

3 Smoke Corrosivity

3.1 Introduction

The combined effects of fire, corrosive smoke and particulates have been defined as ‘fire corrosivity’. Corrosivity of smoke is a well recognised problem that has been studied extensively. Corrosivity of smoke is not an imminent fire hazard, but is mostly a property protection issue, dealing with postfire cleaning and rebuilding of noncritically damaged constructions. Reliable functioning of the machinery and electronic equipment exposed to smoke directly relates to smoke corrosivity and soot deposits. The damaging effect of smoke is a complex phenomenon and depends on both acidic and basic products, as well as on ionic species and products of hydrolysis of smoke components. A review of nonthermal fire damage was published by Tewarson [1].

3.2 Corrosivity of Construction Materials

Metal corrosion can occur in two different scenarios [2]. The first scenario involves metals exposed to smoke under humid conditions, absorbing enough water on their surface to dissolve corrosive gases. Another variant of this scenario considers deposited hygroscopic particles, which contain or absorb water. The first scenario produces local moist conditions and corrosion. The second scenario entails direct precipitation of particles and absorption of gases that produce a uniform cover, which can later absorb atmospheric moisture. This scenario generally results in uniform corrosion of the metal surface.

Water solubility of specific corrosive gases is an important factor determining corrosivity. **Table 3.1** shows the equilibrium distribution of potentially corrosive gases between the gas phase and water-surface film. Oxygen and nitrous dioxide have low solubility in water and therefore have limited contribution to corrosivity. On the other hand, acetic acid, ammonia, hydrogen chloride (HCl) and nitric acid are highly soluble gases, and they will contribute most to the first-scenario corrosion.

Table 3.1 Equilibrium distribution concentration (wt.%) of different gases between gas phase and surface water film		
Gas	Water film (%)	Gas phase (%)
O ₂	3.0 × 10 ⁻²	21
O ₂	6.2 × 10 ⁻⁸	4.0 × 10 ⁻⁶
NO ₂	6.3 × 10 ⁻⁹	1.0 × 10 ⁻⁶
HCHO	3.7 × 10 ⁻⁴	5.0 × 10 ⁻⁸
H ₂ O ₂	3.4 × 10 ⁻³	2.0 × 10 ⁻⁷
CO ₂	1.5 × 10 ⁻³	3.3 × 10 ⁻²
SO ₂	1.8 × 10 ⁻³	5.0 × 10 ⁻⁷
HCOOH	8.6 × 10 ⁻³	5.0 × 10 ⁻⁸
NH ₃	1.9 × 10 ⁻³	1.0 × 10 ⁻⁷
HCl	1.9 × 10 ⁻³	1.0 × 10 ⁻⁷
HNO ₃	3.8 × 10 ⁻³	2.0 × 10 ⁻⁷
Based on data from P. Warneck in <i>Chemistry of Multiphase Atmospheric Systems</i> , Ed., W. Jaeschle, NATO ASI Series, Springer-Verlag, Berlin, Germany, 1986, 6G, p.473 [3]		

Different metals show different susceptibilities to the corrosive effects of smoke. For example, Patton [2] tested four metals typically used in construction, stainless steel, carbon steel, copper/nickel alloy (70:30; CuNi) and Monel alloy. Coupons of these metals were exposed to the gases from polyvinyl chloride (PVC) smoke collected from cone-calorimeter combustion and transferred to the humidity chamber. As **Figure 3.1** shows, the CuNi alloy suffers a significant depth of corrosion even after one hour of exposure, but corrosion of this alloy slows down with time, especially after two days. Surprisingly, stainless steel was more susceptible to corrosion than carbon steel, especially at low exposure time. Monel, as expected, was found to be the metal most resistant to corrosion.

