

The Development and Performance Characteristics of Mixed Flowing Gas Test Environment

WILLIAM H. ABBOTT, MEMBER, IEEE

Abstract—In recent years there has emerged a good understanding of the real nature of field environments in which modern electronics must operate with high reliability. Accompanying these developments have been advances in the art of realistic, accelerated, environmental testing which are designed to simulate the kinetics and degradation mechanisms found in indoor environments. While these differ widely (4 to 5 orders of magnitude in severity), new data have defined four fundamentally different classes of field environments. This demands the development of multiple testing methodologies in order to reproduce dominant mechanisms and chemistries.

Foremost among the laboratory advances is the group of tests and related methodologies known as flowing mixed gas (FMG). Three tests of this type have been developed to achieve realistic simulation through the synergistic effects of 1) low concentrations of the relevant pollutants, 2) humidity, and 3) temperature. These studies have demonstrated the extreme importance of incorporating the sulfide-chloride synergisms into all of the environments in order to simulate the observed corrosion response. It has further been found that by adjusting these variables, large differences can be found in materials reaction rates, corrosion mechanisms, and chemistries.

Data were taken to demonstrate the effects of critical variables on corrosion processes. Relative humidity, reactive chloride concentration, and reactive sulfide concentration were consistently identified as the most important in all cases. Temperature, gas velocity, and NO_2 concentration were far less critical. Sulfur dioxide was also shown to be relatively unimportant for either indoor, field, and/or laboratory mixtures. It has been concluded that three-component mixtures based upon low levels of H_2S , NO_2 , and Cl_2 can be used to satisfy simulation of all reactive environmental classes.

The proposed FMG environments have been developed into practical laboratory test systems. They must, however, be operated within strict limits for the critical variables. Direct environmental analyses, as well as reactivity controls, are mandatory for test verification.

INTRODUCTION

THE SUBJECT of accelerated environmental simulation has been associated with the field of electrical contacts for over 50 years. It has long been known that corrosion and tarnish products can have a significant effect on reliability. However, only within the last five to ten years, has there developed a relatively good understanding of 1) the nature of actual indoor operating environments in terms of chemistries, corrosion mechanisms, and their effects on materials, and 2) laboratory approaches for realistic simulation.

The importance of these matters is not trivial particularly with increasing demands for 1) reliability projections, 2) service cost projections, 3) qualification of new materials and designs, and 4) cost reduction. Some of the earliest studies of

field and laboratory reactions [1], [2] clearly showed the potential consequences of the use of arbitrary and severe environments for laboratory testing. These include:

- 1) artificial film chemistries which can produce misleading electrical results [3], [4];
- 2) unrealistic kinetic response;
- 3) a total reversal of materials performance when compared to field experience.

A fourth and relatively recent finding, which will be developed in this paper, is that many "classical" tests which have been considered severe are both unrealistic and relatively benign when compared to observed field data. These include, for example, tests based on high-concentration one-component, mixtures of SO_2 [6], H_2S [7], or elevated temperature-humidity exposures [8].

In recent years emphasis on realistic, accelerated aging has been placed on incorporating the synergistic effects of natural environments into what has been termed flowing mixed gas (FMG) procedures. Partly through the efforts of a major, industry-sponsored program at Battelle-Columbus, a series of FMG procedures has evolved. These procedures which have their basis in extensive field data, are rapidly finding wide laboratory use in electronics qualification programs ranging from materials evaluation to studies of entire systems.

Three FMG environments exist at present. Scattered details of the chemical makeup of these mixtures already exist in the literature [9]–[11]. However, no publication has adequately described 1) the details of FMG procedures, 2) the purpose of individual procedures with respect to the field, and 3) the effects of such tests on materials with respect to control and verification.

BACKGROUND

Field Environments

One objective of laboratory corrosion exposures is to duplicate environmental effects found in actual field use conditions. In spite of its importance, relatively few relevant field data have been available until recent years. More significant is the fact that indoor data and/or data in actual electronic operating environments have been lacking.

Outdoor exposure data on relevant metals such as copper [12], and even metals common to electrical contacts [13]–[19] have been available. Unfortunately, recent work has shown a vast difference between indoor and outdoor data, with respect to pollutant levels [20]–[22], and reaction kinetics [22]. One important conclusion from this is that outdoor data (including "sherted" exposures) are 1) unrealistic, and 2) usually too

Manuscript received April 2, 1987; revised October 20, 1987. This paper was presented at the 33rd Meeting of the IEEE Holm Conference on Electrical Contacts, Chicago, IL, September 21–23, 1987.

The author is with Battelle, Columbus Division, Columbus, OH 43201.
IEEE Log Number 8718627.

0148-6411/88/0300-0022\$01.00 © 1988 IEEE

severe to address the problems of corrosion in real operating environments. These conclusions apply even to outdoor applications of cabinets, "black boxes," etc.

One reason for the latter effects is the high level of attenuation/modification of environments within structures, enclosures, etc. [22], [23]. This is fortunate since recent work has shown 1) the extreme sensitivity of modern electronics to environments formerly thought to be benign (less than <10 ppb of critical pollutants) and 2) that many technically important materials will corrode rapidly when exposed to such indoor environments [24]–[36]. At least one industry specification for equipment operating environments has recognized these facts and has adopted threshold levels of pollutants in the range of a few parts per billion [37].

Probably the first detailed studies of indoor environments were performed by Campbell and Thomas [1], [2] in the 1930's. Even though this work was mainly for the environments of telephone central offices of that period, it did provide a model for future work on a broader scale. That early work, however, showed the importance of reactive sulfides (S_8 , H_2S) in the corrosion processes. It also was the first to show the presence of chlorides as constituents in the reaction products from the environment. Even the full significance of this observation was not to be shown for another 40 years. Later work clearly showed the dominant effects of chlorides in control of the reactions of palladium in telephone office environments [25], [28], [29]. Other studies have shown the important effects of chlorides in natural indoor environments throughout various industries and applications [9], [14], [24], [26], [31], [33]. However, they have also revealed strong sulfide-chloride interactions in control of corrosion reactions. This is particularly true in the more aggressive environments [3], [33], [34].

In spite of growing emphasis on indoor field data in the 1970's, it has been difficult to compare and place in proper perspective such information. For example, data from one generic application environment such as the telephone central office may or may not compare with another industry's indoor applications. This problem was partially resolved in the 1970's with the introduction of a standard methodology for measuring and classifying indoor environments based on reactivity monitoring [38].

This technique, which has now been applied worldwide at more than 3000 field sites has provided extensive databases for the comparison of field and laboratory results. A full discussion of these data is beyond the scope and purpose of this paper, although prior publications should provide additional information [24], [26], [34], [37].

The significance of this concept may be demonstrated in Fig. 1. These data show typical reactivity distributions for copper [37], [38]. Similar data have been given for porous gold standards [24]. The data represent only several of many possible distributions unique to individual companies, product lines, and generic applications. Data shown are in the same range for generically similar environments as those developed by Rice [26], [35], and Campbell and Thomas [1], as well as product-specific data [40]–[42]. Each of these, however, covers only a portion of the total potential distribution which

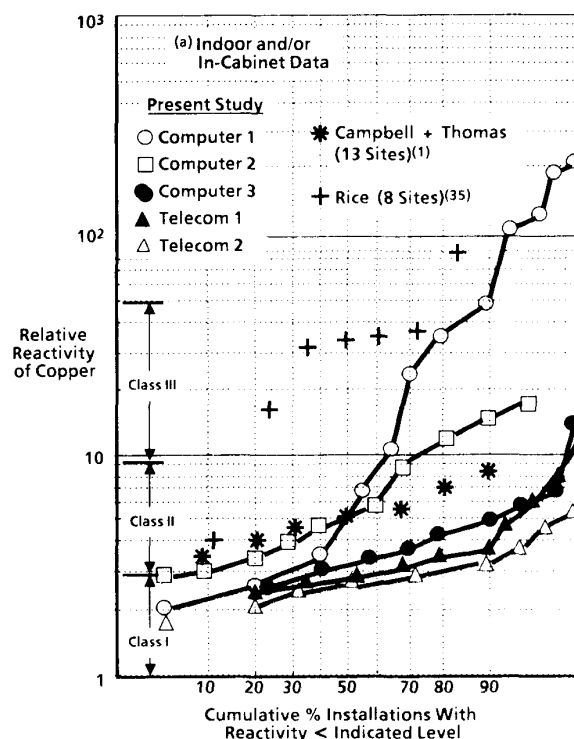


Fig. 1. Typical reactivity distributions for individual manufacturers and/or product lines.

the current work shows to extend over at least 4 to 5 orders of magnitude.

From Fig. 1, the following important principles may be set forth:

1) Real indoor environments for electronics may differ by at least 4 to 5 orders of magnitude in chemical severity [24], [26], [39].

2) The degree of exposure/risk of severe versus benign applications differs widely among manufacturers, even within the same industry.

3) At least four fundamentally different classes of field environment may be demonstrated.

Item 3) provides the basis for this paper and the development of the FMG environments. These have come to be termed the Battelle Class II, III, or IV tests. Since it must be an objective of laboratory test development to simulate the field in terms of kinetics, chemistries, and mechanism(s), one immediate conclusion from Fig. 1 is the following: *No single test procedure can hope to satisfy the requirements for all classes of operating environments.*

However, an equally important principle in the application of such procedures is that *there is often little commercial need or justification for equipment qualification at all or the highest levels of severity.* The concept of environmental classes has been given elsewhere [24], [34], [39]. The important principals relating to corrosion mechanisms and chemistries are summarized in Table I. Within what has been defined as the II through IV classes, it has been shown that environmental corrosion may affect the reliability of electronics. For this reason, an objective of contemporary studies has

TABLE I
DEFINITION OF ENVIRONMENTAL CLASSES BY DOMINANT
MECHANISM(S) AND CHEMISTRIES ON CONTROL COUPONS

Class	Au/Ni/Cu (Porous)		Copper
	Mechanism	Highest . . . Lowest	Chemistry
I	none	—	Cu ₂ O
II	pore	Ni, Cu, Cl, O, (S)	Cu ₂ O, Cu ₂ O ₂ Cl ₂
III	pore and creep	Cu, S, Ni, Cl, O	Cu ₂ S, Cu ₂ O, (?) ^a
IV	creep	Cu, S, Ni, O, Cl	Cu ₂ S, (Cu ₂ O), (?)

