MOLTEN SULFATE-CARBONATE LIQUIDS IN THE EFFlUENTS OF WOOD COMBUSTION FOR POWER PRODUCTION

M. Blander¹, A. D. Pelton², R. Cole¹, J. A. Libera¹, and K. W. Ragland³
¹Argonne National Laboratory, Argonne, IL 60439
²Ecole Polytechnique, Montreal, PQ H3C 3A7
³University of Wisconsin-Madison, Madison, WI 53706

ABSTRACT

Calculations of the combustion effluents of aspen wood chips indicate that molten and solid K⁺,Ca₂⁺/CO₃²⁻,SO₄²⁻ solutions were formed. At 4 atm above 1000°C, a potassium sulfate-rich liquid forms; a corrosive carbonate-rich liquid forms between 875-800°C. These results suggested increasing the temperature range of operation of a gravel bed combustor in a test of a gravel-bed-combustor/gas-turbine system from 800-900°C to 900-1000°C which improved the bed performance considerably. A method deduced for hot gas cleanup could be effective enough to eliminate condensates on the turbine at lower temperatures.

INTRODUCTION

Wood is a renewable fuel that is an alternative to fossil fuels¹⁻⁹; it has much lower contents of sulfur and heavy metals than coal, the ash may be returned to the soil and its' use does not increase atmospheric CO₂. Equilibrium calculations of the inorganic chemistry of the combustion of aspen wood in a gravel-bed-combustor-gas turbine system are presented and discussed with regard to molten salt deposits in the gravel bed and on the turbine¹⁻². These calculations suggest means for avoiding the observed deleterious effects of molten salt deposition in such systems.

CALCULATIONS OF COMBUSTION CHEMISTRY

The calculations were made on the FACT computer program at Ecole Polytechnique in Montreal, which uses the CHEMSAGE¹⁰ computer program for free energy minimization. The FACT system has a large database of more than 6000 solid, liquid, and gaseous species and is flexible enough to allow one to incorporate theoretical
equations that describe solid and liquid solutions. Calculations of the chemistry of the relevant ternary reciprocal molten and solid salt systems, $K^+,Ca^{2+}/CO_3^{2-},SO_4^{2-}$, were made possible by incorporating the equations of the Conformal Ionic Solution Theory for this system$^{[11],[12]}$ and data deduced from an analysis of the available phase diagrams$^{[13]}$ for the four subsidiary binaries. This procedure, in effect, calculates the stabilities and phase diagrams of the ternary system as well as the activities of the constituents for pertinent ranges of temperatures and pressures. Because there are, apparently, no ternary compounds, the Conformal Ionic Solution theory makes it possible to predict the detailed properties of the ternary system from the known properties of the subsidiary binaries.

The specific wood chosen was aspen, which had been used as fuel in tests of a wood-burning gravel-bed combustor developed at the University of Wisconsin-Madison to power a gas turbine$^{[1]-[5]}$. Analysis of the wood showed (in wt %) 85.12 volatiles, 13.66 fixed carbon, and 0.72 ash. The elemental analyses (in wt % on a dry basis) are C-51.57, H-6.24, nitrogen 0.47, sulfur 0.02, and oxygen 39.52. The elemental composition of the ash (in ppm) is Ca-211,700, K-112,500, Mg-35,550, P-11,800, S-7000, Zn-3400, Fe-2600, Mn-1,400, Al-1400, Na-600, B-500 and Cu-300. The wt. % of sulfur (relative to the total weight of wood) from the ash is 0.05, which is about 25% of the relatively low sulfur content of the wood. The elemental analyses of the ash does not add up to 100% because light elements (largely carbon and oxygen) were not included in the analyses.

In order to decrease the complexity of the calculation, we left out three minor elements that play a small role in the degradation of the system performance (Zn, Cu, and Na). The burning of 100 grams of wood was simulated with a large excess of air at temperatures ranging from 700°C to 1150°C. The final gas content of unburned oxygen at 750°C was 4.06 mol %. Table I shows the calculated compositions of the gas phase for constituents present at over 10^{-6} mole fraction at one pressure each for three temperatures (i.e., 750°C, 900°C and 1050°C). Similar calculations were made at 11-13 different temperatures at each of the pressures. The results in Table I illustrate the general trends and provide important clues on methods for eliminating problems in real systems. A significant concentration of potassium is present in the gas phase as KOH molecules. If the total input amount (0.081 g) of potassium was in the 30.69 moles of the gas phase as KOH, it would constitute 6.8 x 10^{-5} mole fraction. At 1050°C, about 30% and 47% of the potassium precipitated (as sulfates) at 1 atmosphere and at 4 atmosphere, respectively, has precipitated. At 900°C (as we will see later, after sulfates have largely precipitated) only 60% (at 1 atm) and 63% (at 4 atm) of the KOH has formed a sulfate condensate. At 750°C 95% (at 1 atm) and 99% (at 4 atm) of the KOH has precipitated (as sulfate and carbonate). These results and the very low sulfur content of the gas ($-10^{-9}$) provide an important clue in improving the performance of a wood-burning power system. Because the molar ratio of sulfur to potassium in aspen wood is 0.3, there is not enough sulfur (as SO_2) to react with the KOH at high temperatures (e.g., above 900°C), and KOH persists in the gas phase to lower temperatures, where CO_2
reacts with the remaining KOH to form carbonates, which can have a negative impact on the performance of a wood-burning power system.

