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Carbon Formation and Metal Dusting in Hot-Gas Cleanup Systems of Coal Gasifiers

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FY 1995 Program Schedule

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Thermochemical Calculations	—	—	—	—				
Literature Review & Analysis	—	—	—	—				
Draft Report				—	—			
Final Report						—	—	—

OBJECTIVES

The product gas resulting from the partial oxidation of carboniferous materials in a gasifier is typically characterized by high carbon and sulfur, but low oxygen, activities and, consequently, severe degradation of the structural and functional materials can occur. The objective of this task was to establish the potential risks of carbon deposition and metal dusting in advanced coal gasification processes by examining the current state of knowledge regarding these phenomena, making appropriate thermochemical calculations for representative coal gasifiers, and addressing possible mitigation methods.

BACKGROUND INFORMATION

There are several possible materials/systems degradation modes that result from gasification environments with appreciable carbon activities. These processes, which are not necessarily mutually exclusive, include carbon deposition, carburization, metal dusting, and CO disintegration of refractories.

Carbon formation on solid surfaces occurs by deposition from gases in which the carbon activity (a_c) exceeds unity. The presence of a carbon layer can directly affect gasifier performance by restricting gas flow, particularly in the hot gas filter, creating debris (that may be deposited elsewhere in the system or that may cause erosive damage of downstream components), and/or changing the catalytic activity of surfaces.

A principal corrosion effect resulting from the formation of carbon layers is the phenomenon of metal dusting,[1-5] which can be a particularly severe form of materials degradation. Metal dusting requires a high carbon activity such that carbon deposition occurs and metastable metal carbides form. It is observed at intermediate temperatures of about 400 - 900°C (750 - 1650°F). Systematic studies of this phenomenon (see, for example, the reviews in references 2, 3, and 5) have shown that the metal dusting process occurs by a series of steps in the following order:

1. Rapid uptake of carbon into the metallic phase leading to supersaturation of carbon in the alloy.

2. Formation of metastable carbides (for steels, Fe_3C).

3. Decomposition of these carbides (which are stable only at $a_c > 1$) when localized deposition of carbon occurs ($a_c = 1$).

4. Development of a loosely adherent layer of filamentary carbon and fine metallic particles, which then act as catalysts for further carbon deposition.

This powdery mixture may also include oxides and carbides. The products can be carried away by the flowing gas. Pits and holes on affected surfaces can be observed in addition to general metal wastage. Carbon formation is a necessary but not sufficient condition for metal dusting - a metastable carbide (typically Fe_3C) must also form since it is its subsequent decomposition that leads to metal wastage. Metal dusting can be distinguished from carburization, normally seen with high-temperature alloys, which results in the formation of stable carbides on and in the solid exposed to a carbon-containing environment (even at $a_c < 1$).

Deterioration of refractories used in coal gasification vessels can occur at temperatures below about 650°C (1200°F) when these materials contain iron or iron alloys (usually castable refractories). An excellent review of this phenomenon, known as CO disintegration, can be found in ref. 6. Carbon deposition from the gas mixture is a necessary step in the process, which then leads to degradation that exhibits many of the same characteristics as metal dusting. Indeed, the basic mechanisms involved in both CO disintegration of iron-containing refractories and metal dusting are similar, although, historically, the studies of the respective phenomena appear to have been conducted independently of each other.

PROJECT DESCRIPTION

This short-term project was begun in November, 1994 to examine issues related to the potential for carbon formation and metal dusting relevant to coal gasification systems. It was funded by the U.S. DOE Office of Fossil Energy through the Morgantown Energy Technology Center and the Advanced Research and Technology Development (AR&TD) Materials Program.

Because carbon deposition and carbide formation are at the root of many of the potential operational and materials problems in coal gasifiers, a major part of this project involved thermochemical calculations of carbon activities and stabilities of iron-containing phases for representative gasifiers and an evaluation of the implications of these results for coal gasification systems. Accordingly, this paper focuses on summarizing the conclusions from this work. Much more detail can be found in ref. 7, which also includes the results from the other parts of the project, including a review of metal dusting, discussion of materials selection considerations for hot-gas cleanup sections of coal gasification systems, and more specific recommendations for followup work.

