7. RECOMMENDATIONS FOR FURTHER EVALUATION OF POSSIBLE DEGRADATION MODES

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. An initial approach is by use of thermodynamic predictions: as demonstrated in Sect. 2, 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) can override thermodynamic considerations related to these phenomena, such predictions must then be experimentally verified. Based on this assessment, the empirical evaluation of the ability of equilibrium thermodynamics and accompanying assumptions on relative reaction kinetics to accurately predict carbon-related degradation tendencies should form the most important part of any relevant test program. The thermochemical calculations described in Sect. 2 unequivocally predict, in the absence of inhibitors, 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) postexposure 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 with carbon-related degradation (Appendix A).

The above tests (designated Type I for convenience) are designed to evaluate whether certain environmental conditions relevant to operating gasifiers can lead to (or prevent) metal dusting. By combining assumptions regarding reaction kinetics with thermochemical calculations, predictions can be formulated and then compared with experimental results. Such tests would evaluate certain factors that can counter thermodynamic tendencies in determining whether carbon deposition and metal dusting will occur. A complementary approach would be to investigate relative materials susceptibility to metal dusting. In this case, using a given gasifier-relevant environment that is known to cause metal dusting of a low-alloy steel (which serves as a baseline), exposures of various compositions and surface treatments (such as conferred by preoxidation treatments) would be conducted and compared. Such experiments (Type II) could also be used to investigate sulfidation tendencies of different materials, and when combined with Type I tests, to determine critical levels of H_2S necessary to suppress metal dusting and avoid degradation by metal sulfide formation.

Experimental methods to evaluate carbon-related degradation phenomena can be broadly categorized into four types: (1) surface reaction studies, (2) laboratory corrosion exposures, (3) rig tests, and (4) test beds. Surface studies involving sensitive analytical probes of composition and structure can be used to investigate catalytic effects and to understand the effects of inhibitors on the carbon deposition process and the effectiveness of potential barrier layers. Laboratory corrosion exposures involve small-scale studies of candidate materials in simulated gas environments.[3,17,30] Analyses are done by following the weight change of coupons, often in a microbalance, and posttest destructive examination and analysis of the specimens. Such tests are useful for determining the susceptibility of a particular material to carbon-related phenomena for a given set of environmental and temperature conditions (including the effects of inhibitors). They can be used to establish the temperature window of susceptibility to metal dusting for given gas compositions and material compositions.[1,2] They are appropriate for the Type II experiments. Rig tests are somewhat more complex. Simulated gases at appropriate velocities flow through tubes of candidate materials.[19,29] Carbon buildup on tube walls can be monitored, and coupons can be exposed and removed at various times for metallurgical and chemical examination. Rig tests are again useful for qualitatively judging the susceptibility of materials as well as for examining the effect of temperature, and could be used for Type II tests. The use of flowing gases allows an erosion component to be included. Test beds connected to actual gasification reactors (such as those at the Federal Energy Technology Center in Morgantown, West Virginia) offer the most realistic experimental conditions outside of operating plants. Such facilities can be used to verify results from laboratory and rig tests and to qualify materials and certain process modifications being considered for new or operating plants. As such, they may be the best approach for Type I tests, particularly if the results are to be used for guidance related to system design or operating parameters.

On the basis of the present work, specific recommendations regarding needed evaluation of possible carbon-related degradation modes are enumerated as follows in order of priority.

1. Experimental validation (Type I) tests should be conducted with a candidate low-alloy steel using variants of a specific gasifier environment in a manner described above. The objective of such a project would be to determine the operating conditions, if any, under which Fe_3C can form and can lead to metal dusting. Such experiments are probably best conducted using a test bed.

2. Type I tests with the candidate low-alloy steel should be used to investigate the effects of a wide range of H_2S levels on carbon deposition and Fe_3C stability. While this study could be part of recommendation 1, these experiments would be specifically targeted at examining the ramifications associated with hot-gas cleaning on materials degradation in the gas-delivery system. With appropriate design, such tests can also be used to determine optimal H_2S levels necessary to avoid carbon-related degradation and sulfidation problems. This investigation could be conducted at the laboratory level.

3. The Type II approach should be used to investigate surface treatments for mitigation of metal dusting, particularly with respect to the stability and long-term reliability of chromia, silica, and alumina scales. These results would have particular relevance to operating procedures that rely on a preoxidation treatment to establish protective oxide layers. Laboratory corrosion exposures would be the preferred method of experimentation. Rig tests or the use of test beds could then be used to qualify specific preoxidation treatments.

4. Given the lack of substantial data on the metal-dusting performance of alumina-forming alloys, a set of Type II laboratory-level experiments incorporating such materials would be beneficial. In particular, the metal-dusting susceptibility of iron aluminides should be explored in greater detail as its excellent sulfidation resistance would allow it to be used in gases with higher H_2S levels (see recommendation 2).