

OBJECTIVES

The overall objective of this project is to study the metal dusting phenomenon from a fundamental scientific base involving laboratory research in simulated process environments and field testing of materials in actual process environments with participation from the U.S. chemical industry, alloy manufacturers, and the Materials Technology Institute (MTI), which serves the chemical process industry. Another objective is to develop a user-friendly knowledge base of materials/corrosion information for application in the chemical and petrochemical industries.

The effort at Argonne National Laboratory (ANL) involves testing off-the-shelf and surface-engineered materials in simulated process environments, developing a user-friendly computerized database of metal dusting/corrosion/mechanical properties of materials, and gaining a fundamental understanding of the metal dusting and associated carburization phenomenon. As part of this effort, alloy manufacturers contributed materials for both laboratory and field testing, participated in a Steering Committee for the project, and conducted in-house evaluation of materials.

STEERING GROUP AND MTI PROJECT MEETINGS

A list of Steering Committee meetings/teleconferences and MTI meetings, in which the project was discussed, is given below:

December 10, 1999 Teleconference

January 25, 2000	Air Products and Chemicals Inc., Allentown, PA
February 21, 2000	MTI meeting, Clearwater Beach, FL
March 16, 2000	Teleconference
June 5, 2000	MTI meeting in St. Louis, MO
July 28, 2000	DuPont Experimental Station, Wilmington, DE
August 31, 2000	Teleconference
October 10, 2000	Teleconference
October 23, 2000	MTI meeting, Charlotte, NC
January 29, 2001	Argonne National Laboratory, Argonne, IL
February 26, 2001	MTI meeting, Clearwater Beach, FL
March 14, 2001	In conjunction with NACE meeting, Houston, TX
June 4, 2001	MTI meeting, Memphis, TN
June 29, 2001	Teleconference

APPROACH

The technical approach involves several steps conducted either sequentially or in parallel and includes participation of MTI members and Argonne National Laboratory in the organization of the work plan and in the conduct of the proposed research to address the metal dusting issue. MTI member companies supplied their in-house metal-dusting data collected over the years and will make available, in the future, their facilities for exposure of candidate alloys and surface-engineered materials for evaluation and assessment.

The approach involves characterization, using thermodynamic modeling, of environments prevalent in several process streams in terms of their chemical activities for carbon, oxygen, and other elements. The results are used to assess the chemical potential and temperature windows for metal dusting to initiate and propagate in metallic materials. The thermodynamic assessment would also establish the consequences of equilibrium and nonequilibrium gas chemistries on the metal dusting process.

The corrosion behavior of commercial alloys in chemical process industries is being evaluated to identify conditions in which metal dusting occurs in practice. MTI has collected metal dusting data (both proprietary and published data from the open literature) for several materials from its member companies. This information is used to establish the effects of alloy chemistry, temperature range, pressure range, exposure time, and exposure environment on the corrosion process by metal dusting.

Bench-scale laboratory experiments are conducted at Argonne with candidate commercial alloys, developmental alloys, and surface-engineered materials, including coatings. Surface modification includes development of oxide scales on candidate alloys by exposures in air and low-pO₂ environments. Surface engineering includes development of pack diffusion coatings and claddings. Experiments are conducted in a wide range of gas chemistries and temperatures that encompass the environments prevalent in various process systems, such as in reformers for the production of hydrogen, ammonia, and methanol. Results are used to establish the conditions for the onset of metal dusting and to evaluate the influence of alloy chemistry on the occurrence of metal dusting.

Candidate commercial alloys, developmental alloys, and surface-engineered alloys will be exposed, at a later date, in several locations in process streams from production plants for hydrogen, methanol, ammonia, and other hydrogen-bearing compounds. Microstructures of the exposed specimens are characterized to assess their propensity to metal dusting. The field-exposure results and the laboratory test data are used to develop performance envelopes for alloys in service with minimum risk of metal dusting.

