F-connector Corrosion in Aggressive Environments -An Electrochemical and Practical Evaluation Brian Bauer - Raychem Corporation

ABSTRACT

The drop has long been considered the weak link in the CATV As future systems require system. shielding greater due to CLI restrictions and higher bandwidth, the drop will receive increasing demands for sustained performance. At the root of many drop problems is corrosion at the F-interface.

As part of a CableLabs funded investigation project, an was conducted into the destructive dynamics of corrosion as it pertains specifically to the F-interface. The electrical performance profile of Fsplice samples exposed to Copper-Accelerated Acetic Acid Salt Spray (CASS) was determined. These samples have been dissected, and much of the mystery behind the discontinuous nature of shielding degradation is explained through the use of Scanning Electron Microscopy and X-rav Spectroscopy. Relative corrosion rates of often used metals within a CATV drop interface, including port, connector, and cable materials are examined. The weakest material link in this connection, found to be the aluminum braid, is studied with regard to relative galvanic coupling to key materials. Corrosion data is offered that is pertinent to the design of future connectors/ cables/ ports.

INTRODUCTION

CATV's F-interface, has long been recognized as one of the weakest areas in a CATV plant. In the case of properly installed connectors, corrosion is probably the largest cause of interface failure. However, very little has been studied with regard to the effects of corrosion.

The F-interface, the focus of consists of the port, this paper, connector and cable. Corrosion is highly dependent upon the compatibility of mating materials and therefore these parts are to be thought of as a system. The way these interface materials interact is crucial to system survival especially corrosive in (coastal, humid, temperature varying, or hiqh precipitation) environments.

This is the first in a three phase series of CableLabs directed F interface corrosion studies. The program objective is to investigate some of the primary material changes and corrosive dynamics of the CATV F-The three phases are to interface. 1) determine the effects of corrosion on the F-interface through the use of Copper-Accelerated Acetic Acid-Salt Spray Test (CASS) 2) investigate the corrosive effects of passing low currents through the F-interface, and 3) compare the above to that of actual environmental conditions in the field.

OBJECTIVES

The primary goal of the first phase was to investigate the electrical performance and material change due to corrosion of the Finterface and to investigate the dynamics involved therein. Particular objectives were as follows.

1) To determine the electrical performance versus time profile of mechanically well stabilized F-interface samples in a corrosive environment (CASS).

2) To determine material changes and key paths of corrosion within the F-connector. Methods used are scanning electron microscopy and xray spectroscopy.

3) To compare the basic corrosive drive of copper acetic acid salt solution to that of deionized water and 3% salt water. This involves measurement of electrode potentials of CATV metals of concern.

4) To investigate the effects of metallic and bimetallic (galvanic) corrosion, due to CASS, on metals typically found within the F-interface.

The method of accelerated salt fog used is CASS ASTM B368 (Appendix A) due to its very aggressive nature of attack. It should be noted that many tests exist for replicating corrosive field environments. Other methods, such as the standard 5% salt spray of ASTM B 117, and cyclic humidity tests such as ASTM G 60, however, have not been effective in degrading the electrical performance in this sort of study within a reasonable time frame. By using CASS, key corrosive information can be attained in a more expedient such electrical manner, as performance profiles, corrosive deterioration paths, and other important patterns. Basic patterns are assumed to occur similarly in other tests of moisture caused corrosion, but results are obtained in a more timely manner using CASS.

ELECTROCHEMICAL STUDY

This section gives the results of the electrochemical corrosion tests performed on CATV F-interface materials. First a background of fundamental electrochemistry will be presented followed by a description of the kinds of electrochemical measurements performed and the results obtained. Then a brief introduction will be given as to how

measurements fit into these а For further corrosion study. introduction to corrosion phenomena reader is referred to the an excellent book by Fontana and Greene [1].

BACKGROUND, ELECTROCHEMISTRY

Chemical energy can be converted to electrical energy by choosing the correct reactants. In the case of the familiar car battery, Figure 1, lead is the reactant at one electrode and lead dioxide is the reactant at the other electrode.



