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Some Aspects of the Chemistry of M.H.D. Seed

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XVII. Some aspects of the chemistry of m.h.d. seed

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The paper reports information assembled from the literature and from experiments about the physical chemistry of potassium sulphate at high temperatures and this enables a first assessment to be made of the difficulty of evaporating it quickly in an m.h.d. combustion chamber and recovering if after it leaves the generator duct.

Measurements of the evaporation rate show that in oxidizing and neutral gases a 50 μm diameter particle, which could be produced by normal powdering methods, should be evaporated within 10 to 20 ms at 2800 °K and this agrees with calculations. The experiments suggest that evaporation should be much faster in reducing gases. Available thermodynamic data has been used to determine the amount of heat used in evaporation of the seed. It amounts to 6·9 % of the calorific value of oil fuel—allowing for seed impurities.

A flue gas containing 0·7 at. % of potassium should begin to condense at 1600 °K and the amount of liquid, solid, or smoke formed will depend on the rate of removal of heat from the flue gas and on the saturated vapour pressure of K_2SO_4. Accurate data for the latter determined by effusion and transpiration methods are reported.

Potassium sulphate reaching metal tubes in the boiler and superheater may form liquids with excess of sulphur trioxide (including pyrosulphates, melting at about 670 °K) in the temperature range 670 to 970 °K. This could cause more severe corrosion than when potassium is absent.

Measurements of the partial pressure of potassium sulphate in equilibrium with coal ash slags up to 2000 °K suggest that it should be possible to reject the slag without loss of potassium if it could be separated from the potassium containing gas at 2000 to 2100 °K according to the ash content of the coal.

Introduction

In an economic open ended m.h.d. system it will be necessary to remove potassium compounds from the exhaust gases so that the seed potassium may be reused. The efficiency with which this must be done depends on many factors, the concentration of potassium in the duct being the principal one. We shall assume that this will be 0·7 at. %, the optimum value in a residual oil-fired system of the type the C.E.G.B. propose for large scale experiments. A different value may be selected for a different fuel and duct configuration and for a different magnet design, but is it unlikely to fall below 0·5 at. %. This is because the gas conductivity would be too low at normal or slightly elevated pressures and at the top flame temperatures achievable without using oxygen, or air heated to an inconceivably high temperature. On the other hand, more than 1·0 at. % would lower the gas conductivity because of the high electron cross-section of potassium atoms and ions. This is discussed by Hart, Laxton & Freck (1965). A concentration of 0·7 at. % would mean adding to the fuel 25 % of its weight of K_2SO_4, the cheapest available potassium compound. To limit the cost of seeding to, say, 2 % of that of the fuel, 98·7 % of the potassium would have to be collected for recycling. Even a loss of 1·3 % may be too much because allowance must be made for the cost of recovery of the rest of the potassium and the cost of its preparation for re-use. But this is taking the narrowest economic view; environmental and social considerations also restrict the amount of potassium seed which may enter the atmosphere. We have taken a minimum target figure of 99 % recovery at the 0·7 at.% level. This means the flue gas must be stripped down to 0·007 at.% of K, before it escapes to the atmosphere.

Separation of the potassium may take place immediately after the m.h.d. duct, perhaps in air-preheating plant (Horn, Sharp & Hryniszak, preceding paper) while the temperature of the seed-laden gas is falling from 2200 to about 1500 °K, or within the conventional boiler and steam superheater plant, allowing it to settle on tubes and be removed by 'soot-blowing', or before the gases enter the stack by filtering or electrical precipitation, just as dust is removed from ordinary flue gas. Each of these will probably make some contribution to the total recovery. If the fuel were a pure hydrocarbon, the potassium would condense in the form of its carbonate, but in any foreseeable large scale economic generator burning coal or residual fuel oil, the gas will contain enough sulphur oxides to convert the whole of the potassium on recycling, if not in one passage, into the more stable potassium sulphate. It will be predominantly in this chemical form that the seed will be condensed, handled and returned to the combustion chamber. Other fuel impurities will also condense and build up in the seed or will have to be separated from it. Residual fuel oil contains around a hundred parts per million each of sodium chloride and vanadium as well as traces of silica and metal oxides, and coal contains from 10 to 25% of ash (alumino-silicates and pyrites). The cases are quite distinct; with oil the trace impurities in the oil will build up to a small extent (3 to 10% by weight) in the sulphate, and may not have to be specially separated, but with coal, the segregation of potassium sulphate from the solid or liquid coal ash will be a major part of the recovery operation because the ash finally rejected must contain little more than its normal content of potassium.

The work has gone through several stages, at first assembling the rather scanty data—physical, chemical and thermodynamic—available from the literature for potassium sulphate at relevant temperatures (1250 to 2750 °K), then making experiments to test extrapolations from lower temperatures and to supply missing data. It has been necessary to report the experiments from time to time to fit in with the progress of the chemical engineering design rather than to await the accumulation of results of unassailable precision. This review of the present position reflects this approach. Thus theoretical predictions and simple experimental results to indicate an expected evaporation rate for potassium sulphate particles in the m.h.d. combustion chamber within rather broad limits suggest that a chamber designed for residual oil combustion should cope with the evaporation of conveniently milled potassium sulphate without difficulty. New experimental data on the vapour and decomposition pressures of pure potassium sulphate and less complete information on mixtures of it with oil and coal ash permits an estimate of the rate of condensation as bulk liquid or solid, or smoke from a cooling m.h.d. exhaust gas. Finally the results of preliminary experiments on the corrosiveness of potassium sulphate rich deposits on metal surfaces and on the segregation of dusts from cold flue gases at the entry of the stack are discussed.