^a ? Indicates unknowns. () Indicates minor amounts (<10 percent).

been to develop simulation techniques appropriate to each of these classes.

Laboratory Testing

Relevant laboratory corrosion studies appear to date from the early work of Vernon [43]. Later work by Campbell and Thomas [1], [2] clearly demonstrated the following principles:

1) Single gas mixtures such as air with H₂S or SO₂ do not simulate indoor field reactions on relevant metals such as silver and copper.

2) Arbitrary, high concentrations of gases such as H₂S or SO₂ may produce:

- unrealistic kinetics,
- unrealistic chemistries,
- a complete reversal in the order of materials performance.

3) SO₂ may not be a significant indoor pollutant.

In spite of these results, such tests as described by 1) and 2) above have been the basis for nearly all internationally developed environmental tests in the field of electrical contacts [6], [7]. It is also worth noting that such procedures are generally based on the use of static (nonflow) environments and without means for control or verification. One partial exception to these statements, and one of the first examples of the recent trend towards flowing gas mixtures is the British "burning gas test" [5]. Unfortunately, this appears to be based largely on an SO₂ chemistry and is difficult to reproduce/control [44].

The late 1960's marked the beginning of an accelerated trend in environmental simulation for electronic corrosion studies. This is the use of dilute, multicomponent mixtures of gases in continuous flow systems. Most of these studies continued to emphasize H₂S as the primary reactive species in combination with SO₂ and/or NO₂ [45]–[51]. However, at least several early studies examined the combined effects of Cl₂ and demonstrated significant effects on the corrosion rates of silver [31], [52] as well as the corrosion rates and film properties of precious metal alloys [52]. More recent work has emphasized the H₂S–Cl₂ or H₂S–NO₂–Cl₂ synergisms [53]–[56] as field data were developed to demonstrate the importance of such interactions relative to the data in Fig. 1.

In spite of a significant volume of laboratory mixed gas data, it is difficult to directly compare the results of different investigators. This can be attributed to two factors, both of

which relate to test control and to verification, as well as to the absence of standards for sample analysis. Reference to most reported laboratory data prior to the last several years fails to show any evidence of verification of test environments by analytical means or confirmation of a "correct" level of chemical reaction/reactivity by use of control samples. The significance of these statements will be developed further in this paper.

In summary, advances in the science of environmental simulation have pointed towards the development of FMG techniques, and specifically, those incorporating the sulfide-chloride synergisms as the best hope for realistic laboratory tests. The following parts of this paper will attempt to define three FMG tests which have evolved from comparative field and laboratory studies. The purposes of the paper are, therefore, to

- define the test conditions,
- define the purposes of such tests,
- define control and verification requirements.
- define the range of expected results on a series of important materials.

DEFINITION OF FMG LABORATORY ENVIRONMENTS

Three test environments have been defined. Each has been developed to reproduce on an accelerated basis the mechanisms and predominant chemistries defined from the field, as given in Table I. The nominal test conditions are summarized in Table II. By definition, no test exists for Class I environments since available data indicate no precedent for environmental effects on reliability.

It is important to recognize that the conditions given in Table II are nominal values actually existing and confirmed in the test environment. Under no conditions can these values be calculated or inferred from external sources such as dilution from standard/analyzed gas cylinders. This does not mean that any gas mixing procedure should be excluded from use in an FMG system. Instead, for whatever method used, gas concentrations in the chamber must be verified by analysis.

Table III summarizes the present understanding of target control ranges for individual variables for Class II and Class III. Also shown is the relative importance of each variable. Data will be given in the experimental section of this paper to justify these conclusions.

PURPOSE OF FMG ENVIRONMENTS

The FMG mixtures must be viewed as moderately accelerated tests specific to each class of field environment. In other words, they can generally not be conducted in matters of hours or even several days. They have been designed to accelerate metallic reactions on a wide range of metals used in electronics. Therefore, they do address actual failure mechanisms involving metallics such as contact and connector corrosion, electromigration, disc media (thin metallic film) corrosion, etc. They have not been studied and are not recommended for other important degradation processes such as structural corrosion, polymer degradation, fretting corrosion, etc.

As will be shown, a variety of materials directly exposed to

TABLE II
DEFINITION OF FMG ENVIRONMENTS BY COMPOSITION

Test/Class	Gas Concentration (ppb)				
	H ₂ S	Cl ₂	NO ₂	%RH	T (°C)
I	—	—	—	—	—
II	10	10	200	70	30
III	100	20	200	70	30
IV	200	50	200	75	50

TABLE III
RELATIVE IMPORTANCE OF INDIVIDUAL VARIABLES IN FMG TEST PROCEDURES

Class	Variable ^a	Very Critical	Important	Less Critical
II	H ₂ S		+ 0/ - 4 ppb	
	Cl ₂	+ 0/ - 2 ppb		
	NO ₂			± 25 ppb
	SO ₂			± 25 ppb
	RH	± 2-percent RH ^b		
	T			± 2°C
	linear velocity			± 50 percent
III	H ₂ S	± 10 ppb		
	Cl ₂		± 5 ppb	
	NO ₂			± 50 ppb
	SO ₂			± 50 ppb
	RH	± 2-percent RH ^b		
	T			± 2°C
	linear velocity			± 50 percent

^a No condensation anywhere.

^b Measured by instrumental means in chamber.

field and laboratory environments will degrade rapidly. Fortunately, this does not occur with most components, such as mated connectors, even in the more severe indoor environments. This fact, together with an intended purpose of FMG tests for reliability estimates imposes one of the perceived limitations of such procedures. This is the need for large sample sizes in order to produce observable results on components as shown in the last section of this paper.

EXPERIMENTAL PROCEDURES

The following sections will present the results of FMG experiments to demonstrate 1) the expected results for the conditions given in Table II, and 2) the requirements for control and test verification.

Data will be given for reactions of specific materials relevant to electronics in coupon form and/or which may be used for control purposes. This paper will not deal with effects on components in detail nor will it deal with acceleration factors. It is intended that such information will be published at a later date. It may be concluded that acceleration factors may be from 1 to 3 orders of magnitude, depending on specific test conditions.

Test System

All experiments were conducted in three FMG test systems. Each system was different in size and design, but all conformed to the information given in Table IV.

TABLE IV
TEST SYSTEM CONSTRUCTION AND OPERATING CHARACTERISTICS

- 1) Type—double chamber; single pass; continuous flow
- 2) Size—200 to 3600 l
- 3) Materials—plexiglass inner chamber
—stainless steel or plexiglas outer
—teflon and stainless steel gas and sampling lines (heated)
- 4) Circulation—single fan; up flow
- 5) Air Exchange—3 to 8 per hour
- 6) Temperature Control—± 2°C inner
- 7) Humidity Control—± 2-percent RH inner
- 8) Gas Analysis
H₂S, SO₂—flame photometric (on line)
NO₂, NO, NO_x—chemiluminescence (on line)
Cl₂—oxidant monitor (periodic)
- 9) Control and Verification—coupon reactivity (see text)

Typical schematic diagrams of FMG systems have been given elsewhere [33], [47]–[50], [57], [58]. As will be shown, any system of similar design *can* give similar results. In practice, however, this has often not been found. The reasons for this are many, but experience has shown that variance with, in order of importance, items 8), 7), 9), and 5) of Table IV has been the primary reasons.

Materials

Extensive use was made of two materials which have evolved as useful controls for the verification of chamber reactions, as given in Table I.

The copper was 0.6 mm thick, commercial, half-hard OFHC from which coupons were sheared to dimensions, 13 mm × 75 mm. These samples were hand finished and cleaned by a modified metallographic abrasion process [37]. This resulted in a standard surface roughness of 0.01 to 0.015 μm CLA.

A minimum of three coupons were used for each data point in the text. Any sample which showed visual evidence of nonuniform corrosion other than the normal interference coloration [59] was rejected.

The preceding finishing procedure also provided a standard substrate for preparation by electroplating of the second major control—porous gold (0.75 μm, acid-hardened Au-0.1 wt % Co) over 1.25-μm sulfamate nickel. The median porosity values were 6 ± 3/cm² as determined by the SO₂ method of ASTM B-583. These samples were actually sheared from larger plated panels to deliberately provide exposed copper edges. Such samples proved useful for evaluating the mechanisms of pore corrosion [24] and surface film creep from pores and edges [34].

The preceding describes the materials actually used. Experience has shown that most of these details other than a requirement for nominally clean surfaces are not critical for the primary purposes for which these materials are used. These are at a minimum:

- | | |
|-------------|--|
| copper | visual confirmation of reaction;
analysis of kinetics and film chemistry; |
| porous gold | visual confirmation of intended mechanism(s);
measurements of creep. |

These items have proved so critical in practice, that the

following operating requirement has been proposed: *FMG tests cannot be conducted in a manner consistent with control and verification without the implementation of Items 8) and 9) of Table IV.*

Analysis

Environmental: All conditions listed in Table IV reflect conditions in the gas phase within the test chamber. Gas analyses for H_2S , SO_2 , and NO_x were checked at least every 24 h using instrumentation given in Table IV. Although continuous analysis was possible, this was not practiced due to long-term corrosion effects on the equipment.

