A FLOWERS OF SULFUR CORROSION CHAMBER FOR TESTING ELECTRONIC HARDWARE

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ABSTRACT
A flowers of sulfur (FoS) corrosion test chamber has been developed by the iNEMI taskforce on creep corrosion on printed circuit boards (PCBs). Besides testing for creep corrosion, the FoS chamber has the potential of replacing the mixed-flowing gas (MFG) chamber as an industry-standard, general-purpose corrosion chamber for testing a whole range of electronic components and assemblies. The iNEMI FoS chamber consists of a 300-mm cube acrylic sealable box maintained at a constant 50ºC. A large area flowers of sulfur tray is the source of sulfur vapor. Household bleach containing sodium hypochlorite provides the chlorine gas. A saturated salt solution dominates the relative humidity in the chamber at its deliquescence relative humidity. The iNEMI FoS chamber can control the sulfur and chlorine concentrations and the temperature and relative humidity (RH) at the desired values. The chamber reaches steady state in a few hours. The paper will describe the details of the chamber design and operation and its use as a low-cost, convenient and easily maintainable replacement for the MFG chamber for a whole range of testing of electronic hardware. Three examples of the use of the chamber will be provided: (1) Effect of relative RH on creep corrosion; (2) Mapping the corrosion rates of silver as a function of temperature and RH; and (3) Characterization of conformal coatings. Progress on the use of the chamber for qualifying surface-mount miniature resistors will also be presented.
Key words: Corrosion, flowers of sulfur, humidity.

INTRODUCTION
Printed circuit boards can suffer corrosion-related failures from number of mechanisms that include open circuits due to corrosion of the interconnects; short circuits due to cathodic anodic filamentation and ion migration; and short circuit due to creep corrosion. There are number of ways of mitigating these failures that include conformal coatings; improving the interconnect metallurgies; replacing silver metallization on printed circuit boards (PCBs) with more ion-migration resistant metallization; and choosing PCB finishes that are more resistant to creep corrosion. The prediction of corrosion-related field failures and their mitigation requires corrosive gas test chambers. In the 1980s, Abbott of Battelle Memorial Institute developed the mixed-flowing gas (MFG) chamber that could be used to test the corrosion resistance of electrical connectors **[1]**. The MFG chamber experienced some initial popularity but over the decades the number of reliability test laboratories equipment with MFG chambers has declined probably because of the high cost and complexity of operating the chambers. The iNEMI task force on creep corrosion embarked on an effort stating in 2013 to develop an alternate to the MFG chamber by developing a flowers of sulfur (FoS) based chamber for testing PCBs for creep corrosion.

The iNEMI FoS chamber was based on the success of work done in IBM by Tofil who tested the robustness of surface-mount technology (SMT) resistors against corrosion in environments high in sulfur-bearing gaseous

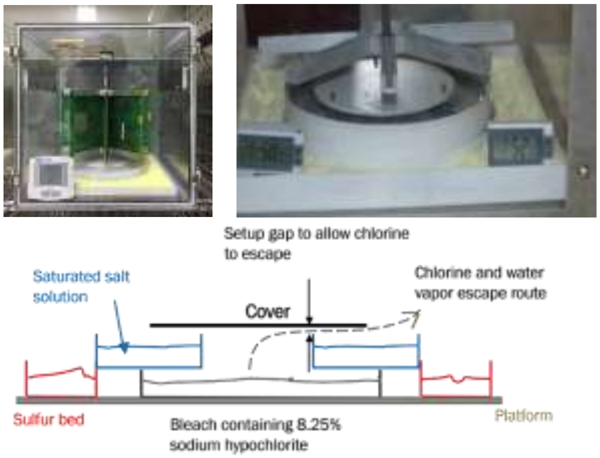


Figure 1: iNEMI FoS test chamber loaded with test PCBs. The tray-like setup below the test PCBs provides the sulfur and chlorine gases and maintains the relative humidity in the chamber at the deliquescence relative humidity of the saturated salt solution in the setup. **[4]**

contamination **[2]**. Tofil's test consisted of exposing resistors under test to sulfur vapors for 20 days in desiccator at 105ºC containing flowers of sulfur. The test proved to be a very successful qualification test for SMT resistors. The iNEMI team modified Tofil's test to include humidity and chlorine gas and lowered the test temperature to 50ºC. The iNEMI modified FoS test proved successful in predicting field creep corrosion. Circuit boards from manufacturing lots that had suffered creep corrosion in the field suffered creep corrosion of similar morphology in the iNEMI FoS test; and circuit boards that did not fail in the field passed the test without suffering creep corrosion. Two round robin tests were conducted to prove the effectiveness of the creep corrosion qualification procedure.