A similar study of the corrosion of carbon steel, stainless steel, Monel 400 and brass was performed in a full-scale test simulating the instrument room of a warship [4]. In this study, carbon steel performed especially poorly in a humid atmosphere, with a 45-fold increase in its corrosion rate at 100% humidity. Increasing the humidity from 70% to 100% in the postfire exposure resulted in a 12-fold increase in corrosion rate. As expected, cables made with crosslinked polyethylene (PE) jackets performed

better than PVC cables, with no noticeable corrosion of brass, stainless steel and Monel, even in a high humidity atmosphere.

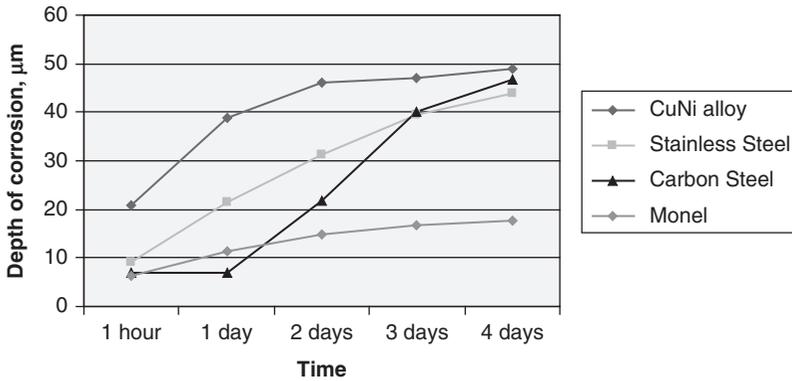


Figure 3.1 Susceptibility to corrosion of different metals exposed to PVC smoke. Based on data from J.S. Patton, *Journal of Fire Science*, 1992, 10, 294 [2]

Acidity of smoke is only one of the contributors to smoke corrosivity. Typically, HCl, hydrogen bromide, hydrogen fluoride and sulfur oxides, as well as organic acids such as acetic acid or formic acid, are responsible for smoke acidity. Acidic gas emissions are measured as the pH of a water extract of the smoke or as the conductivity of aqueous solutions. However, there is no general correlation between acidity of smoke and its corrosivity. For example, **Figure 3.2** shows dependences of smoke corrosivity toward copper (Cu) and the pH of water extracts of smoke. It can be seen that there is no correlation between the acidity and corrosivity of gases. In fact, highly acidic smokes from Neoprene and PVC are less corrosive to copper than are basic smokes from wool and Nylon.

Investigations of fires, as well as large-scale fire tests, have shown that the most serious corrosion damages are observed in the room of the fire's origin, even though the density of visible smoke in adjacent rooms can be as high as that in the room of origin. Because the most corrosive gases tend to be the most polar and the most water-soluble ones, they tend to absorb on surfaces relatively fast and their concentration drops very quickly with increasing distance from the source. This phenomenon is known as the decay of combustion products and is discussed in detail in **Chapter 4**. For example, large-scale tests of burning and smoldering PVC floor coverings showed that about 50% of evolved HCl was deposited on the walls of the room [6]. The concentration of deposited HCl depends on the wall covering (**Figure 3.3**). As expected, porous wall coverings tend to absorb more HCl.