Analysis for Cl_2 , which could not routinely be made in the presence of the other gases was done 1) at initial setup prior to the introduction of other pollutants, but with humidity established, 2) once every 2 days after removal of other pollutants (approximately 1-h effective interruption), and 3) at the end of each test run. Cl_2 analysis is the most difficult and least automated of the pollutants studied

Temperature and humidity were checked twice daily by visual readings of wet and dry bulb thermometers (Taylor Instruments, Model SP-377) mounted in the center of each test chamber. Early in the development process, temperature and humidity were determined electronically (Beckman Model 5412) with equivalent results. The latter method was eventually discontinued due to long-term sensor corrosion and a resultant loss of accuracy.

Gas Stability: The critical need for gas analysis from the test chambers and reaction verification is shown in the data of Figs. 2 and 3. These results, which were obtained for one particular chamber operating with inlet concentrations of 100–1000 ppb, compare analyzed or calculated gas concentrations at the chamber inlet (dry air, high flow) against conditions actually analyzed in the gas phase of the inner chamber.

It is clear that large, unavoidable gas loss mechanisms exist. The primary mechanism is believed to be adsorption and possible irreversible loss by chemical reaction in the adsorbed moisture film on all internal surfaces. This thesis is supported by the strong humidity dependence, as shown in Fig. 2, and the fact that Cl_2 (most soluble and reactive) losses are the highest.

Fig. 3 shows that losses may be reduced by increases in air exchange rate. However, the gas volumes which would be required in a practical test system in order to use this relationship to advantage makes this approach impractical as a means of avoiding the use of analytical equipment.

Additional data in Figs. 2 and 3 show that virtually any internal change, such as chamber loading, will affect these values. Finally, it should be noted that these values strictly apply to only one of several chambers. Each gave slightly different adsorption characteristics. In fact, some systems have been observed in which losses may exceed 90 percent!

From data such as these, it should be apparent why analysis and verification is mandatory in work of this type. It is also apparent why much earlier data in the technical literature must be viewed with caution. In the absence of gas analysis, concentrations are unpredictable but generally far less than intended or calculated.

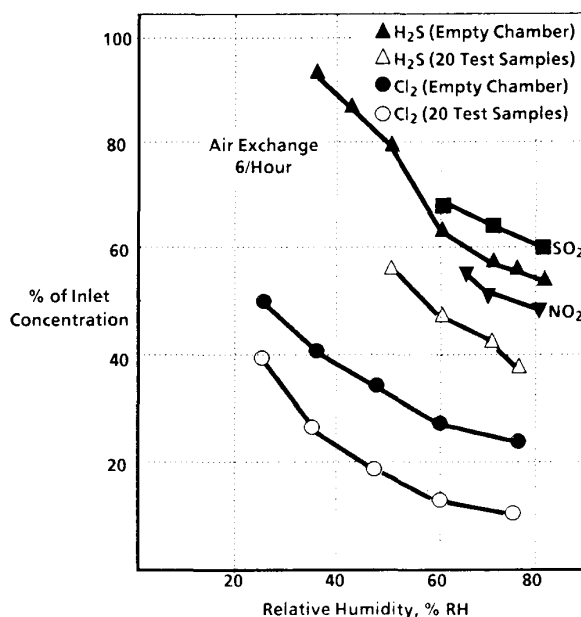


Fig. 2. Analyzed gas concentration in test chamber versus humidity.

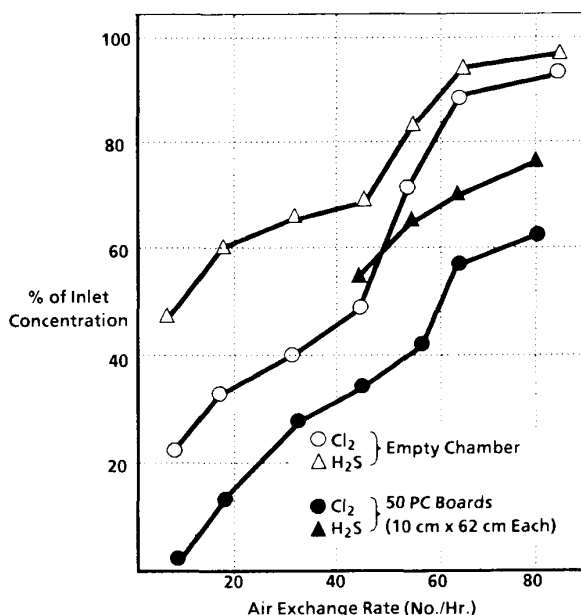


Fig. 3. Analyzed gas concentration in test chamber versus air exchange.

Film Analysis: Most of the kinetic data given in this paper on solid metal coupons were obtained by cathodic reduction of films [37], [59]. Standard conditions used were 0.1N KCl and a current density of $50 \mu\text{A}/\text{cm}^2$. This technique was applied on copper, silver, and the four solid precious metal alloys for which data will be reported. This technique was not applied to the porous gold standards. In this case, SEM/EDAX and ESCA were used to confirm corrosion chemistries.

Contact Resistance: The standard technique of contact resistance probing was used to follow the corrosion of porous gold and the precious metal alloys. The technique conformed to ASTM B-667-80. This included the use of a solid gold, 3.2-

mm diameter, hemispherically ended gold probe. This was calibrated against the recommended electroplated 35Sn–65Ni standard. A minimum of 25 points were probed on each sample. The primary normal force used was 100 g.

These data will be presented mainly to illustrate effects. Contact resistance probing was not used and is not recommended as a primary standard for test validation due to the problems of intralaboratory reproducibility [60]. In addition, the technique is of limited value due to the relatively thick films developed on extended exposure in these procedures. Such films often give contact resistances that are effectively “open.”

FMG TEST RESULTS

Field Data

Fig. 4 shows a typical set of kinetic data for copper and porous gold. These were obtained in one example each of the four classes of environments, as defined earlier. These data are not comprehensive since a broad distribution of similar data will exist within each Class. Instead, they are intended to show the magnitude of corrosion in each Class and to confirm the presence (or absence) of specific mechanisms. As a point of explanation, the contact resistance data in Fig. 4 for Class III were not taken in the region of film creep from edges. They do reflect the effects of pore corrosion (II and III) and creep away from pore sites (III).

These data show

- 1) no corrosion in Class I;
- 2) chloride-driven pore corrosion in Class II, with chemistries of Cu, Ni, Cl, and O [24];
- 3) sulfide-dominated but chloride-accelerated [26], [34] pore corrosion and film creep in Class III;
- 4) sulfide-dominated creep in Class IV.

It is important to note that these data show the speed with which corrosion can occur in a wide range of operating environments. These are, however, data for materials freely exposed to the environments for calibration and sensing purposes. Although component degradation rates may be far lower, such data are useful for the determination of both mechanisms and acceleration factors by comparison with similar coupons in laboratory exposures.

Laboratory

Kinetics: Figs. 5 and 6 present data for the expected response range of the FMG environments of Table II. Copper corrosion kinetics are shown in Fig. 5, together with the actual range of data acquired from many experiments over the last 3 to 4 years. These results were obtained from six test chambers spanning the ranges of operating conditions given in Tables II and IV.

These data demonstrate that a relatively high degree of reproducibility can be obtained. They also show that variability is to be expected. This is one additional reason why reactivity controls are mandatory. Such kinetic data must also provide the basis for calculation of the acceleration factors actually attained in each exposure.

Also shown in Fig. 5 are the extreme kinetic limits

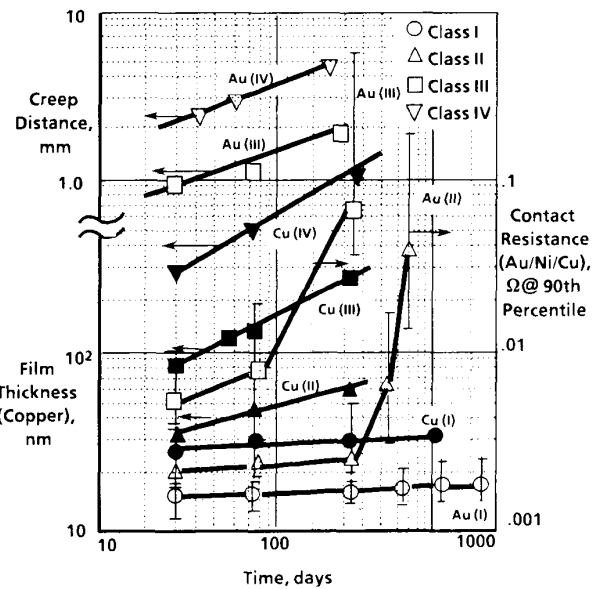


Fig. 4. Typical kinetic responses of copper and porous gold in four classes of field environments.

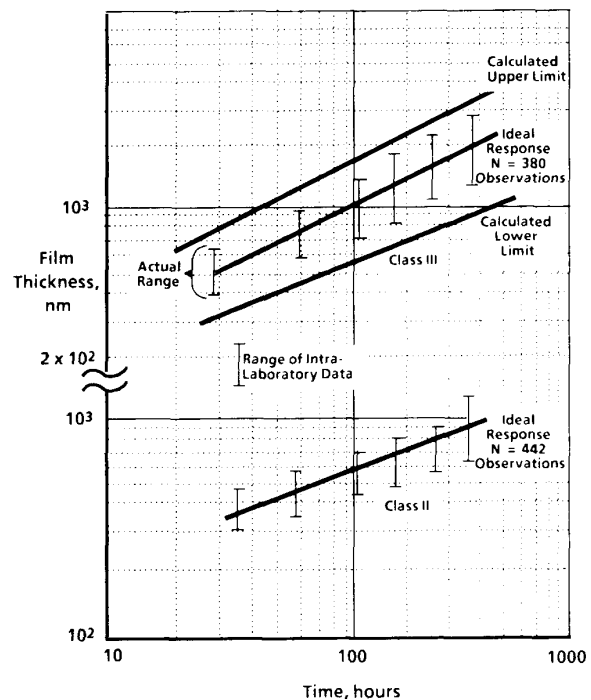


Fig. 5. Corrosion response range of copper controls in FMG mixtures

calculated from the known response of individual variables taken at the limits given in Table III.