Figure 1: Battery Cell, analogous to the corrosion dynamic.

During the course of the battery discharge one of these reactants is "oxidized," which releases electrons. electrons flow through The the electrical circuits and return to the battery where the other reactant is "reduced." Since a transfer of electrons is involved in the electrochemical reaction, a voltage difference is measured between the two electrodes. It is noted that it is only a voltage difference that can be measured. An individual electrode does not have an absolute potential. electrochemistry, the hydrogen In electrode has been arbitrarily set to zero potential, and very often tables will list electrode potentials relative to this standard. The hydrogen electrode is difficult to use in the laboratory, however and in these cases a different "reference electrode" is used (figure 2). In this report we have used a saturated calomel reference electrode. For reference, its potential relative to the hydrogen reference electrode is 0.2425V.



Figure 2: Use of reference electrode to determine electrode potential.

In the battery described above, electrode oxidized, one was one electrode reduced, was and the the electrons flow in outer electrical circuit. In freely corroding systems there is no outer electrical circuit. Therefore, the oxidation (which is the corrosion reaction) must occur in local proximity to the accompany reduction as in figure 3.



Figure 3: Corrosion of Single Metal in Presence of Electrode.

In the case of a single metal oxidation the and corroding, reduction can occur on separate surfaces (that electrically are connected). However, it is still very likely that the reactions will be in close proximity to each other.

Corrosion is an electrochemical process and as such it is driven by the voltage difference between the oxidation reaction and the reduction reaction, as in our battery above. An example of an oxidation would be the dissolution of iron to form iron ions, and an example of the concurrent reduction is the reduction of protons to form hydrogen. (If you drop iron in acid you will see a high degree of bubbling, which is hydrogen evolution.) Some metals have different driving forces (voltages) so it is expected that some metals will corrode less than others. We also see that the corrosion rate will depend on the reduction reaction. If electrochemical reduction could no occur, no corrosion could occur. Typical reductions that accompany the corrosion reaction are proton (or water) reduction to form hydrogen (as mentioned above), and the reduction of oxygen to form water.

One last point should be made concerning corrosion reactions. Since voltages are involved in the driving force for corrosion, we can change the voltage of a given metal to affect a change in the corrosion rate of the metal. One way to change the potential of a metal is to connect it to another metal that has different potential. This is а referred to as galvanic coupling.

In summary, we see that the rate of corrosion depends on the type of metal and the environment of the metal. The environment of the metal includes any coupling to one or more metals, the chemical composition, and the temperature.

DISCUSSION OF ELECTROCHEMICAL RESULTS

Galvanic Series:

In order to predict how metals might tend to corrode we first establish their potentials in solutions of interest. Figure 4 shows the potentials of silver, nickel, copper, tin, cadmium, aluminum, and zinc when immersed in salt water, deionized water, and the CASS test solution.



SINGLE METAL POTENTIALS

Figure 4: Single Metal Potentials with respect to calomel electrode, in various liquid immersions.

Potentials given are all relative to the saturated calomel reference electrode. The data show that the potentials for a given metal is relatively independent of the test solution. Metals that have relatively more positive potentials are considered "noble" and those with more negative potentials are more "active." More noble metals tend to corrode less than more active metals. From the chart, we see that zinc is the most active, aluminum and cadmium are next, tin is in the middle, nickel and copper are relatively

noble, and silver is the most noble. It is very important to stress here that these potentials do not directly correlate into actual corrosion rates. It is entirely possible, for example, that tin and aluminum could corrode at the same rate in a given environment. The reason that the potentials do not correlate directly into corrosion rates is that voltage relates only to the driving force for the reactions. For any chemical reaction there are always activation barriers to overcome before the reaction can proceed. actual The rate of corrosion, therefore, depends not only on the voltage driving force but also on the magnitude of these (called activation barriers Each oxidation and overvoltages). reduction reaction has a different overvoltage and even the same reduction reaction occurring on differing surfaces has a different overvoltage.