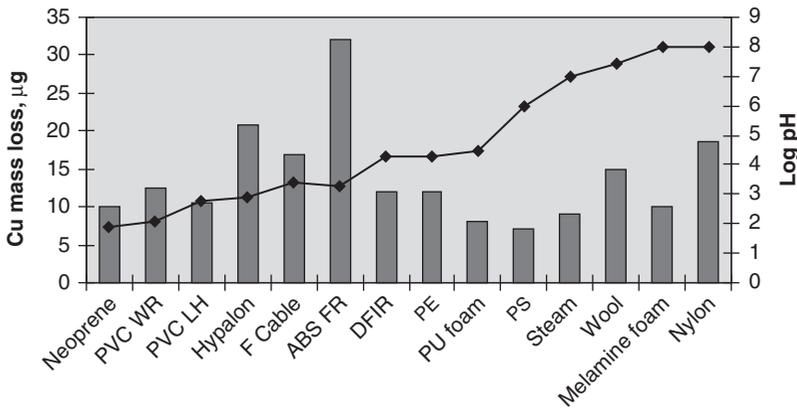


Figure 3.2 Corrosivity (mass loss of Cu) and acidity of water extracts of smoke from different plastic materials. Cu, PVC wire and cable (PVC WR), PVC low halogen (PVC LH), fluorinated cable (F cable), fire retarded acrylonitrile-butadiene-styrene (FR ABS), Douglas fir wood (DFIR), polyethylene (PE), polyurethane foam (PU Foam), polystyrene (PS). Based on data from M.M. Hirschler in the *Proceedings of 39th International Wire and Cable Symposium*, US Army Communications-Electronics Command, Fort Monmouth NJ, Ed., E.F. Godwin, Reno, NV, USA, 1990, p.661 [5]

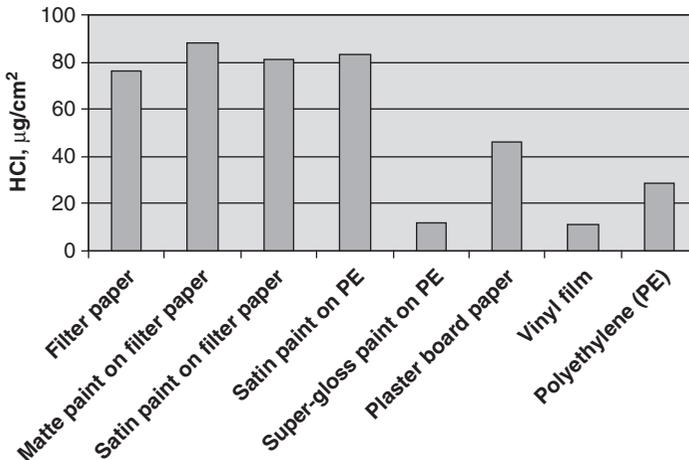


Figure 3.3 Concentration of deposited HCl on wall coverings. Based on data from K.G. Martin and D.A. Powell, *Fire and Materials*, 1992, 3, 132 [6]

3.3 Smoke Corrosivity of Electrical and Electronic Equipment

Fires in telecommunication facilities, computer centres and other research, production or office facilities where large numbers of computers and electronic equipment are present can be very costly, even if the equipment is not directly exposed to the heat, but only to smoke. Exposure of the equipment to smoke gases and soot particulates can result in malfunctions, leading to extensive cleaning or replacement in order for a business to continue operating. The problem was more serious when relay switches were common in electronic equipment, and especially in telecommunications centres. With the conversion to electronic switches, electronic equipment has become more resistant to corrosive gases and soot, however, the problem has not totally disappeared.

If electronic equipment is exposed to combustion gases, one should keep in mind that cleaning should be performed as soon as possible. One reason for this is that corrosion does not stop after the flame exposure ceases, due to deposits of corrosive gases being present on the surface. Deposited soot also undergoes structural changes, becoming more compact with the passage of time and more difficult to remove by regular cleaning procedures. Soot in the particulate fraction of smoke efficiently adsorbs corrosive compounds and corrodes the surfaces by deposition. The presence of high molecular weight, sticky, organic compounds in the non particulate fraction of smoke increases the efficiency of deposition of soot with corrosive compounds on surfaces to enhance corrosion and leakage of current.

Reagor [7] studied the most common cause of corrosion from fires involving combustion of PVC cables and other halogenated plastics (potentially brominated flame retardants and polytetrafluoroethylene). Interestingly, she noticed an important role of zinc-galvanised or zinc-chromated finishes, which are very common as structural elements of the equipment, as well as of heating, ventilation and air conditioning ductwork. Zinc is very reactive toward HCl and forms highly hygroscopic zinc chloride. This electrically conductive solution can move, drip or run onto equipment, resulting in electrical shorting problems. It was found that, in major fires, zinc chloride was the most important compound to remove during cleaning in order to be able to salvage equipment.