In practice, these limits are seldom, if ever, exceeded.

The kinetic equations which approximate ideal Class II and Class III responses are as follows:

$$\bullet \text{ Class III—} X^2 = 6.72 \times 10^3 t - 3.2 \times 10^4 \quad (1)$$

$$\bullet \text{ Class II—} X^3 = 7.0 \times 10^5 t + 2.2 \times 10^7 \quad (2)$$

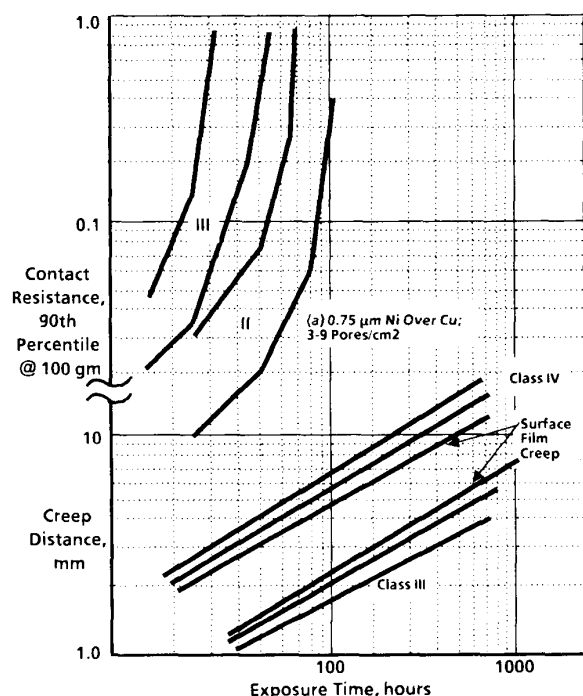


Fig. 6. Corrosion response of porous gold coupon controls in FMG.

where X equals film thickness, in nanometers, and t equals time, in hours.

Both of these equations imply rate-controlling mechanisms of diffusion within the growing film. The forms of these equations are nearly identical to the kinetics for the different classes of field environments. Typically these are

- 1) parabolic within Classes III and IV,
- 2) higher order approaching logarithmic in Class II,
- 3) rapid attainment of a limiting oxide film thickness (oxide only) in Class I.

The equation showing cubic kinetics for Class II is a simple and convenient expression for the observed data. It may be noted, however, that the same data may also be represented by logarithmic kinetics in the Class II region. The latter form which has a theoretical basis is often found in low-temperature oxidation processes [68].

The data in Fig. 5 show the response of copper, an important and recommended control material and one that is easy to analyze by cathodic reduction. Alternate methods for *in situ* monitoring, such as electrical resistance bridges [61] or quartz crystal oscillators [62] have been reported.

The latter methods alone may not be adequate, since the objective of controls should be to verify the correct kinetics (Fig. 5), mechanisms (Fig. 6, Table I), and chemistries (Table I). For example, there may exist a large number of environmental conditions which could corrode copper with kinetics similar to those shown in Fig. 3. Relevant examples are dilute mixtures of

- H_2S in air
- $H_2S + SO_2$ in air
- $H_2S + NO_2$ in air.

We have determined that all will tarnish copper at parabolic kinetics but *none* will corrode porous gold or produce creep at useful rates [24]. In addition, all will produce a predominant Cu_2S chemistry [52] that is not typically observed on field samples, except in the most severe environments (see Table I).

For the purposes of this section, verification is simply a confirmation that the test was conducted in the correct and reproducible manner. The justification for obtaining the correct chemistries and kinetics was discussed earlier. In simple terms, without it field performance cannot be predicted, and the concept of an acceleration factor has little meaning without realistic corrosion.

Examples of these effects are shown in Fig. 7. These particular examples were selected since they are typical of procedures in current national or international specifications. All will corrode copper, but in reality all are relatively benign in comparison with data for Au/Ni/Cu in Figs. 4 and 6.

The missing feature which accounts for this discrepancy is, of course, the sulfide-chloride synergism.

Corrosion Produce Chemistry: Simulation with respect to chemistry is considered important since it has been shown to have large effects on film properties [3], [63], as reflected in electrical performance. Table I describes the dominant chemical features found in what appears to be majority of indoor environments (II, III, IV) in which

- 1) porous precious metal coatings will corrode,
- 2) the environment is likely to affect reliability.

A consistent feature which has now been confirmed worldwide and in virtually all types of operating environments is the presence of some form of "reactive chloride" [22] in the surface films. The ubiquitous nature of reactive chlorides in the field is summarized later in Table VI. It is important to recognize how this term has been defined. It is based solely on the use of silver as a sensor material and the appearance of $AgCl$ as a reaction product. Therefore, by our definition, a site showing reactive chlorides is one in which environmental conditions (chloride concentration and humidity) are sufficient to form $AgCl$ on silver to an extent that it can be detected by cathodic reduction. The data shown in Table V were obtained from a broad cross section of environmental types and equipment applications. The results simply indicate that reactive chlorides are broadly distributed worldwide. There is strong evidence that the absence of this constituent, or more specifically, absence of the chloride-sulfide synergism is the factor accounting for the low rates of reaction shown in Fig. 7 versus the results in Figs. 4-6.

Each of the FMG environments will produce a unique chemistry on copper, as defined by cathodic reduction. These are summarized in Table V. In addition, the ubiquitous nature of reactive chlorides is summarized in Table VI. It is important to recognize how this term has been defined. It is based solely on the use of silver as a sensor material and the appearance of $AgCl$ as a reaction product. Therefore, by our definition, a site showing reactive chlorides is one in which environmental conditions are sufficient to allow $AgCl$ to form on silver to an extent that it can be detected by cathodic reduction (20-30 Å). The data shown in Table VI were

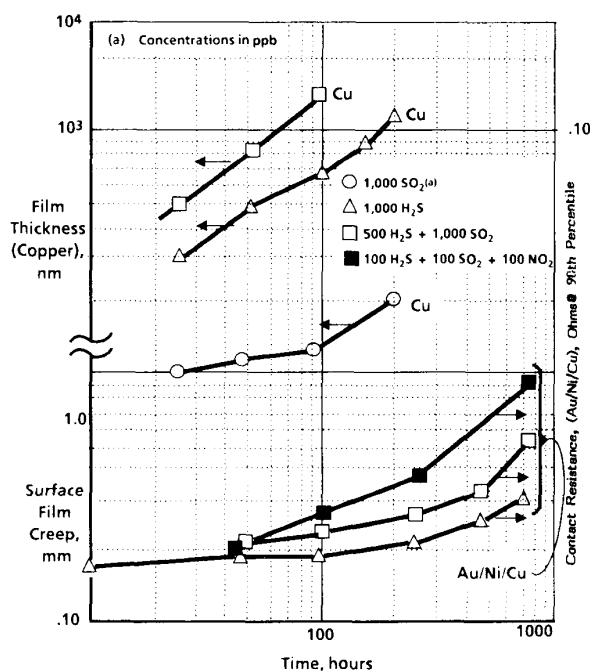


Fig. 7. Typical kinetic responses of copper and porous gold in common H_2S and SO_2 laboratory environments at $30^\circ C$, 70-percent RH.

TABLE V
DISTRIBUTION OF REACTIVE CHLORIDES
AT INDOOR ELECTRONICS SITES

Class	Number of Sites In Statistic	Percent of Sites Showing Reactive Chloride ^a
I	310	20-30
II	630	45-55
III	1495	30-40
IV	520	15-25

^a See text for definition.

TABLE VI
TYPICAL CORROSION PRODUCT CHEMISTRY FOR COPPER
IN LABORATORY FMG ENVIRONMENTS

Class	Number of Films	Major	Percent of Film		
			Cu_2O	$Cu_4O_2Cl_2^a$	Cu_2S
II	3-4	$Cu_4O_2Cl_2$	30-40	50-60	5-10
III	4-5	Cu_2O/Cu_2S	30-40	10-20	30-50
IV	3-4	Cu_2S	10-15	5-10	70-90

^a Sum of all unknowns.

obtained from a broad cross section of environmental types and equipment applications. The results simply indicate that reactive chlorides are broadly distributed worldwide.

Multiple and complex films are indicated by cathodic reduction. Only two of these, but fortunately the major films in most cases, have been chemically identified as Cu_2O and Cu_2S . Some indication of the complexity of these films was

shown earlier by Sharma [64]. Those films which have not been identified are treated as unknown with an average film property calculated from published data for those copper films considered as the most likely for purposes of calculation. Circumstantial evidence and limited ESCA analyses indicate these unknowns to be associated with complex chlorides and/or hydroxychlorides.

A number of factors will affect these percentages. However, significant departure from these ranges probably means a significant departure from the conditions of Tables II and IV, as well as the control ranges shown in Figs. 5 and 6.

For the Au/Ni/Cu controls, the Class II chemistry should be, in descending order, Cl, O, Ni, Cu, S (trace) [24]. Pore corrosion in Class III will show, in order, Cu, Ni, S, O, Cl (low). Creep chemistry in III and IV will show Cu, S, O, Cl (trace). It should again be emphasized that this apparent decrease in chloride with increasing severity in no way decreases its critical importance [24], [26] to the overall reaction process.

Effects of Test Variables: Tables III and IV provide guidelines for control in terms of "permissible" variations of individual variables. This section will attempt to demonstrate the basis for these conclusions.