Figure 5: Single Element Corrosion Rates, CASS exposed, three different configuration sets. Electrochemical techniques can be used to measure actual corrosion rates, but these measurements are not reported on here. What we have done here, instead, is to subject these samples to CASS solution and measure their corrosion rate by monitoring their weight loss with time (figure 5).

Galvanic Couples:

For galvanic corrosion to occur, two or more metals must he electrically connected and some form of electrolyte (eg. moisture) must be present. It is generally true that when two metals are connected the more noble metal will corrode less and the more active metal will corrode more than their respective free-corrosion rates. The solution potential of the metal couple will also fall between the respective potentials of the two metals. If more than two metals are connected, the analysis becomes more complicated. In a conventional Ffitting (figure 6) many metals are in contact in actual bimetal couples and in many cases more than two metal contact is involved.



Figure 6: F-interface. The materials shown are those typically found at the surface of the given parts. Base metal of connectors is usually brass (copper, zinc, lead). Figure 7 shows the potentials we measured in CASS solution of galvanic couples between Al-Cu, Al-cadmium, Al-tin, Al-nickel, cadmium-nickel, Cd-tin, and copper-tin. In the case aluminum bearing couples, of the potential often ends up close to the individual potential of the Al by itself. This does not necessarily mean, however, that Al is corroding at the same rate as it would in the absence of the other metal. Recall. from the above discussion that it is the potential and the activation barriers that control the rate of corrosion. The activation barrier for the accompanying reduction reaction could be lower on the metal couple than on Al itself, thereby increasing the corrosion rate. We have tested Al galvanic couples in CASS solution. Unfortunately we have obtained a wide degree of scatter in the results (averages shown in figure 8). Qualitatively, the corrosion rates follow the predictions from the potentials. That is, aluminum corrodes fastest when coupled with nickel, or silver, copper, significantly less with tin, and less still with cadmium.



Figure 7: Potentials of Galvanic Couples when immersed in solution used to create salt spray in CASS test.

Potentials of Galvanic Couples, CASS solutio



Figure 8: Corrosion Rates of Aluminum when coupled to typical CATV metals, CASS exposed. Average of wide scatter.

These findings also follow results obtained from previous work done by Mansfeld et al using 3% salt water immersion tests [4]. Similar to results here, those tests showed aluminum corroding with elements in the following descending order, silver > copper > 4130 steel >> stainless steel = nickel > Inconel 718 >> Ti-6A1-4V = Haynes 188 > tin > cadmium.

The data gathered and findings here show that both individually and more when coupled. so aluminum corrodes at a much higher rate than these other elements. It is clearly the weakest link in the interface, as is often witnessed when a cable is slit open at the rear of a corroded F-connector in the field. It is therefore imperative to keep moisture from reaching the cable braid. If this is not possible, the use of more

corrosion resistant materials and combinations of materials is desirable. It is often inappropriate to use noble materials, as contacting materials must be electrochemically similar to minimize deterioration.

CASS ELECTRICAL PERFORMANCE <u>TEST PROCEDURE</u>

The practical evaluation of this report consists of exposing samples to the CASS environment and evaluating the results. First, the electrical performance of the F connector interface versus time in an aggressive environment (CASS) is determined. This is followed by an analvsis of the corresponding physical material degradation.

Twenty samples of standard hex connectors were tested crimp for electrical degradation vs time of exposure. CASS The sample configuration, shown in figure 9, consisted of two hex crimp Fconnectors, spliced together with an F-81 barrel splice. Each splice assembly was mounted securely to stabilizing boards. The splice was connected to five feet of quad cable on either side each of which extended outside of the CASS environmental chamber. These non-conditioned cable enda were used to measure the electrical characteristics of the internal sample.

CASS testing was conducted over 56 day period, with electrical performance measurements taken at graduated intervals. Data was collected after 1, 2, 4, 7, 14, 28, and 56 days respectively. Electrical characteristics examined were signal egress, contact resistance, and signal transmission. line The diagram for each of the measurements are shown in figures 10, 11, and 12 respectively.



