



Diffusion and absorption of corrosive gases in electronic encapsulants

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Abstract

Plastic encapsulated microcircuits with aluminum triple track structures were exposed to mixed flowing gas conditions to simulate and accelerate possible environments during long-term storage. No increase in resistance was measured and no corrosion products were observed after 800 h of accelerated exposure. Further experimentation indicated that chloride gas reacts with surface moisture in microscale and macroscale voids within the encapsulant, creating chloride ions. These ions become strongly bound to ion getters present in the epoxy molding compound, trapping the chloride ions within the bulk encapsulant and effectively retarding the diffusion process, which could lead to corrosion at the surface of the die.

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1. Introduction

In the age of consumer electronics, industries that use components in niche applications requiring long-term life in harsh environments, such as military, aerospace, oil drilling and automotive, purchase a miniscule fraction of the microelectronic components that are produced. As a result, there is little marketplace demand for hermetically sealed packages, especially since they are generally orders of magnitude more expensive than their plastic counterparts [1].

The proliferation of affordable, leading-edge plastic encapsulated microcircuits (PEMs) has introduced questions about their reliability in long-term storage applications [2–4]. Because of extended periods of dormancy, there is concern that exposure to elevated temperature/humidity will produce more corrosion in stored devices than in operating devices. Stored devices lack the power dissipation that helps keep condensed moisture off the surface of the die [5].

The diffusion behavior of moisture through electronic encapsulants and the resulting presence of monolayers of water at the die surface have been well documented [6,7]. However, previous research has shown that for corrosion to occur at the die surface within a reasonable amount of time, ionic contaminants must be present [8]. Over the years, sources of mobile ions from the manufacturing process have been identified and removed [9]. This may result in the operating environment becoming a primary source of ionic contamination [10].

The epoxy molding compounds (EMCs) are gas permeable and it is possible that ionic contamination could penetrate into the plastic encapsulated microcircuit in the form of a corrosive gas, such as Cl_2 , H_2S , or SO_2 . The purpose of this paper was to investigate the diffusion behavior of corrosive gases through encapsulants and to document the possible occurrence of ion-induced corrosion in PEMs after long-term exposure to corrosive gases.

1.1. Encapsulants

Predicting gas transport behavior through electronic encapsulants is problematic due to the complex nature of EMCs. Molding compounds consist of an encapsulating resin, typically epoxy cresol-novolac (ECN) or

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biphenyl, with passive and active additives. Passive (inert) components make up the overwhelming bulk of the encapsulant. For example, inorganic fillers, often fused silica, can make up 65–80% by weight of the molding compound. The active components are often a proprietary mix of curing agents (hardeners), accelerators, coupling agents, flame-retardants, stress-relief additives, coloring agents, mold-release agents, and ion getters.

The amalgamation of mold compound materials creates a complex composite structure. The large number of particulates within the encapsulant will result in a large surface area of interfaces. Because the volume percent of inorganic fillers greatly exceeds the percolation threshold, these interfaces can provide diffusion paths for gases, separate from standard bulk diffusion through the encapsulating resin. Predicting bulk diffusion is also difficult, because the resin is often a proprietary blend, rather than a single component.

There has been no direct experimental measurement reported in the literature of the diffusion of industrial gases through encapsulant resins, such as ECN or biphenyls, much less the complex composite structure of EMCs. However, the diffusion behavior of gases through such materials can be predicted based upon previous work in gas transport through polymers or an analysis of the measurement of moisture diffusion through EMC's.