RESULTS

Thermochemical Calculations

Carbon Activities. As discussed previously, the initiation of carbon deposition and metal dusting requires a carbon activity greater than unity. For this reason, the product gas chemistries of eight representative gasifier systems were examined with respect to the chemical activity of carbon. A principal concern is the change in carbon activity brought about by reduction in the gas temperature downstream from the outlet of the gasifier reaction vessel; such cooling may accompany filtration and sulfur removal functions. The selected systems and their nominal effluent gas compositions are listed in Tables 1 and 2. The former table presents the input data for air-blown systems and the latter, data for oxygen-blown systems.

The principal components of the product gas include CO, CO_2, H_2, H_2O, CH_4, and, in the case of air-blown gasifiers, N_2. Minor species include H_2S, NH_3, and COS. A series of thermochemical calculations, based on the SOLGASMIX[8] computer program, was made to examine essentially all of the possible chemical interactions among these species as a function of temperature at representative system pressures. The calculations assumed that the mole fractions of the elemental constituents (C, H, O, S, N) in the compounds composing the reference product gas do not change from point to point in the system, and therefore are constant with temperature. This assumption appears valid given the conditions of forced convective flow in a closed piping system and limited reaction of the gas with its containment system. Based on these calculations, the following generalizations can be applied to all gasifier systems and their attendant product gas compositions:

1. The equilibrium gas composition and, accordingly, the carbon activity, are determined by three principal chemical reactions:

$$2CO\ (g) = CO_2\ (g) + C\ (s) \qquad (1)$$
$$CO_2\ (g) + H_2\ (g) = H_2O\ (g) + CO\ (g) \qquad (2)$$
$$CH_4\ (g) = C\ (s) + 2H_2\ (g) \qquad (3)$$

Thus, changes in the carbon activity of the product gas as a function of temperature (at a given system pressure) are controlled by the temperature dependencies of the standard free energies of these three reactions.

2. In air-blown gasifiers, nitrogen is a diluent. At a given system pressure, the effect of nitrogen on the partial pressures of the other gas species results in both a decrease (reaction 1) and increase (reaction 3) in carbon activity. Its introduction will decrease the carbon activity through reaction 1 and increase it through reaction 3. This effect on the carbon activity is indirect since nitrogen itself is not a reactant. At the nitrogen activities associated with gasifiers, the reactions of nitrogen with carbon or hydrogen are insignificant and products such as NH_3 are relatively unstable.

3. Even at the H_2S concentrations associated with the highest sulfur coals, the sulfur availability is too small to affect the concentration of the principal carbon- or hydrogen-containing species. Therefore, the carbon activity is unaffected by the presence of H_2S.

For air-blown gasifiers, the calculations indicated that the compositions of the gas exiting the gasifier reactor, that is, those shown in Table 1, are at equilibrium with respect to the exit gas temperature. The carbon activity at this point is less than unity. Typically, as the gas is cooled under equilibrium conditions, the CO and H_2 concentrations decrease while the CO_2, H_2O, and CH_4 concentrations increase, and these changes are accompanied by a significant increase in the carbon activity. The temperature at which the carbon activity reaches unity is process- and fuel-dependent, but for the air-blown gasifiers examined, it ranged from a low of 770°C (1420°F) to a high of 880°C (1620°F).

In the case of oxygen-blown gasifiers, where the initial CO content was 54 vol% or greater, calculations showed that the carbon activity of the gas was already higher than unity at the reference reactor outlet temperature. Again, cooling under equilibrium conditions resulted in a decrease in the CO and H_2 concentrations and an increase in CH_4, CO_2, and H_2O levels, while the carbon activity remained at unit activity. In the case of the Texaco gasifier, in which the initial CO content was only 46.5 vol%, the carbon activity was more typical of an air-blown system, and unit carbon activity was not established until the temperature had dropped to 870°C (1600°F).