PROJECT TASKS

Project research focuses on the following tasks:

- Characterize chemical process environments using computer modeling of gas phase reactions
- Perform corrosion testing of off-the-shelf candidate alloys in simulated metal dusting environments
- Develop surface-engineered materials based on results of corrosion tests
- Evaluate the role of system pressure in the initiation of corrosion/metal dusting of materials
- Perform corrosion tests on surface-engineered materials in simulated chemical environments over a wide temperature and pressure range
- Expose candidate alloys and surface engineered materials in several locations in pilot and/or production systems that produce hydrogen, methanol, syngas, and ammonia
- Select the best candidates from monolithic alloys and surface engineered materials and fabricate tube sections for exposure in pilot and/or production units for evaluation
- Develop a database on metal dusting, corrosion, and mechanical properties of materials

BACKGROUND

Process Environments

The predominant process for hydrogen production is steam reforming of light hydrocarbons e.g., natural gas, liquefied petroleum gas, naphtha, or refinery off-gases. This process has been used extensively in the past for hydrogen production and is expected to continue in most of the installations required to meet the increasing demand for hydrogen in the future. The demand for hydrogen is growing in many industries, and refineries in particular must increase hydrogen use to make products acceptable to the environment and to limit production of very heavy resid. Refiners consider hydrogen a

utility, and they emphasize availability, trouble-free response to changing demand, and low-cost investment.

Production capacity in hydrogen plants may range from $<100 \text{ N}\cdot\text{m}^3/\text{h}$ to $>100,000 \text{ N}\cdot\text{m}^3/\text{h}$. For larger capacities, from $1000 \text{ N}\cdot\text{m}^3/\text{h}$ and upward, hydrocarbons are the predominant feedstocks. The production processes may be partial oxidation or steam reforming; for both types of processes, the primary process step is followed by shift conversion and final purification of product hydrogen.

Production of synthesis gas (mixtures of carbon monoxide and hydrogen) is an important first step in the manufacture of numerous chemicals. The most common process for producing synthesis gas is steam reforming, where hydrocarbons are converted by reaction with steam over a nickel catalyst at high temperatures. The synthesis gas from the steam reformer is purified in order to meet the requirements of the downstream process. It can be separated into pure H_2 , pure CO , H_2/CO mixtures, etc. Pure CO is required for the production of isocyanates, polycarbonates, and acetic acid, while for example, synthesis of oxo-alcohols requires an H_2/CO mixture with a molar ratio close to 1. By decreasing the steam/carbon ratio and by increasing the outlet temperature from the reformer furnace, great savings in feedstock consumption and in investment can be obtained.

The steam reformer is the heart of the unit for production of synthesis gas. In the steam reformer, hydrocarbon feedstock is reacted with steam to synthesis gas by the reactions:



All higher hydrocarbons ($n \geq 2$) are completely and irreversibly converted by the first reaction, while in the next two reactions, the strongly endothermic methane-reforming reaction (2) and the exothermic shift reaction (3) are close to equilibrium in the outlet of the steam reformer. The reactions take place over a nickel catalyst placed inside metal tubes. The tubes are arranged in a furnace where burners firing on the outside of the tubes supply the heat.

Metal dusting is a catastrophic corrosion phenomenon that leads to the disintegration of structural metals and alloys into dust composed of fine particles of the metal/alloy and carbon. This phenomenon has been observed in the chemical and petrochemical industries, in reformer and direct-reduction plants, in processes that generate syngas, and in other processes where hydrocarbons or other strongly carburizing atmospheres

are present. Failures have been reported in ammonia plants since reduced energy requirements result in a lower steam/H₂ ratio, whereas CO/CO₂ ratios have tended to increase.

Metal dusting is a process of highly accelerated material wastage that is preceded by the saturation of a material with carbon. The phenomenon is typified by the disintegration of a material (iron- or nickel-base) to a mixture of carbon dust, metal particles, and possibly oxides and carbides. This is usually a localized form of attack, resulting in pits and grooves. Metal dusting occurs at intermediate temperatures of 400-800°C, but this type of corrosion is possible at any temperature at which the carbon activity (a_C) in the gas phase is >1. Such high carbon activities are prevalent in certain locations in several chemical processes, such as methanol production, hydrocarbon and ammonia synthesis, hydrogen production, and syngas generation. Several of these chemical systems have reported metal/component failures by metal dusting. For CO-H₂-H₂O mixtures, carbon activity, which is the thermodynamic driving force for metal dusting, increases with decreasing temperature. Carbon activity values >1000 can be obtained at 500°C in several of the process streams.

Materials can be protected against metal dusting by adding sulfur-containing compounds, such as H₂S, to the process gas. Sulfur in the gas "poisons" the metal surfaces and prevents both carbon ingress and graphite nucleation. However, in many catalytic processes, sulfur-bearing substances cannot be injected since they deactivate the catalysts. To prevent material wastage under such conditions, an appropriate material with high resistance to metal dusting is needed.