Temperature: Fig. 8 shows the effect of temperature on the rate constant for copper at nominal Class III and IV conditions. The data may be described by an Arrhenius equation of the form

$$K = A \exp [\Delta H/RT] \quad (3)$$

where K is the parabolic rate constant and ΔH is in the range of 16 to 17 kcal. This relatively low activation energy is in the range which has been measured for the sulfidation of copper (Cu_2S) [36]. If sulfidation is the rate-limiting process for Classes III and IV, then different activation energies may apply to Class II conditions. This has not been studied.

These data indicate that the III and IV reactions can be accelerated by temperature. However, a practical upper limit of only 40 to $50^\circ C$ exists. This limitation is imposed not by an unrealistic change in mechanism, but by the problems associated with the transport of moisture-laden gas from the chamber environment to external analytical equipment without condensation and large gas losses. In view of these considerations, acceleration by temperature is of marginal value. The maximum added acceleration over nominal conditions according to the above relationship is approximately 50 percent at $40^\circ C$ and 100 percent at $50^\circ C$. With reference to Table IV, the kinetic variation for a temperature control of $2^\circ C$ will be about 20 percent.

Humidity: This variable has always been recognized as an important accelerator of corrosion reactions. Over a range of practical interest (50- to 80-percent RH), the effect of humidity can be approximated by the following relationships:

$$K = B \times \exp [5.68 \times RH] \quad (\text{Class III}) \quad (4)$$

$$K = C \times \exp [3.65 \times RH] \quad (\text{Class IV}). \quad (5)$$

This represents a significant but far lower humidity dependence than is often believed to occur. For example, reference

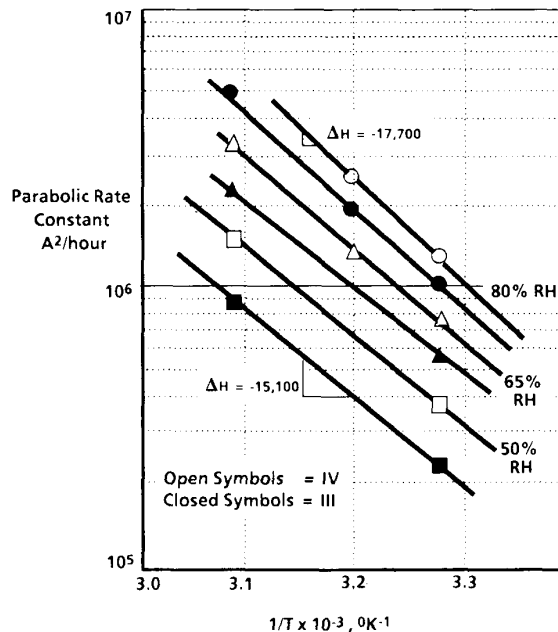


Fig. 8. Temperature dependence of the rate constant for copper in Classes III and IV.

is frequently made to the concept of a "critical" humidity [68] occurring in the range of 60- to 70-percent RH, above which corrosion accelerates rapidly. Such behavior was not found for these types of environments. In fact, these equations were followed to values as low as about 30 percent RH at Class III and IV conditions. These results also correlate with field experience showing significant corrosion rates even into the humidity range of 20 percent for those circumstances in which the sulfide-chloride interactions are present.

Equations (4) and (5) and the absence of a critical humidity are in good agreement with data of Rice [33] who obtained a factor of $4.6 \times \text{RH}$ for a more complex but less reactive FMG environment.

Equations (4) and (5) represent convenient expressions for application over the range of 50- to 80-percent RH. It is interesting to note, however, that these data also follow a relationship of the Brunauer, Emmet, Teller (BET) form [73]. For a second-order reaction the rate constant will take the form

$$K = A \times [B \times \text{RH} / (1 - \text{RH}) \times (1 + C \times \text{RH})]^2. \quad (6)$$

These results confirm the important role of adsorbed water in the corrosion process.

These relationships, together with the practical upper limit of about 80-percent RH suggest that the maximum additional acceleration beyond target values, which can be obtained by increasing humidity, is about 60 percent for the Class III and IV levels (see Fig. 9). This value strictly applies to copper and for other mechanisms the degree of acceleration may actually be less. For example, earlier creep data in these mixed gas environments showed relatively small effects of the humidity variable [34]. Data presently available indicate that humidity can be varied over at least the range of 50- to 80-percent RH without change in rate-controlling mechanisms. Reference to

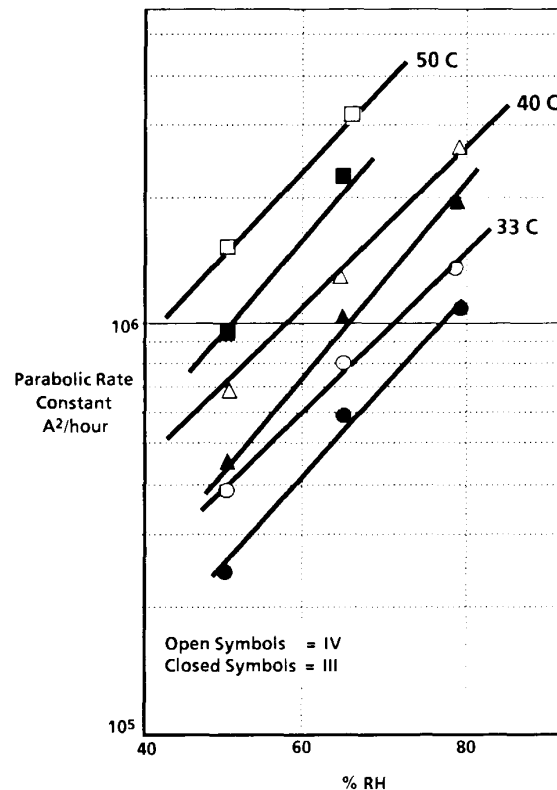


Fig. 9. Effect of humidity on the rate constant of copper in Classes III and IV.

(4) and (5) and Table IV indicates that probable variations in the corrosion rate of copper control samples should be in the range of ± 12 to 15 percent due to humidity variations.

Gas Velocity: Fig. 10 shows little effect of linear velocity beyond relatively low values on either corrosion rates or mechanisms. Few data of this type have been published for FMG environments, but the results are in disagreement with frequently stated "beliefs" that gas velocity should affect rates.

Earlier studies by Lorenzen [31] on the corrosion of silver in FMG mixtures showed a dependence with the one-third power of linear velocity. These results may be in agreement with the present study since silver, by virtue of a gas-phase diffusion rate-controlling process, may be most sensitive to such effects. Ishino [72] reported a velocity dependence for the reduction of copper as the 0.1 to 0.3 power of velocity in H_2S - SO_2 - NO_2 mixtures. It is important to note, however, that those studies were done under conditions of laminar flow/low air exchange rate, and without direct analysis of gases in the test chamber.

An alternative and simple explanation may be available for the apparent velocity dependence shown in earlier data and in the low flow rate data of Fig. 10. The form of the copper reaction curve is an inverse relationship to the air exchange rate curves in Fig. 3. The reaction data, therefore, may simply reflect gas concentration effects due to adsorption losses. These are expected to be high at low air exchange rates and diminish asymptotically at higher rates.

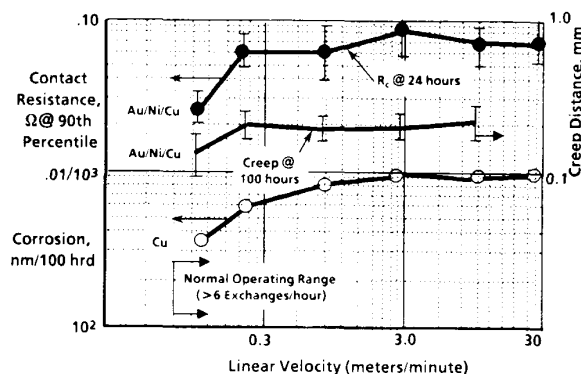


Fig. 10. Corrosion response of copper and porous Au/Ni/Cu versus air velocity for Class III.

In summary, the rate-controlling mechanisms do not appear to be limited by gas phase processes. Corrosion kinetics are independent of velocity within the test chamber other than to the extent that velocity affects gas concentration, temperature, and/or local humidity.

Gas Constituents: The presence of particular gas species and in the correct concentration ranges, is critical to the desired simulation. This section will consider the effects of specific gases.

H₂S: This is considered the primary and possibly the only sulfur species that will drive sulfide reactions in the Class III and IV regions. SO₂ will not [52]; neither will organic sulfides [22]. There are, however, indications that species such as COS may play an important role in atmospheric corrosion [69], possibly in the less severe environments.

The effects of H₂S concentration are twofold. One is the control of mechanisms. This is critical within the Class II region. The upper limit of H₂S has not been precisely defined at which a change to the Class III mechanisms may occur. However, it is known to be in the range of only 15 to 20 ppb. For this reason, control at or below 10 ppb is recommended for Class II.

At Class III and IV levels no new effects on mechanisms have been demonstrated. Therefore, the effects of H₂S concentration are on kinetics and chemistry.

Fig. 11 shows data for the effect of H₂S concentration on the rate constant over limited ranges within the Class III and IV regions. These data may be approximated by a linear relationship of the form

$$K = D \times [\text{H}_2\text{S}]^{1.0} \quad (\text{Class III, IV}). \quad (7)$$

This linear dependence appears to be in general agreement with earlier work summarized by Rice [33] showing a linear relationship between the corrosion rate of copper and reduced sulfur concentration.

