

THERMODYNAMIC AND RHEOLOGICAL MODELING OF COAL ASH BEHAVIOR

Harold H. Schobert and Bong-Jin Jung
Fuel Science Program
Department of Materials Science and Engineering
The Pennsylvania State University
University Park, PA 16802

INTRODUCTION

This paper describes some recent results attained in modelling the behavior of coal ash and slags derived from it. This work is part of a larger effort which seeks to develop a unified model of ash behavior in combustion or gasification systems. A detailed description of the modelling effort has recently been published (1). Briefly, the focus of the model is on the effects of increasing temperature on coal ash and the recognition that ash will undergo a series of transformations which are specified by the composition and temperature of the ash but which may be independent of the configuration of the processing hardware in which the coal is being consumed.

The feature common to all combustion and gasification systems is that the inorganic components of the coal are exposed to temperatures high enough to induce chemical reactions, phase changes, or both. At low temperatures, dehydration reactions and thermally induced structural rearrangements occur, and are particularly important for clays. In low-rank coals, decarboxylation of the coal structure liberates alkali and alkaline earth cations for reaction elsewhere, such as substitution into the clays (2). At higher temperatures carbonate decomposition can occur.

As the temperature continues to increase, a point is eventually reached at which one or more of the low-melting components of the ash will melt. The formation of a liquid phase often marks the onset of troublesome ash behavior, such as clinkering on grates, agglomeration in fluidized beds, and deposition on steam tubes. In each of these instances, the liquid phase acts as a glue to bond solid particles together. The sintering is governed by the Frenkel equation, which relates the interparticle bonding to the viscosity and surface tension of the liquid phase (3).

At a given temperature, the viscosity and surface tension of the liquid phase will be determined by the liquid composition. However, in cases of partial melting (or of a liquid phase remaining after partial crystallization of a melt) it is unlikely that the composition of the liquid phase is the same as the bulk composition as customarily determined by analysis of the ash produced by the standard ASTM ashing procedures. Consequently, before one can apply a model to calculate the viscosity or surface tension, it is first necessary to determine the actual composition of the liquid.

Our approach to calculating liquid phase composition is the thermodynamic model SOLGASMIX (4,5,6). This program is based on minimization of the free energy of the system. An iterative calculation determines the mole fractions of the components which give the minimum Gibbs free energy, consistent with mass balance constraints. In recent work at Penn State, SOLGASMIX has been used with some success to determine the effects of composition on the growth of strength in slag deposits from pulverized coal firing of low-rank coals (7,8).

Numerous models for calculating viscosity as a function of composition are available in the literature. On the other hand, the surface tension of liquids derived from coal ash has been studied very little. Consequently, our recent work has focused on viscosity. The variety of viscosity models available, and the conflicting results occasionally obtained from them, has led us to develop a master program which incorporates six of the major viscosity models and which calculates the viscosity of a given liquid by all six models. This allows us to make an immediate comparison of the calculated results with the experimental data, and will be of assistance in assessing the applicability of the various viscosity models in our overall program.

PROCEDURE

The objective of the present work was to test the combined SOLGASMIX - viscosity program against available experimental data. The material chosen for the test was Martin Lake (Texas) lignite, for which good slag viscosity data and x-ray fluorescence and diffraction analyses of the solidified slag were available. The experimental data derived from an earlier viscosity project, of which the methods and results have already been published (9,10).

The current version of SOLGASMIX used for this work is written in FORTRAN and is running on the Penn State IBM mainframe computer. The viscosity model program is written in FORTRAN and is also running on the mainframe. The input data for SOLGASMIX was the composition determined by x-ray fluorescence analysis of the ash produced by the ASTM ashing procedure. The liquid phase composition was calculated at 25°C intervals in the range 1200 - 1700°C. At each temperature interval, the calculated liquid phase composition was then used as the input data for the viscosity model.

RESULTS AND DISCUSSION

Viscosity

The viscosity was calculated using the six-model program described above. The results for this lignite showed that the best accuracy (agreement between calculated and experimental viscosities) was obtained from the S^2 viscosity model of Hoy et al. (11). These results are summarized in Table 1.