The formation of CH_4 is promoted by decreasing temperature and, in effect, CH_4 becomes a sink for carbon as the temperature is lowered. Accordingly,

Table 1. Gas Composition and Pressures of Reference Air-Blown Gasifiers

Gas Component	Sierra Pacific (MWKellogg)	Wilsonville (Foster Wheeler)	Wilsonville (MWKellogg)	Four Rivers (Foster Wheeler)	Toms Creek
	Concentration (volume %)				
CO	23.89	18.05	18.43	16.50	26.0
CO_2	5.44	8.79	8.10	9.00	5.0
H_2O	5.50	9.11	8.07	9.50	14.0
H_2	14.57	16.57	13.70	12.90	5.0
CH_4	1.35	3.97	0.36	1.40	2.2
N_2	48.65	42.68	51.30	50.50	47.5
H_2S	0.03	0.05	0.02	0.04	0.006
NH_3	0.02	0.32	0.01	0.19	0.15
Ar/Other	0.56	0.48	0.02		
Gas Pressure (bar)	20.26	14.19	20.68	14.18	22.65

Table 2. Gas Composition and Pressures of Reference Oxygen-Blown Gasifiers

Gas Component	Shell	Duke Energy Corp.	Texaco
	Concentration (volume %)		
CO	62.9	54.1	46.5
CO_2	1.3	3.2	15.3
H_2O	0.2	0.0	0.0
H_2	30.8	27.7	35.9
CH_4	0.035	7.0	0.0
N_2	4.4	6.8	2.0
H_2S	0.4	0.0	0.3
Ar/Other			0.1
Gas Pressure (bar)	28.58	22.05	35.13

reaction 3 acts to offset the increase in carbon activity with decreasing temperature resulting from reaction 1. However, without the action of an effective catalyst, reaction 3 is relatively sluggish and tends to be ineffective at temperatures below 800°C (1470°F). Accordingly, calculations of the CH_4 gas concentration assuming equilibrium conditions for reaction 3 can be expected to give unrealistically high CH_4 concentrations at lower temperatures. To examine this effect, another series of calculations was made in which reaction 3 was excluded, and the CH_4 concentration was assumed to remain unchanged as the product gas was cooled. An unexpected finding in these latter calculations was that excluding reaction 3 had only a small effect on the temperature at which unit carbon activity was reached, and this temperature in some cases even decreased slightly. (This result appears to be associated with the relatively high H_2 level in the product gases compared to CH_4 and the combined role of H_2 in reactions 2 and 3.) However, once the temperature dropped below the unit carbon activity threshold, the elimination of reaction 3 significantly increased the carbon activity (or availability of solid carbon) upon further cooling.

The central conclusion to be drawn from examination of carbon activities as a function of temperature is that, from a thermodynamic standpoint, the potential for carbon deposition will exist for all gasifier systems at some temperature below that attained in the reaction vessel. This potential arises from the relatively high CO concentration in the product gas. Based on equilibrium calculations, H_2 will act to offset the extent of carbon deposited through the generation of CH_4, but this reaction is very sluggish at the temperatures at which carbon deposition will occur. The temperature at which deposition becomes possible is directly proportional to the CO content of the gas and may increase or decrease slightly with higher H_2 contents.

Iron-Based Phase Stabilities. Because the formation of a metastable carbide (Fe_3C, for steels) is a necessary condition for metal dusting, determination of solid phase stabilities in different gasifier environments is an important aspect of evaluating the potential for degradation of exposed materials. Accordingly, equilibrium calculations were performed to determine the phase stability of iron-containing reaction products in contact with the product gases of air- and oxygen-blown gasifiers at 600 and 800°C (1110-1470°F), respectively. The Sierra Pacific (M. W. Kellogg) and Wilsonville (Foster Wheeler) reference gas compositions in Table 1 were arbitrarily selected from the air-blown category, while the Shell gasifier composition in Table 2 was selected from the oxygen-blown class. The phase stability relationships were initially determined under equilibrium considerations that limited the carbon activity to that of the most stable carbon-containing phase. Since Fe_3C is not stable at the carbon activity of graphite ($a_c = 1$), the formation of graphite supersedes that of this carbide under equilibrium conditions. However, if the deposition of solid carbon from the product gas is relatively sluggish, such that the carbon activity of the gas can build up above that of graphite, then Fe_3C formation becomes thermodynamically possible, particularly at lower temperatures. Accordingly, a second series of phase stability calculations was carried out in which solid carbon formation was suppressed. The H_2S concentrations used in the calculations were those listed for the given gasifiers in Tables 1 and 2. The H_2S level can vary depending on the coal source and hot-gas cleanup system and that such changes will significantly affect the relative stability of iron sulfide in the system.

