Summary

The papers in this book may be categorized into three areas of interest to oxygen producers and users. The first five papers address established flammability test procedures used principally on nonmetallic materials. They may be subcategorized as to ignition, propagation, and damage potential measurements. The next two papers delve into considerations associated with oxygen systems rather than individual materials. Cleanliness significance and whole component performance are covered. The final three papers present data and philosophy on the testing and selection of metallic materials. Within Committee G-4 there is less of a consensus view on metals than on nonmetals. Many of these ten papers include introductory material and literature reviews for archival use. Others include data to support the use of existing ASTM standards for the evaluation of materials for oxygen service.

The first five papers on established flammability test methods begin with three papers on ignition testing. The avoidance of ignition through selection of ignition-resistant materials is the first line of defense against system fires. Numerous ignition mechanisms have been identified including mechanical impact ignition, autogenous ignition, resonance ignition, particle impact ignition, gaseous fluid impact ignition (adiabatic compression), friction ignition, and others. The first two of these, mechanical impact ignition and autogenous ignition, are the subjects of the first two papers.

Flammability Tests

Coleman J. Bryan reviews the collection and use of mechanical impact ignition test data by NASA. In the NASA test, materials in the presence of oxygen are struck by a falling plummet. The test is conducted in either atmospheric or pressurized environments using either liquid or gaseous oxygen. The material's resistance to ignition is measured by the threshold drop height that produces reactions or by the fraction of reactions that occurs for a fixed drop height. A study of NASA and Rocketdyne testers has produced a calibration procedure that allows essentially identical material rankings to be achieved from apparatus at different laboratories. A material's sensitivity to impact ignition was found to be greater in gaseous oxygen than in liquid oxygen. Impact sensitivity was found to increase with increasing pressures up to 6.9×10^7 Pa (10 000 psig). Extensive tables of NASA mechanical impact test data are presented.

Richard W. McQuaid, Donald G. Sheets, and Mary J. Bieberich review the collection of autogenous ignition temperature data using ASTM Test for Autogenous Ignition Temperature of Liquids and Solids in a High-Pressure Oxygen-

Enriched Environment (G 72) at the David Taylor Naval Ship Research and Development Center. In this test, small quantities of a material are heated to ignition in a pressurized oxidant atmosphere. Materials with higher autogenous ignition temperatures are more resistant to ignition. A study of a single petroleum lubricating oil found that autogenous ignition temperature is a decreasing function of oxygen pressure and of oxygen partial pressure for constant total pressures. Autogenous ignition was observed in oxygen concentrations as low as 2% in nitrogen at 10.3 MPa (1500 psi). The presence of certain metals or metal oxides reduced the autogenous ignition temperature substantially. This effect suggests that resistance to ignition is related to system materials, a factor that must be considered in materials selection.

In the event of ignition of a material, a second line of defense is the selection of a material resistant to propagation. Materials that self-extinguish or propagate slowly are preferred. Tests to evaluate propagation properties include flame speed measurements and oxygen index tests (ASTM Test for Measuring the Minimum Oxygen Concentration to Support Candle-Like Combustion of Plastics [Oxygen Index] [D 2863]). The next two papers on established flammability tests address oxygen index tests.

George K. Ikeda reviews the collection and use of oxygen index data at Air Products and Chemicals Inc. The test described in the paper involves the measurement of the threshold oxygen concentration in nitrogen that will just support downward propagation of combustion in gas streams moving slowly upward. The test has not been widely used for selecting materials for oxygen service yet offers several benefits. The paper discusses a direct relationship between oxygen index values and traditionally accepted material rankings for oxygen service for a spectrum of common materials. A similar direct relationship to heat of combustion data is also noted. Particular value for evaluating dilute oxygen systems is claimed. Specific examples of unique value of oxygen index data in materials selection are cited. The paper suggests that in certain cases oxygen index data provide important information unavailable from other established procedures such as autogenous ignition temperature or heat of combustion. Rationales for use of the data to select materials with precautions against typical misuse are presented. The effects and significances of temperature, pressure, and direction of propagation are reviewed. Tables present oxygen index data for numerous materials.

