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Interactions Between Trace Metals, Sodium and Sorbents in Combustion.

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INTRODUCTION

The proposed research is directed at an *understanding* of how to exploit interactions between sodium, toxic metals and sorbents, in order to optimize sorbents injection procedures, which can be used to capture and transform these metals into environmentally benign forms. The research will use a 17kW downflow, laboratory combustor, to yield data that can be interpreted in terms of fundamental kinetic mechanisms. Metals to be considered are lead, cadmium, and arsenic. Sorbents will be kaolinite, bauxite, and limestone. The role of sulfur will also be determined. The research is divided into five tasks.

Task 1: Combustor Modifications.

The existing laboratory combustor will be modified to allow injection of toxic metal surrogates, and withdrawal of particulate samples for subsequent analysis, without allowing leaks to impact the laboratory room environment.

Task 2: Screening Experiments.

Surrogate trace metals (3, listed above) will be injected through an otherwise "clean" gas flame stabilized in the combustor. Sorbents (3, listed above) will be injected through a port downstream. For each metal/sorbent pair, a statistically correct set of parametric experiments will be performed, quantitatively to determine the effects of a) sodium level, b) sulfur level, c) sorbent injection temperature, d) sorbent residence time, on trace metal capture. Measurements consist of the size segregated composition of the exhaust particulate matter. The objective function is the fraction of metal reactively captured by the sorbent. Solid and surface analyses will provide insight into mechanisms.

Task 3: Mechanisms.

Selected runs (6) from Task 2 will be repeated to obtain time resolved data on metal partitioning, with and without sodium and sulfur. The purpose will be to glean rates and mechanisms from size segregated particulate samples withdrawn. Advanced surface and solid analyses of sampled particulates will aid in mechanism building.

Task 4: Applications.

Three different, well characterized, pulverized coals will be burned, and the partitioning of the three toxic metals, in the presence of sorbents, examined, in the light of the mechanisms uncovered in Tasks 2 and 3. These mechanisms will also be used to determine the optimum application of sorbent injection in the presence of sodium and sulfur.

Task 5: Mathematical Modelling.

Tasks 2 through 4 will be accompanied by mathematical modeling. Empirical model building will be used in Task 2 to correlate, and interpolate the data. Deterministic and mechanistic modeling will be used to correlate and extrapolate the data of Tasks 3 and 4. This modelling will involve models of a) gas/solid reactions, and the appropriate particle size dependencies, b) gas phase reactions, either through partial/global equilibrium arguments (using CET89 software), or through CHEMKIN based detailed reactions, c) aerosol dynamics (using MAEROS), as required and appropriate.

PROGRESS FOR THIS QUARTER

Task 1: The construction of the mini-baghouse and associated equipment is proceeding according to plan. The projected completion date for this portion of this task is December 1, 1995.

Task 5: Development of the anticipated models for examination and analysis of data in Tasks 3 and 4 has begun. A shrinking core model will be used to model the mechinism of mass transfer and reaction in the sorbent particle. The derivation of the model is as follows.

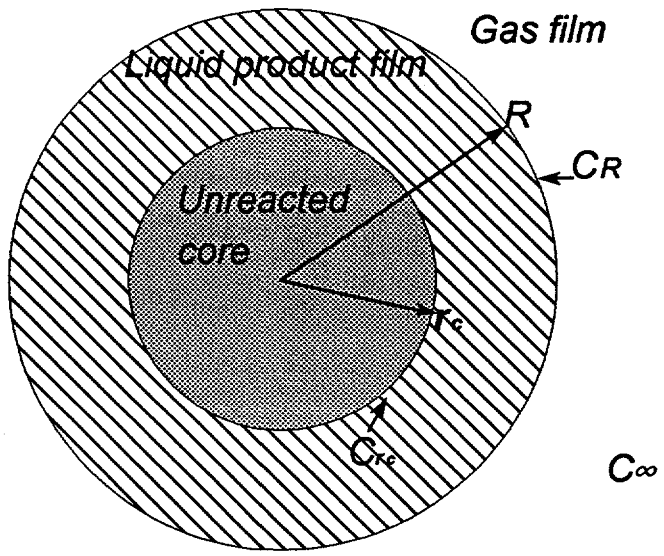
Consider a shrinking core model, with diffusion through gas film, diffusion through product layer, reaction at a thin layer which recedes to make a shrinking core of unreacted reactant (sorbent).