The nature of the recycled seed

Residual fuel oil contains from 1 to 4% of sulphur, and coal available for power generation in the U.K. may contain up to 3% of sulphur. When the fuels are burnt with a stoichiometric amount or a small excess of oxygen the flue gas will contain enough sulphur oxides to ensure that potassium will condense mostly as potassium sulphate from the cool gas. This statement is based on observations on the behaviour of the exhaust gases from a combustion chamber burning oil containing up to 4 % by weight of sulphur and the appropriate amount of potassium added either as finely powdered carbonate, sulphate, or oil soluble naphthenate. Condensed samples consisted of sulphate with less than 1 % of potassium carbonate as would be expected from extrapolated thermodynamic data for such reactions as shown in table 1. These values are based on data of Rossini *et al.* (1952) and Kelley (1961) but they have had to be extrapolated beyond the range of the original measurements. They cannot accurately predict deposit composition without knowledge of the partial vapour pressure of the compounds and of their mixtures, but assuming that mixtures behave ideally and that the carbonate and hydroxide are not less volatile than the sulphate, calculation shows that sulphate would predominate when there is 1 % by volume of oxygen and 0·2 % by volume of sulphur dioxide in the gas. More detailed calculations are in progress using better data to predict the partition of potassium between the three main molecular forms K_2SO_4, K_2CO_3 and KOH, and the minor ones, K_2O, K_2S, KCN, which the thermodynamic data say may occur. These results are not yet ready, but preliminary figures based on less accurate data than is now available, were reported by Hart *et al.* (1965) and Freck (this Symposium). They showed that the minor species were present only in trace amounts at equilibrium, e.g. the ratio of K_2SO_4 to KCN at 1800 °K was 6×10^5 in stoichiometric combustion and $2{\cdot}4 \times 10^{12}$ with 2 % excess oxygen.

TABLE 1. FREE ENERGY CHANGES FOR K_2SO_4 FORMING REACTIONS IN FLUE GAS

reaction	$-\Delta G^0$ (kcal/mole) 1700 °K	$-\Delta G^0$ (kcal/mole) 2100 °K
K_2CO_3 (liquid) $+ SO_2 + \frac{1}{2}O_2 \rightleftharpoons K_2SO_4$ (liquid) $+ CO_2$	41·5	29·4
2KOH (gas) $+ SO_2 + \frac{1}{2}O_2 \rightleftharpoons K_2SO_4$ (liquid) $+ H_2O$	88·4	64·6

TABLE 2. AVERAGE ASH COMPOSITION FOR RESIDUAL FUEL OIL (P/M)

oil source	vanadium	sodium	iron	nickel	calcium, magnesium, silica
A	110	104	25	32	20
B	72	53	7	41	4

Then there are the less volatile fuel impurities which will concentrate in the condensed seed and may affect its physical properties. If only 1 % of the potassium is rejected per cycle these involatile impurities will appear in the seed at a concentration very roughly 100 times greater than in the fuel. Table 2 gives some typical analyses of residual fuel oil ash from two different Middle East sources as supplied to oil-fired power stations in the U.K.

They are subject to uncertainty due partly to the adventitious presence of iron oxide and silica in the oil, which may not be represented properly in the analysis.

The first and second columns in table 3 give suggested analyses, based on the oil ash analyses of table 2 for an m.h.d. seed which has been recycled in the plant until the impurities have reached a steady state concentration.

In practice some segregation of the impurities will occur. Thus a mixture with the composition given in column 1 of table 3, melts at about 1220 °K and separates into two layers if held in a platinum crucible for some time at 1600 °K or below. The smaller layer amounting to about 1 % of the total weight appears in the form of a silica-rich black viscous liquid which appears as a glass on cooling. It contains most of the impurities except sodium and vanadium which largely remain in the sulphate layer. It will be noted that there are discrepancies between the original composition and the final analysis taking the two layers together. This is due to loss by evaporation of K_2SO_4 in the 60 h at 1600 °K needed to attain phase equilibrium, and also to loss of iron and nickel, particularly the latter, to the walls of the crucible.

TABLE 3. ANALYSES OF K_2SO_4 SEED CONTAMINATED BY OIL ASH AND OF THE TWO LAYERS INTO WHICH IT SEPARATES AFTER HEATING AT 1600 °K

	analyses (wt. %)		
species	contaminated seed mixture	glassy layer after separation	sulphate layer after separation
Fe as FeO	0·47	10·9	0·3
Ni as NiO	0·48	2·1	0·04
V as KVO_3	5·00	14·0	4·40
Ca as CaO	0·41	3·5	0·70
Mg as MgO	0·33	3·1	0·80
Si as SiO_2	0·43	53·1	0·20
Na as Na_2O	1·75	2·7	2·50
K as K_2O	45·6	9·2	49·1
SO_3	45·7	0·6	40·8
total	100·2	99·2	98·8
mass of sample (g)	10·0	0·085	8·38
		8·465	

The behaviour of the black glass in an m.h.d. system has yet to be considered, but it would certainly be best to separate it in the liquid form, otherwise it would stick to metal or ceramic heat exchange surfaces.

The condensation of potassium sulphate in the presence of coal ash is clearly a very different problem; not enough is yet known about the interaction of potassium sulphate and hot coal ash to permit a suitable separation process to be specified, but some experiments have been done and these are reported later.

THE PHYSICAL AND THERMOCHEMICAL PROPERTIES OF K_2SO_4

The data required

The first requirement in considering the handling of seed through a generator system will be information on the bulk properties of the K_2SO_4, its heat of formation, evaporation, and decomposition, its specific heat, vapour pressure, melting point, surface tension and viscosity, and the way these are affected by temperature. In this section comment is made on some of these properties beginning with the use of thermochemical data to calculate the heat required to heat up and evaporate the compound.

The heat required for the evaporation of potassium sulphate

The heat required to raise the temperature of 1 mol of potassium sulphate from 298 to 2700 °K, and then to evaporate and dissociate it to K atoms, sulphur dioxide and oxygen, has been calculated in the manner described below to be $391\cdot9 \pm 2\cdot8$ kcal/mole. If 50 % of the K atoms are hydrolysed to potassium hydroxide $343\cdot6 \pm 4\cdot3$ kcal/mole are required. Some of the seed injected into the flame may not have time to vaporize; if only 80 % of it does, the rest remaining as liquid potassium sulphate at 1850 °K, $369\cdot4 \pm 4\cdot3$ kcal/mole would be needed to give 1 at. % of potassium in the vapour—an increase of $7\frac{1}{2}$ %. To obtain a 0·7 at. % concentration of potassium in the plasma, pure potassium sulphate will require 6·1 % of the heat equivalent of the fuel at 10000 c.h.u/lb. Allowing for recycled oil ash impurities, up to 6·9 % of the fuel heat equivalent will be required. The calculations outlined below are made on the assumption that K and KOH are the only K-containing species existing at 2700 °K. Brewer & Mastick (1951) have shown that there is very little K_2O in the vapour phase above 1000 °K and potassium carbonate is largely converted to K and KOH beyond 1800 °K in flue gas at atmospheric pressure. Recent measurements of the decomposition pressure of K_2SO_4 suggest that in the vapour phase it will mostly decompose in the presence of the usual flue gas amount of SO_2 and oxygen beyond 2100 °K.