TABLE 1. Comparison of calculated and experimental viscosity data (S² model (11); viscosity units are poises)

| <u>Temp. °C</u> | <u>Calcd.</u> | <u>Exptl.</u> |
|-----------------|---------------|---------------|
| 1350 | 321 | 220 |
| 1375 | 203 | 160 |
| 1400 | 131 | 110 |
| 1425 | 89 | 77 |
| 1450 | 64 | 55 |
| 1475 | 50 | 38* |

*Extrapolated; experimental data end at 1471°.

When comparing the calculated and experimental results shown in Table 1, it should be borne in mind that these results were obtained with absolutely no a priori assumptions about what the composition of the liquid "should be." The liquid phase composition used as input data for the viscosity model was obtained directly from the minimization of the free energy of a system having the composition of the lignite ash.

As is the case with virtually all viscosity calculation models, the work we have done so far does not provide a prediction of the temperature of critical viscosity, $T_{c,v}$, nor of the viscosity vs. temperature behavior in the non-Newtonian flow region below $T_{c,v}$. However, it would seem that the ability to calculate the amount and composition of the liquid and solid phases afforded by SOLGASMIX may provide the key to development of a means for calculating both of these important slag properties. Efforts to develop $T_{c,v}$ and non-Newtonian viscosity predictions are planned for the future.

Liquid composition

The predicted liquid phase composition changes slightly with temperature, over the range 1350 - 1475°C for which we compared calculated and experimental viscosity data. Nevertheless, the agreement between the SOLGASMIX predictions and the x-ray fluorescence analysis of the solidified slag after a viscosity test are remarkably good, as shown in Table 2, which is given on the next page. The normal SOLGASMIX calculation determines mole fractions of elements and various compounds; however, since the x-ray analysis data are customarily reported as weight percents of the oxides, we have converted the SOLGASMIX output to the same basis for ease of comparison. (In addition, this conversion is necessary to use the SOLGASMIX results as input data for several of the viscosity calculation models.)

Although the reporting of analytical results as oxides and the use of such results as input data for viscosity models are traditions of long standing, in fact a list of oxides does not by itself convey much information about the molecular species actually present in the melt. It is extremely unlikely that very

TABLE 2. Comparison of predicted and determined compositions of Martin Lake lignite ash slag. (Data in weight percent.)

| <u>Component</u> | <u>Calcd. 1350°</u> | <u>Calcd. 1475°</u> | <u>Exptl.</u> |
|--------------------------------|---------------------|---------------------|---------------|
| SiO ₂ | 50.9 | 48.5 | 48.3 |
| Al ₂ O ₃ | 15.9 | 15.0 | 14.9 |
| Fe ₂ O ₃ | 7.1 | 11.9 | 11.8 |
| TiO ₂ | 1.0 | 1.0 | 1.0 |
| P ₂ O ₅ | 0.0 | 0.0 | 0.0 |
| CaO | 11.7 | 10.6 | 10.5 |
| MgO | 3.6 | 3.5 | 3.5 |
| Na ₂ O | 1.0 | 0.9 | 0.9 |
| K ₂ O | 0.5 | 1.1 | 1.1 |
| SO ₃ | 8.3 | 7.5 | 7.5 |

reactive oxide donors such as the alkali and alkaline earth oxides would coexist in a melt, as oxides, with oxide acceptors such as silica or alumina. In fact, the species in the melt are most likely aluminosilicate polymers (12,13). Therefore a real test of the SOLGASMIX predictions is a comparison of the liquid phase molecular species with those found by analysis.

Information on the species in the melt was obtained by x-ray diffraction analysis of the solidified slag after a viscosity test. There are of course limitations to this method, most notably the potential for changes to occur as the melt is cooled, the presence of amorphous phases not detected by diffraction analysis, and the presence of materials in quantities below the detection limits of the equipment. Furthermore, x-ray diffraction analysis is not quantitative. These limitations notwithstanding, the comparison of x-ray diffraction results with SOLGASMIX predictions, shown in Table 3, is encouraging.