It is expected that, over its normal service life, an electronic switch will accumulate 5-10 $\mu\text{g}/\text{cm}^2$ of zinc chloride on its surface. After exposure to fires involving PVC and other halogenated materials, levels of up to 1,000 $\mu\text{g}/\text{cm}^2$ have been observed. It is believed that equipment with contamination levels below 30 $\mu\text{g}/\text{cm}^2$ can be restored to service with little impact on long-term reliability. Equipment with exposures from 30 to 100 $\mu\text{g}/\text{cm}^2$ can also be restored as long as no unusual corrosion problems arise and the environment was controlled soon after the fire. However, if the contamination

levels are above 100 $\mu\text{g}/\text{cm}^2$, the cost of cleaning approaches the replacement cost of the equipment.

In another study, the immediate effect of smoke on the functionality of digital, printed wiring boards was studied [8]. This is particularly important for protecting control rooms of military command centres or nuclear power stations. The tests included study of three possible failure modes of a functional board: (1) circuit bridging; (2) corrosion (metal loss); and (3) induction of stray capacitance. It was found that smoke can increase leakage currents between biased contacts and cause shorts. The shorted electrical signals cause digital systems to receive faulty data and to upset systems, causing failure. High smoke density, high humidity and flaming fires cause more failures than low smoke density, low humidity and smoldering fires. The smoke permanently increased resistance of the circuits tested for corrosion, implying that the contacts were corroded. Failure was also dependent on the type of the boards. For example, high-voltage boards failed permanently, whereas operation was restored for high-speed, low-voltage boards when smoke exposure ceased. It was also found that boards with a protective coating and the use of chip packages with large lead-spacing significantly improved smoke tolerance.

Clean-up procedures for electrical and electronic equipment exposed to smoke from fires were recently reviewed in [9]. It is believed that dry-cleaning methods are not sufficiently reliable and can be used only as an immediate response and precleaning procedure. Sonic cleaning is not suitable because of potential damage to sensitive electronic components. Degreasing cleaners and corrosion inhibitors are also not recommended because of their unpredictable long-term effects. Completely satisfying results can be achieved only with water-based cleaning using slightly alkaline solutions of pH 9-12. Total removal of the flux agent is recommended because it may migrate after water exposure.

3.4 Measurements of Smoke Corrosivity

Measurement of smoke corrosivity can be done according to different chemical or physical principles [10]. The easiest way of assessing corrosivity, which is used in a number of national and international standards, is the indirect measurement of acidity or alkalinity (pH) of the water extraction of effluents. Measurement of electrical conductivity of solutions, together with pH, gives a better idea regarding the presence of ionic species. However, such indirect methods are based on the assumption that higher acidity means higher corrosivity, and that is not always true, as discussed previously. Another method of measuring smoke corrosivity is the direct measurement of the weight loss of metal coupons exposed to smoke. An alternative

to this method is to measure the change of metal resistivity due to the loss of metal thickness. Commercial corrosivity probes based on this principle are being produced. The third method consists of measurements of the leakage of electrical current between closely situated copper strips simulating a printed wiring board.

The International Electrotechnical Commission, IEC 60754 Part 1 method [11] is based on the first principle of indirect measurements by capturing hydrogen halides and titrating them. This method's primary target is electrical cables and, more specifically, PVC cables or cables flame retarded with halogenated fire retardants. In this test, a small amount of a plastic material is heated in the stream of dry air, and gases pass through a 0.1 M solution of sodium hydroxide [9]. The control solution is then acidified with nitric acid, and a known volume of 0.1 M solution of silver nitrate is added. The excess of silver nitrate is then back-titrated with ammonium thiocyanate. This method is not recommended for low concentrations of halogen halides in the smoke.