The evaporation and subsequent dissociation of the sulphate may thus be accounted for with two equations:

$$K_2SO_4 \text{ (crystals)} \rightleftharpoons K_2SO_4 \text{ (liquid)} \rightleftharpoons K_2SO_4 \text{ (gas)} \rightleftharpoons 2K \text{ (gas)} + SO_2 + O_2, \tag{1}$$

$$2K \text{ (gas)} + H_2O + \tfrac{1}{2}O_2 \rightleftharpoons 2KOH \text{ (gas)}. \tag{2}$$

The equilibrium constant of (2) will decide the relative proportions of potassium atoms and potassium hydroxide in the gas, and hence the total heat absorbed.

It is not possible to evaluate directly the heat change in reaction (1) at 2700 °K because there appear to be no data available for the heat capacity of potassium sulphate gas. However, the heats of formation at 298 °K of K_2SO_4 (crystals) and SO_2 (gas) at 298 °K, are known as are the heat capacities of solid, liquid and gaseous potassium and oxygen, both up to 3000 °K, and of sulphur dioxide up to 2000 °K. In the latter case, extrapolation to temperatures a little in excess of 2000 °K is probably permissible without significant error. Sufficient data are already available to calculate directly the heat change in (2) up to 3000 °K.

The sources of data for the calculations which follow are Rossini *et al.* (1952), JANAF Tables (1960 *et seq.*) and Kelley (1961). For reaction (1) $\Delta H_{298} = +314\cdot6 \pm 2\cdot3$ kcal/mole. The heat required to raise the temperature of the dissociation products to 2700 °K is $77\cdot29 \pm 0\cdot45$ kcal/mole K_2SO_4, and so the total amount of heat required to heat up and dissociate 1 mole of crystalline K_2SO_4 at 2700 °K is $391\cdot9 \pm 2\cdot8$ kcal/mole. The heat evolved if reaction (2) goes to completion at 2700 °K is calculated to be $-96\cdot6 \pm 2\cdot9$ kcal.

The amount of heat released by this reaction depends on the extent to which it occurs in the m.h.d. duct gas. The best estimate of this is probably that due to Westinghouse (1963) who used data from JANAF tables (1960 *et seq.*) for the equilibrium constant of reaction (2) and calculated the relative proportion of K and KOH in a gas produced by firing residual oil with a stoichiometric proportion of oxygen at a pressure of 4 atm, with 1 at.% of total potassium in the flue gas. At 2700 °K the ratio is approximately unity. This would be modified slightly by varying the total pressure, the oxygen/fuel ratio and the potassium level, but the effect is small so we used the 1:1 ratio of K to KOH. Thus the total amount of heat required to raise 1 mole of potassium sulphate to 2700 °K in an m.h.d. gas system is

$$(391{\cdot}9 \pm 2{\cdot}8) - \tfrac{1}{2}(96{\cdot}6 \pm 2{\cdot}9) = 343{\cdot}6 \pm 4{\cdot}3 \text{ kcal/mole}$$

or 1·97 kcal/g of K_2SO_4. The potassium in all its forms in the flue gas (0·7 at.%) will require 31 g of K_2SO_4 to be added with each 100 g of residual fuel oil (calorific value 10 kcal/g or 10000 c.h.u./lb.) and will thus consume $31 \times 1{\cdot}97 \times 100/10 = 6{\cdot}1\%$ of the total calorific value of the fuel.

There is of course the possibility that some of the seed remains unevaporated and passes through the duct as liquid beads at the evaporation temperature of 1850 °K. If 20% of the seed fails to evaporate, 0·875 mole of potassium must be added instead of 0·7 mole to obtain the same effect on gas conductivity. The heat required to raise the extra 0·175 mole to 1850 °K increases the over-all percentage of the calorific value of the fuel to 6·46%.

Another factor is the burden of seed impurities. The steady state seed composition appropriate to recycled seed in a residual oil-fired system would take 16·3 g of impurities into the combustion chamber for each 100 g of potassium sulphate. The heat required to evaporate the various compounds in the recycled seed mixture to VO, CaO, MgO, SiO_2, NiO and FeO has been calculated, and it is concluded that it would increase the total heat requirement to 6·6% of the heat value of the fuel (allowing nothing for partial evaporation). There is another small effect, this time beneficial, which must not be overlooked. The oxygen released by the decomposition of potassium sulphate (equation (1)) provides a small amount of oxygen enrichment to the combustion air; it brings into the combustion chamber some oxygen without attendant nitrogen, and this may permit a flame temperature around 10 to 20 degC higher than would otherwise be attainable.

THE VAPOUR AND DECOMPOSITION PRESSURE OF K_2SO_4

Two methods of measurement have been used; a Knudsen cell for the temperature range 1198 to 1310 °K (vapour pressures $2{\cdot}4 \times 10^{-6}$ to $3{\cdot}3 \times 10^{-5}$ atm) and a transpiration method extending to 1800 °K (vapour pressure $2{\cdot}1 \times 10^{-2}$ atm) (Grieveson & Alcock 1960). The results are shown in figure 1. Below the melting point at 1342 °K the data can be represented by the equation

$$\log_{10} p = 6{\cdot}84 - \frac{1{\cdot}47 \times 10^4}{T\,°\mathrm{K}}, \tag{3}$$

where p is the vapour pressure in atmospheres of the gas in equilibrium with solid K_2SO_4 at the temperature T. Above the melting point the appropriate equation (the upper line in figure 1) is

$$\log_{10} p' = 6{\cdot}23 - \frac{1{\cdot}38 \times 10^4}{T\,°\mathrm{K}}, \tag{4}$$

where p' is the 'apparent' total vapour pressure exerted by liquid K_2SO_4. This equation does not accurately represent the experimental results above 1700 °K. This will be explained by what follows.