Assumptions:

1) Spherical particles, of *unchanging total radius R.*

2) Reaction occurs at a plane, at radius $r = r_c$, i.e. no pore diffusion (to be incorporated later).

3) Pseudo steady state, i.e. time to establish steady state is short compared to characteristic time of the process or, $\frac{R}{k_{eff}} \ll t_{characteristic}$ where an expression for k_{eff} is derived below.



Consider the following flows of metal species, W_i, all in units of g-mole/s: through stagnant gas film, assuming a Sherwood Number =2:

$$W_i \quad \frac{moles}{s} \quad = \quad - 4\pi R\, D_M\, (C_\infty - C_R) \tag{1}$$

through product film:

$$W_i \quad \frac{moles}{s} \quad = \quad - \frac{4\pi R\, r_c}{R - r_c} D_{eff}\, (C_R - C_{r_c}) \tag{2}$$

and by reaction at the plane given by $r = r_c$:

$$W_i \quad \frac{moles}{s} \quad = \quad - 4\pi\, r_c^2\, k_{rxn}\, C_{r_c} \tag{3}$$

Eliminating concentrations at the interfaces, the nett consumption rate of metal species i is given by:

$$W_i \quad \frac{moles}{s} = -4\pi R^2 k_{eff} C_\infty \tag{4}$$

where:

$$\frac{1}{k_{eff}} = \frac{R}{D_M} + \frac{R(R - r_c)}{r_c \ D_{eff}} + \left(\frac{R}{r_c}\right)^2 \frac{1}{k_{rxn}} \tag{5}$$

The first term represents (stagnant) gas film diffusion, the second term represents diffusion through a product layer with effective diffusivity D_{eff}, while the third term represents reaction at the plane at radius r_c. The units of each term are in [s/m] or [s/cm] as the case may be.

Now, the shrinking core model with unchanging radius R, allows the conversion of substrate, χ, to be given by:

$$\chi = 1 - \left(\frac{r_c}{R}\right)^3 \tag{6}$$

allowing R/r_c in **Eq (5)** to be eliminated thus:

$$\frac{R}{r_c} = (1 - \chi)^{-\frac{1}{3}} \tag{7}$$

Hence:

$$\frac{1}{k_{eff}(\chi)} = \frac{R}{D_M} + \frac{R[(1-\chi)^{-\frac{1}{3}} - 1]}{D_{eff}} + \frac{(1-\chi)^{-\frac{2}{3}}}{k_{rxn}} \tag{8}$$

Now, if S is the sorbent substrate:

$$\frac{d\chi}{dt} = -\frac{1}{n_S{}^0}\frac{dn_S}{dt}$$
$$= \frac{k_{eff}(\chi)\, 4\pi\, R^2 C_\infty}{\frac{4}{3}\pi\, R^3 \frac{\rho_S}{MW_S}} \tag{9}$$
$$= \frac{3\, k_{eff}(\chi)\, C_\infty}{R\frac{\rho_S}{MW_S}}$$

and so:

$$\frac{1}{k_{eff}(\chi)}d\chi = \frac{3C_\infty}{R\frac{\rho_S}{MW_S}}dt \tag{10}$$

or, substuting for $k_{eff}(\chi)$, and integrating, we get:

This is consistent with the formulation of Szkeley, Evans and Sohn[1], (p81, § 3.3.3) namely:

where:

$$p_{Fp}(\chi) = 1 - 3(1-\chi)^{\frac{2}{3}} + 2(1-\chi) \tag{13}$$

$$\int_0^\chi \left[\frac{R}{D_m} + \frac{R}{D_{eff}}\left((1-\chi)^{-\frac{1}{3}} - 1\right) + \frac{1}{k_{rxn}}(1-\chi)^{-\frac{2}{3}}\right]d\chi = \frac{3C_\infty}{R\frac{\rho_S}{MW_S}}t \tag{11}$$