Table I. Calculated Gas Compositions (Mole Fraction) at 750, 900, and 1050°C at 1 and 4 Atmospheres. (The total moles of gas were always close to 30.69 moles.)

|        | 1 atm          | 4 atm          |
|--------|----------------|----------------|
| 750°C  |                |                |
| N₂     | 0.71863        | 0.71869        |
| CO₂    | 0.13986        | 0.13978        |
| H₂O    | 0.10085        | 0.10086        |
| O₂     | 0.04064        | 0.04064        |
| NO     | 1.9 x 10⁻⁵     | 1.9 x 10⁻⁵     |
| KOH    | 3.1 x 10⁻⁶     | 7.4 x 10⁻⁷     |
| NO₂    | 3.8 x 10⁻⁷     | 7.5 x 10⁻⁷     |
| 900°C  |                |                |
| N₂     | 0.71857        | 0.71856        |
| CO₂    | 0.13988        | 0.13988        |
| H₂O    | 0.10084        | 0.10084        |
| O₂     | 0.04061        | 0.04062        |
| NO     | 7.4 X 10⁻⁵     | 7.4 X 10⁻⁵     |
| KOH    | 2.7 X 10⁻⁵     | 2.5 X 10⁻⁵     |
| OH     | 1.3 X 10⁻⁶     | 8.9 X 10⁻⁷     |
| NO₂    | 6.1 X 10⁻⁷     | 1.2 X 10⁻⁶     |
| 1050°C |                |                |
| N₂     | 0.71848        | 0.71849        |
| CO₂    | 0.13988        | 0.13988        |
| H₂O    | 0.10082        | 0.10083        |
| O₂     | 0.04054        | 0.04054        |
| NO     | 2.1 X 10⁻⁴     | 2.1 X 10⁻⁴     |
| KOH    | 4.8 X 10⁻⁵     | 3.6 X 10⁻⁵     |
| OH     | 8.4 X 10⁻⁶     | 5.9 X 10⁻⁶     |
| SO₂    | 5.3 X 10⁻⁶     | 3.7 X 10⁻⁷     |
| NO₂    | 8.9 X 10⁻⁷     | 1.7 X 10⁻⁶     |

Most of the solid condensed phases formed at the highest temperatures in the calculations (1150°C). All were unreactive and persisted to temperatures of about 800°C and sometimes 700°C, as low as we went in our calculations, 700°C. These compounds are all benign, so, we will not discuss them here.

The total calculation, also included a calculation of the condensation of a calcium-potassium/carbonate-sulfate assemblage of liquid and solid solutions and solid carbonates (Table II) in equilibrium with the gas phase (Table I) and all the other solid compound phases. The calculation required the analyses of known phase diagrams for such systems, which contain information on both liquid and solid solutions, and the
incorporation of fundamental statistical mechanical equations (the Conformal Ionic Solution Theory) for these complex solutions, (defined as "reciprocal salt solutions").[11,12] These equations provide a reliable means for predicting the properties of such solutions with a small amount of phase diagram data[^13] and data on the free energies of formation of the compounds formed.[14] Analyses of the four binary phase diagrams led to values of the parameters describing the non-ideality of the subsidiary binary liquid and solid solutions. These parameters and the free energies of formation of CaCO$_3$(l), CaSO$_4$(l), K$_2$CO$_3$(l), K$_2$Ca(CO$_3$)$_3$ and K$_2$SO$_4$(l) are all one needs to calculate the ternary phase diagram and the activities of all the constituents of the solution phases.