1.2. Gas transport through polymers

The concentration of dry gases in polymers is determined by Henry's Law as

$$C = K_p p \quad (1)$$

where K_p is the sorption constant and p is the partial pressure of ambient gas [11,12]. Assuming steady-state Fickian diffusion, the flow of dry gas molecules can be described by

$$J = D \frac{K_p p}{l} \quad (2)$$

where D is the diffusion coefficient and l is the thickness of the polymeric membrane. Previous experimental and theoretical work has found that the bulk diffusion of small diameter, weakly interacting gases through monolithic polymers is strongly dependent upon the fractional free volume of the polymeric resin [13–17]. Free volume distributions can be measured directly through the use of neutron magnetic resonance (NMR) or positron annihilation lifetime spectroscopy (PALS) [18]. However, these methods can be an expensive and time-consuming. A simpler method is to analytically calculate the fractional free volume (FFV) by

$$\text{FFV} = \hat{v}_f / \hat{v} = \hat{v} - \hat{v}_0 / \hat{v} \quad (3)$$

where v_f is the specific free volume, v is the inverse of the density and v_0 is the volume occupied by the polymer chains. It has been proposed that the diffusion behavior can then be described as

$$D = A e^{-B/\text{FFV}} \quad (4)$$

where A and B are empirical constants. A review of literature performed by Thran et al. [19] showed that the transport of gaseous, non-interacting molecules is strongly dependent on the FFV. Deviations from a linear relationship between the diffusion coefficient and the reciprocal of the FFV were found to be due primarily to variations in the stiffness¹ of the polymer backbone² and the cohesive energy of the polymer. These results required a revision of Eq. (4) to include the effects of stiffness and cohesive energy,

$$\log_{10} D = C_0 - B/\text{FFV} - C_1 E_{\text{coh}} \quad (5)$$

where C_0 and C_1 are obtained through multiple linear regression, E_{coh} is the cohesive energy of the polymer and B is given by

$$B \approx \gamma \frac{v_s^*}{v^*} \quad (6)$$

where γ is an overlap factor,³ v^* is the critical void volume for migration and v_s is the volume of the gas molecule. The diffusion of large, non-polar molecules (N_2 , O_2 , CH_4) was shown to have the strongest correlation to the behavior predicted by Eq. (5). The diffusion behavior of CO_2 gas showed some deviation, suggesting that the polar nature of the molecule causes it to interact with the polymer chain [21]. The smallest molecules (He , H_2) showed evidence of a very different diffusion mechanism than the larger molecules, because their small dimensions allow them to diffuse without assistance from free volume fluctuations [19].

1.3. Moisture diffusion

The migration of moisture through electronic encapsulants has been well documented [6,22–29]. Previous research has found that water molecules are present in epoxy resin in two forms, bound and unbound. The bound molecules are attracted to the polymer chains through hydrogen bonding and become immobilized. It

¹ Polymer chain stiffness is a measurement of the amount of movement and rotation in the polymer chain and is primarily dependent upon the number of double bonds and aromatic groups present in the main chain.

² The dependence on polymer chain stiffness may be because increased chain stiffness can lead to an increase in percolation behavior [20].

³ Between 0.5 and 1. Does not vary significantly between polymers.

is these molecules that cause swelling. The unbound molecules are free to diffuse through the free volume or voids in the resin. Water molecules may also undergo phase transformations as they move through the EMC, initially diffusing as a gas, then condensing in macroscale voids, and finally evaporating and continuing the diffusion process [25].

There are also multiple diffusion paths within the molding compound. Moisture diffusion can occur either through the polymeric resin or along the filler-resin interface (if there is separation between the filler and resin). The diffusion through the polymeric resin can be referred to as ‘bulk diffusion’ and the diffusion through interfaces between polymeric resin and the fillers can be referred to as ‘interfacial diffusion’.

Moisture diffusion in polymers is commonly modeled using the one-dimensional Fickian equation, given by

$$\frac{\partial C}{\partial t} = D \frac{\partial^2 C}{\partial x^2} \quad (7)$$

where C is the moisture concentration, t is time and x is the axis along the concentration gradient. Solving the boundary conditions (see [6]), the diffusion coefficient can be determined through,

$$\frac{M_t}{M_\infty} = 4 \left(\frac{Dt}{\pi l^2} \right)^{1/2} \quad (8)$$

where M_t is the moisture absorbed at time t , M_∞ is the moisture saturation concentration, and l is the thickness of the polymer.