TABLE 3. Comparison of predicted (SOLGASMIX) and observed (x-ray diffraction) species in liquid phase of Martin Lake lignite ash.

| <u>Predicted</u> (a) | <u>Observed</u> |
|--------------------------------------------------|------------------------------------------------------|
| CaAl ₂ Si ₂ O ₈ | CaAl ₂ Si ₂ O ₈ (c) |
| SiO ₂ | SiO ₂ (b) |
| MgSiO ₃ | MgSiO ₃ (c) |
| CaSO ₄ | CaSO ₄ (b) |
| FeO | Fe ₂ O ₃ (c) |
| Fe ₃ O ₄ | |

Notes: (a) Species predicted by SOLGASMIX are listed in decreasing order of abundance; (b) identified as a "major" phase by XRD; (c) identified as a "minor" phase by XRD.

Regarding these results, it should be noted that the calcium aluminum silicate observed by x-ray diffraction was reported as "plagioclase" (14). The term plagioclase refers to a series of

general formula $(Ca,Na)(Al,Si)AlSi_2O_6$ of which the compound listed, $CaAl_2Si_2O_6$ (anorthite), is an end member (15,16). We are not yet certain of the reason for the discrepancy between the predicted and observed iron-containing species.

At the present stage of development of the model, SOLGASMIX itself is not without difficulties. Problems have been encountered in obtaining convergence in the SOLGASMIX calculations for some systems. In particular, the calculations seem extremely sensitive to the amounts of CaO and SO_2 in the ash composition used as input data.

In the context of the development of the unified model of ash behavior, the work reported here indicates that, at least for some ashes, it is possible to obtain useful predictions of the liquid phase composition and viscosity over a range of temperatures using only the initial ash composition as the necessary data. Much work remains to be done. As mentioned, a problem exists with the convergence of the SOLGASMIX calculation for some compositions. The prediction of T_c and the viscosity - temperature curve in the non-Newtonian region remains a target for future investigations. The measurement of surface tension of ash-derived liquids and the development of a method for calculating surface tension vs. temperature from composition are research areas that are woefully under-explored. When these hurdles have all been crossed, there still remains the task of synthesizing the overall model from these components. Of course, any model at any stage of development needs continual testing against available experimental data.

ACKNOWLEDGEMENTS

This research has been supported by the Department of the Interior's Mineral Institutes program administered by the Bureau of Mines under allotment grant number G1164142. In particular, the support of the Pennsylvania Mining and Mineral Research Institute is hereby acknowledged. The authors are also pleased to acknowledge the financial support provided by The Pennsylvania State University Research Initiation Grant Program.

LITERATURE CITED

1. Schobert, H. H.; Conn, R. E.; Jung, B-J. Proc. 4th Annual Pittsburgh Coal Conf. 1987, 423.
2. Falcone, S. K.; Schobert, H. H. In "Mineral Matter and Ash in Coal"; Vorres, K. S., Ed.; American Chemical Society: Washington, 1986; Chapter 9.
3. Frenkel, J. J. J. Physics USSR 1945, 9, 385.
4. Eriksson, G. Acta Chem. Scand. 1971, 25, 7.
5. Eriksson, G. Chem. Script. 1975, 8, 100.

6. Eriksson, G.; Rosen, E. Chem. Script. 1973, 4, 193.
7. Benson, S. A. Ph.D. Dissertation, The Pennsylvania State University, University Park, PA, 1986.
8. Austin, L. G.; Benson, S. A.; Schobert, H. H.; Tangsathitkulchai, M. U.S. DOE Report 1987, No. DOE/FE-70770.
9. Streeter, R. C.; Diehl, E. K.; Schobert, H. H. In "Chemistry of Low-Rank Coals"; Schobert, H. H., Ed.; American Chemical Society: Washington, 1984; Chapter 12.
10. Schobert, H. H.; Streeter, R. C.; Diehl, E. K. Fuel 1985, 64, 1611.
11. Hoy, H. R.; Roberts, A. G.; Wilkins, D. M. Inst. Gas Engineers Pubn. 1964, No. 672.
12. Vorres, K. S. ACS Div. Fuel Chem. Preprints 1977, 22(4), 118.
13. Schobert, H. H. ACS Div. Fuel Chem. Preprints 1977, 22(4), 143.
14. Rindt, D. K. Grand Forks Energy Technology Center, personal communication, 1981.
15. Bowen, N. L. "The Evolution of the Igneous Rocks"; Dover Publications: New York, 1956; p. 45 ff.
16. Berry, L. G.; Mason, B. "Mineralogy"; W. H. Freeman: San Francisco, 1959; Chapter 15.