With reference to Fig. 11, only limited acceleration is possible by increases in the H₂S concentration within the Class III region. This limitation is imposed by mechanistic considerations. Maximum increases (or decreases) from nominal levels of about ± 50 percent are possible. The extent to which acceleration can be applied within the Class IV region has not been fully investigated. Preliminary data indicate that about a

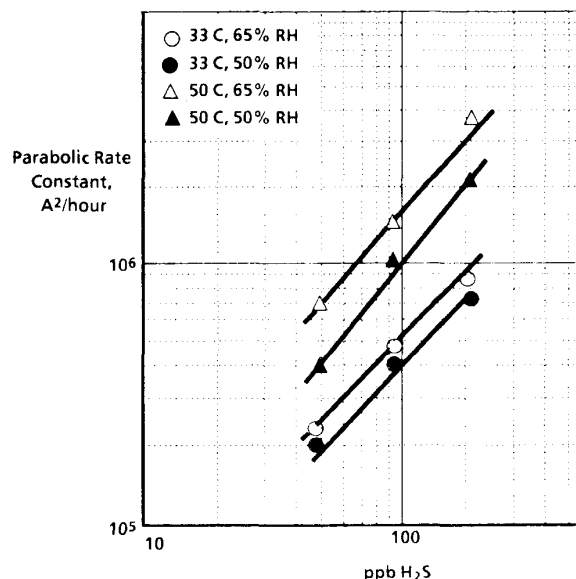


Fig. 11. Effect of H₂S concentration on the rate constant for copper in Classes III and IV.

100-percent increase is possible without unrealistic acceleration.

Finally, limited acceleration from H₂S concentration effects are available within the Class II region. The H₂S concentration dependence has not been fully defined.

NO₂: This species appears to play no direct role in the reaction process although it may for unique metals such as tin and/or solder [67]. NO₂ does, however, accelerate sulfur reactions on silver and copper [52], [68], [69], possibly as an oxidizing agent for H₂S. If this thesis is correct, then other strong oxidizing agents could function in the same role. In fact, recent studies have shown O₃ to be equally effective [70] in the corrosion of silver and copper. Our studies have not, however, shown any significant role of NO₂ in the corrosion of porous gold. Creep appears to be accelerated by small amounts of NO₂ (50 ppb) but large variations in concentration have little added effect [34].

Present data suggest that NO₂ concentration is not critical. Instead, it is believed that some level at or above that of H₂S should be present.

SO₂: This species has an important historical significance in environmental test specifications, as indicated earlier. This is probably due to 1) an emphasis in its use in earlier corrosion studies, 2) the fact that it will corrode many metals—at least at high concentration, and 3) it is present as an important pollutant in the outdoor environments.

Recent work has shown that indoor SO₂ levels are considerably attenuated below outdoor levels [20], [25]. Worldwide, median, indoor levels are in the range of 2 to 3 $\mu\text{g}/\text{m}^3$ with values at the 90th percentile of 30 to 40 $\mu\text{g}/\text{m}^3$ [39]. Since these values are still in the same range as those for H₂S, it is important to determine the role of SO₂ in the corrosion processes.

This questions has been addressed in laboratory experiments in which various levels of SO₂ were added to the

standard Class II and III mixtures. The results in Figs. 7 and 12 show no measurable effects on kinetics or mechanisms up to the limit of study of about 100 ppb. Data not given here also show no effects on chemistry.

These results showing no new or important SO_2 effects are supported by recent regression analyses of field corrosion data. These essentially show a zero exponent on the SO_2 contribution to corrosion for the indoor environments [22].

In summary, no data exist to support the addition of SO_2 in the FMG environments. Conversely, it may be included in such tests at low levels (< 100 ppb) to account for any unique response to materials not yet studied. However, at the current level of understanding, it is a complication for which little justification exists.

Cl_2 : This is perhaps the most critical of the pollutant species. In this case the term "critical" means 1) confirmation of the presence of a reactive chloride, and 2) control of concentration to not exceed specific limits.

The use of Cl_2 does not imply that Cl_2 is the dominant species or is even present to a significant degree in the natural environment. It should be regarded as a convenient laboratory species which will drive the kinetics and produce overall chemistries similar to the field.

Circumstantial evidence suggests that a wide range of halogenated compounds—both inorganic and organic, and at sub parts per billion levels—may produce similar and dramatic effects. At least one study has shown that with one metal of contemporary interest, palladium, these species are not equivalent. It was shown that solid palladium surfaces will be tarnished by Cl_2 (as they are in field environments) [25], [28], [29] and not by HCl [71].

The precise role of Cl_2 in all reactions is not fully understood. In the case of copper reactions, however, there is analytical evidence that its role is to attack the natural Cu_2O film. Earlier work showed the importance of this oxide film in passivating copper against sulfide attack in benign environments [64]. With copper, therefore, the primary role of Cl_2 may be to regulate the pH of the surface film. The high solubility of Cl_2 and its hydrolysis may far outweigh similar effects of SO_2 and account for the negligible effect of the latter, as shown in Fig. 12. The same explanation for the role of Cl_2 may also apply to the corrosion of porous gold with substrate metals of copper and/or nickel.

A full treatment of the effects of Cl_2 and other halogenated species is beyond the scope of this paper. Therefore, the following conclusions will be summarized, but only some can be supported by data in this paper:

- 1) A form of reactive chloride is essential to realistic laboratory simulation.

- 2) Cl_2 is a relevant and convenient pollutant for laboratory use.

- 3) The maximum concentration for Class II is about 10 ppb, and for Class III about 25 to 30 ppb.

- 4) Above the limits just given, unrealistic reactions occur.

Finally, it is equally important to indicate the consequences of variations from these guidelines. First the absence of Cl_2 virtually assures that relevant corrosion will not occur [24], [34] (Fig. 7). Second, attempts to arbitrarily accelerate by

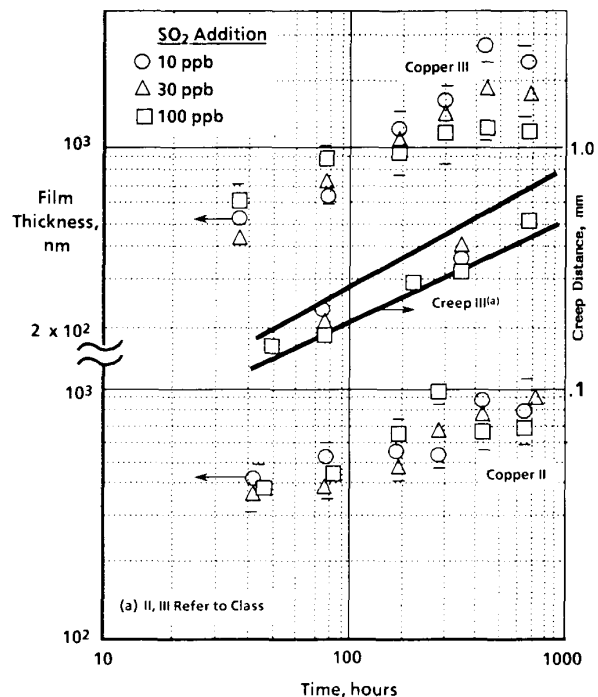


Fig. 12. Effects of SO_2 on the corrosion of copper and porous gold coupon controls.

increases beyond the limits of item 2) may result in totally unrealistic kinetics and a reversal in materials performance.

APPLICATION OF FMG PROCEDURES

Two examples are shown to indicate the general magnitude of effects to be expected on relevant materials and components. The first is a series of common precious metal alloys in coupon form. The second is taken from a connector reliability study.

Precious Metal Alloys

Kinetic data on four precious metal alloys examined in Class II and III are shown in Fig. 13. These data show total film thickness as determined by cathodic reduction. Also shown, for purposes of documentation, are typical values of the amounts of chlorides (AgCl) found on these surfaces. For these materials, the balance is typically Ag_2S .

All of these alloys react according to logarithmic rate equations. This has been interpreted in terms of a rate-controlling mechanism of diffusion via grain boundaries and dislocations in the solid state of the alloy. It should also be noted that the amount of film which will form on these materials in coupon form is sufficient to produce very high contact resistance within periods of exposure less than 24 h.

Not shown are field and laboratory data which would illustrate the following points:

- 1) All of these materials exposed as coupons will tarnish and will have similar, mixed sulfide-chloride chemistries in real environments.

- 2) These alloys will show very low and unrealistic rates in

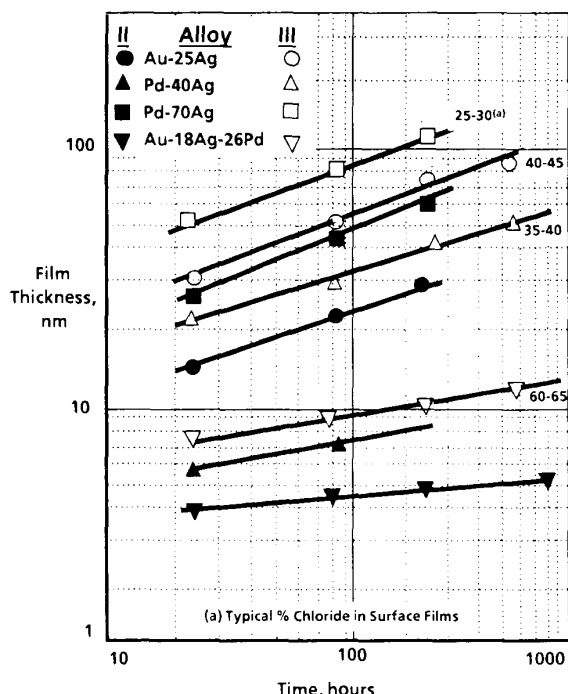


Fig. 13. Corrosion of precious metal alloys in Class II and Class III FMG.

laboratory environments which do not incorporate the S-Cl synergism.

Samples such as these could be considered for control purposes but they are probably not as useful as Cu or Au/Ni/Cu. This is due to the far greater film thickness and *visual effects* for the latter.

