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SUPPORT SERVICES FOR CERAMIC FIBER-CERAMIC MATRIX COMPOSITES

Final Annual Technical Progress Report

June 30, 1999

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LOCKHEED MARTIN ENERGY RESEARCH CORPORATION
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SUPPORT SERVICES FOR CERAMIC FIBER-CERAMIC MATRIX COMPOSITES

ABSTRACT

The Facility for the Analysis of Chemical Thermodynamics (FACT) computer code was used to calculate the vaporization and condensation behavior of germanium (Ge) and lead (Pb) in coal gasification systems. Since condensation occurs at specific temperatures, the elements can concentrate in deposits that foul or corrode structures within an integrated gasification combined-cycle system or form very small particles that may be sticky in particle filter systems or be difficult to collect in a particulate-control cyclone. The calculations were performed in two steps: 1) vaporization from ash constituents at 1600°C at a system pressure of 22.9 atm and 2) condensation of GeX and PbX components at lower temperatures. The calculations indicate that Ge vaporizes as GeS and GeO and condenses through chemical vapor deposition as solid GeO₂. Pb vaporizes primarily as PbS, with some Pb metal, and condenses as PbS. Condensation temperatures for Ge and Pb species depend on the concentration of Ge and Pb in the gasifier feed material. GeO₂ condensation temperatures reach as high as 610°C and PbS as high as 880°C for concentrations in the feed of 100 ppm on a mass basis. Although these concentrations would never be expected in the raw fuel, such levels could be reached if by-product dusts are recirculated into the gasifier feed material. Therefore, the calculations are useful in determining the maximum amount of recirculated material that can be allowed in the feed material to prevent formation of condensates at specific temperatures. The calculations also indicate that chlorine in the fuel has little effect on the behavior of Ge, but increases the concentration of vapor phase Pb as PbCl₄ at temperatures below 800°F, most significantly near 400°F, at which temperature approximately 1/10 of the lead may be in the vapor phase as PbCl₄. It is expected that this vapor would be collected in the system's scrubber.

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1.0 INTRODUCTION

Many advanced power systems will combine two energy cycles to reach efficiencies as high as 47% in converting the chemical energy in coal into electrical energy. The energy cycles always include a typical steam or Rankine cycle, which usually produces 60%–80% of the electrical power. The second cycle usually involves one of three other methods of firing a turbine. The method used in pressurized fluidized-bed combustion (PFBC) is to remove the particulate from the hot flue gas with a high-temperature filter, then directly expand the cleaned gas in a gas turbine. In another concept, the turbine is indirectly fired by using a very high-temperature heat exchanger to transfer the energy to a clean noncondensing working fluid, such as air, which is then expanded in the turbine. The third possibility is to gasify the coal, clean the coal gas, then fire the gas directly into a gas turbine. A steam cycle combined with a gasification cycle is commonly called an integrated gasification combined-cycle (IGCC).

For construction of subsystems in power plants employing these energy cycles, ceramics or advanced alloys are suggested because of their resistance to corrosion and their high-temperature strength. Dense structural ceramics are proposed for use in heat exchangers, which may be used at temperatures as high as 2600°F. Both monolithic and composite ceramics and advanced alloys such as iron aluminide are used to construct hot-gas filters to remove ash from the gas stream at temperatures up to 1600°F. To encourage the acceptability of these subsystems, a better understanding of their long-term performance is required.

The University of North Dakota Energy & Environmental Research Center (EERC) is providing technical assistance and test materials to the U.S. Department of Energy (DOE) Advanced Research and Technology Development (AR&TD) Materials Program investigating ceramic and advanced alloy corrosion in fossil energy systems. The main activity of the EERC is to develop recommendations for appropriate test conditions under which to perform corrosion measurements of structural and particle filter materials. For the year ending in June 1998, we focused on thermochemical equilibrium calculations of the vaporization of nickel from alloys in coal gasification systems (1). For this year (ending in June 1999), we performed similar thermochemical equilibrium modeling of the vaporization and condensation behavior of lead and germanium in oxygen-blown IGCC systems. The elements were chosen through consultation with engineers and scientists working on demonstration-scale IGCC systems. Because these elements vaporize at gasification temperatures and later condense upon cooling, such elements can concentrate in deposits that foul or corrode structures within the IGCC system, or form very small particles that may be sticky in particle filter systems or be difficult to collect in cyclone systems.

2.0 BACKGROUND

For a given system at standard operating conditions, the concentrations of condensable vapor species are dependent on 1) the feed material (including fuel and recycled char) composition, which determines what species can be present in the gas and condensed phases and 2) the local temperature, which determines which species will be thermodynamically stable. Little is known about the vaporization and condensation behavior of elements in gasification systems because very few measurements have been made in operating systems. In addition, gasification conditions are difficult to simulate in the laboratory because of the wide range of gas temperatures and compositions possible in the different systems. Also, operations of these systems are highly proprietary, so access to operating gasifiers is very restricted. For these reasons, computer modeling of the vaporization and condensation behavior of elements is an essential first step in describing potential problems related to this behavior.

In order to predict the vaporization and condensation behavior of the chosen elements, the FACT (Facility for the Analysis of Chemical Thermodynamics) program, developed by C.W. Bale, A.D. Pelton, and W.T. Thomson from Ecole Polytechnique de Montréal, was employed (2). It permits the calculation of stable phases in an ash-gas system over a broad range of temperatures through the minimization of free energy for the system. In addition, it has been partially optimized for the behavior of Pb in aluminosilicate slags. The FACT code is simple to implement because only chemical formulas of possible products and the mole fractions of the elements are needed. A multiple linear regression technique estimates what stable phases are formed by minimizing errors for individual phases.