Important reactions, which can occur in the typical metal dusting environment, are:



Reactions (4) and (5) can produce carbon; Reaction (6) deals with water-gas shift, and Reaction (7) with methane-steam reforming. The dominant reaction in a chemical process can be any one of the above reactions or a combination of them, and the carbon activity will be influenced by the dominant reaction, process temperature, and pressure. Most of the structural materials based on Fe, Ni, and Co are susceptible to this type of degradation even though the conditions of temperature, environmental chemistry, and incubation and kinetic factors for this occurrence may be different.

In a hydrogen plant, the major process components are the fuel gas reformer, process gas boiler, and high- and low-temperature shift reactors. The syngas from the reformer

contains various amounts of gases, such as H₂ (60%), CO (15%), CO₂ (5%), CH₄ (10%), steam (10%), and trace amounts of other compounds. It is produced primarily by steam reforming and partial oxidation of hydrocarbons at temperatures of 800-1400°C. The hot gases are contained in refractory-lined equipment and quenched to about 300°C in a waste-heat boiler or cooled by direct injection of water to the process stream. Most processes deliberately avoid transferring heat through the 800-400°C range because metal dusting occurs at these temperatures, and at present, no alloy can resist this type of corrosion over the long term. Consequently, the energy in high-temperature syngas is not recovered in an efficient manner.

Another example relevant to metal dusting is the formation of filamental coke in several petrochemical processes, which eventually leads to failure of heater alloys by metal dusting. The coke formation involves several sequential steps, such as dissociative chemisorption of hydrocarbon, stepwise dehydrogenation, surface and volume diffusion of carbon, carbide precipitation and transport under a temperature gradient, and regeneration of catalyst or decoking under oxidizing conditions. Further, the process entails cyclic deposition and decoking. Some models have been proposed in the literature for coke formation, which involves dissociative chemisorption and stepwise dehydrogenation leading to adsorption of C and H on the surface sites on the catalyst, diffusion of carbon through the metal and precipitation on the grain boundaries or at the metal/support interfaces, lifting of metal crystallites from the surface of the catalyst, and transport of crystallites to the top of the growing filaments.

Alternatively, C species may react on the surface to develop an encapsulating film, leading to the deactivation of the catalyst. Competition between C accumulation on the surface and C diffusion away from the active sites determines whether the catalyst becomes deactivated or not. This is determined by the composition of gas, hydrogen pressure, and temperature.

Metal Dusting Mechanism

Metal dusting is a high-temperature corrosion phenomenon that occurs in Fe-, Co-, or Ni-base alloys in strongly carburizing gas atmospheres at carbon activities (a_C) >1 in the temperature range of 425-900°C (\approx 800-1600°F).¹⁻⁹ During the metal dusting process, corrosion of metals and alloys occurs, accompanied by formation of fine metal carbide or pure metal and carbon dust. Dusting-related failures have occurred most often in the petroleum and petrochemical industries. This deterioration has been studied for more than 50 years,¹⁰ but its mechanism and driving force are not evident in all cases and no clear approach is currently available to mitigate this problem.

Hochman proposed the following mechanism for the metal dusting of iron: (a) carbon from the gas phase deposits on the metal surface and dissolves in the metal; (b) cementite forms as carbon diffuses into the Fe and the metal becomes supersaturated; and (c) metastable cementite decomposes to Fe and graphite.⁴ Grabke and coworkers

conducted studies and provided additional details on the possible mechanism.^{5-7, 9} According to them, the final product is graphite and Fe. However, there is no conclusive evidence that metallic Fe is present in every case of metal dusting. It is not clear what drives the formation and decomposition of cementite under the same conditions of temperature, pressure, and composition. It is easy to understand that graphite crystallizes from a supersaturated solution. Nevertheless, whether or not recrystallization would lead to decomposition of cementite is not yet clear. The formation and decomposition of chemical bonds require a sizeable free energy change. Cementite is a product of metal dusting, but it is not clear that this compound is essential to initiate metal dusting or is only a product of this step. Furthermore, the susceptibility of even complex Fe- and Ni-base alloys, in which cementite rarely can form, to this mode of degradation suggests that the mechanism is fairly complex and that a single mechanism may not be operative in all cases.

Even though metal dusting is widely prevalent, the general approach to minimize the problem in industry is the unsatisfactory one of excluding the temperature/process conditions that are conducive for the attack. Fixes, such as sulfur poisoning of surface sites and preoxidation of alloy to stabilize chromia on high-Cr alloys, are applied case-by-case, primarily based on past experience of materials performance in such environments.

