproduced by the model.

ACKNOWLEDGEMENTS
The work described in this paper forms just one part of the Grimethorpe Topping Cycle Project and could not have been performed without supporting work from other parts of the Project, carried out by other participants. Their contribution is gratefully acknowledged. The Project is a partnership between the British Coal Corporation, GEC—Alstom, PowerGen and the UK Department of Trade and Industry. The views expressed are those of the authors and not necessarily those of the supporting organisations.

REFERENCES