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SYNERGISTIC CAPTURE MECHANISMS FOR ALKALI AND SULPHUR SPECIES FOR COMBUSTION

Quarterly Report No. 9

for period September - November 1992

DOE Grant Number DE-FG22-90PC90285

Prepared by

T.W. Peterson, F. Shadman, J.O.L. Wendt, and P.O. Mwabe
Department of Chemical Engineering
University of Arizona
Tucson, AZ 85721

Submitted to

Felixa Eskey
Pittsburgh Energy Technology Center
U.S. Department of Energy
P.O. Box 10940
Pittsburgh, PA 15236-0940

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**SYNERGISTIC CAPTURE MECHANISMS FOR ALKALI AND SULPHUR
SPECIES FOR COMBUSTION**

Quarterly Report No. 7

for period March - May 1992

DOE Grant Number DE-FG22-90PC90285

Prepared by

T.W. Peterson, F. Shadman, J.O.L. Wendt, and P.O. Mwabe
Department of Chemical Engineering
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ALKALI CAPTURE MODELS IN A COMBUSTOR

The purpose of this chapter is to present mathematical models that can be used to reproduce the experimental results of Quarterly Reports 7 & 8. In doing so, more insight is shed into the experimentally observed phenomena.

The response surface results (from Quarterly Report #7) and one dimensional particle time-temperature history in a plug flow reactor, are combined to derive the apparent initial reaction rates. A detailed discussion of the assumptions and simplifications made and the limit of their applicability is presented. A computer package for parameter estimation is then used to fit the experimental initial rates to an Arrhenius type equation.

Transport parameters in the combustor are first estimated using the Chapman-Enskog equation and the equations for particle mass transfer coefficients in a quiescent fluid. These are then combined with the experimental results of the effect of particle size to estimate the intrinsic reaction rate kinetics. The two independent approaches are compared and are shown to agree closely. Next, a general capture model in a downflow plug flow combustor, in which it is shown that alkali capture can be predicted for the sodium alone and sodium with SO_2 using the same kinetic parameters by adjusting the effective dewpoint.

ESTIMATING THE INITIAL RATES OF REACTION

The purpose of this section is to estimate the initial reaction rates from response surface experimental results. First, both the particle temperature rate of change and particle velocity are approximated as series function of local flue gas temperature. Alkali

capture results from the response surface experiments is then expressed as a global integral of reaction rates, from which the derivative of the capture function is used to back up the initial reaction rate at point of injection. This can be done for first order reactions and for initial conditions only, because it is only at the limiting point of injection that the gas phase alkali concentration is known and sorbent structure is assumed to be still intact.

Assumptions

- (i) Plug flow reactor, hence a one dimensional flow of flue gas and particles.
- (ii) Low particle to fluid mass loading ($m_p/m_{fg} \ll 1$).
- (iii) Steady logarithmic temperature profile that is independent of capture reactions.
- (iv) Particle temperature follows closely the uncorrected flue gas temperature profile, and also particle velocity follows flue gas velocity.
- (v) Reaction is linear and first order with respect to local concentrations.
- (vi) The dewpoint is a unique point in the combustor between sorbent injection and sampling points, below which no further reactions take place.

Assumption (i), plug flow reactor, is necessary to enable the calculation of particle time temperature history from the measured flue gas temperature profile. This assumption may not hold near the injection point where eddies, particles bouncing off the walls and re-entrainment is expected to take place. Studies on the behavior of small particles (less than $10\ \mu\text{m}$), when injected into a quiescent fluid at $1000\ \text{cm/sec}$, show that the time scale for such particles to assume the characteristics of the fluid field is of the order of 10^{-3} seconds (Hinds, 1977).

Assumption (ii), low particle to fluid loading, is justified. The maximum sorbent flowrate was estimated at 5 gm/min for a flue gas mass flowrate of 450 gm/min, corresponding to a solid/fluid loading ratio of the order of 1 %.

Assumption (iii), steady logarithmic temperature profile independent of capture reactions, is a consequence of the post flame assumption that axial convection is dominant over conduction, no heat sources, and the dominant heat loss is only through the furnace walls. This assumption is much closer to experimental results than a linear temperature profile assumption. It is also not conceivable that any capture reactions can affect the temperature profile.

Assumption (iv), particle velocity and temperature follows that of the flue gas, has been shown to be true (Glass, 1981). In his calculations, the average deviation between particle velocity and that of the flue gas, is less than 2 %.

Assumption (v), linear first order reactions, has been shown by experimental results of the effect of alkali/sorbent loading ratio to be true. Linear assumptions are necessary if 'shooting' methods is to be applied to back up initial reaction rates.

Assumption (vi), that reactions are frozen at a unique point as indicated by the dewpoint, need to be considered in detail. This assumption requires that the thermodynamic dewpoint lie between the point of sorbent injection and the sampling point, and that the dewpoint acts as a distinct cut off point below which no further reactions take place. It is an idealization but one which is realistic as had been shown in thermodynamic equilibria studies. Under this assumption, rates can be extracted only if the dewpoint lie relatively closer to the sorbent injection point than to the sampling

point. Changing the injection point, in such a case, would result in a larger marginal change in the time scale available for gas-solid reactions. Experimental results shows that this is the case of the sodium and excess sulphur environment. In the case where the dewpoint is nearer the sampling point down stream, and if the time scale this represent is longer than that which is necessary for complete reaction, changing a sorbent injection point may not result in a difference in capture as there is still enough relaxation time for complete capture to take place. This is apparently the case with the results of sodium with excess chlorine and sodium only runs. The results from the excess chlorine and sodium alone environments reflect more of the marginal effect of sorbent sintering with temperature, than the effect of injection temperature on reaction rates. For these reasons, the experimental data for sodium with excess sulphur are the only ones to be used for deriving the initial reaction rates.

