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SUPPORT SERVICES FOR CERAMIC FIBER-CERAMIC MATRIX COMPOSITES

Annual Technical Progress Report

June 22, 1998

Report Prepared by
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PO Box 9018
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under
19a-SS112V

for

OAK RIDGE NATIONAL LABORATORY

Oak Ridge, Tennessee 37831

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LOCKHEED MARTIN ENERGY RESEARCH CORPORATION

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Office of Fossil Energy
Advanced Research and Technology Development Materials Program

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SUPPORT SERVICES FOR CERAMIC FIBER-CERAMIC MATRIX COMPOSITES

Research sponsored by the U.S. Department of Energy, Fossil Energy Advanced Research and Technology Development Materials Program, DOE/FE AA 15 10 10 0, Work Breakdown Structure Element UNDEERC-4.

1.0 INTRODUCTION

Many advanced power systems will combine two energy cycles to reach efficiencies as high as 47% in the conversion of 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 electric 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 indirectly fired cycles, a very high-temperature heat exchanger is used to transfer 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).

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, which is reported here, is to perform thermochemical equilibrium calculations to develop recommendations for test conditions under which to perform corrosion measurements of structural and particle filter materials. The modeling is primarily being performed to determine possible mechanisms of corrosion, especially by species that vaporize in the gasifier then condense on downstream surfaces. During 1995–1996, a methodology was proposed and ash was collected for testing the corrosion resistance of materials in air-blown fluidized-bed gasification systems such as the Sierra Pacific Power Company Piñon Pine Project.¹ For this year, the focus was on the stability of nickel in structural and filter alloys. This work was done in an effort to explain the existence of nickel-containing condensates found downstream of particulate filters in an EERC pilot-scale coal gasifier which operates under conditions similar to the Piñon Pine system, and to determine possible operating conditions that could reduce the wastage of nickel from structural and filter alloys.

2.0 EXPERIMENTAL METHODS

For a given system at standard operating conditions, the corrodent compositions are dependent on 1) the fuel (and sorbent in a fluidized-bed system), which determines what species will be present in the gas and condensed species, and 2) the temperature of the material, which determines the stable chemical and physical form of the elements. In general, corrodents in gasifier systems are not well understood. 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 and the lack of published data due to the highly proprietary nature of the technologies.

In order to calculate possible corrosion pathways in coal gasifiers, 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. 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.

The FACT code was used to determine nickel species that are thermochemically stable in the product gas from a coal gasifier. Nickel was modeled because in two tests of the transport reactor demonstration unit (TRDU) at the EERC, a pilot-scale entrained-bed gasifier, there were indications that Ni speciation can differ significantly when the gasifier temperature, the amount of water vapor (from 14% to 20%), and the amount of carbon monoxide (from 5% to 36%) are changed. Higher TRDU temperatures yielded less nickel in the vapor phase, which is indicative of chemical rather than physical vaporization pathways. Modeling focused on nickel carbonyl and nickel hydroxide, which are volatile and chemically stable at low temperatures, and on the individual reactions of formation and decomposition that are typically obscured by total equilibrium calculation. The nickel species considered in the modeling are listed in Table 1.

3.0 RESULTS AND DISCUSSION

The modeling indicates that at high temperatures, nickel can vaporize from alloys by forming nickel hydroxide gas ($\text{Ni}(\text{OH})_2$). Nickel carbonyl gas ($\text{Ni}(\text{CO})_4$) will form from $\text{Ni}(\text{OH})_2$ gas at lower temperatures. $\text{Ni}(\text{CO})_4$ is a coordination compound, where the nickel atom is in a tetrahedral arrangement with four carbonyl groups. Hence, the transition from hydroxide to carbonyl involves reduction of Ni^{2+} to Ni^0 . At equilibrium, nickel carbonyl formation can be expressed by the following gas-phase reaction:

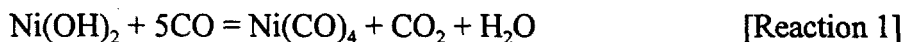


Figure 1 shows the equilibrium constant of Reaction 1 as a function of temperature. Below 677°C, nickel carbonyl predominates, and above that temperature, nickel hydroxide gas is the preferred species. Figure 2 shows nickel speciation for TRDU Tests PO50 and PO51 as predicted by the FACT code. The role of $\text{Ni}(\text{CO})_4$ is demonstrated by lower levels of nickel in the gas phase at higher temperatures. This agrees with the observations made during the TRDU tests.