Connector Reliability

FMG Conditions: Fig. 14 shows data for three designs of commercial edge card connectors which were examined under Class II and III conditions. Although it is not important to the present discussions, all systems had the following features:

- 1) Au/Ni/Cu in contact with Au/Ni/Cu;
- 2) 0.4 to 1.25 μm Au on springs; 1.25 μm Au on card tabs; 1.25- μm Ni underplate;
- 3) 100- to 130- μg nominal force;
- 4) unlubricated; 25 cycles insertion and withdrawal prior to exposure.

One of these designs could be considered typical of a high-reliability ("high end") product, while samples 2) and 3) might be found in lower cost, shorter design-life applications.

Several important conclusions can be reached from these data. First, comparison with Fig. 6 shows the vast (but fortunate) difference between coupon and component degradation rates. This is due to the well-known "shielding" effect of component housings. This is further illustrated by comparison of mated and unmated data in Fig. 14.

The major feature in these data, however, concerns the magnitude of *measurable degradation in finite sample sizes* in such tests. It is typically low. This fact points to one of the main issues and purposes of such tests. These are 1) reliability

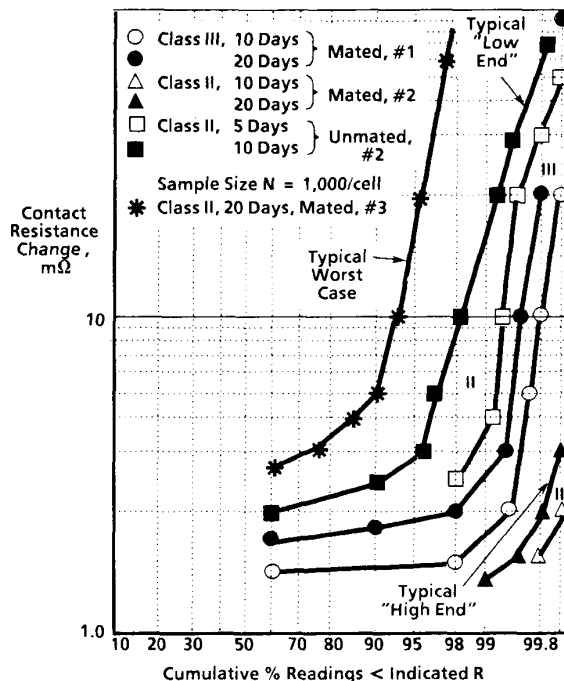


Fig. 14. Examples of connector Delta R distributions for Class II and Class III FMG.

estimates, and 2) service life projections. Towards these goals the data in Fig. 14 would actually project to unacceptable failure rates for some products and applications.

These facts also point to several of the disadvantages perceived by some in the use of such tests. These are as follows:

- 1) They are not quick tests (5 to 30 days typical).
- 2) They demand large sample sizes to support modern failure rate estimates.

Comparison to Non-FMG Conditions

Some data are available to compare the performance of one particular connector in the field to more classical, non-FMG and/or non-S-Cl environments. The results shown in Fig. 15 are in good agreement with the conclusions reached from Fig. 7 for coupon data. These are as follows:

- 1) Severe single-gas H_2S and/or SO_2 environments are relatively benign.
- 2) Application of such procedures at the component level is likely to result in projections of artificially high reliability.

SUMMARY AND CONCLUSIONS

At the present time, a relatively good understanding exists of the chemical nature of the indoor electronics environments as well as their effects on materials. Four classes of field environments have been defined based on corrosion mechanisms. All exhibit strong synergistic effects with particular emphasis on the sulfide-chloride-humidity interactions. These conclusions have been demonstrated worldwide, in all of the major areas of product application, and in most industries. We have also demonstrated that relevant materials, including the

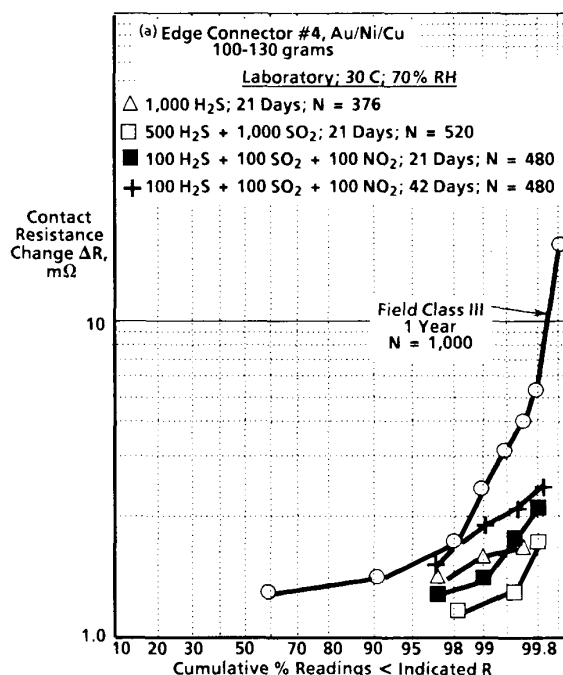


Fig. 15. Effects of common H_2S and SO_2 laboratory environments versus field performance of connector hardware.

precious metals, may degrade rapidly in at least three of those classes. Also, one class of environment exists in which corrosion neither occurs at a significant rate, nor has any influence on reliability.

These observations strongly argue for the development and use of multiple testing procedures. This approach also requires that individual users gain a far better understanding of the range of environments for specific products. Available data argue strongly against the approach of qualification of all components in the most severe environments. In fact, on the basis of component use, exactly the opposite is probably closer to actual application conditions.

These facts have been used in the development of three test environments based on low levels of pollutants in a flowing gas mixture. All are based on the H_2S - NO_2 - Cl_2 interactions at constant, controlled, temperature and humidity. Any or all of these tests can be conducted in the same equipment.

These tests and procedures have been developed into practical systems ranging in size from those used in basic materials research to those used for full-scale systems evaluation. It has been demonstrated that any of these systems can yield similar results. Therefore, no single design exists or needs to exist. However, for the successful conduct of these procedures, proper control and verification is mandatory. These features have largely been lacking in existing environmental test specifications. Some of the reasons and consequences associated with the lack of proper control have been shown in this paper. Due to unavoidable gas loss mechanisms, it may be argued that any attempts to conduct these procedures without analytical controls will result in tests conducted at an effective severity far lower than intended.

We have concluded that two types of control are mandatory. One is direct analysis of the environment actually existing in

the test chamber. The second is verification by reactivity monitoring. For the latter, copper and porous-gold-electroplated coating are useful and strongly recommended.

Finally, FMG procedures cannot be regarded as all-inclusive of all potential failure mechanisms. They are specifically designed to examine long-term corrosion from natural environmental influences. They are not designed to examine, for example, influences such as infant mortality due to surface contamination, organic contamination, fretting, etc. Neither can they be considered as "quick look" corrosion tests applied to small sample sizes, particularly in component evaluation.

In summary, the FMG procedures offer a significant advance in the art of environmental aging. They exhibit realistic degradation mechanisms and chemistries for a wide range of materials. They must be used with some caution. The interpretation of data from such tests must be accompanied by good engineering judgement.

REFERENCES

- [1] W. E. Campbell and U. B. Thomas, "Tarnishing studies on contact materials," in *3rd Int. Research Symp. on Electric Contact Phenomena* (Univ. of Maine, Orono, 1966), p. 83.
- [2] —, "Tarnish studies," *Trans. Elect. Soc.*, vol. 76, p. 303, 1939.
- [3] W. H. Abbott, "Effects of test environment on the properties of silver films," in *11th Int. Conf. on Electric Contact Phenomena* (Berlin, 1982), p. 294.
- [4] W. H. Abbott and H. R. Ogden, "The influence of environment on tarnishing reactions," in *Proc. 4th Int. Conf. on Electric Contact Phenomena* (Swansea, 1968), p. 35.
- [5] British Standards Institution, "Sulphur dioxide test for contacts and connections," B52011, 1977.
- [6] IEC 68-2-42, IEC 50B 272, 1986, DIN 40 046 Part 36, Jeida 39
- [7] IEC 68-2-43, IEC 50B 272, 1986, DIN 40 046 Part 37, Jeida 38
- [8] MIL-STD-202E, 1973.
- [9] B. Wiltshire, "A survey of contact atmospheres in UK telephone exchanges," *Brit. Telecom. Tech. J.*, vol. 2, no. 1, p. 74, Jan. 1984.
- [10] U. Cosack, "Survey of corrosion tests with pollutant gases and their relevance for contact materials," in *13th Int. Conf. on Electric Contacts* (Lausanne, Switzerland, 1986), p. 316.
- [11] T. Hayakawa *et al.*, "Silverplated stainless steel for contact applications," in *Proc. Int. Conf. on Electric Contacts* (Nagoya, Japan, July 1986), p. 41.
- [12] D. H. Thompson *et al.*, "The atmospheric corrosion of copper results of 20-year tests," *ASTM Spec. Tech. Publ.* 175, p. 77, 1955.
- [13] L. Borchert *et al.*, "Investigation of corrosion behavior of contact materials used in telecommunications," in *9th Int. Conf. on Electric Contact Phenomena* (Chicago, IL, 1978), p. 273.
- [14] J. C. Mollen and M. Trzeciak, "Analysis of copper films after field exposure," *Electrical Contacts*, p. 37, 1970.
- [15] R. V. Chiarenzelli, "Tarnishing studies on contact materials," in *3rd Int. Research Symp. on Electric Contact Phenomena* (Univ. of Maine, Orono, 1966), pp. 83.
- [16] R. V. Chiarenzelli, "Air pollution effects on contact materials," in *Electrical Contacts* (Univ. of Maine, Orono, 1965), p. 63.
- [17] B. E. Blake, "Summary report of the ASTM Section 6 field tests," in *Int. Symp. on Electric Contact Phenomena* (Graz, Austria, 1964), p. 531.
- [18] C. Leygraf and S. Zakipour, "Field and laboratory corrosion tests of Au- and Sn-plated contact materials," in *Proc. 9th Int. Conf. on Metallic Corrosion* (Toronto, Ont., Canada, 1984).
- [19] J. L. Jostan *et al.*, "Langzeitkorrosionsprüfungen An Elektrowerkstoffen," *Metalloberfläche*, vol. 39, pt. 1-5, pp. 45, 93, 145, 165, 190, 1985.
- [20] N. Honma *et al.*, "Sox and dust concentrations in contact atmosphere," *Electrical Contacts*, p. 24, 1980.
- [21] D. W. Rice *et al.*, "Atmospheric corrosion of nickel," *J. Elect. Soc.*, vol. 127, p. 563, 1980.
- [22] W. H. Abbott, "Studies of natural and laboratory environmental reactions on materials and components," 9th Progress Rep., Aug. 1986, unpublished data.