Velocity Profile

For a plug flow, constant cross section reactor, the conservation of mass and the ideal gas equation of state can be combined to give the first series approximation of the local flue gas velocity as a linear function of local flue gas temperature (θ). Flue gas molecular weight is estimated using the CET89 program. The flue gas velocity equation is then of the form:

$$v_f \text{ (cm/s)} = c \theta \quad (1)$$

At a mass flowrate of 450- 480 gm/min, the velocity temperature coefficient, c is 0.12 cm/K.sec

Temperature Profile

The post flame energy equation can be written in the form of;

$$c_p \dot{m}_{fg} \frac{d\theta}{dx} = k \frac{d^2\theta}{dx^2} - h(\theta - T_\infty) \quad (2)$$

with all parameters assuming their usual meaning. If the axial convective terms are taken to be dominant over axial conduction, Equation 2 becomes,

$$\frac{d\xi}{dx} = -\frac{h}{\dot{m}_{fg} c_p} \xi + \frac{T_\infty}{\dot{m}_{fg} c_p} \quad (3)$$

which gives a logarithmic temperature profile of the form:

$$\frac{d\theta}{dx} = -a\theta + b \quad (4)$$

At a constant mass flowrate of 450 gm/min, the mean values of parameters, a and b as; $a = -2.85 \times 10^{-3} \text{ cm}^{-1}$ and $b = 1.83 \text{ K/cm}$.

The time rate of change of a particle temperature, if taken to be uniform throughout the particle and follows that of the flue gas, can then be expressed as:

$$\frac{d\xi}{dt} = \frac{d\theta}{dx} \cdot \frac{dx}{dt} = (-a\xi + b) c \quad (5)$$

hence

and $a_1 = -3.42 \times 10^{-4}$, $a_2 = 0.2196$. Equation 6 will later be used as a time to temperature integral transform function expressed explicitly as:

$$dt = \frac{d\theta}{a_1\theta^2 + a_2\theta} \quad (6)$$

$$dt = \phi(\theta)d\theta$$

$$\text{with} \quad (7)$$

$$\phi(\theta) = \frac{1}{\theta(a_1\theta + a_2)}$$

Capture Reaction Formulation

Both Lagrangian and Eulerian formulations of alkali capture can be used to derive the capture equations. The practice adopted here is to use a Lagrangian formulation with respect to the 'particle phase' to derive the initial kinetics and later, use an Eulerian formulation with respect to the gas phase to predict global capture characteristics. The two formulations are coupled through the particle number density, which depends on the mean particle size and the alkali to sorbent loading ratio in the flue gas. A lagrangian formulation of a global capture function $g(t)$, for particles moving uniformly with flue gas and undergoing gas-solid reaction after injection is given as:

$$g(t) = \int_0^t R_g(c_p, \theta(t)) dt \quad (8)$$

The initial conditions are at $t=0$, $\xi=T$ and $C_i = p_i/RT$

R_g is the global capture rate in gm Na_2O /gm sorbent-sec, θ is the local flue gas temperature, and C_i is the local alkali gas phase concentration. For particle sizes under

2.0 μm , which were used in the response surface experiments, capture has been shown to be independent of particle size, hence $R_g(C_{\text{NaOH}}, \theta)$ is safely taken to be kinetically controlled, although it may also contain some parameter term to account for structural change with extent of reaction. Equation 8 is only useful if the alkali concentration is far in excess such that capture by particles does not change the volume concentration of alkalis in the flue gas. In a flow system, in which capture changes the alkali concentration significantly, it is important to re-express Equation 8 in terms of dimensionless initial alkali-sorbent loading ratio. The alkali to sorbent equivalence ratio(φ) remains constant and does not change with extent of capture, hence Equation 8 can be re written as:

$$g(\varphi, t) = \int_0^t R_g(\varphi, \theta(t)) dt \quad (9)$$

Provided that all experiments are carried at same initial alkali concentration, p_{io} , it can be taken for granted that $R_g(\varphi, \theta)$ is a unique, continuous and monotonic function. Equation 9 can be transformed into a temperature integral by introducing the time temperature transform Equation 7, together with the initial and final conditions that at $t=0$, $\theta=T$. and at the end condition that at $t = \tau_d$, $\theta = T_{\text{dwpt}}$.

Hence:

$$g(\varphi, \tau_d) \rightarrow g(\varphi, T) = \int_T^{T_{\text{dwpt}}} \frac{R_g(\varphi, \theta)}{\theta(a_1\theta + a_2)} d\theta \quad (10)$$

$g(\varphi, T)$ is the response surface experimental results that are presented in terms of alkali/sorbent equivalence ratio and injection temperature. Equation 10 is a function of

a limit parameter (injection temperature T), and temperature history, θ .

$g(\varphi, T)$ is in the form of :

$$I(\alpha) = \int_{a(\alpha)}^{b(\alpha)} f(\alpha, x) dx \quad 11$$

The derivative of Equation 11 can be obtained using Liebnitz theorem (Greenberg, 1988), and is given as:

$$I'(\alpha) = \int_{a(\alpha)}^{b(\alpha)} \frac{\partial f(\alpha, x)}{\partial \alpha} dx + f(b) \frac{db}{d\alpha} - f(a) \frac{da}{d\alpha} \quad 12$$

Applying Equation 12 to Equation 10, and by replacing $a(\alpha)$ with T , and $b(\alpha)$ with T_{dwpt} = constant, together with the fact that $R_g(\varphi, \theta)\phi(\theta)$ is not a function of T , then at constant initial alkali concentration, and fixed equivalence ratio, the derivative of the capture response surface is:

$$\frac{\partial g}{\partial T} = \frac{-R_g(\varphi, T)}{a_1 T^2 + a_2 T} \quad 13$$

from which the initial global reaction rate, $R_g(\varphi, T)$, at point of injection can be calculated. Combining Equation 13 with the response surface results of Table 1, the initial global reaction rate is given as:

$$R_g(\varphi, T) = -0.313\tau^3 + (0.486 + 0.162\varphi)\tau^2 - (0.166 + 0.0816\varphi)\tau$$

14

$$\tau = \frac{T(K)}{1273}$$

6.1.5 Apparent Intrinsic Reaction Rates

Experimental results showed that alkali capture was linear with respect to the equivalence ratio upto $\varphi=0.5-0.6$. It was also shown by both the AA bulk analysis and SEM analysis of individual reacted particles that 50% sorbent utilization is the maximum that could be obtained in our system. These observations lead to a further assertion that capture results at $\varphi=1$ approaches an excess alkali environment. The reaction rate parameters derived at $\varphi=1$ should, therefore, approach intrinsic parameters in which the effect of particle-particle interaction or the effect of particle 'starvation' is negligible.