With regard to moisture absorption behavior of PEM's, existing literature is in some disagreement. Some experiments have shown that the simple Fickian model faithfully predicts moisture diffusion behavior [6,26–28]. Other researchers have found that different models, such as a simple quasi-steady state (QSS) [25] or dual-mode sorption model [27], provide a more accurate description. A QSS model developed by Tencer [25] is based on a container with a permeable wall to illustrate the QSS approach. The governing equation is

$$\frac{dc_i}{dt} = \frac{AP}{V_L + V_{\text{wall}}LK/2} (c_a - c_i) \quad (9)$$

where c_a is the ambient moisture concentration, c_i is the moisture concentration of air inside the container, P is the permeability (defined as the product of D and the solubility partition coefficient K), V is the volume of the enclosure, L is the wall thickness, A is the surface area of the wall, and V_{wall} is the volume of the wall. The Tencer model addresses the importance of moisture permeability vs. diffusion constant of wall materials and is applicable to microelectronic packages. For thin walls and/or absorbing walls, such as hermetically sealed packages, the first term, which is a function of P , pre-

dominates. It is also a function of the container's geometry (V and A). For thick and/or absorbing walls, such as PEMs, the second term (depending on D) prevails. The moisture diffusion kinetics do not depend on the container/package geometry, only on the wall thickness.

In a moisture sorption study of polymers by Belton et al. [27], deviations from Fickian behavior were observed and were attributed to the dual mode sorption theory. This theory is based on the observation that water molecules exist in two states in plastic encapsulants, bound and unbound.

Attempts to predict moisture diffusion behavior as a function of polymeric properties have primarily focused on cross-link density and free volume. Aronhime et al. [30] has reported that the free volume determines the maximum moisture absorption while the cross-link density of the polymer determines the diffusion rate. He showed that an increase in cross-link density in epoxy resins resulted in an increase in free volume, an increase in equilibrium moisture absorption and a decrease in the moisture diffusion rate. Thus an increased ion diffusion rate in biphenyl resins is consistent with their decreased cross-link density due to their lower functionality. However, Belton et al. [27] reported that an increase in post mold curing in epoxy resins resulted in an increase in free volume, an increase in equilibrium moisture absorption and an increase in the moisture diffusion rate.

To better understand the transport behavior of gases through electronic encapsulants and their effect on ion-induced corrosion, two sets of experiments were performed. The first set examined the occurrence of ion-induced corrosion and the second set examined the absorption of chlorine gas into epoxy encapsulants.

2. Ion-induced corrosion

Two types of test chips fabricated by Sandia National Laboratories were used for this experimentation. The purpose behind the use of both test chips was to simultaneously track both moisture and gas ingress in the same environment. The first test chip, an ATC5.0 Moisture Test Chip, monitored the moisture content at the die surface. The moisture test chip consists of unpassivated, interdigitated 2 mm wide aluminum tracks patterned over a porous silicon film (see Fig. 1). An increase in the local relative humidity results in molecules, or monolayers, of water condensing in the pores. This absorption effect triggers a non-linear increase in measured capacitance in the pF range.

The second chip, an ATC2.6 Assembly Test Chip, monitored the presence of corrosion products on the die surface. The assembly test chip consists of eight interdigitated, 2 mm wide aluminum triple tracks patterned over a silicon substrate (see Fig. 2). Four of the tracks

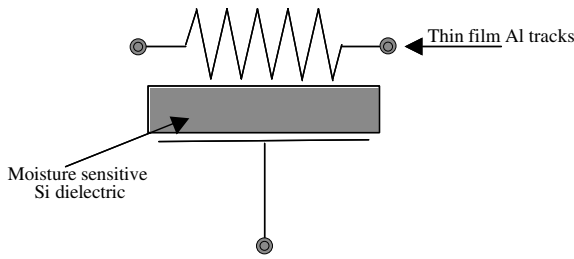


Fig. 1. Electrical schematic of the ATC5.0 test chip from Sandia National Laboratories.