- [23] F. B. Benson *et al.*, "Indoor-Outdoor air pollution relationships," EDA-NERC 27709, 1972.
- [24] W. H. Abbott, "The corrosion of porous gold platings in field and laboratory environments," in *13th Int. Conf. on Electric Contacts* (Lausanne, Switzerland, 1986), p. 343.
- [25] M. Antler, "Field studies of contact materials in telephone central offices," in *11th Int. Conf. on Electric Contact Phenomena* (West Berlin, FRG, 1982), p. 297.
- [26] D. W. Rice, "Corrosion in the electronics industry," presented at Corrosion/85, Boston, MA, Mar. 1985, paper 323.
- [27] S. P. Sharma, "Atmospheric corrosion of Cu, Ni, and Ag," *J. Elect. Soc.*, vol. 125, p. 2005, 1979.
- [28] C. A. Haque and M. Antler, "Atmospheric corrosion of clad palladium and palladium silver alloys—Part I: Film growth and contamination effects," *Electrical Contacts*, p. 183, 1981.
- [29] S. P. Sharma *et al.*, "Development of Pd and Pd-Ag Alloy: Part II—Film chemistry," *Electrical Contacts*, p. 203, 1981.
- [30] W. H. Abbott, "Field and laboratory studies of the contact resistance of an amorphous metal alloy," *Electrical Contacts*, p. 253, 1980.
- [31] J. Lorenzen, "Atmospheric corrosion of silver," *Proc. Inst. Env. Sci.*, p. 110, 1971.
- [32] D. W. Rice *et al.*, "Atmospheric corrosion of cobalt," *J. Electrochem. Soc.*, vol. 126, no. 9, p. 1459, 1979.
- [33] D. W. Rice *et al.*, "Atmospheric corrosion of copper and silver," *J. Electrochem. Soc.*, vol. 128, p. 275, 1981.
- [34] W. H. Abbott, "The effects of test environment on the creep of surface films over gold," in *Proc. 12th Int. Conf. on Electric Contact Phenomena* (Chicago, IL, 1984), p. 47.
- [35] D. W. Rice *et al.*, "Indoor corrosion of metals," *J. Electrochem. Soc.*, vol. 127, p. 891, 1980.
- [36] B. Chattopadhyay and S. Sadigh-Esfandiary, "Sulphidation of Cu and Cu-Ni alloys in H₂S/argon mixture," *Corrosion Sci.*, vol. 13, p. 747, 1973.
- [37] ISA Specification, ISA-d571.04.
- [38] W. H. Abbott, "The measurement of equipment operating environments to evaluate corrosion related failure mechanisms," IEC Doc. 65 (Montreal/USA), May 7, 1965.
- [39] —, "Field vs. laboratory experience in the evaluation of electronic components and materials," *Materials Perform.*, vol. 24, p. 46, 1985.
- [40] R. Currence *et al.*, "Characterizing the machine internal environment for specifying and testing contact materials," in *Proc. ECSG* (Anaheim, CA, 1986), p. 23.
- [41] M. A. Lunn, "Control equipment component failure and its relationship to environmental corrosivity," in *TAPPI 1983 Engineering Conf.*, p. 53.
- [42] J. Steer, *Pulp and Paper Canada*, vol. 85, no. 8, 1984.
- [43] W. H. J. Vernon *et al.*, "Laboratory study of the atmospheric corrosion of metals," *Trans. Faraday Soc.*, vol. 27, p. 255, 1931.
- [44] M. Antler and J. J. Dunbar, "Environmental tests for connectors and contact materials: An evaluation of a method involving sulfur dioxide," *IEEE Trans. Comp. Hybrids, Manuf. Technol.*, vol. CHMT-1, p. 17, 1973.
- [45] W. A. Crossland, *et al.*, "The accelerated tarnish testing of contacts and connectors employing silver alloy contacts," *Electrical Contacts*, p. 265, 1973.
- [46] J. Potinecke, "Behavior of contact surfaces consisting of Ag and Pd-Ag alloys in tarnishing environments," *Electrical Contacts*, p. 139, 1975.
- [47] K. L. Schiff, *et al.*, "The tarnishing behavior of gold base alloys in corrosive environments," *Electrical Contacts*, p. 37, 1975.
- [48] J. Potinecke, "Behavior of contact surfaces consisting of gold alloys in H₂S-NO₂-SO₂ atmospheres," in *8th Int. Conf. on Electric Contact Phenomena* (Tokyo, Japan, 1976), p. 275.
- [49] K. L. Schiff, "Technical realization and experimental performance of corrosive gas test equipment for accelerated testing of electrical contacts," *Electrical Contacts*, p. 43, 1977.
- [50] K. L. Schiff and R. Schnabl, "A comparative evaluation of accelerated corrosive gas tests applied to separable connector contacts," in *9th Int. Conf. on Electric Contact Phenomena* (Chicago, IL), p. 309.
- [51] K. L. Schiff and H. Becker, "Surface analysis of tarnished precious metal alloys after exposure to different corrosive environments," in *9th Int. Conf. on Electric Contact Phenomena* (Chicago, IL), p. 295.
- [52] W. H. Abbott, "Effects of industrial air pollutants on electrical contact materials," *Electrical Contacts*, p. 94, 1973.
- [53] E. S. Sproles *et al.*, "Results of exposure of palladium-based contact materials to Cl₂ and H₂S ambients," in *11th Int. Conf. on Electric Contact Phenomena* (West Berlin, FRG, 1982), p. 143.
- [54] S. P. Sharma *et al.*, "Development of a gentle accelerated corrosion test," *J. Electrochem. Soc.*, vol. 125, no. 12, p. 2002, 1978.
- [55] S. P. Sharma and F. Bader, in *Proc. Annual Connectors and Interconnections Symp.*, (ESCG Inc., Philadelphia, PA, 1981), p. 257.
- [56] T. R. Long and K. F. Bradford, "60 Pd-40Ag as an electrical contact material to replace palladium," in *8th Int. Conf. on Electric Contact Phenomena* (Tokyo, Japan, Aug. 1976), p. 55.
- [57] J. P. Baron *et al.*, "Search for a test simulating the environment of industrial atmospheres for contacts and connections," in *9th Int. Conf. on Electric Contact Phenomena* (Chicago, IL, 1978), p. 287.
- [58] W. J. Curren *et al.*, "Design and operating characteristics of a mixed gas environmental chamber," presented at Corrosion/85, Boston, MA, paper 326.
- [59] W. E. Campbell and U. B. Thomas, Bell Telephone Systems Monograph B-1170, 1939.
- [60] ASTM Committee B-4, "Task force report on contact resistance probing," Oct. 1979 and ASTM B667-80, unpublished data.
- [61] R. C. Allen and M. Trzeciak, "Measuring environmental corrosivity," *Electrical Contacts*, p. 29, 1979.
- [62] S. Zakipour and C. Leygraf, "Studies of corrosion kinetics on electrical contact materials by means of quartz crystal microbalance," *J. Electrochem. Soc.*, p. 873, May 1986.
- [63] W. H. Abbott and H. R. Ogden, "The influence of environments on tarnishing reactions," in *Proc. 4th Int. Res. Symp. on Electric Contact Phenomena* (Swansea, 1968), p. 35.
- [64] S. P. Sharma, "Reaction of Cu and Cu₂O with H₂S," *J. Electrochem. Soc.*, vol. 127, p. 21, 1980.
- [65] U. R. Evans, *The Corrosion and Oxidation of Metals*. London, England: E. Arnold, 1960, p. 486.
- [66] T. E. Graedel *et al.*, "Carbonyl sulfide: Potential agent of atmospheric sulfur corrosion," *Science*, vol. 212, p. 663, May 1981.
- [67] H. G. Tompkins, "The interaction of some atmospheric gases with a tin-lead alloy," *J. Electrochem. Soc.*, vol. 120, no. 5, p. 651, 1973.
- [68] J. Guinement and C. Fiaud, "Laboratory study of the reaction of silver and copper with some atmospheric pollutants," in *13th Int. Conf. on Electric Contacts* (Lausanne, Switzerland, 1986), p. 383.
- [69] D. Simon *et al.*, "Study of the contamination of contact materials, silver and silver palladium alloys in air containing hydrogen sulfide and nitrogen dioxide," in *13th Int. Conf. on Electric Contacts* (Lausanne, Switzerland, 1986), p. 333.
- [70] W. H. Abbott, unpublished data.
- [71] S. P. Sharma, "Reaction of palladium with chlorine and hydrogen chloride," *Electrical Contacts*, p. 203, 1981.
- [72] M. Ishino *et al.*, "Effect of gas flow velocity on tarnish kinetics of contact materials," *Electrical Contacts*, p. 23, 1979.
- [73] S. Brunauer *et al.*, *J. Amer. Chem. Soc.*, vol. 60, p. 309, 1938.