Michael A. Benning reviews an exploratory program at Air Products and Chemicals Inc. to measure oxygen indices at elevated pressures. Wider acceptance of oxygen index use requires an understanding of the effects of pressure. The test program found pressure and temperature to be significant variables while Reynolds numbers to 1500 and gas velocities to 57 cm/s were found to have little effect. Increasing pressure was found to produce a decrease in the oxygen index value, but typically the rank order was preserved. Exceptions to the rule appeared to be predictable. Oxygen index data for the materials tested appear to approach an asymptotic value at higher pressures with the curves falling only slowly at 2 MPa (300 psi). The nature of the curves was modeled with a straightforward physical analysis and an excellent curve fit was achieved. Data for six plastics and elastomers are included.

Where both ignition and propagation are possible, the third line of defense is to choose a material with a small damage potential. This strategy involves minimizing the material's heat of combustion. Heat of combustion test data are well established and have bearing on ignition and propagation tendencies, but they have the most direct effect on destructive potential.

Robert Lowrie reviews the collection and use of heat of combustion data by ASTM Test for Gross Calorific Value of Solid Fuel by the Adiabatic Bomb Calorimeter (D 2015) at Airco Central Research Laboratories. The test involves forced combustion of a material in an oxygen atmosphere and measurement of the thermal energy that is released. Precision of heat of combustion measurements is excellent among various laboratories. Materials with low heats of combustion are desired for oxygen systems not only to minimize direct damage potential but also to lessen the possibility that ignition of the material will promote the ignition of nearby materials. A material with negligible heat of combustion poses no significant fire hazard. Meaningful collection of heat of combustion data for oxygen material selection is discussed. Analysis is made of material selection examples from ASTM Guide for Evaluating Materials for Oxygen Service (G 63) and from open literature reports.Tables detail heats of combustion for numerous common materials.

Oxygen Systems

Beyond the testing of specific system materials for flammability, system factors must be considered. Materials assembled into a system may demonstrate combined properties differing from those of the constituents. Also, required materials that are individually inadequate may be offset by other system properties. System operational factors play a role. Pressurization rates, cleanliness, and component interactions are all important. The next two papers are not associated with established ASTM standards but review system related factors.

Jack Stradling, David L. Pippen, and Gene W. Frye review the testing of whole components at NASA. This paper observes that at very high pressures above 20.7 MN/m^2 (3000 psi) traditional material selection methods may be inadequate. Also, the most compatible materials are not always practical. The alternative suggested by the paper is to test the whole component in an environment at least as severe as it would see in service. To qualify a component, the paper proposes that an adequate test procedure use pressures and temperatures 10% above the highest operational values and pressurization rates twice those of operation. A life-cycle test under these severe conditions is recommended that includes at least 50 cycles in each operational mode. Disassembly and inspection is vital following qualification. Lesser testing of refurbished or spot-tested components is said to be reasonable.

Strict system cleanliness is a well-known requirement in oxygen service. The removal of both liquid and particulate contaminants is essential. These contaminants may be flammable or may through impact promote the ignition of other materials.

Barry L. Werley reviews the literature and presents new data on the hazards of oil films in oxygen systems. Ignition of oil films is the associated hazard, but systems often need to be cleaned far below the level of film ignitability to eliminate the hazard because migration of thin oil films can create flammable regions in service, and migration can often occur at film thicknesses well below those that enable ignition. Migration was inhibited on rough surface finishes. This factor has to be considered when surface finishes in an oxygen system are chosen. Data are presented to identify limits above which film propagation has been demonstrated for ignition under the influence of burning hot wires, shock waves, rapid compression, mechanical impact, and open flames. Migration data are presented for the mechanisms of gravity, centripetal acceleration, gas flow, and thermal gradients. Two significant migration mechanisms of frozen film chipping and vaporization-condensation are not reviewed and are in need of study. Present cleaning technology is thought to be adequate to achieve properly cleaned systems.