Besides relatively large amounts of carbonate solids, there was a significant amount of liquid both at high temperatures (>1000°C) and at lower temperatures, as well as solid solutions all containing Ca$^{2+}$, K$^+$, SO$_4^{2-}$, and CO$_3^{2-}$. These liquids and solids contain various amounts of these four ions and have compositions that can be characterized by two of the four cation and anion fractions:

\[
X_K = \frac{N_K}{N_{Ca} + N_K} = 1 - X_{Ca}
\]  

\[
X_{CO_3} = \frac{N_{CO_3}}{N_{SO_4} + N_{CO_3}} = 1 - X_{SO_4}
\]

where $N_j$ is the number of moles of the designated ions. The total number of moles of the solid or liquid solution, $N_T$, given in Table II is calculated as follows:

\[
N_T = N_{SO_4} + N_{CO_3} = (N_K/2) + N_{Ca}
\]

Examination of Table II reveals that the solid solutions formed are mainly potassium sulfate, with a small amount of calcium and carbonate ions in solid solution. The high-temperature (1000-1025°C) liquid is largely molten potassium sulfate with a relatively small concentration of calcium sulfate, which decreases with decreasing temperature, and even smaller amounts of carbonates. These high-temperature liquids can be avoided by operating the gravel bed at temperatures ≤ 1000°C at 4 atm. However, at 4 atm, molten carbonate liquid also forms at lower temperatures (below 875°C). These liquids are largely mixtures of potassium and calcium carbonates and constitute a major condensate with undesirable physical and corrosive properties in this system.
| T°C | Liquid Soln. | Solid Soln. | $X_{CO_3}$ moles | $X_{CO_2}$ moles | $K_2C_2A_5(CO_3)_3$ moles | CaCO₃ moles |
|-----|-------------|-------------|------------------|------------------|--------------------------|-------------|
| 1   | 10000       | 10000       | 4.6 x 10⁻⁴       | 0.001            | 6.2 x 10⁻⁴               | 0.000       |
|     | 10000       | 10000       | 6.3 x 10⁻⁴       | 0.001            | 6.4 x 10⁻⁴               | 0.000       |
|     | 10000       | 10000       | 6.6 x 10⁻⁴       | 0.001            | 7.2 x 10⁻⁴               | 0.000       |
|     | 10000       | 10000       | 6.5 x 10⁻⁴       | 0.001            | 1.000                    | 0.000       |
|     | 10000       | 10000       | 6.5 x 10⁻⁴       | 0.001            | 1.000                    | 0.000       |
|     | 10000       | 10000       | 6.5 x 10⁻⁴       | 0.001            | 1.000                    | 0.000       |
|     | 10000       | 10000       | 6.5 x 10⁻⁴       | 0.001            | 1.000                    | 0.000       |
|     | 10000       | 10000       | 6.5 x 10⁻⁴       | 0.001            | 1.000                    | 0.000       |
| 4   | 700         | 700         | 1.8 x 10⁻⁴       | 0.001            | 6.2 x 10⁻⁴               | 0.000       |
|     | 700         | 700         | 6.3 x 10⁻⁴       | 0.001            | 6.3 x 10⁻⁴               | 0.000       |
|     | 700         | 700         | 6.3 x 10⁻⁴       | 0.001            | 6.3 x 10⁻⁴               | 0.000       |
|     | 700         | 700         | 6.3 x 10⁻⁴       | 0.001            | 6.3 x 10⁻⁴               | 0.000       |
|     | 700         | 700         | 6.3 x 10⁻⁴       | 0.001            | 6.3 x 10⁻⁴               | 0.000       |
|     | 700         | 700         | 6.3 x 10⁻⁴       | 0.001            | 6.3 x 10⁻⁴               | 0.000       |
|     | 700         | 700         | 6.3 x 10⁻⁴       | 0.001            | 6.3 x 10⁻⁴               | 0.000       |

Table II. Amounts of Carbonate-Sulfate Solids and Liquids Condensed fromCombustion Effluents.
APPLICATION TO GRAVEL-BED COMBUSTOR/GAS TURBINE SYSTEM

We applied our calculations to tests of the gravel-bed combustor developed at the University of Wisconsin-Madison to power a gas turbine.[1-5] This combustor burns wood chips in a downdraft mode on top of a refractory MgO gravel bed. The gravel bed holds up the wood chips, facilitates carbon burnout, and holds up some of the ash. The fuel bed was typically about 10 cm deep on top of the gravel. Because of the high downward air flow, the combustion zone in the fuel bed was only 3- to 5-cm thick. The combustor was run with excess air to limit the combustor temperature. An ash layer built up with time at the fuel/gravel interface, and some of the ash passed through the bed to the turbine.

An Allison Model 250 gas turbine (designed to be run at a full power of 300 kW at 1000°C and 7 atm) was directly connected to the combustor and run for 250 hours. In these tests[2] the turbine inlet temperature was 800-900°C, with some excursions above 1000°C, and the inlet pressure was 4 atm. The average turbine blockage (percentage decrease of flow per unit time for a fixed pressure drop) due to deposits binding the gravel chips was 0.19% per hour, which is excessive for long-term operation. The turbine blade deposits[5] were primarily CaO, MgO, and K₂SO₄, and no carbonates were detected, probably because they precipitated in the relatively cool gravel bed. In other tests, a pressure control valve was used in place of the turbine. These tests established that MgO was a much better bed material than the original acidic Al₂O₃, which probably reacted with the base, KOH. As suggested by our calculations in Table II, we recommended running the bed at higher temperatures (900-1000°C). This change gave considerably less bed deposition than running at 800-900°C.