$$R_g(1, \tau) = \sum_{k=1} a_k \tau^k$$

15

$$a_1 = -0.247$$

$$a_2 = 0.648$$

$$a_3 = -0.313$$

Equation 15 gives the experimentally derived initial reaction rates, in an excess SO_2 environment, which fall within the range of 0.08-0.10 gm Na_2O /gm sorbent/sec. The reaction rate per particle, R_p , becomes:

$$R_p = R_g \cdot \frac{\rho_p \pi d_p^3 (1-\epsilon)}{6} \left(\frac{\text{gm Na}_2\text{O}}{\text{particle. sec}} \right) \quad 16$$

For a first order gas-porous solid reaction, R_p can be expressed in terms of local alkali

concentration, particle diameter and particle porosity as:

$$R_p = k_{int} \cdot \frac{P_{NaOH}}{RT} \cdot \frac{\varepsilon \pi d_p^3}{6} \cdot 31 \quad (17)$$

$$R_p = \left(\frac{cm^3 \text{ gas}}{cm^3 \text{ solid. sec}} \right) \left(\frac{gmol}{cm^3 \text{ gas}} \right) \left(\frac{cm^3 \text{ solid}}{particle} \right) \left(\frac{gm \text{ Na}_2\text{O}}{gmol \text{ NaOH}} \right)$$

where the units of k_v is already shown to be in $cm^3 \text{ gas}/cm^3 \text{ porous solid. sec}$. Combining Equation 14, Equation 15 and Equation 16, and Equation 17, the kinetic reaction rate at $\varphi=1$, is then given as:

$$k_v(\tau) = \left(\frac{3.37 \times 10^3 \rho_p \cdot \frac{1-\varepsilon}{\varepsilon}}{P_{NaOH}} \right) \sum_{k=1} a_k \tau^{k+1} \quad 6.18$$

$$\tau = \frac{T(K)}{1273}$$

a_k 's are already given in Equation 6.15. Using the values for $\rho_p = 2.64 \text{ gm/cc}$, $\varepsilon=0.58$ (Tsuzuki, 1969; Uberoi, 1990), and $P_{NaOH} = 100 \text{ ppm}$ (corresponding to an alkali recovery of 40%), the rate parameter, k_v , can be calculated using Equation 18. A plot of Equation 6.18 is shown in Figure 1. with the rate found in the range : $4-10 \times 10^6$ ($cm^3 \text{ gas}/cm^3 \text{ solid. sec}$).

The form of Figure 1 suggest that the intrinsic rate can be fitted to an Arrhenius type equation of $k_v = k_0 \exp (-E/RT)$. The best fit of k_v is given by:

$$k_v = 4.5 \pm 0.5 \times 10^7 \exp (-5300 \pm 150 (\text{cal/gmol})/RT) \text{ cm}^3 \text{ gas}/\text{cm}^3 \text{ solid. sec}$$

Figure 1 also shows the best fits of k_v that was achieved with activation energy of 6, 10

and 20 kcal/gmol (values given in in the figure). It is apparent from the plot that activation energies between 6-10 kcal/gmol are realistic. However, activation energy of 20 and above did not give good fits. From this work the rate of sodium capture in gm Na₂O/gm sorbent.sec is best given by;

$$\frac{d[Na_2O]}{dt} = 0.0323 \, k_v \cdot V_s \cdot C_{Na} \quad 19$$

where [Na₂O] is in gm Na₂O per gm sorbent

$k_v = 4.5 \pm 0.5 \times 10^7 \exp (-5300 \pm 150(\text{cal/mol})/RT) \text{ cm}^3\text{gas}/\text{cm}^3\text{solid}.\text{sec}$

V_s = Sorbent pore volume in cm³/gm sorbent.

C_{Na} = Sodium concentration in gmol Na/ cm³ gas.

Figure 1: Initial reaction rate kinetics derived from experimental data.
 An activation energies under 10 kcal/gmol is shown to adequately fit the data with
 best fit achieved with 5.3 kcal/gmol

GOVERNING MECHANISMS OF CAPTURE

A coarse kaolinite (1-100 μm size) was used to evaluate effect of particle size on sorbent utilization, a phenomena that could not be discriminated from the narrow size-range particle experiments. The normalized results of sample 352, 353, 362, and 363 given in Quarterly Report #7, show that two regimes of alkali/ sorbent interactions exist. These are: (1) Small particle size range (below $3\mu\text{m}$), for which no size dependent capture is exhibited and (2) Large particle size range, for which a clear size dependence is shown. To evaluate the governing mechanisms, we first estimate relevant transport parameters such as bulk diffusivity, effective diffusivity and interface mass transfer coefficients. We then interpolate, from the experimental results, the particle size for which both transport and kinetic rates are in same order of magnitude. This is referred to as the point of inflection. If we assume that the gas solid reaction is first order with respect to gas phase concentration of sodium, then the point of inflection is independent of concentration or extent of reaction (Romans et al, 1990; Sohn and Szekely, 1972), but instead, depends only on the non dimensional ratios of reaction rates and transport rates.

Figure 2 show fraction particle utilization plotted against impactor lower cut off diameter for sample 352 and 353. The figure is derived by normalizing sorbent utilization with the utilization of the smallest particle size, in this case the $0.65\mu\text{m}$ particle.

Figure 2: Normalized sorbent utilization for run 352 and 353, showing the point of inflection at $2.00\mu\text{m}$ particle.

Two lines extrapolating regions of transport dependence and regions of kinetic dependence show that the particle size corresponding to the point of inflection is $2.0 \mu\text{m}$. At the point of inflection, the characteristic dimensionless ratio of transport rates to kinetic rates(either Damkholer number or Thiele modulus) are of the order of unity. With the transport coefficients known, an order of magnitude calculations for kinetic reaction rates was calculated for comparison. The possible governing mechanism can then be discriminated.

Gas Phase Alkali Concentration

In Quarterly Report #7, it was shown that flue gas alkali concentration backed from impactor samples is much lower than alkali concentrations that are calculated from feed flowrates to the furnace. Alkali concentrations, backed up from impactor results, is to be used in evaluating reaction kinetics. Table 1 show AA results for impactor 352 and 353. The sampling probe diameter is 0.336" and the furnace diameter is 6". Under isokinetic sampling conditions, the gas phase alkali concentration is calculated to be in the range of 65-70 ppm, which corresponds to an alkali recovery of 25%. A concentration of 70 ppm is consistent with the 100 ppm used previously in Section 6.1.

