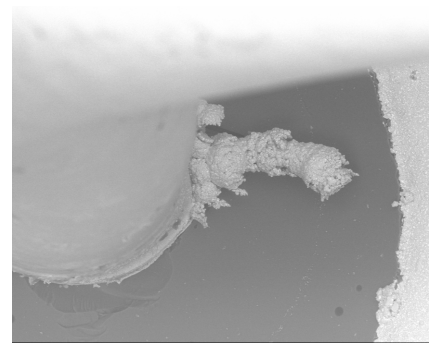
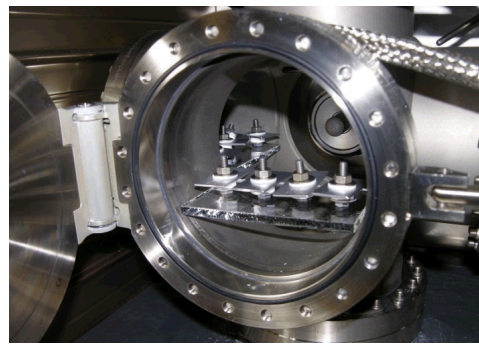
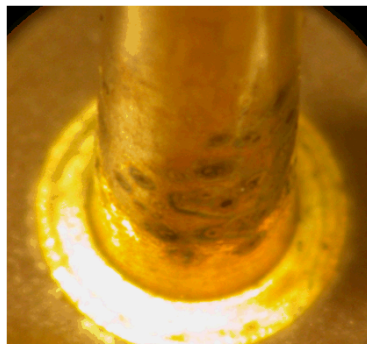
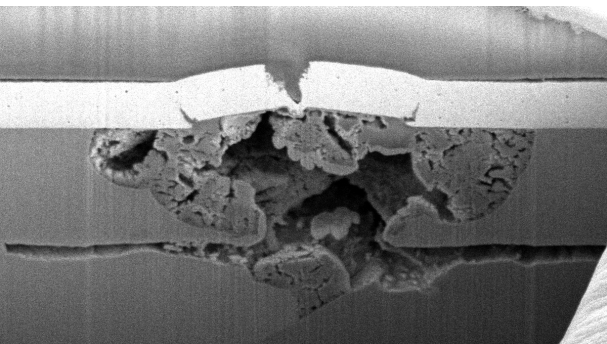


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# A Review of Standardized Atmospheric Corrosion Test Methodologies for Microelectronics and Other Applications

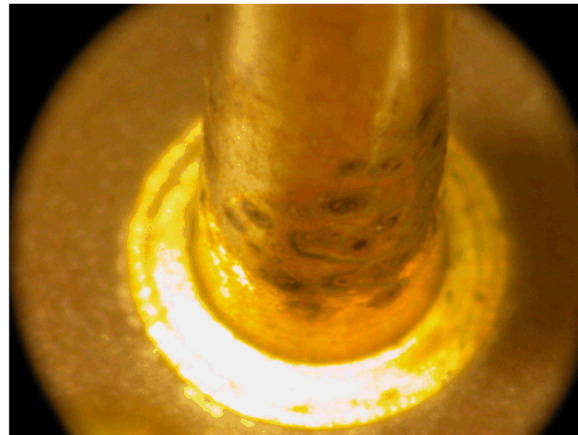
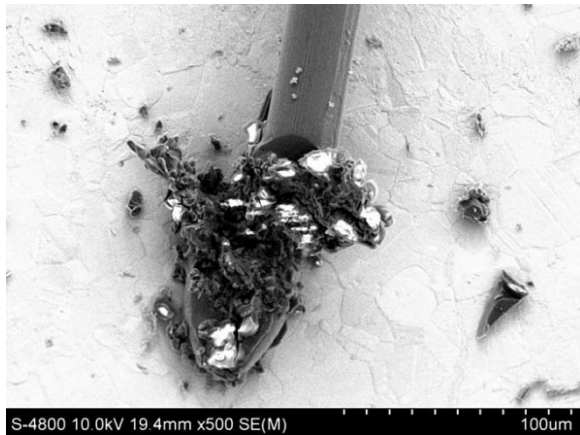
D.G. Enos