When graphite was allowed to form, phase stability calculations for both air-blown gasifiers indicated that iron oxide (FeO) predominated as the most stable iron-containing phase at 800°C (1470°F), and both iron sulfide ($Fe_{0.877}S$) and iron oxide were stable phases at 600°C (1110°F). Under these same conditions, only the $Fe_{0.877}S$ phase was stable in the case of the oxygen-blown Shell gasifier. When the formation of solid carbon was suppressed but CH_4 formation (reaction 3) was allowed, the results for the air-blown gasifiers were unchanged - FeO and $Fe_{0.877}S$ were the principal phases at 600°C (1110°F), and FeO alone was predominant at 800°C (1470°F). However, if the reaction to form CH_4 was suppressed along with the one to form solid carbon, then Fe_3C and $Fe_{0.877}S$ became the predominant phases at 600°C (1110°F) for both air-blown gasifiers. At 800°C (1470°F), Fe_3C was the single predominant phase in the case of the Sierra Pacific gasifier, while $Fe_{0.877}S$ and FeO were predominant in the case of the Wilsonville gasifier. When the formation of graphite was suppressed in the case of the oxygen-blown Shell gasifier, the $Fe_{0.877}S$ phase remained stable and the Fe_3C phase did not appear even when the CH_4 reaction was suppressed. Only by lowering the H_2S content of the gas to below 0.20 vol% at 600°C (1110°F) and 0.32 vol% at

800°C (1470°F) could stability be conferred to the Fe_3C phase, where it co-existed with $Fe_{0.877}S$. At H_2S concentrations below 0.09 vol% at 600°C (1110°F) and 0.20 vol% at 800°C (1470°F), Fe_3C became the sole predominant phase. Similar calculations indicated that nitrogen-containing reaction products with iron would not be expected to form under equilibrium conditions even for air-blown gasifiers. A summary of the phase stability relationships for these three gasifiers is shown in Table 3.

For the air-blown gasifiers, the appearance of the Fe_3C phase coincided with the disappearance of the iron oxide phase, which was a result of the oxygen activity of the system being reduced by the relatively high carbon activity. These phase stability calculations indicate that the formation of Fe_3C is precluded thermodynamically under conditions where an oxide can form, a finding that suggests that FeO should be effective in mitigating metal dusting. The sulfide reaction product in the air-blown gasifiers was found to co-exist with either the oxide or the carbide. However, in the oxygen-blown Shell gasifier, the oxide was unstable and, because of the relatively high H_2S concentration (1.4 vol%), the sulfide existed to the exclusion of the carbide. It follows that at higher H_2S concentrations, the sulfide can act effectively to exclude the formation of Fe_3C in the same manner as an oxide, while at lower H_2S levels where it co-exists with the carbide, its effectiveness as a barrier to Fe_3C will depend on the relative nucleation and growth rates of the carbide vis-a-vis the sulfide. Because the reaction rate to form iron sulfide is significantly faster than that of iron oxide at 600°C (1110°F), the stability of iron sulfide in this temperature range, as shown by these calculations, could be a significant factor in inhibiting the formation of Fe_3C. A general conclusion from these stability calculations is that the removal of H_2S by a hot-gas cleanup system may have less effect on the formation of Fe_3C (and therefore on metal dusting) in the two air-blown gasifier environments, where the iron oxide phase can exist and is unaffected by the removal of sulfur, than in the Shell product gas environment, where iron sulfide provides the only significant potential barrier to Fe_3C formation.