An effort is underway to make the iNEMI FoS test chamber an industry standard, general-purpose corrosion chamber for testing the reliability of electronic components and assemblies. This paper reviews the design of the test chamber and its success in predicting creep corrosion. Three examples are presented to illustrate the use of the chamber as an industry-standard, general-purpose corrosion chamber: (1) Effect of relative RH on creep corrosion; (2) Mapping the corrosion rates of silver as a function of temperature and RH; and (3) Characterization of conformal coatings. A potential use of the chamber for qualifying SMT resistors at a more reasonable temperature of 60ºC will be discussed.

FLOWERS OF SULFUR CHAMBER DESIGN AND PERFORMANCE

The iNEMI FoS chamber test setup has been described in detail in **References 3-12** and repeated here for the convenience of the reader. The FoS chamber shown in

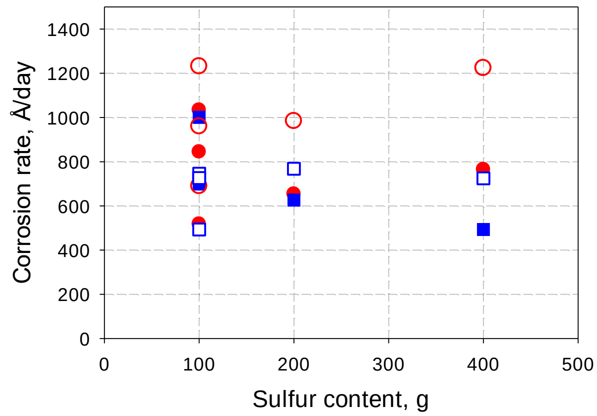
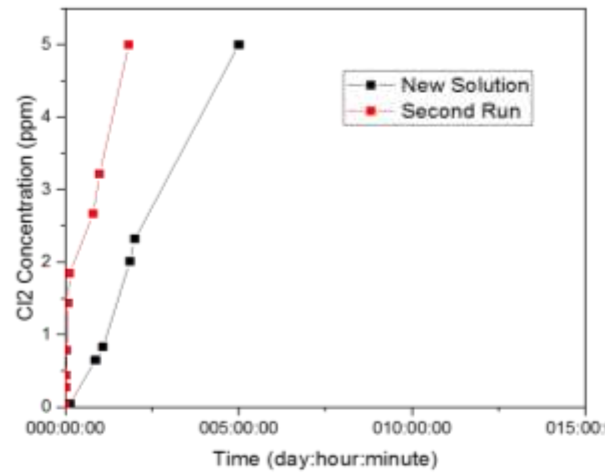
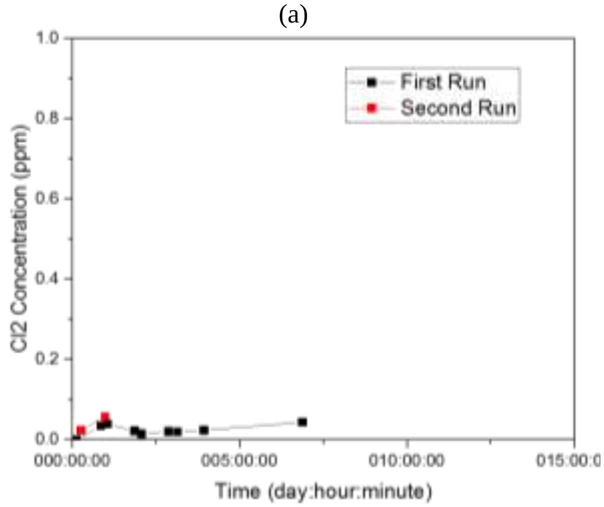


Figure 2: Effect of sulfur content on the copper and silver corrosion rates. The red circular dots are for copper corrosion rates and the blue square dots are for silver corrosion rates. The open dots are for mass gain method and the solid dots for coulometric reduction method. The relative humidity of 46-57%, during the test, was maintained using ammonium nitrate saturated salt solution. **[3]**

Figure 1, is a 300-mm cube acrylic box with 8-paddle wheel rotating at 20 RPM. Each paddle can accommodate one printed circuit board. The chamber can thus accommodate a total of 8 printed circuit boards. The setup to control the sulfur and chlorine gas concentrations and the relative humidity in the chamber is described in **Figure 1**. The sulfur is provided in a 275-mm square tray, 20-mm deep, with a 195-mm circular opening in the center. The sulfur concentration is controlled by placing the chamber in an oven maintained at a constant 50ºC. The household bleach, consisting of an aqueous solution of 8.25% sodium hypochlorite Clorox™, is contained in a 145-mm diameter petri dish that sits inside the sulfur tray on the same platform as the sulfur tray. The saturated salt solution is in a 190-mm diameter tray with a circular opening of 65-mm diameter in the center, which is covered by a circular plate with 1-mm gap to allow controlled escape of the chlorine gas from the bleach. The cover plate also throttles the escape of water vapor from the bleach such that the saturated salt solution can dominate the relative humidity in the chamber at its deliquescence relative humidity. The relative humidity can be maintained at incremental values in the 15-80% range. The chamber reaches steady state in a few hours. It is most challenging to achieve low humidity in the chamber because of the water vapor given off by the household bleach that is also the source of the chlorine gas. The chamber design described here has been able to overcome this challenge. With zinc chloride saturated solution in the chamber at 50ºC, the chamber design allows the humidity to stabilize at about 15%, which is the deliquescence relative humidity of $ZnCl_2$.