Table 1: AA data used to estimate gas phase alkali concentration

Impactor #	Sampling time (mins)	AA reading of total mass of Na sampled. (ppm in 30ml dissolving acid)	Equivalent flue gas concentration (ppm)
352	30	85.40	70.1
353	30	78.10	64.2

Two lines extrapolating regions of transport dependence and regions of kinetic dependence show that the particle size corresponding to the point of inflection is $2.0 \mu\text{m}$. At the point of inflection, the characteristic dimensionless ratio of transport rates to kinetic rates(either Damkholer number or Thiele modulus) are of the order of unity. With the transport coefficients known, an order of magnitude calculations for kinetic reaction rates was calculated for comparison. The possible governing mechanism can then be discriminated.

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352	30	85.40	70.1
353	30	78.10	64.2

Transport Coefficients

The Chapman-Enskog equation (Bird, Stewart & Lightfoot, 1960) for the molecular diffusivity of two gas pairs is given as:

$$D_{AB} = 1.8583 \times 10^{-3} T^{\frac{3}{2}} \frac{\left(\frac{1}{M_A} + \frac{1}{M_B} \right)^{\frac{1}{2}}}{p \sigma_{AB}^2 \Omega_{D,AB}} \quad 20$$

With D_{AB} in cm^2/s , T in K, p in atm, σ_{AB} in Angstrom units and $\Omega_{D,AB}$ is a dimensionless function of the temperature and the intermolecular potential field for a molecule of A and B. M_A and M_B are molecular weights of species A and B. In the absence of data for NaOH gas, $\text{CO}_2\text{-N}_2$ parameters (Reid et al, 1977) are used:

$$\Omega_{D,AB} = \left(\frac{\epsilon_A}{k} \cdot \frac{\epsilon_B}{k} \right), \quad \sigma_{AB} = \frac{1}{2} (\sigma_A + \sigma_B) \quad 21$$

	M_i	$\sigma_i(\text{\AA})$	ϵ/k
CO_2	44	3.941	195.2
N_2	28	3.798	71.4
Air	28.9	3.711	78.6

Sample calculations for D_{AB} at 1500 K is shown in Equation 6.22,

$$D_{\text{CO}_2\text{-N}_2} = \frac{1.858 \times 10^{-3} 1500^{\frac{3}{2}} \left(\frac{44+28}{44 \times 28} \right)^{\frac{1}{2}}}{(3.8695)^2 (0.842)} \quad 22$$

giving D_{AB} as $2.0 \text{ cm}^2/\text{s}$.

Knudsen diffusivity, for NaOH in metakaolinite, is determined by,

$$D_k = 9.70 \times 10^3 \frac{d}{2} \left(\frac{T}{M_A} \right)^{\frac{1}{2}} \quad 23$$

where d , is the average pore diameter in centimeters, and T is the temperature in Kelvin. Punjak (1988) measured the average pore size of metakaolinite as

$d = 180 \times 10^{-8} \text{ cm}$, and a porosity of 0.58. Substituting into Equation 23, the Knudsen diffusivity at 1500 K is $D_k = 0.054 \text{ cm}^2/\text{s}$. This compares with $0.036 \text{ cm}^2/\text{s}$ calculated by Punjak at 800°C . At such small pore size, Knudsen diffusivity would be expected to dominate. The effective diffusivity is calculated by Equation 24,

$$D_e = \left(\frac{D_{AB} D_k}{D_{AB} + D_k} \right) \quad 24$$

giving

$$D_e = 0.052 \text{ cm}^2/\text{s}$$

Film diffusion coefficient, k_m , can be calculated from Nusselt number correlation for a spherical particle in a fluid flow field by Equation 25 (Levenspiel, 1976):

$$Nu = \frac{k_m d_p}{D_{AB}} = 2 + 0.6 Sc^{\frac{1}{3}} Re^{\frac{1}{2}} \quad 25$$

Where Re is particle Reynolds number based on particle slip velocity and Sc is the fluid Schmidt number. For gases, Sc is of the order of unity. The velocity of particles of size less than $10 \mu\text{m}$ diameter, has been shown to approximate that of the flue gas velocity (Glass, 1981), making the particle Reynolds number to approach zero. A Nusselt

number of 2 is therefore justified. The film diffusion co-efficient becomes:

$$k_m = \frac{2D_{AB}}{d_p} \quad 26$$

Substituting Nu, and D_{AB} into Equation 25, the interface transport coefficient k_m for a $2.0 \mu\text{m}$ particle at 1500 K, is:

$$k_m = 2 \times 10^4 \text{ cm/s}$$

Kinetic Reaction Rate Parameters

The particle size for which both transport and kinetics are the same order of magnitude has been determined as $2.0 \mu\text{m}$. Runs 352 and 353 had sorbents injected at port 3, at a temperature of 1200°C (1500 K). The impactor derived gas phase sodium concentration was 70 ppm.

First, let us assume that the dominant transport controlling mechanism, for large particle size, is intraphase diffusion. The characteristic ratio of kinetics reaction rate and intraphase diffusion rate is the Thiele modulus. Thiele modulus, for a spherical reacting particle, assuming first order kinetics, is given as:

$$\phi = \frac{d_p}{6} \sqrt{\left(\frac{k_{\text{intr}}(1 - \epsilon_0)}{D_e} \right)} \quad 27$$

where k_{intr} is the volume intrinsic reaction rate in $\text{cm}^3\text{gas}/\text{cm}^3 \text{ solid} \cdot \text{sec}$, ϵ_0 is particle porosity and d_p is particle diameter in cm. The value of Thiele modulus for which both intrinsic rates and diffusion rates are same order of magnitude is suggested by Smith (1981) as 0.3. Substituting this in Equation 27, for a particle size of a $2.0 \mu\text{m}$, and an

effective diffusivity of 0.052 cm²/s, the intrinsic reaction rate parameter is calculated as:

$$k_{\text{intr}} = \left(\frac{0.09 \times 36 \times 0.052}{0.42 \times 4.0 \times 10^{-8}} \right) = 10.0 \times 10^6 \frac{\text{cm}^3 \text{gas}}{\text{cm}^3 \text{solid} \cdot \text{sec}} \quad 28$$

which compares very well with the apparent volume rates (k_v) that were calculated from the response surface analysis shown in Figure 1 which at 1500 K is, $k_v = 8.00 \times 10^6$ cm³gas/cm³solid.sec.