Materials Reliability Department



# Atmospheric Corrosion of Microelectronics and Connectors

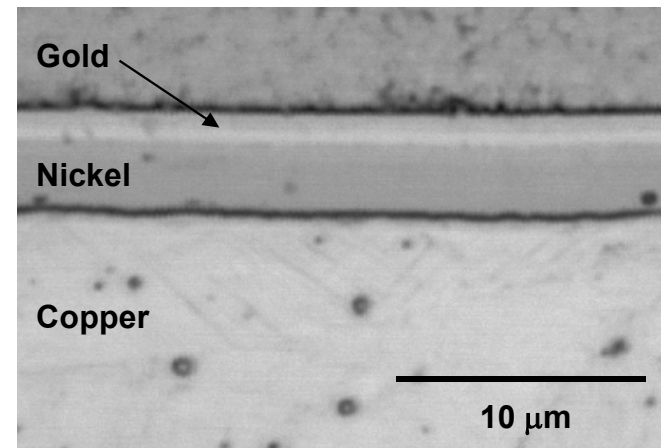
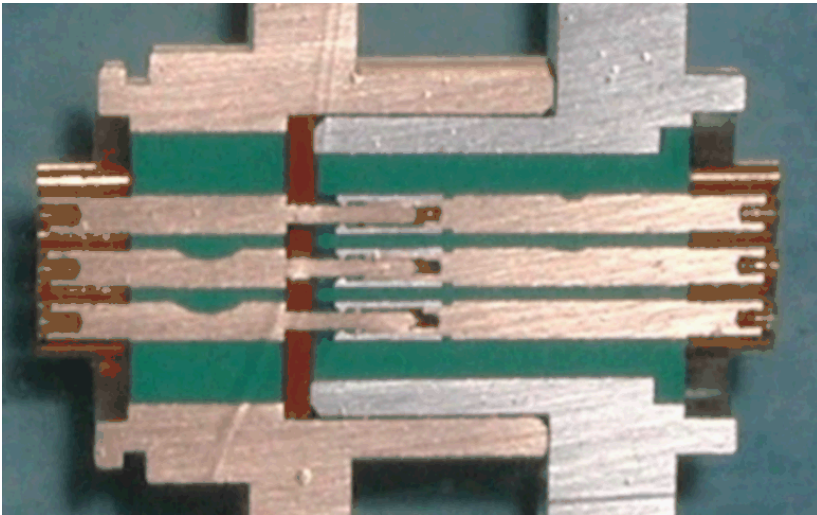
- In microelectronic devices, very small amounts of attack can have a significant impact on performance
- Impact can be direct (Failure of a key feature) or indirect (corrosion product film impacts performance)



- How do you evaluate the long term performance of such devices?

# First Step - Assess the System of Concern

- Appropriate test protocol selection requires an understanding of the situation being simulated



- Material Behavior
  - What information do you need to know?
  - Extent of corrosion?
  - Nature of corrosion product?

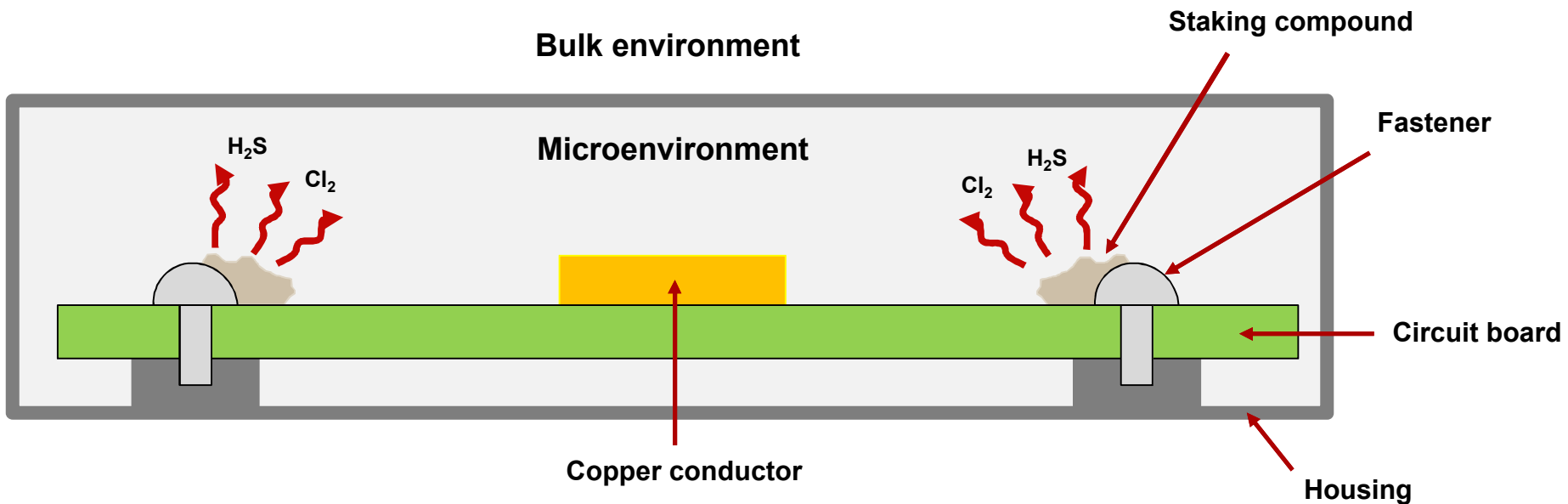
# First Step - Assess the System of Concern