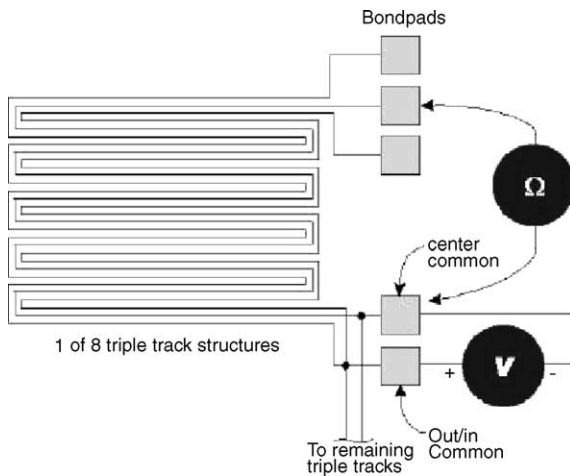


Fig. 2. Electrical schematic of ATC2.6 Assembly Test Chip from Sandia National Laboratories.

have a 5000 Å thick SiN passivation layer. The other four have cut-outs in the passivation layer, allowing the biased tracks to be exposed. The aluminum, triple-track structure was chosen because aluminum corrosion can induce an increase in electrical resistance and eventually an electrical open [31–33]. Any corrosion of the aluminum traces, which would decrease the conductive cross-sectional area, was expected to result in an increase in resistance in the kΩ range.

Both chips were encapsulated in a commercially available epoxy-molding compound (Sumitomo EME-7320CR). Information on this encapsulant is detailed in Table 1.

Six moisture test chips and six assembly test chips were exposed to a Class III mixed flowing gas (MFG) environment. A picture and schematic of the airflow in a MFG chamber can be seen in Figs. 3 and 4, respectively. Many studies have demonstrated that MFG exposure is a realistic, accelerated, environmental test that can be designed to simulate the kinetics and degradation mechanisms found in contaminated environments [34–41]. As a result, MFG tests are widely used as accelerated corrosion tests for electrical contacts and connectors. A review of the various classes of MFG environments is provided in Table 2.

Half of the chips in each group were biased at 5 V. Chips were removed every 200 h for capacitance (ATC5.0) and resistance (ATC2.6) measurements. Total exposure time was 800 h (33.5 days). Using the acceleration factor for Battelle Class III MFG testing stated in [39], that two days in the MFG chamber approximately equals one year in the field use, the total test exposure is approximately equivalent to a 16-year lifetime in a moderate industrial setting.



Fig. 3. Image of MFG chamber at CALCE EPSC.

Table 1
Commerically available EMCs investigated in this study

	EME-7320CR	AMC-2	MG15F	MG36F-25A
Company	Sumitomo	Cookson	Dexter	Dexter
Usage	Anti-popcorn	Low stress/anti-popcorn	High power	General use
T_g	130–155 °C	147 °C	190 °C	170 °C
Resin type	Biphenyl	ECN	N/A	N/A
Filler	N/A	Fused silica (70%)	N/A	N/A
Transfer pressure	85 kgf/cm ²	N/A	N/A	N/A
Mold cure	45 s at 180 °C	N/A	N/A	N/A
Post-mold cure	8 h at 175 °C	No post-mold cure	10 h at 175 °C	2 h at 177 °C

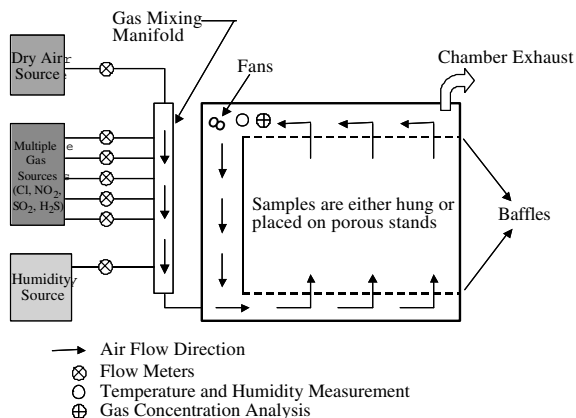


Fig. 4. Schematic of airflow in MFG chamber.