Now, let us assume that the controlling transport mechanism for the large particle size is the interface film diffusion. The characteristic dimensionless ratio of film diffusion rate and kinetic rate is the Damkholer number given as:

$$Da = \frac{k_{\text{intr}}(1-\epsilon)d_p}{6k_m} \quad 29$$

At point of inflection (2.00 μm particle), the suggested Damkholer number at which transport rate is same order of magnitude as kinetic reaction rate is 0.1 (Smith, 1981).

substituting, with k_m from Equation 25, the intrinsic reaction rate parameter is:

$$k_{\text{intr}} = 143.00 \times 10^6 \text{ cm}^3 \text{gas/cm}^3 \text{solid} \cdot \text{sec}$$

The latter value of k_{intr} is two orders of magnitude larger than that estimated from response surface experimental results. Consequently, film diffusion as a rate limiting step, is rejected. The same conclusion had been arrived at from the $1/d_p$ dependence of the experimental sorbent utilization results.

Governing Mechanisms of Capture

The conclusions from this Section are:

- The initial rate kinetics derived by response surface analysis are in close agreement with those estimated from coarse kaolinite experiments. These are two independent approaches that give the same result.
- The rate controlling step, for kaolinite particles of size range greater than $3.00\mu\text{m}$, is likely to be the intraphase diffusion. Kinetics is controlling for sizes under $3\mu\text{m}$.
- Sorbent utilization drops with increase in particle size, from typically 50% for a $2\mu\text{m}$ particle to under 10% utilization for a $10\mu\text{m}$ particle. This result is important in practical design and selection of sorbent size.
- The apparent activation energy calculated is much lower than that of the bench scale studies of Punjak (1988).
- No significance should be attached to the actual values of the apparent activation energies, as this may include all gas phase alkali-sorbent surface interactions including sorbent sintering which can not be isolated in our present set up. The overall rates, however, are realistic and reasonable. Further experimentation is necessary to determine the nature of surface reactions that govern alkali capture. It is evident that activation energies in the range of 10-20 kcal/gmol should give acceptable model results.
- Kinetic rates are correlated by a first order reaction with respect to sodium concentration in which $k_v = 6.0 \times 10^7 \exp(-6 \text{ kcal/RT}) \text{ cm}^3\text{gas/cm}^3\text{solid.sec}$

GENERAL CAPTURE MODEL IN A PLUG FLOW COMBUSTOR

The reaction of a porous particle with a gaseous species in a confined flow environment, is a fairly complex process whose complete analysis needs consideration of a large number of physical and chemical rate processes. It involves mass transport of gaseous reactants and products in the surrounding gas phase, mass transport in the interior of the porous particle, reaction on the internal and external surfaces of the particle and effects of structural changes that the particle undergoes as reaction proceeds. The problem of solving a classical diffusion reaction equation is further complicated with the difficulty in the choice of boundary conditions at the outer particle radius. Unlike the case of fixed bed reactors where the outer gas phase bulk concentration assumes a steady profile, and hence constant relative to the particle, in a continuous flow process described by our reactor, the particles 'see' a gas phase alkali concentration and bulk phase temperature that changes as the particle moves down the flowfield.

Development of Model Equations

The model of capture presented here consists of a series of first order ordinary differential equations of the initial value type. As was stated earlier, an Eulerian approach is to be adopted in this section. The capture equation is first formulated as a species conservation equation in the fluid phase. Auxiliary equations of particle number density, temperature profile, and the ideal gas law are then combined with conservation equation to solve for the alkali gas phase concentration profile along the axial length of the combustor. Assumptions that were discussed in earlier, also apply here. Unless otherwise stated, all symbols here are as have been used throughout the body of the text.

the text.

In order to develop appropriate mathematical relationships amongst the system variables, consider a small flow field bounded by the wall of the reactor and cross sections 1 and 2 at a distance Δx apart (Figure 3).

Figure 3: Flowfield (control volume) between section 1 and 2.

The gas phase conservation of species can be written as:

$$UC|_x - D_p \frac{dC}{dx} \Big|_x = UC|_{x+\Delta x} - D_p \frac{dC}{dx} \Big|_{x+\Delta x} - R_v \Delta x$$

30

$$\frac{d(UC)}{dx} - D_p \frac{d^2C}{dx^2} - R_v = 0$$

D_p is the reactor dispersion characteristics, which for a plug flow reactor, approaches zero. R_v is the reactor volumetric capture rate in $\text{gmol Na/ cm}^3 \text{ gas. sec.}$ R_v can be formulated to account for the effect of particle loading in the control volume in consideration. Two scaling assumptions are necessary to scale reaction rates that were derived at initial injection conditions at unity loading ratio. These are:

- Capture kinetics derived for $\varphi=1$, approaches that of intrinsic rates at excess alkali concentrations.
 - Capture scales linearly with respect to the net alkali concentration after injection.
- Consequently, the simplified formulation of the volumetric rate is a product rate per particle multiplied by the particle number density.

$$R_v(\varphi, \xi) = R_p(1, \xi) \cdot \frac{\#particles}{cm^3}(\varphi) \quad 31$$

Reaction rate per particle at a local alkali concentration p_i , and local flue gas temperature ξ , is given by

$$R_p(1, \xi) = k_0 e^{-\frac{E}{R\xi}} \left(\frac{p_i}{R\xi} \right) \left(\frac{\pi d_p^3 \epsilon}{6} \right) \quad 32$$

with k_0 , and E already been determined. The number of particles per unit volume of gas can be derived for a given initial alkali concentration p_{i0} and alkali/sorbent equivalence ratio(φ) as follows:

$$\dot{M}_{Na_2O} = \left(\frac{31 p_{i0} \dot{M}_{fB}}{M_{wfB}} \right) \quad 33$$

The initial total alkali/sorbent equivalence ratio(φ) is

where m_p is the sorbent (particle) mass flowrate. Particle number density is then given

$$\varphi = \frac{\dot{M}_{Na_2O}}{\dot{M}_p \times 0.27} \quad 34$$

as;

$$\frac{\# \text{ Particles}}{cm^3 \text{ gas}} = \left(\frac{M_w}{\dot{M}_{fg} R\xi} \cdot \frac{6\dot{M}_p}{\rho_p \pi d_p^3 (1-\epsilon)} \right) \quad 35$$