The IEC 60754 Part 2 method [12] is based on DIN/VDE 0472 Part 813 [13]. It also is based on the absorption of effluent gases, but the decomposition of a polymer specimen (1 g) is performed in a quartz tube furnace preheated to 935 °C. The effluent gases pass through washing bottles filled with distilled water. The pH and the conductivity of the solution are measured afterward. Although this Part 2 method is designed only for halogen-containing gases, it is still an indirect method of assessing corrosivity.

The Centre National d'Etudes des Télécommunications (CNET) test uses only 600 mg of a pelletised or pulverised material, which is pyrolysed at 800 °C. The smoke is contained within the chamber, at controlled humidity and temperature (**Figure 3.4**), and the corrosivity is evaluated based on the change in resistance of a circuit that has been cooled to accelerate the deposition of smoke. This method represents the first example of direct measurement of smoke corrosivity because resistance is changed due to current leakage. The method is designed to test materials and is not suitable for testing real manufactured parts [14]. The International Organization for Standardization, ISO 11907 Part 2 test [15] is based on the CNET test.

Another corrosion test was developed in Germany and is based on a quartz furnace described in the DIN 53436 standard [16]. This furnace is also used for smoke toxicity testing in Germany. It consists of a moving-tube furnace configured in such a way that a constant level of smoke is created for the duration of the combustion period (generally 30 minutes). Air is passed through the furnace at a specific rate. The corrosion sensor, like the one in the CNET test, is a printed wiring board that is cooled down to promote deposition of corrosive gases. Change of resistivity is recorded as the measure of corrosion. This test also allows use of metal coupons that

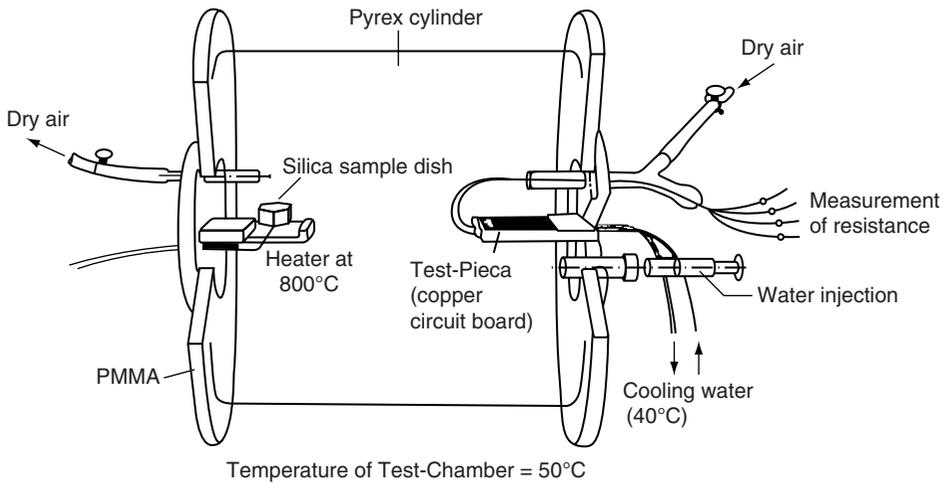


Figure 3.4 Schematic of the CNET corrosivity test chamber

will be exposed to the smoke, and corrosivity will be assessed as a weight gain [17]. The furnace can operate in flaming or non flaming (smoldering) mode. This test was developed into the ISO 11907, Part 3 test [15].

In the US, the American Society for Testing and Materials, ASTM D5485 test [18] is used to directly assess corrosivity of smoke. The test can use the cone calorimeter fire-test instrument or can be a stripped-down version of the cone calorimeter test designed only for smoke corrosivity. The cone calorimeter test, ASTM E1354 [19], is widely accepted as a bench-scale test for measurement of heat release, smoke, carbon monoxide and CO₂. In ASTM D5485, the instrument is equipped with a gas sampling collection device mounted above the cone heater. This device is used for taking a sample stream of smoke and passing it through an 11.2 litre exposure chamber (Figure 3.5). In the exposure chamber, two circuit board corrosion targets are mounted (one of the targets is protected and is used as a reference to compensate for temperature variation). Sampling lasts for 60 minutes or until 70% weight loss of the tested specimen has occurred. The advantage of this test is that relatively large samples (10 × 10 cm) can be tested, which allows for assessment not only of materials but of parts of assemblies and composites. This test is known as the cone corrosimeter and was also adopted by the ISO committee on plastics as ISO 11907, Part 4 [20].