In the transpiration apparatus it was possible to observe the effect of flue gas constituents and it emerged that the evaporation of potassium sulphate was markedly lower when sulphur dioxide and oxygen were added to the nitrogen carrier gas, and a minimum vapour pressure was recorded when these gases were present above certain partial pressures. This effect was interpreted as due to the suppression of partial decomposition of potassium sulphate molecules in the gas phase according to the equation

$$K_2SO_4 \text{ (gas)} \rightleftharpoons 2K \text{ (gas)} + SO_2 + O_2. \qquad (5)$$

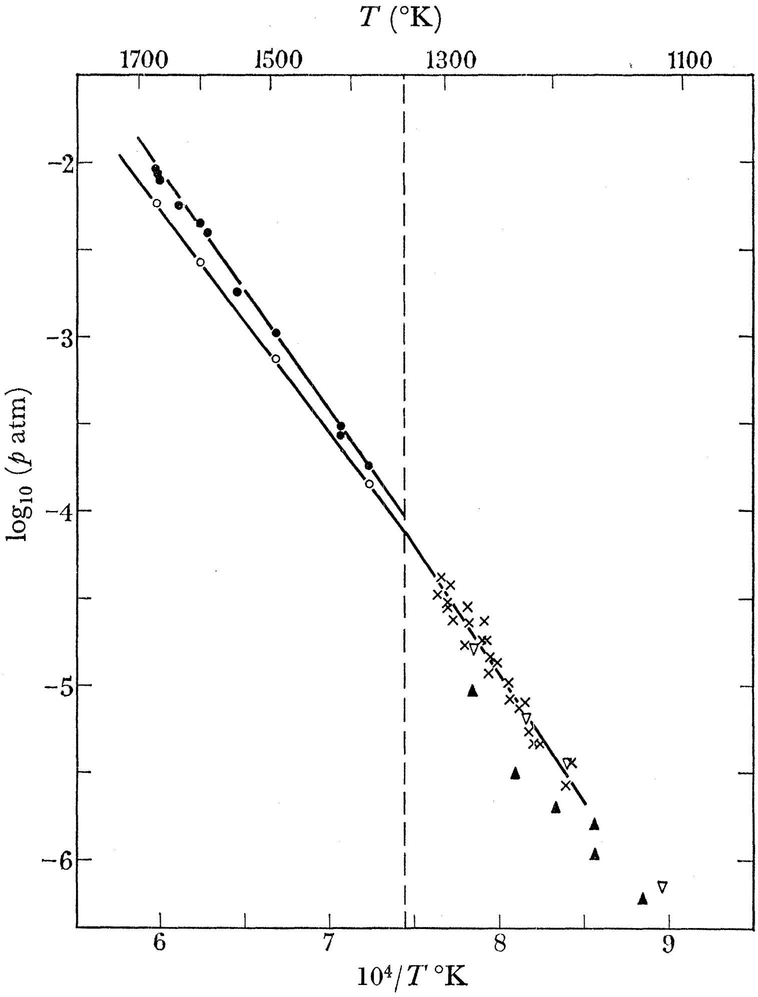


Figure 1. Saturated vapour and decomposition pressure of potassium sulphate. Transpiration method: ●, decomposition not suppressed; ○, decomposition suppressed. Knudsen cell method: × (▲, ▽, Kröger).

Thus the lower of the two lines on the left of figure 1 refers to the true vapour pressure of K_2SO_4 molecules with decomposition suppressed and the upper one to a total pressure made up of an equilibrium mixture of K_2SO_4 and its decomposition products but expressed in terms of K_2SO_4 vapour. The actual total pressure can be calculated from the weight loss in the two sets of transpiration measurements if it is assumed that (5) is in fact correct. If this is done then the pressure p' at 1700 °K, i.e. $1{\cdot}29 \times 10^{-2}$ atm is increased to an actual pressure of $3{\cdot}29\times10^{-2}$ atm account being taken of SO_2 and O_2 as well as potassium atoms. The equation for the lower line is

$$\log_{10} p'' = 5{\cdot}37 - \frac{1{\cdot}27\times10^4}{T\,^\circ\mathrm{K}}. \tag{6}$$

Equations (3) and (6) may be interpreted in terms of the Clausius–Clapeyron equation

$$\log_{10} p = \text{const.} - \frac{\Delta H}{2{\cdot}303RT}, \tag{7}$$

where ΔH is the heat of evaporation or sublimation, and R is the gas constant. From the constants in equations (3), (6) and (7) the latent heat of sublimation of potassium sulphate is 67·3 kcal/mole, and the latent heat of evaporation 58·3 kcal/mole. These figures are each subject to an uncertainty of $\pm2{\cdot}0$ kcal.

The temperature at which the partial vapour pressure of potassium sulphate molecules above the liquid would be 1 atm is found from equation (6) to be 2368 °K and the entropy of vaporization at this temperature is $24{\cdot}6\pm2{\cdot}5$ cal $\mathrm{degC^{-1}\,mole^{-1}}$. This is in good agreement with the value predicted by Trouton's rule of 22 cal $\mathrm{degC^{-1}\,mole^{-1}}$ which suggests that we are correct to assume that liquid potassium sulphate evaporates to monomeric molecules under sufficient pressure of sulphur dioxide and oxygen to suppress decomposition.

The difference between the latent heat of evaporation and sublimation gives the latent heat of fusion. From the data the value is $9{\cdot}0\pm4{\cdot}0$ kcal/mole which is satisfactory in view of the value of $9{\cdot}0\pm0{\cdot}1$ kcal/mole determined by Kelley (1961).

From equations (4) and (6) it is possible to calculate for any temperature within this range the total vapour pressure of liquid potassium sulphate when it is free to decompose and also when its decomposition is suppressed and from the two values obtain the equilibrium constant for the assumed decomposition reaction. These values and the validity of reaction (5) may be tested by using weight loss data with varying sulphur dioxide and oxygen partial pressures. So far the measurements are not sufficiently refined for this interpretation.

On the assumption that (5) is the appropriate equilibrium reaction the amount of sulphate decomposed in a flue gas containing 0·2 vol % of sulphur and 1 vol % of oxygen is 0·34 % at 1400 °K and 50 % at 1900 °K. This ignores the effect of water vapour which will give rise to some KOH and so increase the decomposition, but this effect is appreciable only at the higher temperature.

Allowing for this amount of decomposition we may calculate that a flue gas bearing 0·7 at. % of potassium (a partial vapour pressure of K_2SO_4, not counting its decomposition products of 0·0035 atm) should begin to condense at 1600 °K, and that 90 % of the potassium should be condensed, if equilibrium is allowed to be attained, at 1420 °K, i.e. about 80 degC above the melting point.