$$t^* = g_{Fp}(\chi) + \sigma_s{}^2\, p_{Fp}(\chi) \tag{12}$$

and

$$g_{Fp}(\chi) = 1 - (1-\chi)^{\frac{1}{3}} \tag{14}$$

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[1] Szekely, J., Evans, J.W., Sohn, H.Y. Chapter 3 in Gas-Solid Reactions, Academic Press, New York (1976)

and

$$t^{*} = \frac{k_{rxn}}{\frac{\rho_S}{MW_S}R} C_A^{\infty} t$$
$$\sigma_s^2 = \frac{k_{rxn}R}{6D} \tag{15}$$

Consequently:

$$\frac{R\chi}{D_M} + \frac{R}{2D_{eff}}\left[1 - 3(1-\chi)^{\frac{2}{3}} + 2(1-\chi)\right] + \frac{3}{k_{rxn}}\left[1 - (1-\chi)^{\frac{1}{3}}\right] = \frac{3C_{\infty}\ t}{R\frac{\rho_S}{MW_S}} \tag{16}$$

which is consistent with **Equation 12** (same as Eq 3.3.33, of Skeley et al. ,1976), with the gas film diffusion term neglected.

Let the overall metal sorbent reaction be given as:

$$\mathbf{M}(\mathit{metal}) + \mathbf{S}(\mathit{sorbent}) \rightarrow \mathbf{R}(\mathit{rxn\ product}) \tag{17}$$

W, the weight fraction metal in the partially reacted particle isgiven by:

$$\begin{aligned} W &= \frac{gm\ metal}{gm\ particle} \\ &= \frac{moles\ R \times MW_M}{initial\ moles\ S \times [(1-\chi)MW_S + \chi MW_R]} \\ &= \frac{n_S^0\,\chi \times MW_M}{n_S^0\,[(1-\chi)\times MW_S + \chi \times MW_R]} \end{aligned} \tag{18}$$

or *W* is related to χ thus:

$$W = \frac{\chi MW_M}{MW_S + \chi(MW_R - MW_S)} \tag{19}$$

Combining **Equations 16** and **19**, it is possible to obtain a relationship between *W* and R, for various values of the other parameters. R can be solved from the quadradic equation:

$$R = \frac{-B + \sqrt{B^2 + 4A}}{2A} \tag{20}$$

where:

$$\begin{aligned} A &= \frac{\frac{\rho_S}{MW_S}}{3C_\infty t}\left[\frac{\chi}{D_M} + \frac{1 - 3(1-\chi)^{\frac{2}{3}} + 2(1-\chi)}{2D_{eff}}\right] \\ &= \frac{\frac{\rho_S}{MW_S}}{3C_\infty}\left[\frac{1}{D_M \tau_2} + \frac{1}{2D_{eff}\tau_1}\right] \\ \tau_2 &= \frac{t}{\chi} \\ \tau_1 &= \left[\frac{t}{1 - 3(1-\chi)^{\frac{2}{3}} + 2(1-\chi)}\right] \end{aligned} \tag{21}$$

and:

$$\begin{aligned} B &= \frac{\frac{\rho_S}{MW_S}}{C_\infty k_{rxn} t}\left[1 - (1-\chi)^{\frac{1}{3}}\right] \\ &= \frac{\frac{\rho_S}{MW_S}}{C_\infty k_{rxn}}\left[\frac{1}{\tau_3}\right] \\ \tau_3 &= \left[\frac{t}{1 - (1-\chi)^{\frac{1}{3}}}\right] \end{aligned} \tag{22}$$

For product layer diffusion control only:

$$R_{product\ layer\ control} = \sqrt{\frac{\tau_1 6D_{eff}C_\infty}{\frac{\rho_S}{MW_S}}} \tag{23}$$

For gas film control only:

$$R_{gas\ film\ control} = \sqrt{\frac{\tau_2 3D_M C_\infty}{\frac{\rho_S}{MW_S}}} \tag{24}$$

For reaction control, at the surface at r_c,:

$$R_{reaction\ control} = \frac{\tau_3 k_{rxn} C_\infty}{\frac{\rho_S}{MW_S}} \tag{25}$$

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