The major factor for binding the MgO chips together at 800-900°C is likely to be the formation of a carbonate-rich sulfate-carbonate liquid (Table I), which can be present in larger amounts than the solid compounds. For example, at 4 atm and 825°C, the amount of a liquid rich in calcium-potassium carbonate was 1.0 x 10⁻³ mol whereas, except for CaO (3.06 x 10⁻³ mol), which is a high-melting, relatively benign solid, the amounts of other solids are low. The formation of an alkali-calcium/carbonate-sulfate liquid is likely to predominate the binding of MgO gravel chips upon crystallization of the liquid. Although the solid compounds can have some influence on degradation of bed performance, that effect is likely to be small relative to the influence of alkali-calcium/carbonate-sulfate liquids. Our calculations indicate that avoidance of regimes of temperatures and pressures were such liquids might form (Table II) appears to be one useful strategy for improving bed performance. For example, at pressures of 1-4 atm, condensation of liquids in the gravel bed could be avoided at about 900-1000°C.

There are some indications that the formation of these corrosive liquid melts anywhere in the system could be avoided. First, we see in Table II that they did not form
at 1 atm much below 1000°C. If the gas were sent through a turbine at a fairly high pressure, the adiabatic expansion of the gas would lead to both lower pressures and temperatures. We see in Table II that the temperature range for stability of this carbonate-rich liquid narrows in going down in pressure so that there may be a pathway for the adiabatic expansion of the gas from high pressure to 1 atm, where no liquid condenses. In addition, one might be able to introduce acidic materials (SiO₂, Al₂O₃) to precipitate the potassium as solids which can be physically separated from the gas phase.

DISCUSSION

The original purpose of our investigation was to improve the operation of a gravel-bed wood combustor operating in the vicinity of 4 atm at temperatures of 800-900°C. As can be seen in Table II, a molten carbonate forms in this range of temperatures at that pressure. The formation of a relatively large amount of molten carbonate is likely to be a primary cause for rapid degradation in the performance of the gravel bed. Raising the bed temperatures to a range of 900-1000°C appears to solve the major part of the problem. Tests of this conclusion indicated that molten ash deposition in the gravel bed was greatly reduced when operating at 900-1000°C rather than 800-900°C.

Although raising the temperature solves the problem with the gravel-bed combustor, the problem could arise again downstream in the turbine. In the expansion through the turbine, the gas would expand from a high temperature and pressure to atmospheric pressure and an intermediate temperature. During this expansion, condensation of a liquid phase as corrosive (and erosive) as the carbonates must be avoided. Even the solid phases (sulfates and carbonates) could pose a significant problem, since solid condensates could erode high-speed turbine rotors. The best method for avoiding condensation in the turbine is hot-gas cleanup, which can be performed by additives that react to form solid condensates that can be separated with cyclones and/or filters. The basic KOH molecule, leads to most of the condensation below 1000°C. Acidic additives such as SiO₂ and Al₂O₃ could react with KOH to form separable solids. For example, a mixture of SiO₂ and Al₂O₃ would be possible reactants which form solid products that are separable by a cyclone and/or filter. Yet another method is suggested by the calculations, which indicate that KOH would react with a higher concentration of added SO₂ to form K₂SO₄. One should be able to reduce the amount of KOH considerably by increasing the partial pressure of SO₂. This can be done by adding a small amount of SO₂ gas (roughly equivalent to the amount of KOH) or a relatively unstable sulfate such as MgSO₄ or CaSO₄. If the residual pressure of SO₂ is raised from calculated values of the order of 10⁻⁹ to 10⁻⁵ mole fraction in the process, the amount of gaseous KOH would decrease by 99% at equilibrium at 1000°C. At lower temperatures, the levels of KOH in the gas would be even lower. If these acidic compounds (Al₂O₃ + SiO₂ or SO₂ or MgSO₄ or CaSO₄) are added before entry into a cyclone and/or filter
system, one might be able to separate the condensing solid sulfates. After separation of solids in a cyclone/filter system, one might react a small amount of unreacted SO₂ with a fixed bed of a basic material or might introduce a basic additive to reduce the SO₂ emissions to levels well below environmental constraints. The disadvantage of the use of SO₂ is that it must be carefully controlled to guarantee conformance with environmental laws. The advantage of gaseous SO₂ is that it would tend to react more completely with bases than solid acidic materials and can more readily be metered and mixed with the combustion effluents. The significance of our calculations is that they provide baseline data which can be combined with chemical, physical, and operational data on a wood-burning-combustor turbine system operating at about 4 atm to define the chemistry and to deduce solutions to problems which arise. In addition, our calculations have provided solutions to problems with a gravel bed combustor and possible solutions to potential problems with turbines caused by condensates.

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