Combining Equation 33 and Equation 34, Equation 35 becomes;

$$\left(\frac{\# \text{ Particles}}{cm^3} \right) = \left(\frac{1}{0.27\varphi} \right) \cdot \left(\frac{186}{\rho_p \pi d_p^3 (1-\epsilon)} \right) \cdot \left(\frac{P_{io}}{R\xi} \right) \quad 36$$

The volumetric reaction rate of Equation 31 in $gmol \text{ Na}/cm^3 \text{ gas} \cdot sec$, at any alkali concentration, and any alkali/sorbent equivalence ratio is then given as:

$$R_v(\varphi, \xi) = \left(\frac{1}{0.27\varphi} \right) \cdot \left(\frac{P_{io}}{R\xi} \right) \cdot \left(\frac{\epsilon}{1-\epsilon} \right) \cdot \left(\frac{31}{\rho_p} \right) \cdot \left(k_o e^{-\frac{E}{R\xi}} \right) \cdot \frac{P_i}{R\xi} \quad 37$$

It is noted that all terms in Equation 37 are known with the only adjustable parameters being the kinetic terms of k_o and E . Returning to the gas phase capture balance Equation 30 and with the dispersion term already dropped, the gas phase equation can be written as:

The auxiliary equations are:

$$\frac{d}{dx}(UC_i) = -\left(\frac{1}{0.27\varphi}\right)\left(\frac{p_{io}}{R\xi}\right)\left(\frac{\epsilon}{1-\epsilon}\right)\left(\frac{31}{\rho_p}\right)\left(k_o e^{-\frac{E}{R\xi}}\right)\frac{p_i}{R\xi} \quad 38$$

$$\frac{d\xi}{dx} = -a\xi + b$$

$$C_i = \frac{p_i}{R\xi} \quad 39$$

$$U = c\xi$$

Combining Equation 38 and 39, the capture equation is in the form:

$$\frac{dp_i}{dx} = -\beta(p_{io}, \varphi, k_o, E, \xi) p_i \quad 40$$

$$\beta = -\left(\frac{31}{0.12}\right)\left(\frac{1}{0.27\varphi}\right)\left(\frac{p_{io}}{R\xi^2}\right)\left(\frac{\epsilon}{1-\epsilon}\right)\left(\frac{1}{\rho_p}\right)k_o e^{-\frac{E}{R\xi}}$$

The initial conditions at point of injection x_o , are:

$$\begin{aligned} \xi(x_o) &= T \\ p_i(x_o) &= p_{io} \end{aligned} \quad 41$$

The model parameters are $\rho_p = 2.64$ gm/cc, $\epsilon = 0.58$, $R = 82.05$ cm³atm.g-mol⁻¹K⁻¹, 1.987 cal/gmol K, $p_{io} = 100 \times 10^{-6}$ atm, $k_o = 5.97 \times 10^7$ cm³ gas/ cm³ solid.sec and $E = 6$ kcal/gmol.

Equation 40 is a linear first order ODE and can be solved numerically by the implicit trapezoidal computation scheme. The trapezoidal rule combines the inherent stability of the implicit schemes with the added advantage of a second order accuracy

(Ferziger,1981). The computation scheme is implemented in FORTRAN program MODEL.FOR and is included in the appendix. Step by step computation is carried with the stop conditions set by the alkali dewpoint, the sampling point, complete alkali capture or maximum sorbent utilization.

The first approach is to use the model parameters to predict sodium capture in the sodium and excess SO_2 environment. This is the same environment from which the kinetic parameters were extracted. Some form of close agreement would naturally be expected. It is expected that some form of over prediction should be the case as we use the initial kinetics that are linearly scaled with respect to alkali concentration. An improvement in this model would require inclusion of some structural parameter term that changes with the extent of particle conversion. Parametric studies can, however, be carried for this system to investigate marginal effect of choice of such parameters as the activation energy, and the probable alkali dewpoint.

The next step is to investigate the use of the same model parameters on an independent environment. In our earlier arguments, the effect of SO_2 on sodium capture was attributed, to a large extent, on the changed dewpoint. The model parameters can then be applied to the sodium alone system by using the dewpoint position corresponding to sodium only environment.

Modelling of the sodium with chlorine system will first be attempted using the bench scale kinetic parameters of Uberoi (1990). A later modification of the bench scale kinetics, in which the reactant was proposed to be sodium hydroxide in equilibrium with sodium chloride, was suggested by Gallagher (1992). Using the present model and the

experimental data derived from sodium alone environment, comparisons can be made between the two kinetics and the unlikely reaction mechanism can be eliminated.

Model Results

The simulation results for sodium capture profiles in an excess SO_2 environment is shown in Figures 2 and 3. In this simulation, sorbents were injected at port 3 at a temperature of 1600 K. It is shown that 99% capture in under 1 second can be achieved by a kaolinite flowrate that is equal to an alkali to sorbent equivalence ratio of 0.1- 0.25.

Figure 4 shows a comparative plot between experimental results of capture response surface for sodium in excess SO_2 , regression fit of the same capture response surface, and model predicted results. These plots show that what has been observed experimentally can be described mathematically, which was the purpose of our modelling. Different capture characteristics can then be predicted in the same manner by adjusting the kinetic and dewpoint parameters.

Figure 5 shows model prediction results plotted against experimental results for sodium in excess SO_2 environment. Overprediction is shown which is consistent with what was expected.

Figure 2: Model prediction of percent alkali capture at various alkali/sorbent equivalence ratio plotted against furnace axial distance.

Figure 3: Model prediction of unaptured alkali concentration along the furnace for various alkali/sorbent equivalence ratio.

Model prediction using best fit kinetic parameters that have been derived from the same data.

$$k_o = 5.97 \times 10^7 \text{ cm}^3 \text{ gas/cm}^3 \text{ solid.sec}$$

$$E = 6 \text{ kcal/mol}$$

$$T_{dwp} = 1100 \text{ K}$$

Sodium (100 ppm), SO_2 (500 ppm)

Figure 5: Model prediction of water insoluble sodium capture plotted against experimental results. The kinetic parameters used in the model were derived from same results.