A few determinations of the dew point of potassium sulphate from flue gas in a 6 in. square magnesia-lined duct have been made in the range 1400 to 1500 °K. An alumina tube with a closed end was inserted into the duct and its end viewed through a port at the side of the duct. The probe was cooled below the gas temperature by means of an air stream passed down a platinum tube to its tip. Probe end temperatures were measured with a disappearing filament pyrometer. The fuel was burnt with 1 to 5 % (v/v) excess oxygen and up to 0·2 at. % of K as 5 μm sulphate powder. Condensation as shown by the growth of a droplet of liquid potassium sulphate on the probe did not take place at a given partial pressure of potassium sulphate unless the surface temperature was nearly 30 degC below that given by equation (4). Errors of temperature measurement may be a cause of this discrepancy and supersaturation near the condensing surface another.

The effect of impurities on vapour pressures and on the temperature of condensation has not yet been determined. It is expected to be very small.

The absorption of potassium in a coal-fired system

Data were required on the equilibrium absorption of potassium seed by coal-ash slags at various temperatures appropriate to liquid slag handling to assess the possibility of separating potassium vapour from hot slag, e.g. by removing the liquid in a cyclone. An isopiestic method was used in which an inert carrier gas was passed at a measured rate over a large platinum dish containing liquid potassium sulphate at the outer end of the hot zone of a furnace tube and then, towards the centre of the furnace, over groups of small platinum dishes at increasing temperatures which were measured by thermocouples. After sufficient time for equilibrium to be reached, the samples were removed and analysed. Potassium, estimated at K_2O, was retained in the melts and the amount could be related to the partial vapour pressure of potassium sulphate in the gas stream at a given temperature, by the expression

$$p_{K_2SO_4} = K_s N_{K_2O}, \tag{8}$$

where N_{K_2O} is the molecular fraction of potassium oxide in the condensed phase and $p_{K_2SO_4}$ the partial pressure of potassium sulphate (atmosphere) calculated from the loss of weight to the gas stream from the platinum dish. When the condensed phases contained only SiO_2 or $SiO_2/Al_2O_3/CaO$ mixtures the solubility constant K_s was found to be related to temperatures by an expression of the type

$$\log_{10} K_s = A - \frac{\Delta H}{2{\cdot}303RT}; \tag{9}$$

A is a constant and ΔH, with a value of around 52 kcal/mole for K_2O, was plainly the heat of reaction of gaseous K_2SO_4 with liquid silica,

$$K_2SO_4\ (\text{gas}) + SiO_2\ (\text{liquid}) = K_2SiO_3\ (\text{liquid}) + SO_2 + \tfrac{1}{2}O_2. \tag{10}$$

With natural coal ash slag (with mol. fractions of 0·59 SiO_2, 0·2 Al_2O_3, 0·07 CaO, 0·07 FeO) ΔH was less than 52 kcal below 1600 °K, but from 1600 to 1900 °K it was the same as for the synthetic mixtures. Table 5 gives some values of K_s.

By extrapolation to higher temperatures it is possible to calculate the temperatures at which the slag would have to be heated before separation in a cyclone, so that it did not carry out more potassium than it carried into the system which, in an average British coal ash, would amount to about 0·04 at. % of the flue gas. Figure 2 shows the loss of seed potassium to the slag if separation were carried out at various temperatures. On the basis of 1·0 atm. % of potassium in the flue gas, 2223 °K would give complete separation. At 0·7 mol % 2173 °K would suffice and if 5 % loss of potassium to the slag were permitted

2100 °K. These figures are for 20 % ash in coal. For a 10 % ash, coal separation at 2080 °K would do. These are formidable but not impossible gas temperatures for cyclone operation. The practical task would be less severe if only a part of the coal mineral were to evaporate.

Table 5. Equilibrium concentration of K_2O in coal ash slags exposed to K_2SO_4 vapour

T (°K)	$p_{K_2SO_4}$ (10^{-4} atm.)	mol. fraction of K_2O in slag, N_{K_2O}	$K_s = p_{K_2SO_4}/N_{K_2O}$ (10^{-4} atm.)
1468	1·11	0·129	8·60
1493	1·1	0·110	10·1
1518	2·11	0·158	13·4
1538	2·11	0·137	15·4
1578	3·55	0·193	18·4
1673	8·16	0·213	38·3
1698	8·16	0·178	45·8
1753	13·4	0·212	63·2
1788	13·4	0·140	95·7
1798	13·4	0·142	94·4
1923	51·2	0·165	310·0

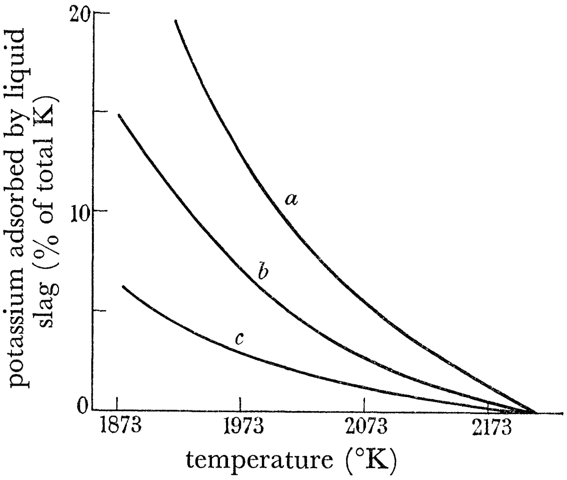


Figure 2. Equilibrium absorption of potassium by coal ash slag. For 1 at. % K: (*a*) 20 % ash in coal; (*b*) 10 %; (*c*) 5 %.

Viscosities and surface tension of liquid seed

(*a*) *The surface tension of potassium sulphate*

The surface tension of liquid potassium sulphate has been determined by Jaeger (1917) by the maximum bubble pressure method within the range 1343 to 1933 °K. The values show a linear relation with temperature,

$$\gamma = 228{\cdot}3 - 0{\cdot}063\,T, \tag{11}$$

where γ is the surface tension (dyne/cm), and T the temperature (°K). The surface tension at 1400 °K is nearly twice that of water at ordinary temperatures.