Steam Injections. Kinetic effects can be expected to play an important role relative to carbon deposition in gasifier systems, considering that deposition is possible only at reduced gas temperatures. (These effects, particularly those associated with H_2S and NH_3, are discussed in a subsequent section.) In fact, on the basis of the reactions controlling carbon deposition (reactions 1-3), it appears more fruitful to approach the problem of carbon deposition in gasifiers by inhibiting the reactions kinetically rather than by attempting

Table 3. Predominant Solid-State Phases Of Iron When Exposed To Reference Product Gas Compositions

Gasifier System	Temp. (°C)	Predominant Phases		
		Fully Equilibrated	Carbon Deposition Suppressed	Carbon Deposition and CH_4 Formation Suppressed
Sierra Pacific (MWKellogg)	600	Graphite, FeO, FeS	FeO, FeS	FeS, Fe_3C
	800	Graphite, FeO	FeO	Fe_3C
Wilsonville (Foster Wheeler)	600	Graphite, FeO, FeS	FeO, FeS	FeS, Fe_3C
	800	FeO	FeO	FeO, FeS
Shell (Oxygen-blown)	600	Graphite, FeS	FeS	FeS*
	800	Graphite, FeS	FeS	FeS**

* Fe_3C also is stable if $H_2S < 0.2$ vol%
**Fe_3C also is stable if $H_2S < 0.32$ vol%

thermodynamic fixes, that is, rather than by altering the concentrations of major gas species. An example is shown by the effect of adding steam to one of the reference air-blown product gases, namely, the Sierra Pacific reference composition (Table 1). Equilibrium calculations were made in which the concentration of steam was doubled from the initial level of 5.5 vol% to a level of 11 vol% without changing the relative concentrations of the other gases. Even such a large steam injection did not eliminate the potential for carbon deposition, although it did lower the temperature at which unit carbon activity was achieved from 850°C (1560°F) to 798°C (1468°F). Accordingly, the injection of steam would not of itself eliminate the possibility of carbon deposition, although by lowering the threshold temperature for carbon deposition it could possibly aid inhibiting techniques based on kinetic effects.

Another aspect of increasing the steam content of the product gas concerns the effect on corrosion products formed by reaction with the containment material. By increasing the oxygen potential of the gas, steam injection could promote the formation of oxide reaction products which may serve to prevent development of Fe_3C. Accordingly, the effect of doubling the steam content of the Sierra Pacific gasifier to 11% was also examined from the standpoint of its effect on the phase stability of iron-containing reaction products. As noted above, if the formation of solid carbon is suppressed, the predominant phases formed in the nominal Sierra Pacific product gas, containing 5.5% H_2O, are FeO and $Fe_{0.877}S$ at 600°C (1110°F) and FeO at 800°C (1470°F). Increasing the H_2O content to 11% in this case did not change the stable ensembles at either temperature. In the case where the formation of both solid carbon and CH_4 (reaction 3) was suppressed, increasing the H_2O content to 11% had no effect at 600°C (1110°F) but was beneficial at 800°C (1470°F). $Fe_{0.877}S$ and Fe_3C were retained as the predominant phases at 600°C, while at 800°C, the Fe_3C phase, predominant in the nominal atmosphere, was, in fact, supplanted by FeO. It appears that H_2O additions could provide an overriding effect on iron carbide formation at higher temperatures, where the carbon activity of the gas is more moderate, but very large additions would be required at lower temperatures to offset the larger carbon activities that can accrue if solid carbon deposition and CH_4 production fail to keep pace with carbon-forming reactions (such as reaction 1).

Conditions That Influence Kinetics of Carbon Deposition

As shown in a previous section, essentially all representative gasifiers operate under conditions in which carbon formation is thermodynamically possible in the hot-gas cooler and cleanup sections. However, such calculations do not take account of the kinetics of the gas equilibration or carbon deposition processes since all chemical reactions are assumed to proceed sufficiently rapidly that thermodynamic equilibrium is achieved. Typically, methods exist to increase or decrease the rates of reaction either through gas-phase modifications or by altering the surfaces on which deposition is to take place.