Model Prediction in Sodium Only Environment

Thermodynamic equilibria studies showed that the dominant gas phase species in the case of sodium alone and sodium with SO_2 is sodium hydroxide. An extension of this observation was that the effect of SO_2 on alkali capture is through the elevated dewpoints of the condensate sulfate which results in reduced gas phase residence time. Experimental results of previous reports showed that the presence of SO_2 resulted in a slight reduction in capture of under 10% at 1300°C , with larger reductions at lower temperatures which were attributed to the effect of raised dewpoint. It follows that the kinetics of capture reactions derived from sodium with SO_2 environment should give good prediction of capture in sodium only environment if the above arguments are to be valid.

Figure 6 shows model prediction of sodium capture in sodium alone environments, using sodium in excess SO_2 kinetics, plotted against experimental results. A dewpoint of 973 K has been used in the prediction calculations. Extrapolation of the continuous capture results shows that a dewpoint of 973 K is the likely one for sodium alone case.

Good agreement between experimental results and model prediction is shown. It is noted that in this case both kinetic parameters and experimental data were obtained independently. The results of this section confirm the hypothesis that in both sodium alone and sodium with SO_2 , capture reactions proceed as a gas solid reaction between sodium hydroxide and metakaolinite.

Model prediction of sodium capture in sodium only environment using best fit kinetic parameters that were derived from sodium in excess SO₂ environment.

$$k_0 = 5.97 \times 10^7 \text{ cm}^3 \text{ gas/cm}^3 \text{ solid} \cdot \text{sec}, E = 6 \text{ kcal/mol}, T_{\text{dwpt}} = 973 \text{ K}$$

Figure 6: Model prediction of sodium capture in sodium only environment plotted against experimental results.

Effect of Chlorine

Bench scale capture studies of Uberoi (1990) analyzed sodium capture results by proposing that sodium chloride reacts with metakaolinite to form nephelite as given in Equation 42

The simulated flue gas in the bench scale experiments was 80% N₂, 15% CO₂, 3% O₂, 2% H₂O, and between 50 and 500 ppm Na, at a temperature of 800°C. The kinetics of this reaction was then given as $k_o = 1.92 \times 10^{10} \text{ cm}^3 \text{ gas/ cm}^3 \text{ solid} \cdot \text{sec}$, $E = 32 \text{ kcal/mol}$. If indeed the above reaction proceeds through the hydroxide-metakaolinite reaction, then complete reaction mechanism can be written as;

Gallagher (1990) suggested that the rates that were calculated using Equation 42 could have been underestimated especially if the effect of water in the system was not accounted for. To account for NaCl-NaOH-H₂O equilibria, it was then proposed that the species of interest can be related by stoichiometry as follows.

$$[NaCl] = [Na] - [NaOH] \quad 45$$

$$[HCl] = [NaOH] \quad 46$$

$$[H_2O] = [H_2O]_o - [NaOH] \approx [H_2O]_o \quad 47$$

where $[Na]$ is total sodium concentration and $[H_2O]_o$ is the total water concentration which is much higher than other reactants' concentration. These relationships can be used in an equation for the equilibrium coefficient K_{eq} .

$$K_{eq} = \frac{[NaOH] [HCl]}{[NaCl] [H_2O]} = \frac{[NaOH]^2}{([Na] - [NaOH]) \cdot [H_2O]_o} \quad 48$$

The concentration of NaOH can then be found explicitly.

$$[NaOH] = \frac{1}{2} (-K_{eq}[H_2O]_o + \sqrt{(K_{eq}^2[H_2O]_o^2 + 4K_{eq}[H_2O]_o[Na])}) \quad 49$$

The initial reaction rate given by Uberoi (1990) was calculated with respect to total sodium concentration $[Na]$ and can now be transformed to a reaction rate with respect to NaOH concentration such that

$$\begin{aligned} \text{Rate} &= k[Na] = k'[NaOH] \\ k' &= \frac{k[Na] \text{ Bench scale}}{[NaOH]} \end{aligned} \quad 50$$

The transformed rates can be written as

$$k' = \frac{k [Na]}{\frac{1}{2} (-K_{eq}[H_2O]_o + \sqrt{(K_{eq}^2[H_2O]_o^2 + 4K_{eq}[H_2O]_o[Na])})} \quad 51$$

where k is the bench scale kinetics of Uberoi (1990)

Since the NaOH concentration is much lower in the presence of sodium, it can be seen that the transformed rates should be much higher than what was calculated in bench scale. Using the results of Equation 51, Gallagher calculated new modified intrinsic rates from the bench scale kinetics as given in Table 1

Table 1 Sodium reaction rate calculations

Temp (K)	1023	1073	1148
ΔG°_f (kJ/gmol)	127.24	127.29	127.35
In (K_{eq})	-14.96	-14.27	-13.34
[Na] (ppmv)	55	127	482
[NaOH] (ppmv)	0.6	1.3	3.9
In k (Bench scale)	16.13	16.86	17.84
In k' (Transformed)	20.66	21.47	22.65

Figure 7 shows results of model predicted sodium capture using the bench scale kinetics of Uberoi (1990) and the transformed kinetic data as suggested by Gallagher (1992) which has been reproduced in Table 1, plotted against our experimental capture results that were obtained in a sodium alone environment. The results show no correlation between experimental results and model predictions using the bench scale kinetics. On the other hand, good correlation is shown between experimental results and model prediction using the transformed kinetics. It is concluded from these results that in the presence of chlorine and water, the capture reactant is the hydroxide.

Figure 7 Model prediction of sodium capture in a sodium only environment plotted against experimental results. Kinetic parameters from Uberoi (1990) and Gallagher (1992) are compared.

This Work in Perspective

The capture reaction model presented in this chapter can be used to reproduce experimentally observed phenomena. It has been applied successfully as a predictive model to carry out parametric studies on the effect of k_p , E and the dewpoint on overall capture. It has also been used to resolve the issue as to what species, NaCl or NaOH, participates in sodium metakaolinite capture reaction. The bench scale kinetics of Uberoi (1990) which appear extremely slow, give model prediction results that correlate well with experimental data, but only after they have been transformed to account for the NaCl-NaOH-H₂O equilibria. This work has shown conclusively that in all the three cases considered, sodium alone, sodium with chlorine and sodium with SO₂, it is the gas phase sodium hydroxide that reacts with metakaolinite to form nephelite. Whereas the effect of sulfur sodium capture is exhibited through the changed dewpoint, that of chlorine has been shown to be exhibited through changed gas phase equilibria composition.