Figure 9: Layout of CASS chamber and configuration for sample stabilization.

Signal Egress

Signal egress measurements, figure 10, were taken using an HP 11940A close-field probe. The probe is a balanced magnetic field sensor which provides an output voltage proportional to the strength of the magnetic field at its tip. When the probe is held close to the sample, field radiated magnetically the couples to the probe and produces a larger output voltage. This frequency-preserved voltage is amplified by the pre-amplifier and is read by the spectrum analyzer for display.

Egress measurements were probed at the rear of each of the two connectors, A and B, where the jacket just meets the connector. The chamber was temporarily turned off and the lid removed for ventilation

readings. while taking egress otherwise Samples remained undisturbed through the duration of Other measurements were tests. conducted outside of the chamber the cable terminates whereby externally.

The voltage values were read into a PC using a program which reads, stores, displays, and charts The frequency range taken results. was between 0 and 1000 Mhz. Egress levels are displayed in dB micro The levels shown are good volts. indicators and not relative are absolute calibrated to values. extremely Typically an corroded sample exceeds 20 dB microvolts higher than when pre-exposed. Nearly all samples remained just within this level up to 56 days.



Figure 10: Configuration of equipment for signal egress measurements.

Contact Resistance

Contact resistance measurements, figure 11, are taken at the externally located cable ends. The Cambridge Technology Model 510 Micro-Ohmeter was connected to each of the two outside connectors and the contact resistance was displayed and recorded.



Figure 11: Contact Resistance measurement setup.

Signal Transmission

Signal transmission is measured with the equipment shown in figure 12. Radio Frequency signal is provided by the internal tracking generator of the HP 8590B Spectrum Analyzer. The signal was subsequently amplified by the

Amplifier Research Amplifier and pre-Amp. A feedback loop was constructed to keep the swept signal in range and consistent. This signal transmitted externally into the drop sample and received directly by the spectrum analyzer. The results were automatically read, stored, and displayed by computer. Again the frequency range was from 0 to 1000 Mhz. Signal level is shown in dBmV.



Figure 12: Setup for signal transmission measurement.

MICROSCOPY AND MATERIAL CHARACTERIZATION PROCEDURE

After samples were tested for electrical performance degradation during CASS exposure, samples were examined for corresponding moisture paths and material change.

The scanning electron microscope was used to take electron generated micrographs for the purpose of showing paths of moisture salt spray product deposition. Note that the presence of salt spray products doesn't necessarily mean that significant corrosion has occurred. It does, however, show that an electrolyte is provided. Actual corrosion is evident when material has been extracted (ie plating goes away exposing the base metal).

X-Ray Spectroscopy

X-ray spectroscopy was used to characterize surface materials. This method determines elements through analysis of irradiated electron wavelengths. Elements found on a surface are represented by the peaks of the energy spectrum shown in figure 13.



Figure 13: X-Ray Spectum of elements at surface of an F-connector.

This spectrum shows the deposited CASS products on a 3-day exposed sample. Similar technology, Energy Dispersive X-Ray Spectroscopy, was used to map out the presence of a particular element within a chosen surface area (figure 14). This allows one to determine the locations of material degradation (actual corrosion), particularly where plating has been removed and base metal is exposed.



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Figure 14: Energy Dispersive X-ray mapping of connector mandrel surface. Bright surface on left represents element of concern, in this case Copper, existing at surface.

The SEM micrographs give an excellent representation of surface discontinuity and depth of field, figure 15. By initially making cursory observations of many contact areas of the corroded samples, key areas of material degradation were determined. This was followed by low magnitude, broad x-ray mapping of these areas to give a useful material profile.

Areas found to be of greatest concern 1) the mandrel post, 2) the mandrel face which contacts the F-81, 3) leakage paths (the internal wall of the crimped component, the nut threads, and the swivel joint). The two former areas are those which make and must preserve outer conductor contact.