The poisoning effect of H_2S on carbon deposition reactions has long been known.[9-11] This compound is also routinely added to gas mixtures of high carbon activity to reduce degradation that involves carbon deposition as a precursor to carburization.[2,5,12-14] It is generally assumed that the sulfide acts to reduce the catalytic activity of surfaces with respect to carbon deposition.[5] The presence of water vapor has also been reported to inhibit deposition of carbon,[15] but not necessarily catalytically. Rather, water vapor can react with the deposit to form gaseous products or shift the equilibria of reactions 1 - 3 so as to reduce CO decomposition.[15] However, as discussed above, relatively large concentrations of water vapor would be required to materially affect carbon deposition in the typical gasifier.

The formation of stable surface layers of certain types of oxides has been shown to be effective in decreasing carbon formation and/or reducing the susceptibility to metal dusting (perhaps by preventing deposition on reactive surfaces). These oxides include chromia, silica, and, possibly, alumina.[1,16,17] Other surface oxides, such as Fe_2O_3 and Fe_3O_4, and carbides can actually increase carbon formation.[3,6,18,19] In addition to oxidation effects, alloying or material selection and surface condition can also affect deposition by controlling the types of carbides that form or the phase distribution of the alloy components.[20] Surface roughness increases carbon deposition rates.[3,20] As may be expected, the surface crystallography can have an important effect (see, for example, ref. 21).

Influence of System Operating Parameters on Carbon Deposition and Metal Dusting.

Coal gasification processes are typically targeted to the generation of a product gas containing a relatively high concentration of CO. As discussed above, this high CO concentration essentially guarantees that a carbon activity greater than unity will be achieved on cooling the gas downstream of the gasifier reaction vessel. Calculations indicated that the prospects of drastically reducing the thermodynamic potential for carbon deposition by additions of H_2O do not appear feasible, given the amounts of H_2O that would be required. Hydrogen additions offer another thermodynamic avenue for reducing the carbon activity on cooling, but this would involve a radical change in the gasification process or a separate source of H_2. Furthermore, there is no assurance that the rate of the chemical reactions involving any of these additions (particularly H_2) could compete with that of the CO decomposition reaction as the gas is cooled. Thus, the operating parameter variations that appear most effective for inhibiting carbon deposition come down to the H_2S and NH_3 levels maintained in the product gas and the rate and degree of cooling between the gasifier and the gas turbine. The oxygen activity of the product gas is another operating parameter that may be important, since it could be manipulated to maintain oxide films as carbon deposition barriers on metals otherwise susceptible to metal dusting. Alternatively, barrier surface oxides could be established by a preoxidation procedure, either by treating individual components before system assembly or by operating the gasifier in an oxidizing (combustion) mode prior to the start of gasification.

As discussed elsewhere,[7] instances of metal dusting have been reported in operating gasification systems. However, it appears that most gasifiers have not been plagued by serious metal dusting and deposition problems to date, particularly in contrast to many other chemical processes containing comparable CO concentrations. One probable reason relates to the possibility that the carbon activities in these systems are not sufficient to form Fe_3C to the exclusion of oxides or sulfides of iron (see above). In addition, the relatively high H_2S contents that generally exist in the product gas ahead of the filtration and sulfur removal systems should assure that there is sufficient sulfur available to inhibit carbon deposition or carbide formation over the most crucial temperature range during gas cooling. Once the gas is cooled by water quenching, the kinetics of carbon deposition would no longer be favorable, with or without H_2S. If H_2S is the key to preventing carbon deposition, this problem would assume greater significance with the adoption of hot sulfur-removal processes in future gasifiers, since the H_2S will then be removed in a temperature regime where carbon deposition and metal dusting are possible. The operating parameters that then would become critical are the temperatures of the hot-gas clean-up system and the downstream piping, and the level to which H_2S has been reduced in the gas flowing through these sections.