The fast reaction rates and intrinsic kinetic parameters that have been extracted in this work need to be considered in perspective with those of previous workers. First, there is no doubt that significant alkali capture was recorded. EDX analysis results independently confirmed the results of the AA analysis and hence the order of magnitude of water insoluble sodium content. The sorbent residence time scales were of the order of 1-2 seconds and so the reaction rates so far calculated are reasonable. Second, the kinetic parameters that were extracted from sodium with excess SO₂ runs were applied in our model to predict the results sodium alone runs with very good results achieved.

It is thus clear that both the reaction rates and the kinetic parameters extracted are realistic. The apparent activation energy that fits our experimental results, however are much lower than previously reported. By varying both the pre-exponential factor, k_0 and the apparent activation energy, E , we have shown that good agreement between model prediction and experimental data can still be achieved upto $E=10$ kcal/mol. Activation energy of 20 kcal/mol however, does give poor prediction of alkali capture. The transformed bench scale kinetic parameters with an activation energy of 37 kcal/mol show good prediction results but only in a narrow temperature range between 1000°C - 1100°C. Figure 8 shows that the transformed kinetics tend to over predict at high temperatures and under predicts at low temperatures. Our kinetics predict experimental data with the same consistency across the temperature range. Given that bench scale kinetics were obtained from single temperature experiments, while our present kinetics have been obtained from a wide temperature range, we believe that the kinetics derived in this work best describes mechanisms that govern alkali capture in a combustor.

Model prediction using:

Left : Kinetics of Uberoi (1990) as modified by Gallagher (1992)

Right: Kinetics from this work

Figure 8: Percent deviation between model predicted capture and experimental capture, plotted against sorbent injection temperature. Kinetic parameters from this work gives better prediction at all temperatures.

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APPENDIX : LISTING OF COMPUTER PROGRAM MODEL.FOR

```

      IMPLICIT REAL *8 (A-H,O-Z)
      REAL *8 K0
      CHARACTER *20 OUTPUT,INPT2,LOOP
      COMMON /PARA/K0,E,PHI,A,B,C,PA0,RHOP,POR

      LOOP='TRUE'
C     THIS PROGRAM PREDICTS ALKALI CAPTURE IN THE KINETICALLY
CONTROLLED REACTION
C     REGIME
C     The program stops iteration when either temperature is below the dewpoint
C     or the sampling point is reached
C     or all the alkali is captured, PA=0
C T     Temperature in K
C Pa0   Gas phase initial concentration ppm
C PA    Gas phase concentration of NaOH in ppm
C PHI   Alkali to sorbent equivalence ratio
C Theta BET surface function, theta=1 at injection
C G     Capture by reaction in gm Na2O/gm sorbent
C X     Furnace axial position in cm
C A,B   Temperature profile constants dT/dX=aT+b
C C     Particle velocity profile dX/dt=cT
C Alpha Empirical constant for particle sinter
C R     Gas constant 1.987 cal/gmmol
C
      POR=0.58

      OPEN(UNIT=7,FILE='INPUT.TXT',STATUS='OLD')
      READ(7,10) OUTPUT
      READ(7,10) INPT2
10     FORMAT(A12)
      READ(7,*) K0,E,RHOP,A,B,C
      READ(7,*) PHI,PA0,X,T,TDWPT,DX
      CLOSE(7)
      OPEN(UNIT=8,FILE=OUTPUT,STATUS='UNKNOWN')
      WRITE(8,*) 'CAPTURE MODEL FOR ',OUTPUT,'E=',E
      WRITE(8,20)'T','ER','g* expt','g* model'
20     FORMAT(A12,2X,A12,2X,A12,2X,A12)
      PA0=PA0*1E-6
C     Start computation
      OPEN(UNIT=9,FILE=INPT2,STATUS='OLD')
      DO WHILE('TRUE')
        READ(9,*,END=70)TEMP,PHI,GEXPT
        TEMP=TEMP*1273
        DO WHILE(T.GT.TEMP)
          A1=1-A*DX/2
          A2=1+A*DX/2
          A3=B*DX

```

```

        T=T*A1/A2+A3/A2
        X=X+DX
    ENDDO
T2=T
PA=PA0
CAPT=0
DXP=10
GS=0
DO WHILE(X.LE.388)
    CALL RV(T,ALPHA,BETA)
    A1=(1-ALPHA*DX/2)
    A2=(1+ALPHA*DX/2)
    A3=BETA*DX
    PA=PA*(A1/A2)+A3/A2
    X=X+DX
    CAPT=100*(PA0-PA)/PA0
    GS=0.27*PHI*(PA0-PA)/PA0
    A1=1-A*DX/2
    A2=1+A*DX/2
    A3=B*DX
    T=T*A1/A2+A3/A2
    IF(T.LE.TDWPT) GOTO 50
    IF(GS.GE.(0.13))GOTO 50
ENDDO
50  WRITE(8,60)T2/1273,PHI,GEXPT,GS
60  FORMAT(F8.4,8X,F6.3,8X,F7.4,8X,F7.4)
    T=1600
    X=30
    ENDDO
70  STOP
    END

C    Volumetric rate calculations
    SUBROUTINE RV(T,ALPHA,BETA)
    IMPLICIT REAL *8(A-H,O-Z)
    REAL *8 K0
    COMMON /PARA/K0,E,PHI,A,B,C,PA0,RHOP,POR
    R=1.987
    R2=82.05
    RT=EXP(-E/R/T)
    RT=k0*RT*PA0*31*POR/(((1-POR)*R2*T*T*0.27*PHI*RHOP)
    RT=RT/C
    BETA=0
    ALPHA=RT
    RETURN
    END

```

Input file for MODEL.FOR

SOEXPT.TXT

SO2EXPT.DAT

5.97E7,6000,2.64,0.002847,1.83,0.12

1.0,100,30,1600,1123,2

LINE 1 : OUTPUT FILE NAME

LINE 2 : FILE CONTAINNING EXPERIMENTAL RESULTS TO BE COMPARED

LINE 3 : k_0 , E, Particle density (g/cc), Temperature gradient coefficients

A,B: $dT/DX=AT+B$ and flue gas velocity coefficient C, $dX/dt=CX$

LINE 4 : ϕ , Initial sodium concentration (ppm), Initial conditions for temperature profile; X, T(K)

TDWPT (dewpoint temperature) and DX.

END

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