(a)



(b)

Figure 3: Chlorine concentration in chamber as a function of time at (a) 13-18% relative humidity and (b) 74-80% relative humidity. The first run (black plot) was made with fresh saturated salt solution and fresh Clorox™. The second run (red plot) was made with fresh Clorox™ but keeping the same saturated salt solution. **[5]**

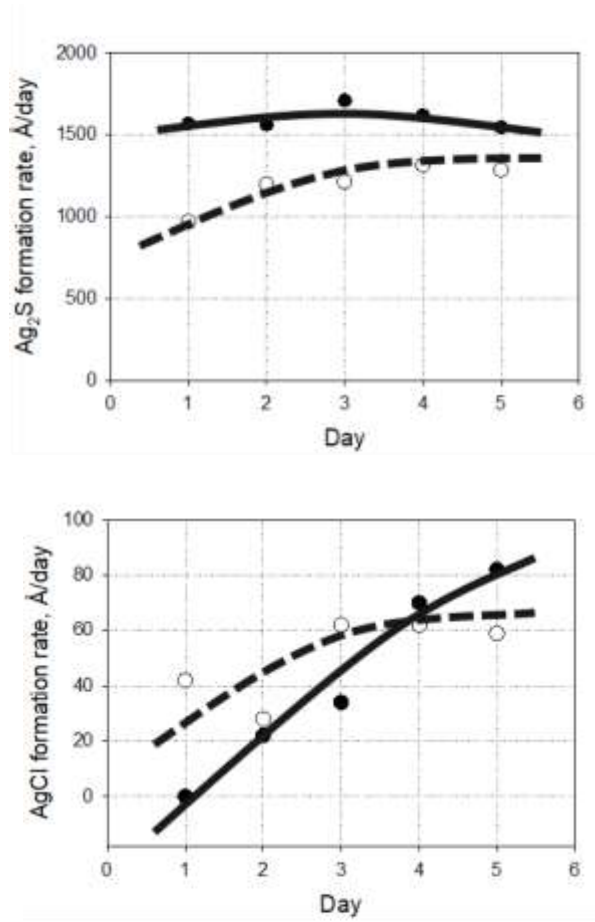


Figure 4: The formation rates of AgCl and Ag_2S are shown as a function of days for Clorox containing 4.12 and 8.25% sodium hypochlorite by the dotted and the solid curve, respectively. The sulfur content was 200 g. The relative humidity was controlled to 59% using sodium nitrite saturated salt solution.

Sulfur vapor concentration: The sulfur vapor concentration thermodynamically depends only on the temperature of the chamber if there is enough sulfur in the chamber to bring the airborne sulfur concentration to equilibrium value in a reasonable amount of time, say, a few hours. Results shown in **Figure 2** confirm the thermodynamic position that the sulfur content, indirectly measured by the copper and silver corrosion rates, is independent of the sulfur content in the chamber, within the limits of the accuracy of the corrosion rate measurement techniques. Given the space available in the tray, the amount of sulfur was standardized at 200 g.

Chlorine concentration: The source of chlorine in chamber is Clorox™ containing 8.25% sodium hypochlorite. It is expected that the chlorine content in the chamber will increase with time as shown in **Figure 3**. An interesting observation to note is that chlorine gas is absorbed by water. Therefore, when two runs are made back to back starting with fresh saturated salt solution, the chlorine content in the chamber in the 2nd run is greater than in the 1st run because the saturated salt solution is in a near chlorine-saturated condition during the 2nd run and therefore absorbs less chlorine. Also notice that the two plots in **Figure 3** show that the chlorine concentration is a strong function of humidity in the chamber. At higher relative humidity, the chamber walls adsorb more water which in turn absorbs more chlorine gas, thus, lowering the chlorine concentration in the chamber.