(*b*) *Viscosity of pure fused potassium sulphate and the effect of impurities from fuel-oil ash*

Viscosity measurements have been made at temperatures between 1273 and 1673 °K on pure potassium sulphate and also on recycled oil-fired seed. The viscosity of the pure material was 1·70 cP at 1520 °K which is similar to that of water at 274 °K (1·70 cP). A mixture of composition 87·5 % K_2SO_4, 6 % Na_2SO_4, 5 % V_2O_5 and 1·5 % K_2SiO_3 (w/w) had a viscosity approximately 7 % greater than that of the pure salt. The effect of temperature is given by the following equations:

$$\log_{10} \eta \ (K_2SO_4) = 1825/T - 0{\cdot}96, \tag{12}$$

$$\log_{10} \eta \ (\text{mixture}) = 1904/T - 0{\cdot}98, \tag{13}$$

where η is the viscosity (cP) and T the temperature (°K).

The measurements were made in a Pt/20 % Rh capillary viscometer held in a furnace tube with a 10 cm hot zone constant to ±4 degC. The capillary was calibrated with fused potassium nitrate at 623 to 770 °K. The viscosity of this substance has been studied carefully by several workers (cf. Dantuma 1928). A small correction for thermal expansion of the capillary was applied to measurements made at higher temperatures.

The evaporation and decomposition of potassium sulphate in an m.h.d. combustion chamber

Early experiments in any m.h.d. programme by-pass the problem of seed addition by adding the potassium as an oil-soluble compound, or as extremely finely ground potassium sulphate, or carbonate (which evaporates more easily than sulphate) all of which would be too expensive to use on a large scale. In a working plant there are two main possibilities; the recycled seed can be blown in with the preheated air at a selected point in the chamber as a 50 μm powder or as an atomized liquid (it might be carried in from a falling rain air-preheater), or it can go in with the fuel as a suspension. Whatever is done the 2700 °K gas entering the generator duct must carry with it the requisite amount of potassium in thermal equilibrium and preferably with no seed unevaporated. It is also desirable that evaporation and decomposition of the seed should not impose any limitations on the combustion chamber design, so it should be achieved well within the 20 to 30 ms residence time planned for a residual fuel oil combustion chamber. Coal firing will need a larger combustion chamber with a longer residence time so the problem of seed evaporation may not loom so large.

It was found that potassium sulphate ground to a fine powder ($\ngtr$ 40 μm), suspended in fuel oil (the oil/sulphate mixture was vigorously agitated in a small tank just before the injector) was completely evaporated at a flame temperature of 2050 °K in an Urquhart 2 gal/h combustion chamber, which had an average residence time of 0·6 s. This was shown by collecting a sample of condensable matter at the outlet of the chamber on an air-cooled metal probe; unevaporated particulate material appeared to be absent and the ratio of potassium carbonate to sulphate in the condensed solid was the same no matter if the seed added to the oil was all one or a mixture of both. Unfortunately the burner jets would not work for long with more than 7 % by weight of sulphate in the oil; they became clogged with solid residue. This limited the potassium content to about 0·2 at. % for runs of more than an hour or so. Blowing in the same seed powder with the burner air was also tried. Unfortunately little of it evaporated and there was evidence in the flame tube of unevaporated powder even when it had been milled ('micronized') before the injection of 5 to 10 μm particles. At this stage calculations were made of the rate of evaporation in flue gas of K_2SO_4 particles of various sizes up to 76 μm in diameter. The calculations were based on the assumption that heat transfer to the particles was rate controlling and used measurements of the vapour pressure of K_2SO_4 and an assessment of the heat required to raise its temperature, and evaporate it to potassium sulphate molecules. It was assumed that the subsequent decomposition to potassium atoms would take place rapidly in the gas phase. For a 50 μm particle plunged into gas at 2800 °K, the calculations gave the following results:

(*a*) approximately 2 ms would be required to heat the particle to 2000 °K;

(*b*) if diffusion from the surface is rate limiting, the particle would evaporate at 2000 °K and at a rate of 1·25 μm/ms;

(*c*) if effusion or evaporation is limiting the temperature of evaporation would be 1800 °K with a rate of 2·0 μm/ms;

(*d*) 50% of full conductivity would be attained in 4 ms with diffusion limitation including time of heating; for 90% of full evaporation about 10 ms would be required.

Laboratory experiments were made to test the calculated evaporation times. They were of three kinds: (*a*) direct microscopic observations of the evaporation of a droplet of molten potassium sulphate suspended in a slow-moving gas stream in a furnace tube; (*b*) spectroscopic determination of *K*-emission resonance radiation in a premixed shielded flame at about 2200 °K to which fine particles were added with the air/oxygen mixture; and (*c*) estimation of the evaporation from particles suspended in a shock-heated gas with a 10 ms dwell-time at a peak temperature of 2700 °K. The results all support the calculations. The experiments exposed some interesting features about the evaporation process to which we draw attention.

(*a*) *Direct observation of the evaporation of* K_2SO_4 *droplets*

The method of Frössling (1938) was used in which a droplet about 2 mm in diameter is suspended from a platinum wire in a furnace tube through which flows a gas of controlled composition. The particle temperature, measured by thermocouples and an optical pyrometer could be maintained at points in the range 1470 to 1770 °K and the evaporation followed by projection microscopy and measurement of the weight change at the end of a run. Fuchs (1959) shows theoretically that the diffusion limited evaporation rate (g/s) from a spherical particle is directly proportional to the radius of the particle. Table 6 compares calculated values of the constant of proportionality with experimental values for particles with diameters between 0·2 and 0·39 cm.

The agreement between the two sets of values lends support to the assumptions made in the calculations. The line *A* in figure 3 shows the temperature coefficient of the evaporation rate is approximately consistent with an expression of the type, rate $= A\mathrm{e}^{-E/RT}$. The mean value of E, which may be described as an energy of activation for evaporation, is 69 kcal/mole. This is only slightly higher than the sum of the heat of evaporation, 58·3 kcal/mole and the calculated energy of activation for diffusion, 5·8 kcal/mole; no doubt a very little of the sulphate decomposes as it leaves the surface.

Extrapolating the experimental data represented in figure 3 to 2000 °K, an evaporation time of 6 ms may be calculated for a 50 μm particle to evaporate in an m.h.d. combustion chamber at a gas temperature of 2800 °K. To this must be added 2 ms for heating the particle to 2000 °K (at which temperature evaporation would take place) making a total evaporation of 8 ms. A 100 μm particle would require about 30 ms. These figures refer to an atmosphere corresponding to stoichiometric or 1 % oxygen-rich combustion.

