CONDENSATION PROCESSES IN
COAL COMBUSTION PRODUCTS

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ABSTRACT

Slag vaporization is a serious problem in high-temperature coal combustion and gasification processes. Cooling of process gas streams causes the slag vapors to condense, but they do not necessarily do so at equilibrium. Predicting the compositions and properties of the condensing species requires modeling the nucleation processes occurring in these systems.

This is a report on our progress toward modeling this nucleation process and toward implementing the model with a computer code suitable for design calculations.

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INTRODUCTION

An important difference between coal and the other common sources of energy, i.e., oil and natural gas, is that in addition to the combustible material, coal contains significant quantities of normally involatile material commonly referred to as slag. In high temperature combustion and gasification processes, the slag will vaporize, ionize, and significantly change in chemical composition. As the combustion or gasification gases cool on subsequent passage through process equipment, the slag will condense, often with very deleterious effects. For example, in gasification processes even small concentrations of slag vapors can result in poisoning of catalysts and fouling (with eventual plugging) of heat exchanger tubes. In the Open-Cycle Gas Turbine Process the gas must be scrubbed to remove both solid particles and slag vapors. If slag vapors are not removed before the turbo-expander, nucleation will occur in the expander, leading to erosion of the turbine blades and excessive wear on other moving parts.

In MHD power generation, slag condensation is also detrimental. Slag particles or aerosols greatly decrease the electrical conductivity of the combustion plasma and are therefore usually removed from the combustion gas before entering the MHD channel. Slag rejection is also necessary to reduce seed losses and to prevent excessive fouling of the MHD electrode surfaces. However, problems can occur even under high-slag-rejection conditions because of aerosols which can form by the nucleation of the previously vaporized silicates. The high-work-function droplets

thus formed will dramatically decrease the electrical conductivity of the combustion plasma and thereby reduce the power generation. Martinez-Sanchez, Kolb and Kerrebrock (1) have shown that in small, research-sized generators, the cooling which occurs in the MHD channel is too small to cause any condensation, but that in large, base-load, MHD plants the cooling is more rapid and lasts for a longer time. The cooling is therefore so large that, in the power generation region of the MHD channel, the gas crosses into the two-phase region and achieves a supersaturation so high that nucleation is certain to occur. However, with previous computer codes (which are limited to equilibrium calculations only) one could not quantitatively assess the effect on generator operation since the thermal and electrical properties of the aerosol formed depend not only on equilibrium considerations but also on the *nucleation and chemical reaction kinetics*.

The most general of the computer codes now available is the NASA program "Computer Program for Calculation of Complex Chemical Equilibrium Compositions, Rocket Performance, Incident and Reflected Shocks, and Chapman-Jouguet Detonations" developed by Gordon and McBride. This program was developed primarily to describe the properties of rocket exhausts and the products of explosive reactions, but is very general and can be applied, with some modification, to coal-combustion reactions. The program can calculate both phase and chemical equilibria; but its phase equilibria calculations are limited to the condensation of pure components only.

During the first year of this project[†], we obtained a copy of this computer program and modified it to calculate the rate of homogeneous nucleation for non-reactive gases and for systems where the rate of gas-phase chemical reaction is much faster than the rate of nucleation. We showed that the barriers to nucleation have a significant effect on the rate of condensation for rapidly cooling gases. We also showed that the chemical equilibria has a similarly large effect on the condensation conditions. These conclusions, and appropriate illustrative calculations and figures were presented in Progress Report C00-4947-1.

[†] This project was begun under contract ER-78-02-4947.A000. Because both the principal investigator and the coprincipal investigator changed institutions (from Clarkson College to The Johns Hopkins University) at the end of its first year, a new contract was awarded to Johns Hopkins University for the purpose of continuing the research. We shall refer to the entire project (both contracts) in this report as one unit.

PROGRESS IN THE PAST YEAR

In the past year, we have again made significant progress, particularly in two areas. We have developed a theory which predicts the rate of condensation nucleation for chemical reactive systems[†]; we have improved our computer codes and made additional computer studies on the effects of other process variables on the rate of homogeneous nucleation.

We began our analysis of the problem of nucleation with simultaneous chemical reaction by first considering a simple bi-molecular reaction, i.e.,

We allow a nucleus to grow either by the direct addition of a "C" molecule from the vapor phase (which is formed by homogeneous gas-phase chemical reaction) or by the reaction of "A" and "B" molecules to form "C" molecules on the surface (or in the bulk) of the nucleus. Similarly, we allow a nucleus to decrease in size by the direct evaporation of "C" molecules or by the decomposition of "C" molecules back to "A" and "B".

The rate at which a cluster containing "i" molecules of species "C" grows to size "i+1" is then:

$$f(i) = (\beta_c + k[A][B])a(i) \quad (2)$$

[†]We include below a brief description of this theory. A complete derivation will be available in a preprint in the near future.

where β_c is the rate "C" molecules condense on the surface of the cluster (this we determine from kinetic theory for dilute gases), [A] and [B] are the concentrations of the reacting species on the surface of the cluster, k is the surface reaction rate constant, and $a(i)$ is the surface area of a cluster of size "i". The rate a cluster will decrease from size "i+1" to size "i" is

$$b(i+1) = (\gamma(i+1) + k'[c]) a(i+1) \quad (3)$$

where $\gamma(i+1)$ is the evaporation rate of "C" molecules and k' is the reaction rate constant for the reverse reaction.