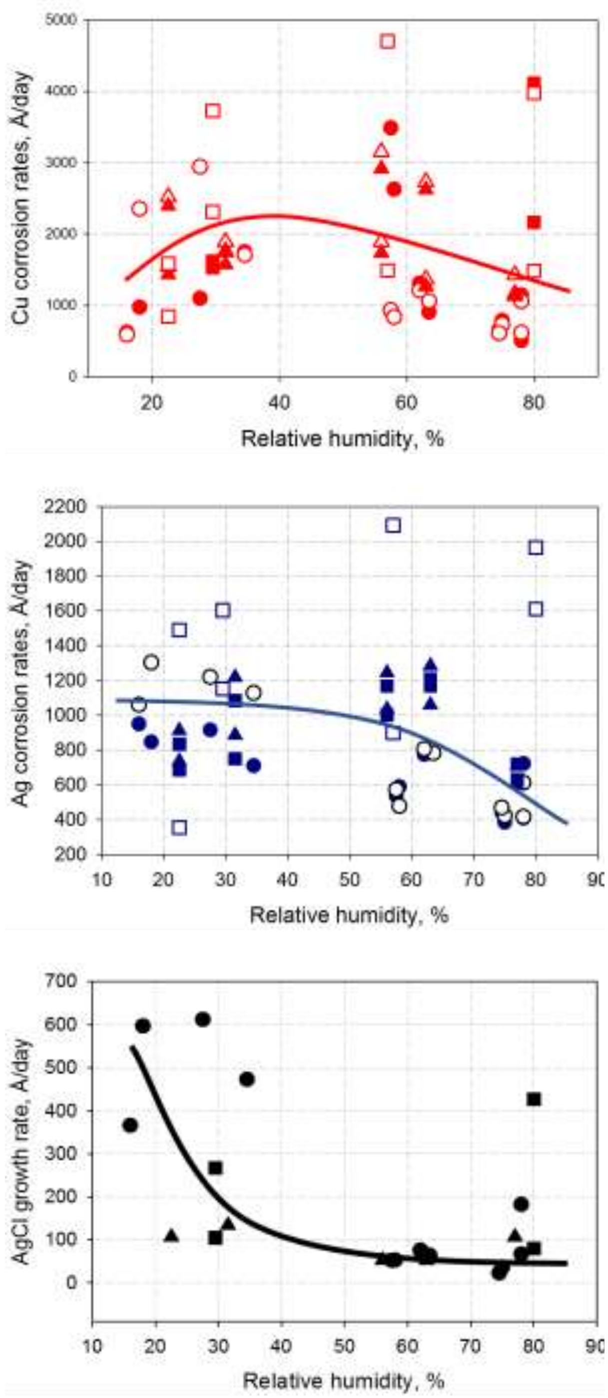


Figure 5: Effect of relative humidity on Cu and Ag corrosion rates and AgCl formation rate averaged over a 5-day period. The test was run with 200 g sulfur, 100 ml Clorox^{TM}, $NaNO_2$ saturated salt solution at 50°C. **[4]**

Humidity and gas concentration time dependent variations: It is important to know how the gases and the humidity in the chamber vary with time. The humidity in the chamber takes a few hours to get to the deliquescence relative humidity of the saturated salt solution. Beyond that, the relative humidity stays constant if the salt solution remains saturated. It is good practice to ensure sufficient amount of solid salt in the solution for the test duration. As mentioned earlier the concentration of sulfur and chlorine gases are measured indirectly by the rate of formation of sulfides and chlorides, respectively, as shown in **Figure 4**. The AgCl formation rate keeps rising over time as the Clorox^{TM} gives off chlorine gas. The Ag_2S formation rate is quite constant in agreement with the thermodynamic concept that the sulfur vapor concentration is only a function of the chamber temperature.

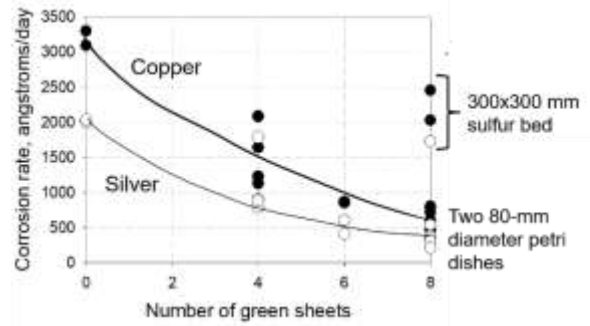


Figure 6: The effect of loading (number of PCBs) on copper and silver corrosion rates. The solid dots are for copper corrosion; the open dots for silver corrosion. The green sheets are PCBs. The test was conducted at 50°C chamber temperature. The sulfur was contained in two 80-mm diameter beakers and KCl saturated salt in two 100-ml beakers. No Clorox was used in this test. **[10]**

Relative humidity dependence of corrosion rates: The effects of relative humidity on copper and silver corrosion rates as measured at three companies, IBM, iST and Lenovo, using mass gain and coulometric techniques are shown in **Figures 5**. The copper corrosion rate tends to rise with humidity as expected in the low humidity range and decreases with humidity in the higher humidity range. The decrease of copper corrosion rate with humidity in the high humidity range is probably because of the decrease of the chlorine gas content due to high humidity. The silver corrosion rate tends to decrease with relative humidity over the complete humidity range probably because of decreasing chlorine gas concentration with increasing relative humidity.