Several other examples can be cited, such as hydrogen production by reforming reaction, but it is evident from the information presented above that metal dusting of materials is an issue in several chemical/petrochemical processes, and a detailed understanding of the causes for metal dusting and long-term solutions to minimize the problem could lead to substantial improvements in process efficiency, materials performance, process downtime, and reliability of operation. Further, the knowledge base developed in the U.S. will aid in the advancement of processes in the domestic industry, lead to development of better and improved metal-dusting-resistant alloys, and result in establishment of a data bank for selecting suitable materials for application in different process environments.

TECHNICAL PROGRESS

Gas Phase Reactions

Chemical process environments were characterized by computer modeling of gas-phase reactions under both equilibrium and nonequilibrium conditions. Calculations were made to evaluate carbon activities for different gas mixtures as a function of temperature at atmospheric pressure (14.7 psia) and at plant system pressures. Chemical compositions are listed in Table 1 for several gas mixtures that include the reformer streams and laboratory simulation environments. Carbon deposition process can be influenced by two possible reactions, as follows:

Table 1. Chemical compositions of gas mixtures relevant for metal dusting study

Gas species	Composition in mol %						
	Gas 1	Gas 2	Gas 3	Gas 4	Gas 5	Gas 6	Gas 7
CH ₄	4.1	1.1	0.2	-	-	-	-
CO	7.2	18	8.4	17.5	17.6	12.7	70.0
CO ₂	5.7	5.6	5	8.3	8.3	10.1	4.0
H ₂	43.8	52	36.3	74.2	72.2	77.2	25.25
H ₂ O	39.2	23	35	0	1.96	0	0.007
N ₂	-	-	15	-	-	-	-
Ar	-	-	0.1	-	-	-	-

Gases 1, 2, and 3: Reformer outlet gases.

Gases 4, 5, and 6: Used in ANL experiments.

Gas 7: Used in Special Metals Program.



Since the gas composition is maintained fairly constant during the passage through the waste-heat boiler, either Reaction 1 or Reaction 2 may dictate the carbon activity in the stream at different temperatures. If it is dictated by Reaction 1, the carbon activity will be directly proportional to H₂ and CO partial pressures and inversely proportional to H₂O partial pressure. On the other hand, if the carbon activity is dictated by Reaction 2, then it will be directly proportional to the square of the CO partial pressure and inversely proportional to CO₂ partial pressure. In addition, if gas phase equilibrium does prevail, albeit at high temperatures and/or for long residence times, then the calculated carbon activity value will be the same (i.e., irrespective of Reaction 1 or 2) since thermodynamically the gas composition will adjust to give the most stable (lowest free energy) composition. Therefore, carbon activity was calculated as a function of temperature from 496°C or 925°F to the maximum test temperature and for 1 atm to the maximum test pressure for various gas mixtures (Table 1) assuming Reaction 1 or 2 is dominant and the gas phase is in thermodynamic equilibrium.

Carbon Activity Calculations

Table 2 lists the carbon activity values calculated for the seven gas mixtures (Table 1) at 593 and 704°C (1100 and 1300°F), based on whether Reaction 1 or 2 was dominant or equilibrium between different gas species prevailed at the elevated temperature. Figures 1-3 show plots of carbon activity as a function of temperature for the three gas mixtures listed in Table 1. Figure 1 shows six curves for Gas Mixture 1, as follows:

Table 2. Carbon activity values at 593°C (1100°F) and 704°C (1300°F) based on reactions 1, 2, and equilibrium. Calculated for gas mixtures listed in Table 1.

Gas #	593°C (1100°F)			704°C (1300°F)		
	Rxn 1	Rxn 2	Eqm	Rxn 1	Rxn 2	Eqm
1	0.4	1.2	0.3	0.05	0.08	0.09
2	2.0	7.9	0.7	0.24	0.53	0.25
3	0.4	1.9	0.2	0.05	0.13	0.04
4	∞	5.0	1.3	∞	0.34	0.8
5	32.3	5.0	1.2	3.8	0.34	0.7
6	∞	2.2	0.01	∞	0.15	0.02
7	117.4	165.4	32.6	13.8	11.1	6.2