In inert gas at atmospheric pressure, nickel carbonyl will readily decompose to nickel and carbon monoxide.³ In pressurized CO-rich gas, however, carbonyls are known to exist down to temperatures of 250°C. One possibility for nickel to remain in the gas phase is shown in equilibrium Reaction 2:

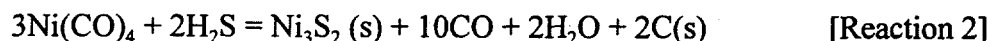


TABLE 1

Nickel Species Used in Thermochemical Equilibrium Modeling

<u>Nickel Species (gas, liquid, solid)</u>
Ni(g,l,s)
NiO(g,s)
Ni(OH) ₂ (g)
Ni(CO) ₄ (g,l)
NiS(g,s)
Ni ₃ S ₂ (s)
Ni ₆ S ₄ (s)

At very high CO(g) pressures (on the order of 10 atm), Reaction 2 is driven to the left, supporting the existence of gaseous nickel carbonyl formed from nickel sulfide, itself a solid corrosion product of nickel. Note that carbonyl decomposition is accompanied by the formation of solids (nickel subsulfide and carbon). This would typically occur on filters and in vessels that are allowed to cool down, but not in a system that is at temperature and where flow velocities are high. Furthermore, Reaction 2 suggests that systems with high water vapor pressures promote the formation of nickel carbonyl. This is not observed in existing gasification systems, and neither is it predicted by the FACT model. For the gas composition of a full-scale oxygen-blown gasifier, the model predicts complete decomposition of nickel carbonyl at 20% water vapor, irrespective of the partial pressure of CO(g). At higher total pressures but temperatures below the dew point of water, carbonyl will decompose and form nickel carbonates.

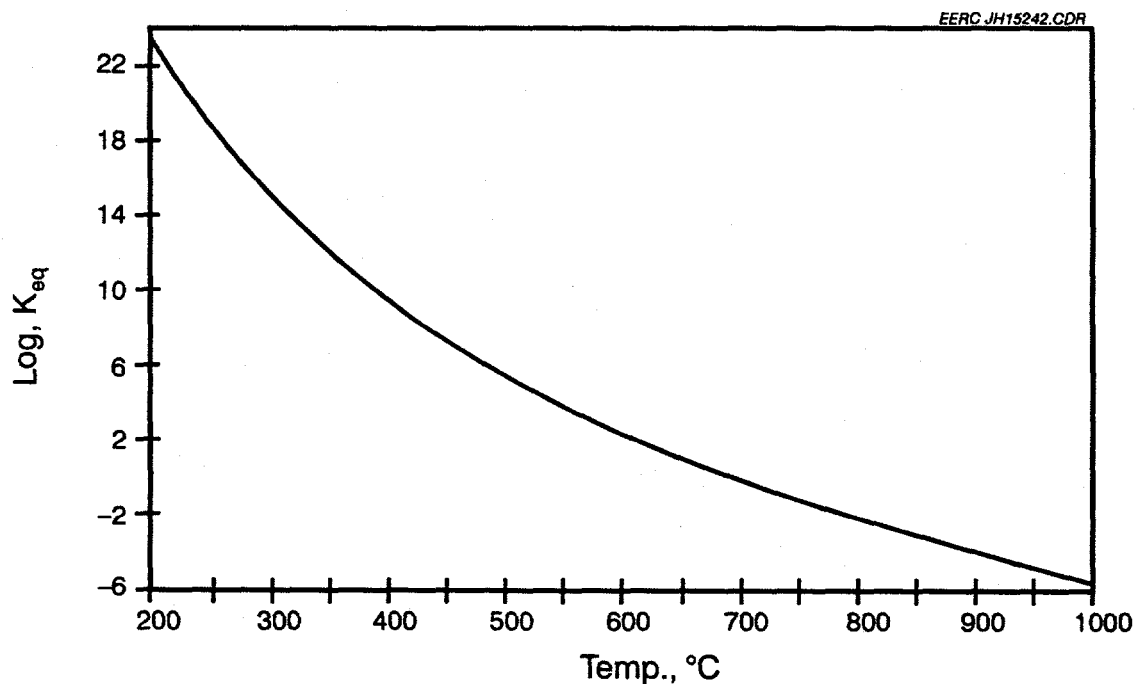


Figure 1. Equilibrium constant for Reaction 1.