2.1. Ion-induced corrosion (results)

Results of the capacitance measurements are displayed in Fig. 5. The increase in capacitance over time indicates that moisture diffused through the molding compound to the die surface. Using these results, the diffusion coefficient of moisture through Sumitomo EME-7320CR at 35 °C and 75% RH was determined to be $7.5 \times 10^{-9} \text{ cm}^2/\text{s}$ [6]. A saturation moisture concentration of 0.21% was also calculated.

Results from resistance measurements are displayed in Fig. 6. Note that there is no change in resistance over the 800 h of exposure. Decapsulation of the test chips and optical examination of the aluminum tracks revealed no evidence of corrosion products. The lack of corrosion on the triple track structures and at the bond pads in the assembly test chip suggests either the MFG environment did not induce deterioration of aluminum traces or the ingress of corrosive gases was somehow retarded or hindered by the electronic encapsulant.

2.2. Ion-induced corrosion (discussion)

When running accelerated tests, it is important to determine if it is reasonable to expect failure during the

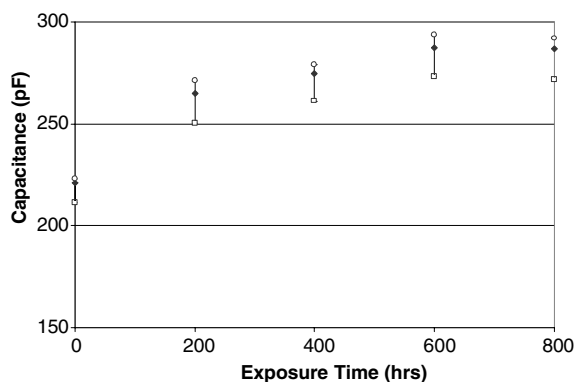


Fig. 5. Change in capacitance in ATC5.0 test chips as a function of time in Class III MFG environment. Dry capacitance reading is 150 pF (from Sandia).

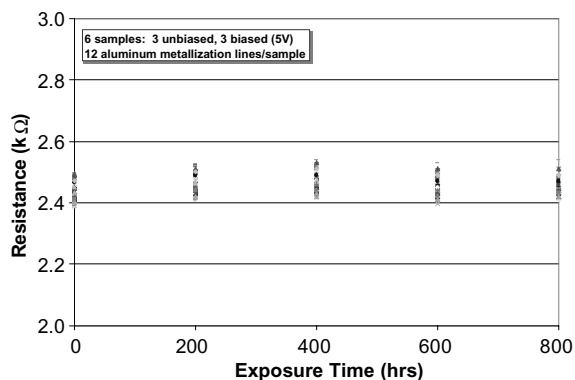


Fig. 6. Change in resistance in ATC2.6 test chips as a function of time in Class III MFG environment. Note that there is no noticeable change in resistance after 800 h.

exposure time. This section will review previous literature for experimental data supporting or challenging the assumption of 800 h as an appropriate exposure time under Class III MFG conditions.

Experimental work on unpassivated, unencapsulated die showed that exposure to an 85 °C/85% RH/10 V environment with high amounts of Cl₂ gas (1000 ppb)

Table 2
A listing of MFG environments

	Class II	Class III	Class IV
Environment	Light industrial/business office	Moderate industrial; particulates present	Heavy industrial; extremely corrosive
Temperature, °C	30 ± 2	30 ± 2	50 ± 2
Relative humidity, %	70 ± 2	75 ± 2	75 ± 2
Chlorine (Cl ₂), ppb	10 ± 2	20 ± 5	50 ± 5
Nitrogen dioxide (NO ₂), ppb	200 ± 25	200 ± 25	200 ± 25
Hydrogen sulfide (H ₂ S), ppb	10 ± 4	100 ± 10	200 ± 10
Sulfur dioxide (SO ₂), ppb	100 ± 20	200 ± 50	300 ± 50

No test exists for Class I environments since available data indicates no precedent for environmental effects on reliability [40].

induced failures, defined as an electrical open, after approximately 100 h [42]. Median life was less than 600 h. While this modified HAST environment is more extreme in temperature and humidity than the Class III MFG environment, Abbott [40] has found that single gas environments, even at very high concentrations, can retard the corrosion process in comparison to multiple gas environments. Therefore, it is reasonable to expect that unpassivated, unencapsulated dies exposed to a Class III MFG environment would begin to fail within an order of magnitude of the 100 h seen in Iannuzzi [42].