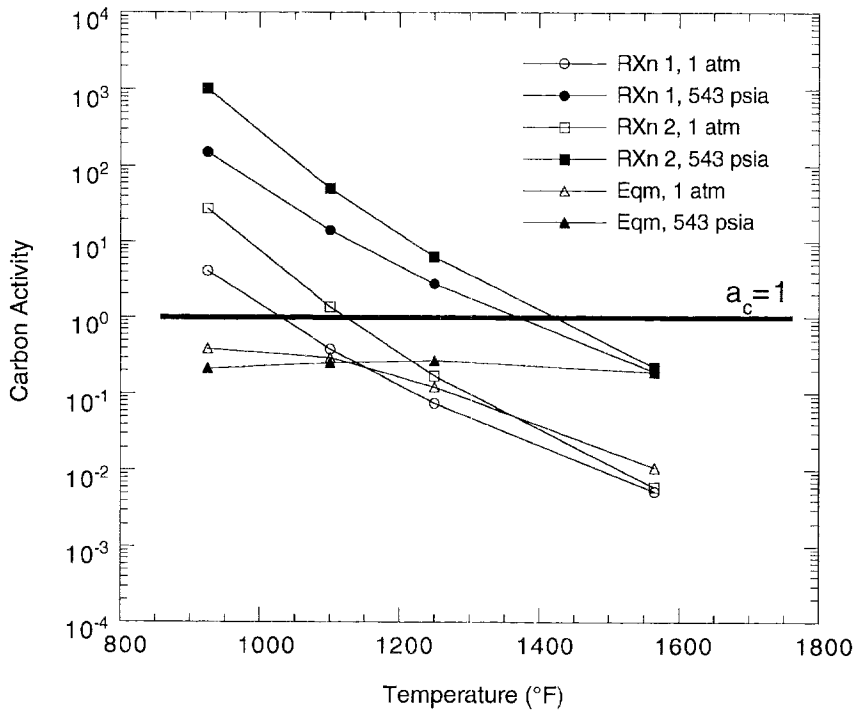


Fig. 1. Carbon activity curves calculated as a function of temperature for Gas Mixture 1.

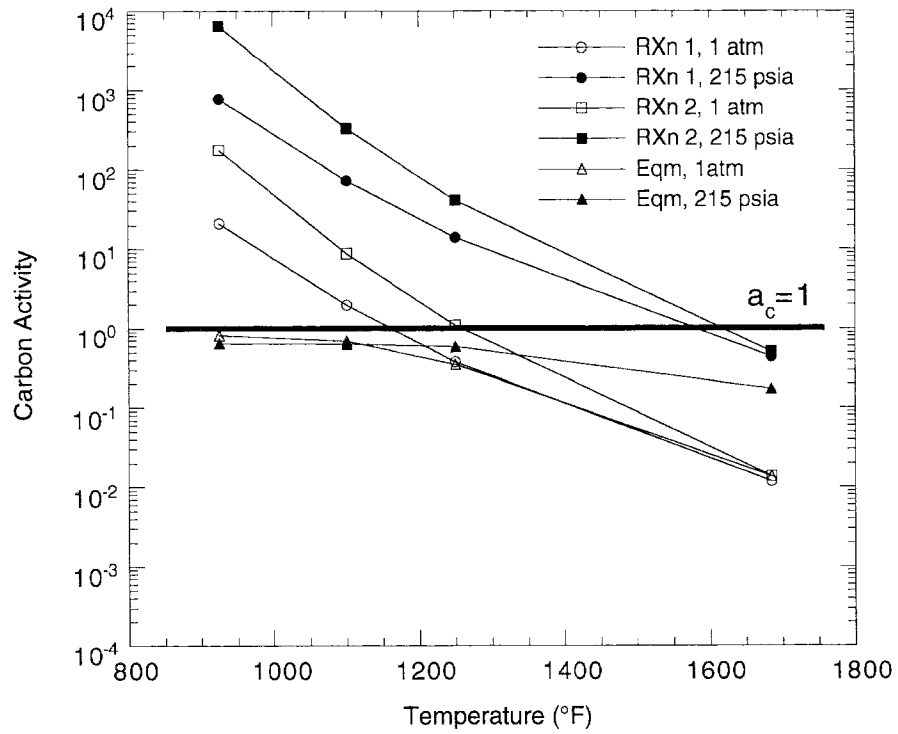


Fig. 2. Carbon activity curves calculated as a function of temperature for Gas Mixture 2.