Nucleation occurs when more clusters of size "i" grow to size "i+1" than clusters of size "i+1" shrink to size "i", or

$$J = f(i) n(i) - b(i+1) n(i+1) > 0 \quad (4)$$

where $n(i)$ is the number (or concentration) of clusters of size "i". We have solved this equation in terms of "measurable" quantities and we obtain

$$J = Na_o \left(\frac{\sigma a_o}{9\pi kT} \right)^{\frac{1}{2}} (\beta_c + k[A][B]) \exp \left\{ -\frac{2}{3} - \frac{4}{27} \left(\frac{\sigma a_o}{kT} \right)^3 / \ln^2 \left[\left(\frac{\beta_c + k[A][B]}{\beta_c^e + k[A]^e[B]^e} \right) \frac{[C]^e}{[C]} \right] \right\} \quad (5)$$

In this equation, the reaction rate constant, k , is the only variable which cannot be determined from equilibrium measurements.

When no surface chemical reaction occurs, one recovers:

$$J = Na_o \left(\frac{\sigma a_o}{9\pi kT} \right)^{\frac{1}{2}} \beta_c \exp \left\{ -\frac{2}{3} - \frac{4}{27} \left(\frac{\sigma a_o}{kT} \right)^3 / \ln^2 (\beta_c / \beta_c^e) \right\} \quad (6)$$

Comparison of equations (5) and (6) shows that the chemical reaction affects the rate of nucleation in two ways. There is a small effect on the pre-exponential term since the arrival rate β_c is increased by the rate at which reaction occurs on the surface of a cluster. However, there is a very important effect on the exponential term in equation 5. Instead of a logarithm of the supersaturation, P/P_e , we now obtain a ratio of effective arrival rates β^*/β_e^* . Note that this effective arrival rate includes both the increase due to the surface reaction, i.e., the $k[A][B]$ term, and an increase due to the fact that the surface of the nucleus contains fewer "C" molecules; as the supersaturation increases, a smaller fraction of the surface will be "C" molecules and therefore the evaporation rate and the backward reaction rate must necessarily decrease.

We have generalized this derivation to treat the multiple complex chemical reactions which occur in the condensation of SiO_2 . We allow clusters of SiO_2 to grow either by the direct condensation of gaseous SiO_2 molecules or by the surface reaction of SiO and O_2 . We can then write the following reactions:

For conditions where the reacting species have a much higher gas-phase concentration than the product species, it is a reasonable approximation to assume that the surface concentrations of the reacting species are given by their equilibrium isotherms. The nucleation rate is then identical to Equation (5) except that the $k[\text{A}][\text{B}]$ reaction term becomes

$$(k_{10} + k_{11})[\text{SiO}][\text{O}_2]^{\frac{1}{2}} + k_{12}[\text{SiO}][\text{O}] .$$

This result will allow us to realistically predict the nucleation conditions for SiO_2 condensation. The important yet unknown quantities in this equation are the rate constants for reactions 10, 11 and 12.

It is difficult for the reader to appreciate at this stage the full significance of the advance that we have made since we have not yet had time to computerize the theory and thus make sample calculations. However, we should note that a scheme for generalizing nucleation theory has been sought for many years and that our work to date has shown the way.

We have also made considerable progress in improving our computer code and studying the effect of process conditions on the nucleation rate. In particular, we have studied the effect of hydrogen and water on the condensation of SiO_2 .

Hydrogen and water affect the condensation of SiO_2 in two ways. First, there can be competition for oxygen atoms between the hydrogen and the SiO . If SiO molecules cannot react with O atoms because of this competing reaction, condensation will not occur. Second, SiO_2 molecules can react with H_2O to form Si(OH)_4 . This compound is much more volatile than SiO_2 and, at low temperatures, even more volatile than SiO . The formation of Si(OH)_4 , therefore, can significantly decrease the driving force for condensation, particularly when the vapor-phase concentration of water is high.

Our computer results show that the hydrogen to oxygen ratio is important whenever there is less oxygen than is necessary for complete combustion. These results are illustrated in Figure 1 which shows the nucleation temperature plotted versus the ratio of moles of O_2 to moles Si for various hydrogen concentrations. One sees that there is a very dramatic decrease in the nucleation temperature at low O_2 concentrations due to the competition between the reactions

For the available oxygen. At higher oxygen concentrations, there is still a noticeable depression of the nucleation temperature, because at these higher *temperatures* most of the hydrogen is in the form of OH^- and not water.

At even higher hydrogen (or steam) concentrations, the additional reaction for the formation of Si(OH)_4 further affects

the nucleation temperature. However, at conditions which are presently expected in MHD processes, the water concentration is not high enough to produce sufficient quantities of Si(OH)_4 to affect the nucleation conditions.

We have also devoted significant amounts of time during the last year looking for data and generating numerical expressions for the thermodynamic properties of slag-related compounds. Of particular difficulty has been finding temperature-dependent data for the surface tension (which is needed in the nucleation rate expression), since few others are interested in surface tensions under these extreme conditions. We expect to have to continue our efforts in this area despite the fact that it is not central to this project.

Finally, we are continually improving our computer code. We are presently incorporating our theory for nucleation with simultaneous chemical reaction and shall have illustrative results in the near future.

REFERENCES

1. Martinez-Sanchez, M., C. E. Kolb and J.L. Kerrebrock,
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on Plasma Conductivity in Open Cycle, Coal Fired MHD
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Figure 1: Nucleation temperatures for the condensation of SiO_2 . A - no Hydrogen; B - Hydrogen mole fraction $X = 0.000233$; C - Hydrogen mole fraction $X = 0.001165$. All curves at 1 atm. total pressure and silicon mole fraction $X = 0.000233$.