Table 6. Calculated and experimental specific evaporation rates of potassium sulphate droplets in slow moving gas

temp (°K)	evaporation rate (g cm^{-1} s^{-1}) experimental	evaporation rate (g cm^{-1} s^{-1}) calculated
1470	$2{\cdot}6\times10^{-6}$	$3{\cdot}6\times10^{-6}$
1620	$3{\cdot}1\times10^{-5}$	$4{\cdot}6\times10^{-5}$
1770	$1{\cdot}8\times10^{-4}$	$2{\cdot}4\times10^{-4}$

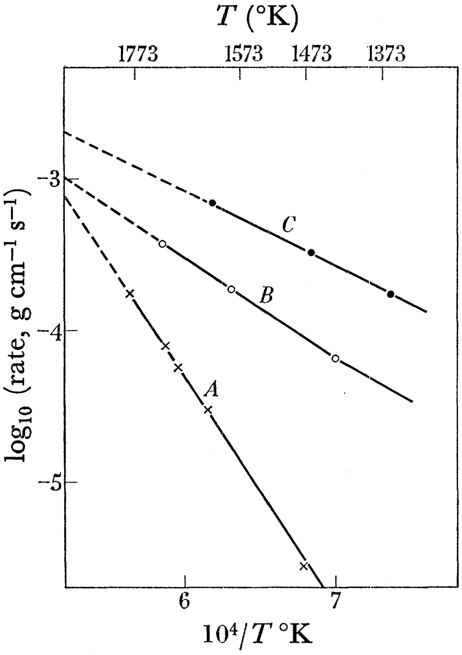


Figure 3. Rate of evaporation of a K_2SO_4 droplet at various temperatures; *A*, in nitrogen; *B*, in nitrogen with 10 % CO; *C*, in nitrogen with 10 % H_2.

In mixtures of nitrogen and hydrogen or carbon monoxide the rates of evaporation were much higher. Curves *B* and *C* on figure 3 show this. The temperature coefficient is much lower than in neutral or oxidizing atmospheres but even at a particle temperature of 1800 °K evaporation in a reducing atmosphere may be still several times greater than in an oxidizing one. This could certainly explain our good results in the 2050 °K oil burner with sulphate suspended in oil in which the particles may be surrounded by reducing gases for most of their life in the combustion chamber, and the bad results with the same size particles introduced in an air suspension.

Reducing gas will react with potassium sulphate molecules at or near the particle surface. This will assist evaporation by replacing potassium sulphate molecules by more volatile and easily diffusible products KOH, K, H_2S, SO_2, and by liberating heat of reaction at the surface, so improving apparent heat transfer and evaporation. In the reducing part of a flame front round a particle of fuel, hydrogen atoms or hydrocarbon radicals could add very greatly to both these effects by diffusing rapidly across the cooler gas layer near the particle. The following reactions are possible:

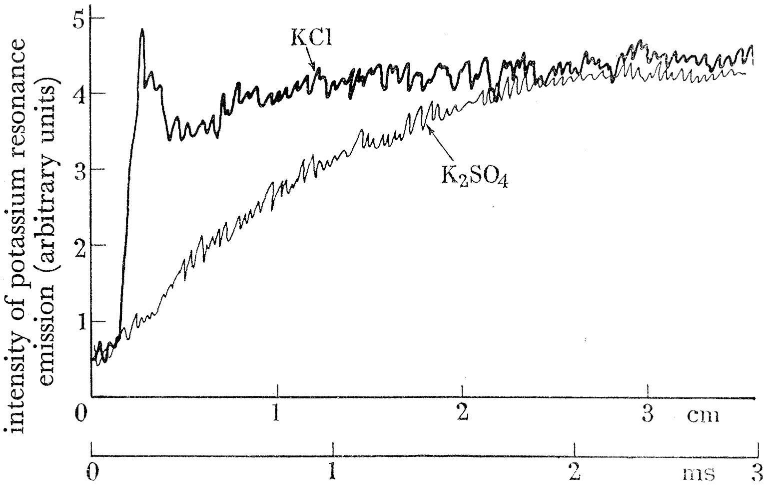
$$K_2SO_4\ \text{(liquid)} + 4H_2 = 2KOH\ \text{(gas)} + H_2S + 2H_2O, \tag{14}$$

$$K_2SO_4\ \text{(liquid)} + CO = K_2SO_3\ \text{(gas)} + CO_2. \tag{15}$$

The work described in the next section suggests that the gas phase decomposition of K_2SO_4 molecules is a relatively slow process.

(*b*) *Development of potassium atom concentration in a premixed flame containing particles of potassium sulphate*

The following method has been developed for the smaller particles which could not be observed directly. Potassium sulphate was added as an atomized spray of a dilute solution in water to the unburnt gases of a premixed hydrogen/oxygen/nitrogen flame burning on a water cooled burner similar to that described by Padley & Sugden (1958). The intensity of resonance radiation at 7699 Å which is due to K atoms was measured along the flame from the reaction zone and the growth of intensity was used to calculate the rate of decomposition of the sulphate. The flame consisted of three concentric zones and it was to the inner one of 15 mm diameter that the metal salt spray was added. The outer flames were fed with the same gaseous reactants at rates which would give the same burnt gas velocity as the inner flame. The central flame was thus well shielded and provided a steady-state flow system in which the time of reaction was measured in terms of distance along the flame; 10 cm was equivalent to 6 ms. A suitable temperature range over which the decomposition of potassium salts could be studied was 1600 to 1800 °K and burnt gas temperatures were varied over this range by altering the oxygen proportion from 3:8:1 to 3:8:1·4 for H_2, N_2 and O_2 respectively, so all flames were fuel-rich. The gas temperature



upper scale, distance along burnt gas column
lower scale, reaction time from flame zone

FIGURE 4. Emission of potassium radiation from gas at 2000 °C when atomized potassium salts are added.