For 1998–1999, the FACT code was used to calculate the vaporization and condensation behavior of Ge and Pb species that are stable in the product gas from an oxygen-blown entrained-flow coal gasifier. These two elements were chosen based on discussions with scientists and engineers who are operating demonstration-scale systems and the analysis of samples provided by these contacts. Because of the proprietary nature of the operations of the systems, the specific companies contacted will not be revealed.

The calculations were performed in two steps in order to diminish the effect of competing system conditions. The first step was to calculate the molar fractions (partial pressures) of Ge and Pb components in the vapor phase at 2900°F (approximately the highest temperature in an oxygen-blown entrained-flow gasifier) in the presence of syngas with fractional mass concentrations of 1) $\text{H}_2\text{S} = 0.013$, $\text{H}_2 = 0.022$, $\text{CO} = 0.522$, $\text{CO}_2 = 0.298$, $\text{N}_2 = 0.015$, $\text{H}_2\text{O} = 0.119$, and $\text{CH}_4 = 0.010$ and 2) the addition of 100 ppm of Cl_2 .

Total gas pressure in the system used for these calculations was 430 psi. Calculations were performed for four mole fractions of Ge and Pb in the ash of the gasifier feed materials (consisting of coal and char): 1×10^{-4} , 1×10^{-5} , 1×10^{-6} , and 1×10^{-7} . These calculations were performed for vapor-phase sulfides, oxides, metallic species, and hydrides in the absence of chlorine and, separately, in the presence of chlorine in the syngas.

The second step was to calculate the molar fractions of Ge and Pb components condensed from the vapor at lower temperatures for the four elemental concentrations. The syngas composition and pressure used in this stage of calculation were the same as that applied in the first calculation step.

3.0 RESULTS AND DISCUSSION

The calculations indicate that at 2900°F for the concentrations modeled, all of the Ge and Pb components exist in the vapor phase. Figures 1a and 1b illustrate the distribution of Ge and Pb components in the vapor for mole fractions of Ge = 1×10^{-4} and Pb = 1×10^{-5} in the feed ash. The figures indicate that Ge primarily vaporizes as GeS and GeO, while Pb vaporizes as PbS and Pb. Concentrations of other species are at least 2 orders of magnitude less.

Figures 2a and b show the relative mole fractions of Ge and Pb components in the vapor and condensed phases as a function of temperature for Ge = 1×10^{-4} and Pb = 1×10^{-5} mole fractions in the feed ash. At this concentration, Ge undergoes chemical vapor deposition below approximately 1150°F, converting from GeS and GeO vapors to solid GeO₂. X-ray diffraction (XRD) analysis of samples collected from operating gasifiers has identified this condensed Ge phase. In contrast, Pb condenses primarily through physical vapor deposition, changing from PbS vapor (with 1/10 as much Pb metal vapor) to PbS solid at approximately 1400°F. XRD has also confirmed this phase in the samples analyzed.

As expected, the condensation temperatures of the Ge and Pb components depend on the mole fraction of these elements in the feed material and, in both cases, decreases with lowering metal content. The temperature dependence of the condensation behavior of Ge and Pb components is listed in Table 1. In all ranges of temperature, no Ge or Pb liquid phases were predicted. Uncertainties, however, may occur in the prediction of liquid phases if components expected to form in experimental tests are not included in the FACT code database because of the lack of thermodynamic parameters.

The presence of chlorine in the gas has no effect on the concentrations of Ge in the gas or condensed phases, but does have a significant effect on the concentrations of Pb vapor at lower temperatures. Figure 3 shows the effect of 100 ppm of HCl in the syngas on the vapor concentrations of Pb at lower temperatures for a feed material ash mole fraction of 1×10^{-4} . It shows that at temperatures below 800°F, chlorine increases the concentration of Pb in the vapor phase, and the increase becomes very significant near 400°F when approximately 1/10 of the Pb can be in the vapor phase as PbCl₄.

4.0 CONCLUSIONS

Condensation temperatures for Ge- and Pb-derived components were identified using the FACT thermochemical equilibrium computer code. Ge condenses via chemical vapor deposition from GeS and GeO in the vapor to GeO₂ solid. Pb condenses physically from PbS vapor to PbS

TABLE 1

Condensation Temperatures of Ge- and Pb-Derived Components as a Function of Mole Fraction of Ge and Pb in Coal Ashes

Mole Fraction	Condensation Temperature of GeO ₂ , in °F	Condensation Temperature of PbS, in °F
1×10^{-4}	1130	1616
1×10^{-5}	1022	1436
1×10^{-6}	950	1275
1×10^{-7}	878	1148

solid. The condensation temperatures depend on Ge and Pb contents in the feed ash, but can be as high as 1130°F for Ge or 1616°F for Pb at mole fractions of 1×10^{-4} . Although these concentrations would never be expected in the raw fuel, such levels could be reached if by-product dusts are recirculated into the gasifier feed material. Therefore, the calculations are useful in determining the maximum amount of recirculated material that can be allowed in the feed material to prevent formation of condensates at specific temperatures. The presence of chlorine in coals has little effect on the behavior of Ge, but increases the concentration of vapor phase Pb as PbCl₄ at temperatures below 800°F, most significantly near 400°F at which temperature approximately 1/10 of the lead may be in the vapor phase as PbCl₄. Neither Ge or Pb condensed phases contain liquids

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(a)

(b)

Figure 1. Species present in the vapor phase at 2900°F: a) Ge species and b) Pb species.

(a)

(b)

Figure 2. Relative concentrations of vapor and condensed species: a) Ge at 0.0001 mole fraction in the feed material ash and b) Pb at 0.00001 mole fraction in the feed material ash.

Figure 3. Relative vapor concentrations of Pb in the presence and absence of chlorine at lower temperatures.

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