VOC contamination in chamber: The FoS chamber has limited volume and the gases in the chamber remain trapped in it for the duration of the test, unlike the MFG chamber in which the gases are continuously flowed in and out of the chamber. Therefore, there is concern that the volatile organic compounds (VOCs) and other gases given off by the test PCBs and components will build up in the chamber and unrealistically influence the corrosion mechanism. **Figure 6** shows clearly that PBC loading decreases copper and silver corrosion rates which may be due to the PCBs giving off VOCs that redeposit on the PCB metallization thus giving some protection to the PCB metallization from corrosion. One way to address this concern of the buildup of VOC contamination is to low-temperature pre-bake the PCBs and components before inserting them in the chamber. In view of this observation, the iNEMI creep corrosion qualification test includes the pre-bake step. Ten-day creep corrosion testing was conducted on pre-baked and unbaked PCBs from lots that had failed in the field. As shown in **Figure 7**, creep corrosion could be reproduced only on the PCBs that were pre-baked.

EXAMPLES OF THE iNEMI FoS CHAMBER APPLICATIONS

An example of FoS testing of a PCB assembly from a lot that suffered in the field is shown in **Figure 8**. The creep corrosion morphology shown in **Figure 8** is very similar the morphology experienced in the field. A difference from field experience was that in the FoS creep corrosion test, the termination of the surface-mount capacitors corroded; whereas in the field there are no known occurrences of capacitor termination corrosion.

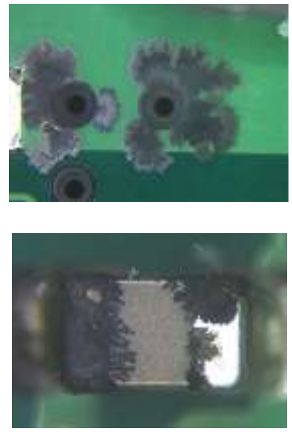
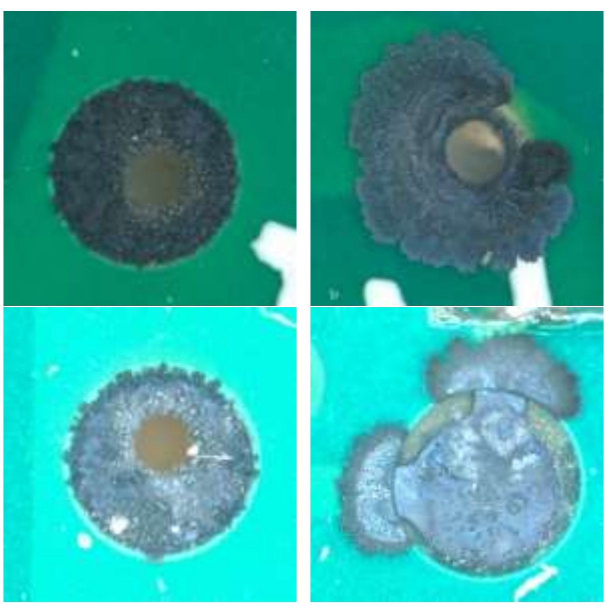


Figure 8: 5-day FoS run using KCl saturated solution. The PCB board was prebaked in flowing nitrogen gas at 100ºC for 10 hours. The top figure shows creep corrosion on the PCB. The lower figure shows silver migration out of a capacitor termination. The surface mount resistors on the board did not suffer corrosion.

Effect of humidity on creep corrosion: It is generally believed that high humidity promotes corrosion. But as shown earlier in this paper, high humidity can lead to the lowering of some gaseous contamination such as chlorine gas that gets adsorbed on surfaces under high humidity conditions. Creep corrosion tests, done using the iNEMI FoS chamber, as a function of humidity have shown that for some PCB finishes, such an ImAg, creep corrosion is more pronounced in the lower humidity range; whereas for other PCB finishes, such as ENIG, creep corrosion is more pronounced in the higher humidity range as shown in **Table 1**. This is the first reported effect of relative humidity on creep corrosion.