In Canada, a test for the creation of acid gases from the combustion of polymeric materials in a tube furnace has been used to estimate the corrosiveness of smoke [14]. The gases emitted are trapped, and the acidity of the water extract is measured. An analysis of test conditions showed how the results can be significantly altered by small differences in the way the test is conducted [21]. The basis for this test is the assumption

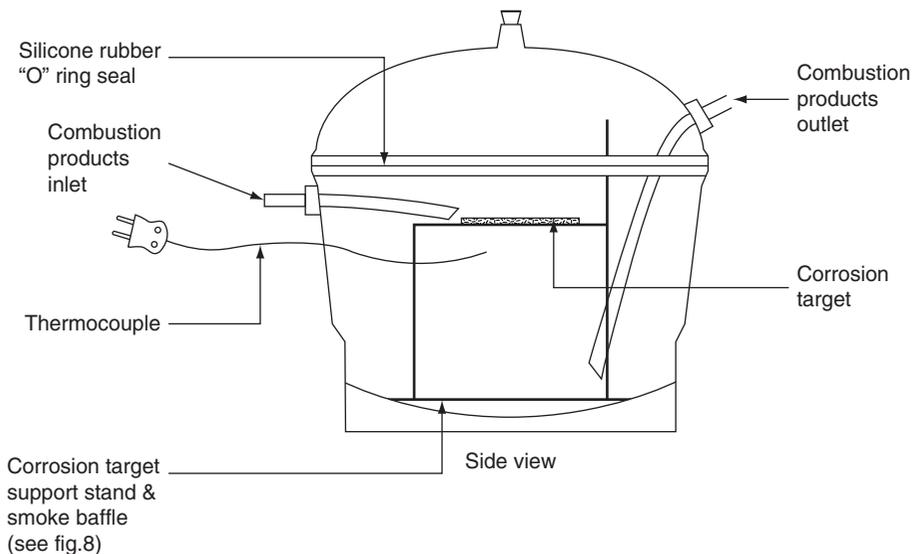


Figure 3.5 Smoke exposure chamber of ASTM D5485 [18] corrosivity test

that acid gases are the only corrosive products of any importance in polymer smoke. As was discussed earlier, this hypothesis has been proven to be wrong.

The fire propagation apparatus (FPA) described in ASTM E2058 [22] was originally developed at Factory Mutual (now FM Global) and is used there for assessing smoke corrosivity [1]. The FPA uses a resistivity corrosion probe similar to that used in the cone corrosimeter, and the probe is inserted directly into the sampling duct of the FPA. The corrosion is tested in the dynamic mode for the time of about 10 minutes of sample combustion, and for an additional 10 minutes while deposited corrosive gases attack the probe.

Factory Mutual also operates 5000 kW and 20,000 kW flame propagation calorimeters, which are capable of running combustion tests of cable arrays in their real configuration and measuring smoke corrosivity, amongst other parameters. Another possibility is running such tests in enclosed spaces simulating real rooms. Recently, a report [10] was issued of a study of smoke corrosivity of power cables and communications switch assemblies in a 272 m³ room in a realistic configuration. It was shown that the use of water (sprinklers) increases the non particulate fraction of smoke and thus makes soot with corrosive compounds stick tightly onto surfaces, resulting in the enhancement of corrosion. It was also noted that switch assemblies produced a more sooty type of smoke, which came from the printed wiring boards flame retarded with brominated flame retardants and caused more corrosion than a PVC cable array.

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