<u>SEM</u>



Mandrel Post, At Midlength, 500x



Mandrel Post



Mandrel Face



Inner Crimp Wall

Figure 16 SEM, Aluminum Braid Pre vs 56 Day Exposure

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Braid, Pre Exposure 500x



Braid, After 56 Days CASS, 150x



Braid, After 56 Days CASS, 1000x



Typical Crystal Structure Due To CASS, 5000x

Rear of Connector

Micrographs of connector components, figure 15, show that much of the moisture and salt sprav deposition into the rear of the connector has occurred along the crimp wall where the metal has been bent during crimping. These crimp bends have provided a channel for moisture to migrate. SEM's suggest that the moisture spends little time these 'channels', in depositing generously into the base of the post moving and beyond, towards the post/braid. Upon electrolyte arrival to the aluminum braid, figure 16, the largest degree of corrosion is observed.

Front of Connector

Little moisture has succeeded in migrating through the front of the connector during these tests. As seen in the SEM's of the nut, moisture has migrated approximately to the middle of the nut threads but little beyond. A significant amount of salt spray solution migrated to the mandrel face via the swivel Although the mandrel face joint. showed a fair degree of chloride buildup from incoming moisture, it was not significant enough to break contact or migrate to the center As a result the center conductor. conductor itself in samples of this test showed no signs of moisture or corrosion.

DICUSSION OF RESULTS: ELECTRICAL AND MATERIAL

The electrical characteristics of the samples varied with respect to time but did not show continuous degradation, (figure 17). The samples initially showed a decrease in signal leakage after the first 24 hours. This initial improvement may be explained by 1) settling of the contacting materials, providing an improved contact of metals, 2) electrolytes migrating within the swivel and other areas, figure 18, improving shielding due to better electrolytic continuity within interstices, and as a result 3) an improved impedance match is attained.

Signal Egress, CASS Exposed Samples As Measured with Near Field Probe



Signal Egress, CASS exposed Samples As Measured with Near Field Probe



Figure 17: Profile of signal egress; above categorized by frequency, below by length of exposure.

Figure 18 SEM, F-interface Components, Improved Shielding 3 Day Exposure



Mandrel Post



Post/Nut Interface



Figure 19 X-Ray Map Material Characterization, Connector Mandrel Post

Cadmium

Chromium



Figure 20

Cadmium



Figure 21 X-Ray Map Material Characterization, Connector Mandrel Post 56 Days CASS









The impedance, directly related to shielding effectiveness, is inversely proportional to capacitance. The capacitance is affected by any changes in the dielectric constant of substances between current carrying surfaces.

Results suggests that the moist CASS solution enters the interstitial voids in the F-interface, greatly reducing the dielectric constant between metal surfaces (eg. cable braids mandrel post). Hence the impedance, and resulting signal egress decreases significantly.

This improved shielding occurs during the very initial stages of corrosion, that is, before significant amount of material has left the key metal components such as the mandrel post, figure 20. From the x-ray mapping we see that the post has maintained material character, good cadmium and chromium plating coverage, similar to the pre-exposed sample, figure 19.

As the metal components continue to corrode at key junctions, any improvements in electrical performance due to initial material settling and electrolyte deposition begin to be counter balanced by loss of contact due to corrosion at dissimilar metal interstices. This crossover occurs somewhere between 28 and 56 days, figure 17.

Finally, signal egress has degraded significantly after 56 days. Upon inspection of samples exposed to this time, figure 21, we begin to see that a significant degree of the cadmium plating on the connector post has gone away.

The corrosion of the aluminum which interfaces with the post, as is expected based on data from electrochemistry experiments, was quite extreme. When examining the xray maps of the corroded post, we see some of the plating on surfaces has gone away after 56 days. However, a amount relatively great of the aluminum braid has degraded in this This is witnessed by the time. micrograph, figure 16, which shows a braid section from one of the CASSexposed connectors. The sample has corroded from an original diameter of approximately .0062 inches to less than .0052 inches (a volume decrease of 30%) at some points. Even if the entire plating depth of the connector (cadmium and chromium) post had corroded, it represents less than 1% of the aluminum's corrosion penetration. This follows quite well with what we would expect based on bimetallic and corrosion the potentials performed in which electrochemical tests. show aluminum as the most corrosive element in the system.

severe With such material degradation, continuous longitudinal and circumferential contact is lost. The effect was a substantial increase in signal egress figure 17 by 56 days. The outer conductor contact resistance, figure 22, degraded less dramatically, as some degree of contact, at mandrel face and somewhat at braid/post, was maintained.