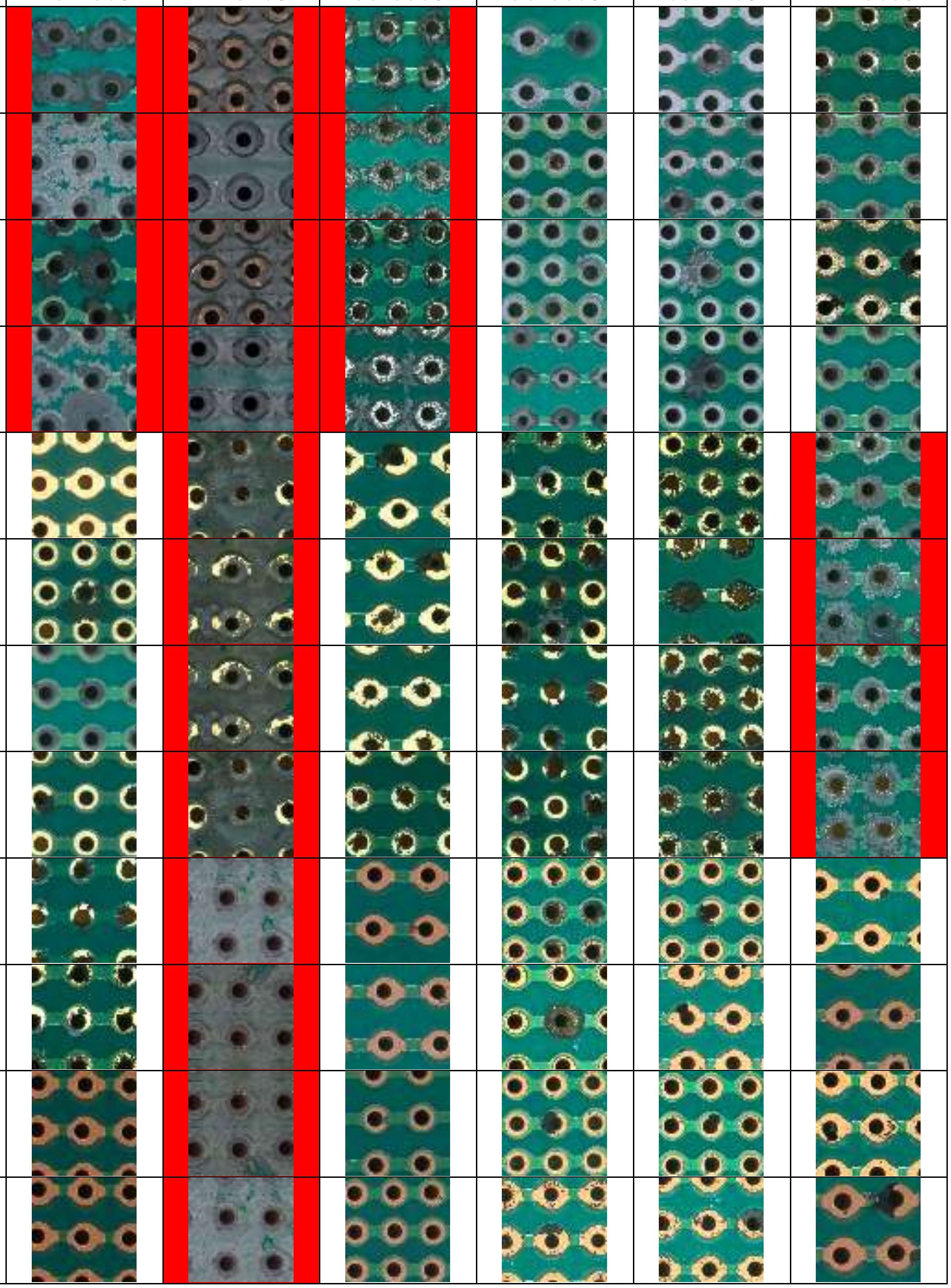
Not prebaked Prebaked

Figure 7: Effect of prebaking. Creep corrosion in the FoS test occurred only on PCBs that had been prebaked in flowing N_2 gas at 100ºC for 24 hours. **[9]**

Effect of temperature and relative humidity on metal corrosion rates: To contain the rising computing energy costs, data center administrators are resorting to cost cutting measures such as not tightly controlling the temperature and humidity levels and in many cases resorting to air side economizers with the associated risk of introducing particulate and gaseous contaminations into their data centers. There is therefore a need to determine the effect of temperature and humidity on metal corrosion in corrosive environments. The corrosion rates of copper and silver in corrosive environments displayed on psychrometric chart would be great aid in determining the risk of running data centers outside the temperature-humidity recommended range. **Figure 9** shows an approach to achieve this end. The corrosion rates of thin serpentine films of copper and silver can be measured by measuring increases in their electrical resistances as they corrode. These measurements can be done in the iNEMI FoS chamber at different relative humidity levels. In addition. the films can be joule heated to introduce the temperature variable thus making corrosion measurements over the temperature-humidity range of interest. **Figure 9** shows that the silver corrosion rate, in a corrosive environment with sulfur vapors and chlorine

Table 1: Creep corrosion occurrence as a function of PCB finish and relative humidity. The micrographs showing creep corrosion are highlighted with red background. [5]

Finish	Days	Run number and relative humidity					
		Run #11 13-19%	Run #12 27-37%	Run #13 55-59%	Run #16 56-68%	Run #14 69-77%	Run #15 74-80%
ImAg NR330	5						
	10						
ImAg EF8000	5						
	10						
ENIG NR330	5						
	10						
ENIG EF8000	5						
	10						
OSP NR330	5						
	10						
OSP EF8000	5						
	10						



gas, is a strong function of temperature with little dependence on relative humidity. The figure also shows the silver corrosion rates across a portion of the psychrometric chart.