Testing and Selection of Metallic Materials

Finally, the subject of metals flammability is one for which few consensus test methods are in use. Metals are typically much more resistant to ignition than other materials likely to be used in oxygen systems. Metal flammability has been studied by various laboratories and for various goals. ASTM Committee G-4 is in the early stages of addressing metals testing and selection. The final three papers in this book discuss metals flammability and the selection of metals for oxygen service. These papers should provide a foundation for future efforts of Committee G-4 as consensus standards on metals test and evaluation are pursued.

Raymond W. Monroe, Charles E. Bates, and Coultas D. Pears analyze metals flammability data collected at Southern Research Institute. This paper presents a thorough review of the open literature including a detailed discussion of metal autogenous ignition mechanisms. Two burn ratios are proposed for predicting the flammability of metals. Each ratio is calculable from the physical properties of the metal and is useful in predicting whether a metal is likely to self-quench, burn as a liquid, or burn as a vapor. Both burn ratios are calculated for five metals and indicate increasing flammability in the following order: silver, 90:10 copper/-nickel, carbon steel, tin babbitt, and aluminum. The five metals were fractured while carrying electric currents at pressures to 6.9 MPa (1000 psig) oxygen gas and gas velocities to 425 m/s. Ignition and propagation characteristics ranked the materials in the same order as the burn ratios, lending support to the validity of the burn ratio approach.

R. Jenny and H. Wyssman review metal flammability tests under the influence of friction at Sulzer Brothers Ltd. This paper reviews graphical models of metal ignition in terms of heat balance at elevated temperatures. The models are expanded to demonstrate the effects of a frictional heat input. The assorted heat inputs and dissipations are then related through Arrhenius theory, frictional testing, and measured ignition temperatures. Rates of oxidation heating in the frictional tests are obtained from a difference in the drive power necessary to experimentally achieve given temperature levels in oxygen as compared to inert gas. Frictional ignition is reported for three pairs of metals: Monel K500 against itself, tin bronze against itself, and cast iron against stainless steel. Monel was most resistant to ignition. Unexpectedly, tin bronze was the least resistant. However, following ignition, the propensity for combustion to propagate away from the frictional zone yielded a best-to-worst ranking in an anticipated sequence of Monel, tin bronze, and cast iron-stainless steel. Reconciliation of the two different rankings, perhaps in terms of transition temperature effects or protective oxides, remains for future work.

Joseph W. Slusser and Keith A. Miller present a thorough review of metals selection for a hypothetical control valve for 1.7-MPa (250-psi) oxygen service. The exercise involves not only flammability considerations, but mechanical and performance considerations, together with industry guidelines that influence the engineering judgements in selecting any component. To support the analysis, a review of pertinent literature is made, and promoted ignition test data are reviewed on four candidate metals tested at Air Products and Chemicals, Inc. Promoted ignition resistance is rated as one of the most important parameters for a metal to have. In order of preference the four candidate materials were ranked as Monel 400, type 304 stainless steel, cast iron, and carbon steel. Each valve component had different demands for flammability resistance relative to the application itself. Copper-bearing alloys such as Monel are rated highest, but the paper suggests that in many applications stainless steel and cast iron may be adequate for various components in such a valve. A significant contribution in the paper is the thought process by which a component is evaluated.

This collection of papers represents an overview of both coarse and selected minute details that compose the evaluation of materials for oxygen service. The volume should meet its goals of supporting the use of ASTM standards, introducing newcomers to the subject of oxygen compatibility, and spurring future Committee G-4 projects. However, the collection is not complete.There are material test procedures undergoing standardization which have not been discussed herein and which will need support. There are worthwhile points of view that have not been heard. These aspects provide bases for and encourage future symposia.

Barry L. Werley

Corporate Research Services Department, Air Products and Chemicals, Inc., Allentown, PA 18105; editor