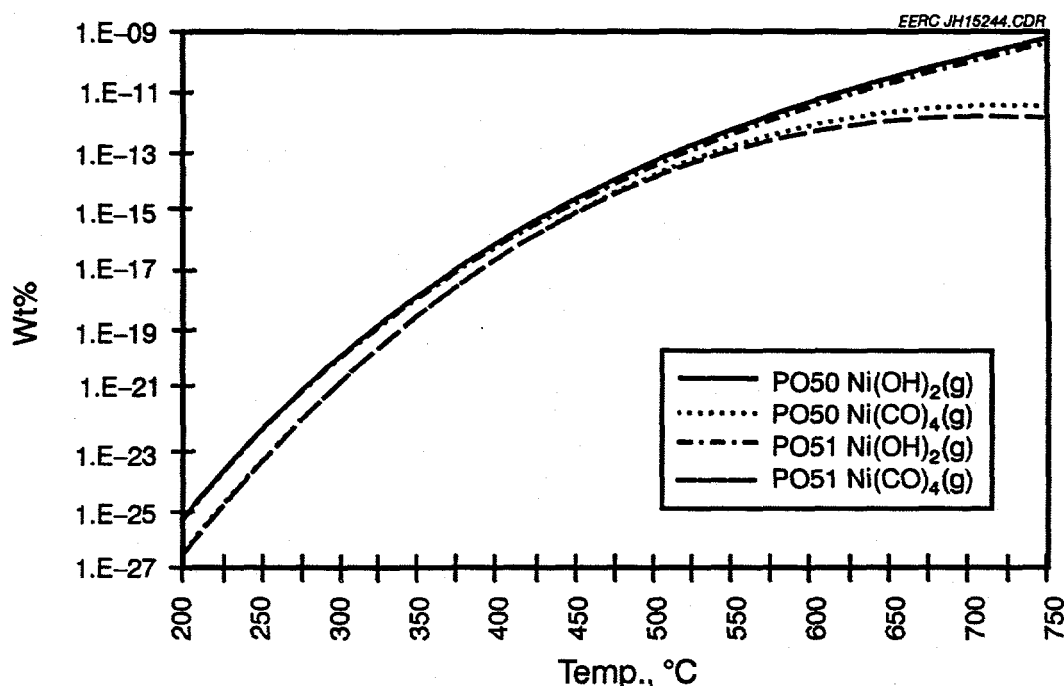
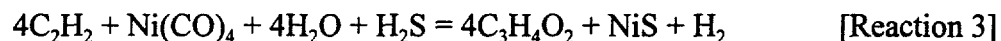


Figure 2. Nickel fraction in the gas phase.

Other mechanisms were sought that would inversely correlate concentrations of nickel carbonyl and water vapor. Reactions of gaseous hydrocarbons with double and triple carbon bonds present themselves as likely reactants. For example, formation of acrylic acid (gas) from acetylene involves nickel carbonyl, as illustrated in Reaction 3. Acetylene is used here only because it is the smallest hydrocarbon with a triple bond. Similar gas components may also produce the required reaction conditions.



Although water vapor will coexist with nickel carbonyl, a high concentration of water will drive the equilibrium of Reaction 3 to the right and will promote the precipitation of nickel sulfide.

Using data from a full-scale oxygen-blown gasifier, the relationship of $Ni(CO)_4$ and water vapor was determined using the FACT code. The initial nickel concentration was assumed to be 100 ppbv. Equilibrium conditions in the product gas were set by maintaining a constant $CO:CO_2$ ratio. This way, gasification could be modeled without the water-gas shift reaction converting carbon monoxide and water to carbon dioxide and hydrogen. Although thermochemically feasible, the water-gas shift reaction is too slow to have a significant effect at the temperatures of interest, below 300°C.

Figure 3 shows that above a water content of 5% in the produced gas, nickel carbonyl formation is drastically reduced and concentrations are negligible below 250°C. Between 3% and 5%, nickel carbonyl is very sensitive to water vapor, and below 3% water vapor, the concentrations can reach 0.1 ppbv. Nickel carbonyl is more stable at 200° than at 250°C in this moisture range, while the opposite is true at water contents greater than 5%. Note that these calculations assume nickel in equilibrium with solid (sub)sulfides that consume more than 99.9% of the nickel. In real systems, this equilibrium may not be fully reached.