An ideal approach for setting the H_2S content in gasifiers incorporating hot sulfur-removal systems would be to maintain an H_2S level that is sufficient to inhibit carbon deposition and metal dusting in piping sections ahead of the gas turbine but is too low to cause corrosion by sulfidation. Barnes et al. demonstrated that, for high-chromium Fe-Ni-Cr alloys at 1000°C (1830°F), at H_2S levels up to 100 ppm, sulfur adsorption on carbides formed on the alloy surface progressively inhibited carbon pickup.[22] Higher levels of H_2S also reduced internal carburization, but promoted the formation of a surface layer of chromium sulfide which led to increased corrosion.[22] Whether such a critical range of H_2S exists for the present case cannot be determined on the basis of current information, but it becomes a critical consideration in establishing the desired operating parameters for future gasifiers.

The NH_3 concentration of the product gas is another operating parameter that is reported to affect the kinetics of carbon deposition and metal dusting.[2] However, as discussed above, NH_3 is relatively unstable in the given product gas chemistry and may be relatively difficult to control. As in the case of H_2S, the level of NH_3 required to inhibit carbon deposition and metal dusting is an unknown in the case of the gasifier product gas and would need to be evaluated experimentally.

There is no obvious way to escape the temperature window for carbon deposition if the product gas is maintained at the exit temperature of a hot-gas cleanup system. However, cooling the gas immediately downstream from the cleanup system would afford a way of limiting any metal dusting concerns if a low-alloy steel is used as the connecting piping to the gas turbine. The gas temperature would need to be lowered to below about 400°C (750°F) to suppress any possibility of metal dusting of the low-alloy steel, assuming no other means of inhibition were employed.

Although of limited value in inhibiting carbon deposition (see above), steam additions, by increasing the oxygen activity of the product gas, could improve the stability of oxide films (FeO on iron or low alloy steels, Cr_2O_3, Al_2O_3, SiO_2 on appropriate alloys) which form on metals that otherwise might be susceptible to metal dusting. Steam additions would also decrease the temperature at which unit carbon activity is achieved in air-blown gasifiers, and such a temperature decrease could prove valuable in avoiding the operative temperature window of metal dusting for certain materials.

FUTURE WORK

There are a number of ways to examine various operating and environmental conditions in which carbon deposition and metal dusting might be expected in the product gas streams of coal gasification processes. The initial approach is by the use of thermodynamic predictions: as demonstrated in this project, knowledge of appropriate reactions and free energies is used to calculate carbon activities and phase stabilities and therefore to determine if a driving force for carbon deposition and metal dusting exists for a given gas mixture as a function of temperature and pressure. However, because other factors, such as kinetics, effects of inhibitors, and particular material conditions, actually determine the extent to which reaction products form, such thermodynamic predictions must then be experimentally evaluated. Indeed, based on this assessment, the experimental determination of the ability of equilibrium thermodynamics and accompanying assumptions on relative reaction kinetics to accurately predict carbon-related degradation tendencies forms the most important part of any relevant test program. The thermochemical calculations described above unequivocally predict carbon deposition in certain temperature ranges for all of the examined gasifiers. More importantly, it was shown that Fe_3C, a necessary precursor to metal dusting damage of steels, can become stable in these gasifier environments when carbon deposition and CH_4 formation are sluggish, as they may well be in many gasifier systems. It is therefore important to determine experimentally the temperature and environmental conditions under which Fe_3C can form and lead to degradation of the steel. The necessary steps in such a process include (1) specification of a representative gas composition, specifically one in which Fe_3C is predicted to be stable over a certain temperature range and under appropriate kinetic conditions, (2) exposure of a susceptible material in these environments, and (3) post-exposure analysis to correlate the occurrence of carbon deposition and metal dusting with the different environmental conditions. In a similar manner, an experimental validation approach can be taken with respect to verifying the effects of H_2S and steam injection on carbon deposition and Fe_3C stability. These types of experiments would help resolve the questions associated with (admittedly limited) observations that operating experience with coal gasification plants to date has not indicated significant problems that can be associated with carbon-related degradation.

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