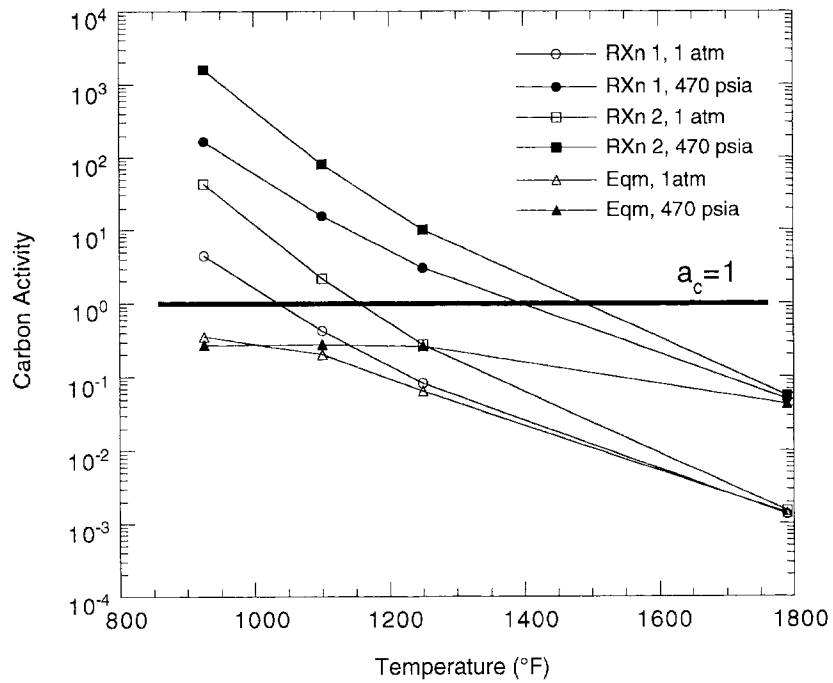


Fig. 3. Carbon activity curves calculated as a function of temperature for Gas Mixture 3.

Case 1:	Reaction 1 dominant, P = 1 atm (14.7 psia)
Case 2:	Reaction 1 dominant, P = 37 atm (543, psia)
Case 3:	Reaction 2 dominant, P = 1 atm (14.7 psia)
Case 4:	Reaction 2 dominant, P = 37 atm (543 psia)
Case 5:	Equilibrium condition, 1 atm (14.7 psia)
Case 6:	Equilibrium condition, P = 37 atm (543 psia)

Similar curves are shown in Fig. 2 for Gas Mixture 2, and in Fig. 3 for Gas Mixture 3. The maximum pressure values for Gas Mixtures 2 and 3 are 15 atm (215 psia) and 32 atm (470 psia), respectively.

The implications of the carbon activity calculations are as follows:

1. Under nonequilibrium conditions, Reaction 1 at 1 atm pressure results in the lowest carbon activity for all three reformer gas mixtures. Even under these conditions, the carbon activity is 1 or higher at temperatures below $\approx 565^{\circ}\text{C}$ ($\approx 1050^{\circ}\text{F}$) for Gas Mixtures 1 and 3 and below $\approx 621^{\circ}\text{C}$ ($\approx 1150^{\circ}\text{F}$) for Gas Mixture 2. At 496°C (925°F), the carbon activity values are ≈ 4 for Gas Mixtures 1 and 3 and ≈ 20 for Gas Mixture 2. These carbon activities can result in carbon deposition at 496°C (925°F) and may lead to metal dusting of several alloys, depending on the incubation time and alloy composition.
2. Reaction 2 always results in higher carbon activity. This trend is evident at all temperatures and pressures for the present calculations. Furthermore, this trend is independent of the gas mixture. The differences in the absolute value of the carbon activity established under Reaction 1 versus Reaction 2 control can be used to assess the role of these reactions in carbon deposition and associated metal dusting. For example, if an experiment is run in Gas Mixture 1 at 579°C (1075°F) and 1 atm, Reaction 1 control (with a_{C} of ≈ 0.6) would result in no carbon deposition, whereas Reaction 2 control (with a_{C} of ≈ 3) would result in carbon deposition. If a metal-dusting-susceptible alloy is used in this experiment, the results will clarify the role of Reaction 1 versus 2 in the carbon deposition/metal dusting process..
3. Increased system pressure increases a_{C} calculated for both reactions, irrespective of the gas composition. The carbon activities increase in direct proportion to the total pressure, and the values could be extremely large at lower temperatures. Furthermore, the effect of increased pressure is to widen the temperature window in which $a_{\text{C}} \gg 1$. For example, in Gas Mixture 1 with