was first measured along the flame by sodium D-line reversal, and later from the total potassium resonance emission along the flame. The liquid particles were considerably less than 10 μm in diameter and the particle of salt left by evaporation of the water would be well below 1 μm in diameter, which is expected to evaporate in less than 1 ms. This was borne out by the fact that with a wide range of potassium salts (but not the sulphate) the intensity of emission had reached its full decomposition value very quickly. Figure 4 shows a typical recorded trace for potassium chloride and sulphate. The chloride trace rises rapidly even showing an initial peak which we have ascribed to a 'non-equilibrium' atom concentration due to the influence of radicals in the tail of the combustion zone, and indeed other potassium salts show an even sharper initial peak, but with the sulphate there is no peak and the intensity of radiation rises slowly. It is inferred that this is due to the slowness of the gas phase decomposition of sulphate molecules. From the intensity growth curve we calculated the first-order decomposition constant, k, for the reaction

$$\mathrm{K_2SO_4} \rightleftharpoons 2\mathrm{K}+\text{products} \tag{16}$$

from the expression

$$2{\cdot}303\log_{10}(I_t/I_f-I_t) = kt, \tag{17}$$

where I_f is the final emission intensity and I_t that at time t. k is given by the expression

$$\log_{10} k = 7{\cdot}38\pm 0{\cdot}4-\frac{31\,500\pm 3\,000}{2{\cdot}303RT}. \tag{18}$$

The time for 99 % decomposition at 1800 °K is 1·4 ms. Thus even at the relatively low temperature around an evaporating potassium sulphate pellet the time for decomposition is fairly small. But this refers to reducing gases and to very low concentrations of potassium (less than 0·001 at. %). More work is needed to explore the order of the decomposition and the rate constants for decomposition in neutral or oxidizing gases and at higher total concentration of the salt itself.

(*c*) *Evaporation of* $\mathrm{K_2SO_4}$ *particles in a shock-heated gas*

Small quantities of micronized potassium sulphate particles have been exposed to the hot gas behind a reflected shock wave. The tube permitted a dwell time of 10 ms at a temperature in the region of 2700 °K. The particles were examined microscopically after treatment and the loss by evaporation estimated from the change in average diameter of the particles in a sample. The accuracy of the method was limited by inadequacy of the size determination, but the results indicated clearly that a particle of about 50 μm diameter would evaporate almost completely in less than 20 ms in an oxygen rich or neutral atmosphere.

The conclusion drawn from the collected experiments is that the calculated evaporation time is approximately correct for neutral atmospheres when the rate controlling process is heat transfer or diffusion of the evaporation products away from the particle. The calculated time is adequate for the evaporation of 50 μm powder in a 2700 or 2800 °K flame in 10 to 20 ms. The effect of reducing gases may be to reduce significantly the evaporation time, so it may be better to add the potassium sulphate mixed with the fuel, or in a fuel rich zone in the combustion chamber, rather than with the air.

Condensation of seed

Seed is removed from the cooling combustion gas in two ways: by direct condensation of the vapour molecules as liquid or solid on a cooled surface and as submicron particles of fume. The latter precipitates on nuclei when the gas phase becomes supersaturated as a result of loss of heat usually in the boundary layer near a cooled surface, and also in the bulk gas when it loses heat by radiation. The proportion of each form of condensation in the plant following the m.h.d. duct has been determined by the method described by Sherwood & Pigford (1952).

First the quantity of seed vapour transferred to a cooling surface in the absence of fog precipitation is calculated and then from heat transfer calculations the amount of gas in the temperature régime, which would become supersaturated and so liable to form fog, is determined. Fog formed in a boundary layer would be acted upon by two transport processes thermophoresis and photophoresis, which would drive it towards the cool surface. Away from the cooling surface eddy diffusion would sweep the fog back into the bulk gas. The balance between these transport processes would give rise to a point of no return in the boundary layer, after which diffusing vapour or fume would all deposit on the cooling surface.

Calculations show that if gas cooling by radiation is ignored little fog would be produced from an unsaturated gas if the cooling surface were more than 400 degC below the gas temperature which would then be in excess of 1800 °K. This is because the boundary layer can remain unsaturated during diffusion of K_2SO_4 to the surface. But radiation cooling can only be ignored in quite narrow ducts; in an experiment in a 6 in. diameter cylindrical duct with a gas-wall temperature difference of 300 degC, and a heat loss rate of 1000 B.t.u. $ft.^{-2}$ h^{-1} heat transfer by radiation in a section of the duct in which the gas cooled from 1900 to 1600 °K was five times that by convection and approximately 85 % of the potassium sulphate was condensed as fog. On the other hand a small temperature difference (not more than 50 degC) between gas and condensing surface also avoids fume formation. This condition is best achieved in condensing on liquid surfaces, especially on droplets of liquid. In such an experiment the condensation from a flue gas containing 0·1 mol. % of K_2SO_4 on a liquid droplet suspended from the closed tip of an air cooled alumina tube was observed.

Drops falling from the tip were collected in a platinum crucible and weighed. The amount collected was nearly twice that predicted from the mass transfer equation using a gas temperature measured by sodium D-line reversal, a liquid temperature by optical pyrometry and extrapolated values of gas viscosity and diffusivity. In view of the uncertainties in the calculation the agreement is reasonable and certainly confirms that fume does not occur in this type of condensation.

The corrosiveness of potassium sulphate deposits in boiler plant

It is usual to operate the superheater tubes in a conventional oil-fired boiler at a steam temperature of 810 °K and to use the cheaper low chromium alloy steels without incurring inconvenient metal loss. Above this temperature the corrosion rate increases rapidly and even high chromium steels cannot be used satisfactorily above steam temperatures of

870 °K. These limitations are usually explained in terms of the fusion of sodium and vanadium-containing oil–ash deposits which occurs at 800 °K in the presence of sulphur dioxide and oxygen. Sodium pyrosulphate melts at 675 °K, but it is only stable in the presence of considerable amounts of sulphur trioxide in the gas phase.

The behaviour of potassium sulphate-rich recycled seed deposits is different in several important respects, the most striking of which is the very much greater stability of potassium pyrosulphate. In experiments this was found to be stable at its melting point of 680 °K under only 100 p/M of SO_3 (or SO_2 if there is excess O_2 and a metal surface is present to catalyse the conversion to SO_3) and to remain liquid up to 750 °K with 0·2% SO_3. A eutectic occurs in the $K_2O/V_2O_5/SO_3$ system at 753 °K and some liquid remains well towards 970 °K. Thus throughout the temperature range 680 to 970 °K a potassium sulphate-rich deposit will not be free from some liquid phase and so corrosion of metal heat exchange surfaces might be more severe than when normal oil ash is present. The physico-chemical study of the deposits must of course be supported by actual corrosion tests, simulating as accurately as possible, plant conditions. It is an aspect of seed behaviour which seems far removed from the m.h.d. duct, but it could impose an economic burden if superheater tubes had to be made more resistant, i.e. of higher chromium materials, than in conventional plant.

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