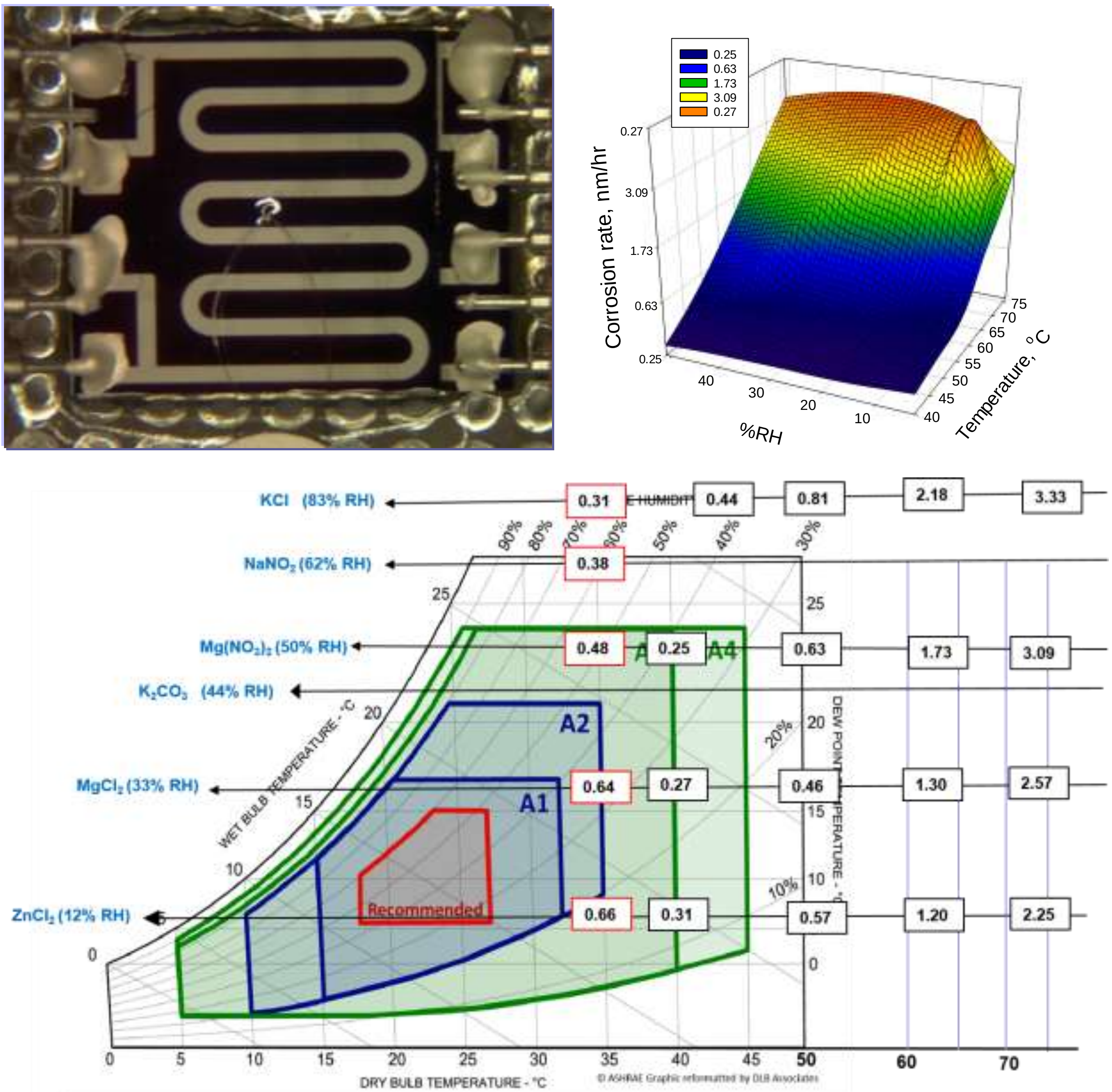


Figure 9: The corrosion of serpentine silver thin film can be used to map out the silver corrosion rates across a region of the psychrometric chart of interest. The top right figure shows silver corrosion rate as a function of temperature and relative humidity. The bottom figure shows silver corrosion rates on the psychrometric chart.

Conformal coating characterization: Serpentine silver and copper thin films can also be used to characterize conformal coatings **[13]**. The corrosion rates of bare thin films and thin films coated with the conformal coating under test can be measured in the iNEMI FoS chamber. In **Figure 10,** the slopes of the curves are the corrosion rates of the underlying silver thin films. From the figure, it is clear that both the FP04 and FP08 fluoro-polymer coatings provide good protection against corrosion and that the FP08 coating is superior to the FP04 coating. In addition, tests can be done on various coating thickness to determine the optimal coating thickness.