4.0 CONCLUSION

Nickel carbonyl forms at lower temperatures in the vapor phase in a pressurized gasification system as described by Reaction 1. Subsequent decomposition of $\text{Ni}(\text{CO})_4$ may proceed according to Reaction 2 or Reaction 3. Although Reaction 2 is thermochemically more favorable, Reaction 3 is suggested to describe nickel equilibrium in the product gas. This conclusion is based on the following hypothesis and observations. First, Reaction 2 occurs at higher temperatures than Reaction 3 and requires the precipitation of solids, including carbon, at temperatures $> 600^\circ\text{C}$. No such precipitation has been observed in this (dynamic and circulating) section of the gasifier. Second, Reactions 2 and 3 have opposite dependence on water vapor. Reaction 3 is in agreement with observations made in hydrotreatment processes (fuels treated with hydrogen), where nickel carbonyl appears to be more problematic in a "dry" gas than in a wet gas. And finally, the temperature profiles shown in Figure 2 are closely followed by the activities of double-bonded and triple-bonded hydrocarbons, supporting the reactant types of Reaction 3.

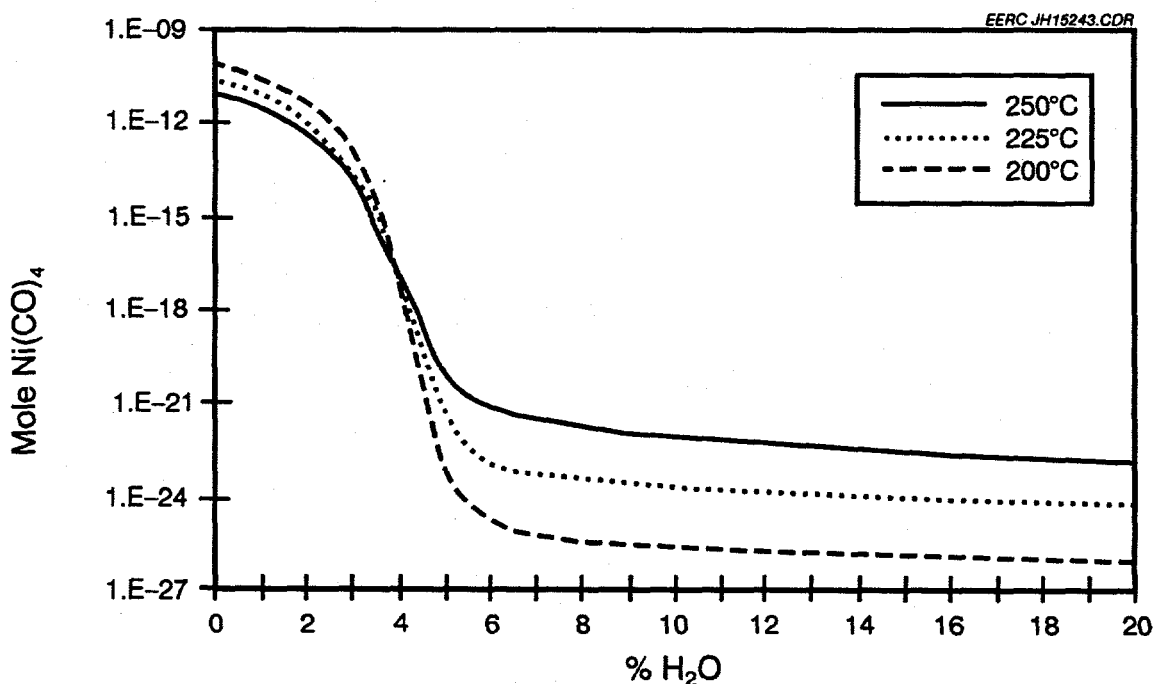


Figure 3. Equilibrium concentrations of nickel carbonyl in coal gasifier product gas.

Based on Reaction 3, gaseous carbonyl formation can be greatly reduced by maintaining water vapor above 5% (volume basis) in the product gas, thus reducing the vaporization of nickel from structural and filter alloys. Below 400°C, this moisture content should reduce carbonyl concentrations by several orders of magnitude compared to moisture contents of less than 3%.

5.0 REFERENCES

1. U.S. Department of Energy. *Proceedings of the Tenth Annual Conference on Fossil Energy Materials*; Knoxville, TN, May 14-16, 1996.
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3. Kirk, R.E.; Othmer, D.F., Eds. *Encyclopedia of Chemical Technology*; Interscience Publishers, Inc.: New York, 1952; Vols. 8 and 9.