

## 5. 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 in Sect. 2, 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 in Sect. 2 indicated that the prospects of drastically reducing the thermodynamic potential for carbon deposition by additions of H<sub>2</sub>O do not appear feasible, given the amounts of H<sub>2</sub>O that would be required. Hydrogen additions offer another approach for reducing the carbon activity on cooling, but this would involve a radical change in the gasification process or a separate source of H<sub>2</sub>. Furthermore, there is no assurance that the rate of the chemical reactions involving any of these additions (particularly H<sub>2</sub>) could compete kinetically 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 are the H<sub>2</sub>S and NH<sub>3</sub> 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. However, long-term stability and integrity of such oxides may be problematical.

As discussed in Appendix A, 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 is that the carbon activities in these systems are not sufficient to form Fe<sub>3</sub>C to the exclusion of oxides or sulfides of iron (see Sect. 2). In addition, the relatively high H<sub>2</sub>S contents that generally exist in the product gas ahead of the filtration and sulfur removal systems should ensure that sufficient sulfur is 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, carbon deposition would be appreciably slowed, with or without H<sub>2</sub>S. If the H<sub>2</sub>S is the key to preventing carbon deposition, this problem would assume greater significance with the adoption of hot sulfur-removal processes in future gasifiers because the H<sub>2</sub>S 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 cleanup system and the downstream piping, and the level to which H<sub>2</sub>S has been reduced in the gas flowing through these sections.

An approach for setting the H<sub>2</sub>S content in gasifiers incorporating hot sulfur-removal systems would be to maintain an H<sub>2</sub>S level that is sufficient to inhibit carbon deposition and metal dusting in piping sections ahead of the gas turbine but that is too low to compromise the corrosion resistance of the gas-containment material. Barnes et al. demonstrated that, for high-chromium Fe-Ni-Cr alloys at 1000°C (1830°F), at H<sub>2</sub>S levels up to 100 ppm, sulfur adsorption on carbides formed on the alloy surface inhibited carbon pickup.<sup>32,33</sup> Higher levels of H<sub>2</sub>S also reduced internal carburization but promoted the formation of a surface layer of chromium sulfide, which led to increased corrosion.<sup>33</sup> Whether such a critical range of H<sub>2</sub>S exists for the present case cannot be determined on the basis of current information, but it becomes an important consideration in establishing the desired operating parameters for advanced gasifiers.

The NH<sub>3</sub> concentration of the product gas is another operating parameter that is reported to affect the kinetics of carbon deposition and metal dusting.<sup>2</sup> However, as discussed in Sect. 2, NH<sub>3</sub> is relatively unstable in the given product gas chemistry and may be relatively difficult to control. As in the case of H<sub>2</sub>S, the level of NH<sub>3</sub> required to inhibit carbon deposition and metal dusting in gasifiers is unknown and would need to be evaluated experimentally.

There appears to be no 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. Disadvantages of this approach include the additional surface area of the heat exchanger and, in the case of integrated combined cycle units, a reduction in the gas turbine inlet temperature.

Steam additions are of limited value in inhibiting carbon deposition (see Sect. 2); however, by increasing the oxygen activity of the product gas, steam additions could improve the stability of oxide films (FeO on iron or low-alloy steels; Cr<sub>2</sub>O<sub>3</sub>, Al<sub>2</sub>O<sub>3</sub>, or SiO<sub>2</sub> on applicable alloys) that 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 (see Sect. 2). Such a temperature decrease could prove beneficial by allowing a gasifier to operate above the temperature window of metal dusting for certain materials.