Iannuzzi also found that die encapsulated in RTV silicone rubber were much more robust under the severe environment, with no failures occurring before 2000 h of exposure. In fact, the silicone rubber encapsulation was a much greater factor in survivability than the presence of a SiN passivation layer. The most probable reason for this behavior is silicone's resistance to moisture diffusion and absorption. The moisture diffusion rate of Sumitomo EME-7320CR, a biphenyl epoxy, at 35 °C/75% RH (7.5×10^{-9} cm²/s) is only 1/4th that of silicone at 85 °C/85% RH (3.3×10^{-8} cm²/s) [43]. In addition, the saturation level of Sumitomo EME-7320CR at 35 °C/75% RH is approximately an order of magnitude higher than silicone at 85 °C/85% RH (0.04%). The absence of moisture at the die surface more than likely caused the large improvement in the reliability of the silicone encapsulated aluminum structures. Since EMC's do not provide the same level of protection, encapsulated microcircuits should be expected to display the effects of corrosion within 2000 h of exposure.

More recent work suggests that the material makeup of commercial encapsulants will impede the migration of industrial gases through EMC's. From experimental work using electrolyte solutions, Lantz and Pecht [10] showed that ion getters present in the molding compounds will bind with ions from external sources. These reactions effectively halt the diffusion process, preventing migration of the ions until all ion getters are effectively neutralized. This causes ions to move as a front, with diffusion rates at low concentrations (0.15 M NaCl) being much lower than moisture diffusion rates.

While chlorine gas is a neutral compound, it can be a source of ionic contamination as a result of the following reaction with surface moisture:



where $K = 2.6 \times 10^{-5}$ at 25 °C. This generates a weakly acidic solution of chloride ions on the surface. Because of the low solubility of the chlorine in water (0.52 g Cl₂/100 g H₂O at 85 °C and 1 atm [44]) and because the equilibrium constant governing the formation of chloride ions is so low, the concentration of chloride ions on the surface is probably small. As moisture diffusing

through molding compounds can also condense in macroscale voids, this chloride reduction reaction could also take place within the bulk encapsulant.

At both reaction sites, the ion getters present in the encapsulant will bind to the chloride ions. Since the corrosion process, especially in regards to aluminum, requires electrolyte, the trapping of chloride ions would explain the absence of resistance changes and corrosion products in the samples used in this experiment.

If chloride ions are trapped in the encapsulant material, an increase in chloride should be observed after long-term exposure to chloride gas. To verify this hypothesis, three types of electronic encapsulants were exposed to two different gaseous environments.

3. Absorption of gaseous ions

The three types of electronics encapsulants (see Table 1) were selected to replicate the broad range of EMC's used in electronics packaging. The corrosive environments, detailed in Table 3, were simulated in a MFG chamber (see Fig. 3). These two environments were selected to investigate the possibility of synergistic effects in the absorption of gaseous ions into EMCs.

Samples were exposed to the test environments for up to 12 days. All samples were handled using power-free vinyl gloves. All equipment, instruments, and glassware that came into contact with samples were first subjected to a rigorous cleaning process, consisting of an initial cleaning, a wash with methanol, and a final rinse in deionized (DI) water. After exposure to the corrosive gases, the EMC samples were carefully removed from the chamber and ground into powder using a low-speed drill. A small amount of powder, approximately 0.05 g, was then placed into a beaker containing 100 ml of DI water. The beaker was sealed and the powder/water mixture was allowed to boil for 60 min. The resulting solution was analyzed for sulfide (S²⁻) and chloride (Cl⁻) ions using ion chromatography (IC).

3.1. Absorption of gaseous ions (results and discussion)

The results of IC are displayed in Figs. 7 and 8. At the lower levels of 50 ppb of chlorine gas in the Class IV mixed flowing gas environment, no measurable increase in the chloride concentration of the EMCs was detected.⁴ At the higher exposure level of 300 ppb of chlorine gas, a sharp increase in chloride concentration

⁴ The detection limit of IC for chloride concentration was 250 ppb, with a variability of approximately 250–500 ppb per sample reading.