OUTER CONDUCTOR CONTACT RESISTANCE, AVERAGES



Figure 22: Outer Conductor Contact Resistance. The mandrel did show some corrosion, figure 14, but near field probe measurements show less signal leakage at that junction.

No sign of corrosion degradation was found at center conductor/leaf spring interface. As a result, the signal transmission and inner contact resistance integrity was nearly maintained (figures 23 and 24).



Figure 23: Signal Transmission



CENTER CONDUCTOR CONTACT

Figure 24: Inner (Center) Conductor Contact Resistance

As compared to connectors tested in previously unpublished CASS results, samples in this program corroded and degraded at a much slower rate. This can be attributed to lower fretting corrosion [2] as is known to occur on many electrical contacts which are typically not held stable.

One of the phenomena which can be attributed to fretting is the nature of samples to 'heal' over This has been witnessed often time. in the field, whereby a sample begins with particular shielding а effectiveness, the signal degrades, improves again, and so on in a discontinuous fashion. Fretting corrosion, and the removal of fretting corrosion products, has been suggested as a way in which discontinuity in signal degradation can occur [2], figure 25.



Figure 25: Process of Fretting Corrosion

Fretting occurs when a metal contact area corrodes, micromotions re-expose corroded surfaces, these areas additional oxide develop films/ corrosion products, cycling until contact is lost. The 'healing' experience, unfounded in this test program, occurs in the field when 1)

removed upon larger vibration or impact, creating better shielding as metal to metal contact is almost restored and 3) signal degrades again through general and fretting corrosion. This may cycle until contact can no longer be restored. In this series of tests, healing has been successfully eliminated through means of stabilizing samples.

SUMMARY/CONCLUSIONS

1. Stabilized samples show an initial slight decrease in signal leakage followed by gradual increase through 56 days CASS exposure. Signal Transmission and Contact Resistance more gradually degrade over this time frame.

2. Initial decreased signal leakage, occurring after 24 hours, corresponds to wetting of the many contact surfaces, with no significant sign of corrosion. Samples gradually corrode and are quite degraded by 56 days. Key paths of moisture ingress and corrosion, are along the crimp bends and into the swivel. Moisture is deposited at the base of the post, finally wicks which into the braid/post interface. Some post material was degraded and a large amount of the aluminum braid was corroded after 56 days.

3. The CASS chamber solution, when used as an immersion bath for drive corrosive (potential) measurements, is qualitatively quite comparable to that of 5% salt water, and deionized water. The metal elements of concern fall within the same ranking for each of the solutions.

4. The corrosion of aluminum is significantly higher than other Finterface elements. The single metal corrosion rates in CASS are, in decreasing order; aluminum >> cadmium > Nickel Tin > Copper Silver. In the CASS enviroment, the aluminum corrosion rate decreases with element coupled in the following order; Copper > Nickel ~ Silver > Tin > Cadmium.

RECOMMENDATIONS

In environments for which the Finterface may be exposed to moisture, the following is suggested. These recommendations are ideal from a scientific point of view, but do not take into account other factors such as economics and tradition.

1. Use braid materials which are both less generally corrosive and are more compatible with contacting surfaces.

2. Use moisture sealing methods in order to repel electrolytes and hence minimize corrosion rates.

3. Mechanically stabilize the cable surrounding the interface to limit fretting corrosion.

4. Implement all of the above while using materials which are both more noble and are electrochemically more compatible (eg; Copper braid/ nickel plated post or silver plated copper braid/silver plated post).

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