DISCUSSION

The original FoS chamber in 2013 contained just sulfur and KCl saturated salt solution in beakers. We originally had two ways of moving the air in the chamber: a forced air setup and the 8-paddle wheel setup we now use. Along the way we introduced Clorox™ as a source of chlorine. The challenge was to allow the chlorine to come out of the Clorox™, without the water vapor from the Clorox™

interfering with the domination of the relative humidity by the saturated salt solution. It took a lot of effort and design iterations to invent the Clorox™ setup shown in **Figure 1**. Along the way we discovered the loading effect of the PCBs, shown in **Figure 6,** that led to the necessity of pre-baking the PCBs for creep corrosion to occur. Without the pre-baking, creep corrosion was not occurring in the FoS chamber. In general, PCBs and components that can contaminate the chamber with VOCs must be pre-baked.

With the newly developed ability to have sulfur vapors and chlorine gas in the chamber at various relative humidity levels in the 15 to 90% range, the effect of relative humidity on creep corrosion was studied for the first time. The surprising, non-intuitive discovery was that creep corrosion can occur on ImAg finished PCBs in the low relative humidity range and not under high humidity conditions. On the other hand, ENIG finished PCBs tended to suffer creep corrosion in the high humidity range.

With the two additional applications of the iNEMI FoS chamber dealing with the measurement of silver corrosion as a function of temperature and relative humidity and with the ability to characterize conformal coatings, the ability of the in the iNEMI FoS chamber to be an industry-usefulness of the standard, general-purpose iNEMI FoS corrosion chamber is amply demonstrated.

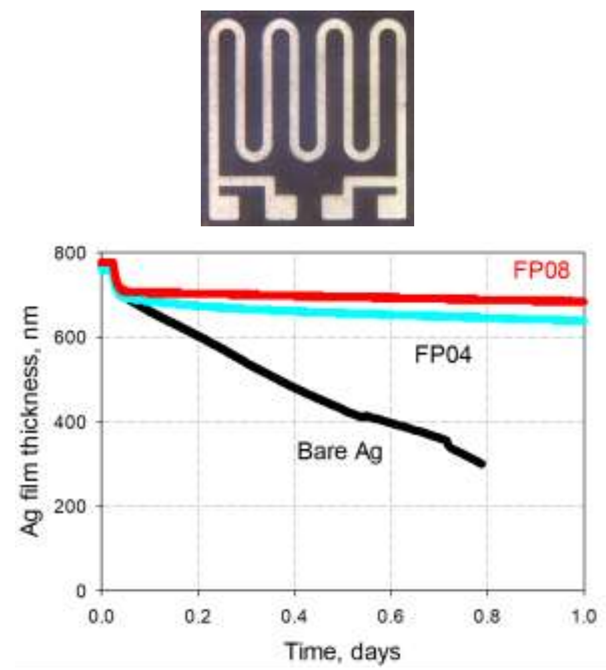


Figure 10: Conformal coating characterization can be done by coating a serpentine silver film with the conformal coating of interest and measuring and comparing the corrosion rate of the coated silver to a bare silver thin film. The slope of the curves above are the corrosion rates for thin films coated with FP08 and FP04 conformal coating and a bare thin film. [13]

A challenge facing the industry is to test and qualify surface-mount resistors near the application temperature. The present industry-standard method is to subject resistors to 105ºC in a sulfur-saturated environment. At this high temperature of test, the failure mechanism is probably distorted from what it is at the application temperature. While this very harsh test has proven itself by passing only very robust and reliable resistors, it is probably rejecting weaker resistors that would otherwise perform reliably in the field. The iNEMI FoS chamber may provide a qualification test at a more reasonable lower temperature with a minor modification of in-situ monitoring the resistance of the resistors under test. Since the resistors will not be disturbed during their resistance measurement, very small changes in resistance could indicate the start of resistor degradation, shortening the test time and allowing the test to be run at lower, more realistic temperatures.

CONCLUSIONS

The iNEMI FoS chamber has proven to be a convenient, low cost alternative to the MFG chamber. The relative humidity and sulfur concentration can be well controlled. The chlorine concentration released from the sodium hypochlorite containing Clorox™ rises over time in a relatively controlled manner. The creep corrosion tests done in the chamber has proven very successful in identifying PCB finishes prone to creep corrosion. The test has revealed for the first time that ImAg finished PCBs have higher propensity to creep corrosion in the low humidity range; whereas ENIG finished boards suffer more creep corrosion in the higher humidity range. The chamber has also been successfully used to measure silver corrosion rates across a range of temperature and humidity and to characterize conformal coatings. Future work may involve testing surface mount resistors are lower, more realistic, close to application temperatures.

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