Table 3
Accelerated testing environments

	MFG (Class IV)	Single gas exposure (Cl ₂)
Environment	Heavy industrial	N/A
Temperature, °C	50 ± 2	30 ± 2
Relative humidity, %	75 ± 2	Uncontrolled
Chlorine (Cl ₂), ppb	50 ± 5	300 + 30/ – 30
Nitrogen dioxide (NO ₂), ppb	200 ± 25	0
Hydrogen sulfide (H ₂ S), ppb	200 ± 10	0
Sulfur dioxide (SO ₂), ppb	300 ± 50	0
Ultraviolet exposure	No	Yes

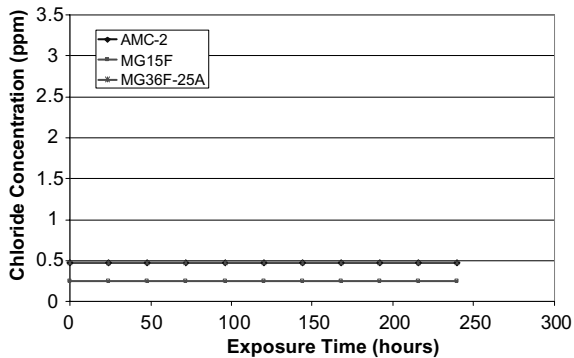


Fig. 7. Chloride concentration in EMCs subjected to a Class IV MFG environment and exposed to ultraviolet light.

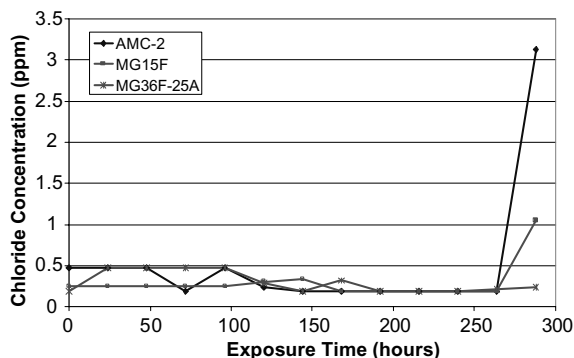


Fig. 8. Chloride concentration in EMCs exposed to 300 ppb chlorine gas environment.

was detected in two of the three molding compounds after 250 h of exposure.

The prepared solution diluted concentrations by 1/2000th. This would result in concentrations of approximately 3–7 ppb of chloride in the solution due to chlorides present in the encapsulant manufacturing process.⁵ The concentrations of 1 and 3 ppm, measured

⁵ Current EMCs have approximately 5–15 ppm of extractable chloride.

after exposure⁶ to chlorine gas, are equivalent to 2000–6000 ppm of chloride in the encapsulant. This is a significant amount of chloride and concurs with Lantz's findings [10] that suggest that ion getters are very effective in trapping electrolytes.

4. Conclusions and future work

The results suggest that PEM's will not be susceptible to corrosive environments, even when stored for long periods of time at controlled temperatures. This is a continuation of experimental research that has compared the reliability of plastic and hermetic integrated circuits [45]. However, temperature cycling or highly accelerated stress testing (HAST), can induce delamination between the encapsulant and die and the encapsulant and the leadframe. This provides an additional pathway for moisture and corrosive gases to diffuse to the die surface. Delamination at the die surface will remove ion getters from being in physical contact with the surface moisture. This may result in the initiation of corrosion and eventual electrical failure.

As part of continuous improvement and cost containment, encapsulant materials are constantly modified and replaced. There is currently no discussion in the literature on the effect of formulation on ion diffusion. The influence of free volume, functionality, cross-link density, filler material and concentration on gaseous diffusion rates has not been determined. Future material changes could create diffusion paths that might increase PEM's susceptibility to corrosive gases.

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⁶ 250 h at 300 ppb of chlorine gas.

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