## Atmosphere/Environment

- What do you know/can you measure in terms of the ambient environment?
  - Temperature, RH, gas species, gas velocity, UV light, etc.
  - Is it consistent or does it vary?
- What environment is important?
  - Does a microenvironment exist?

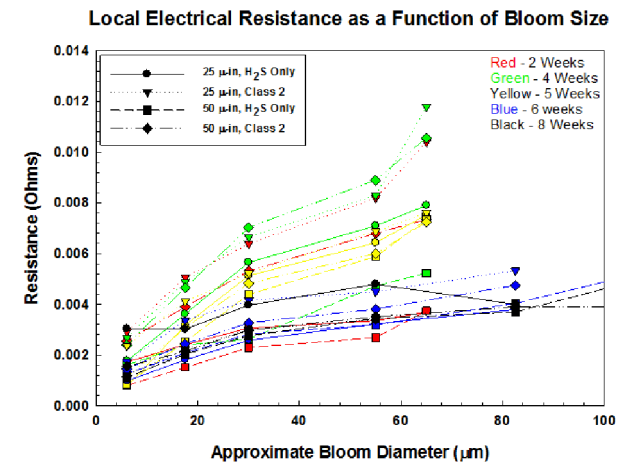
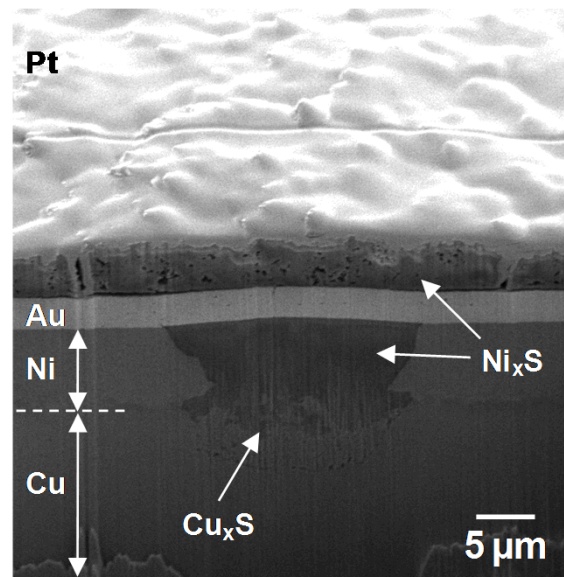
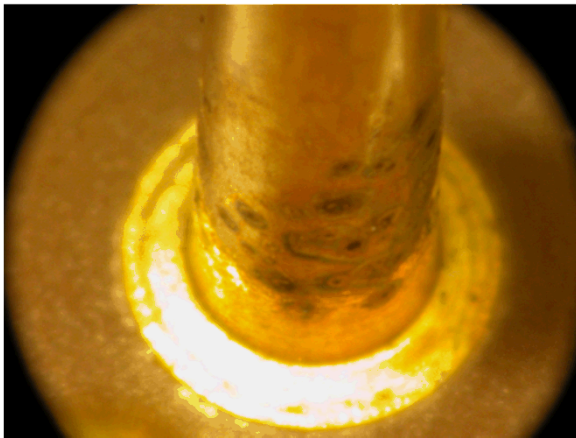
# Microenvironments

- While the bulk environment can be important, if a system with a restricted geometry is being considered, the local environment could be radically different.
- Consider a copper trace inside a microelectronic device



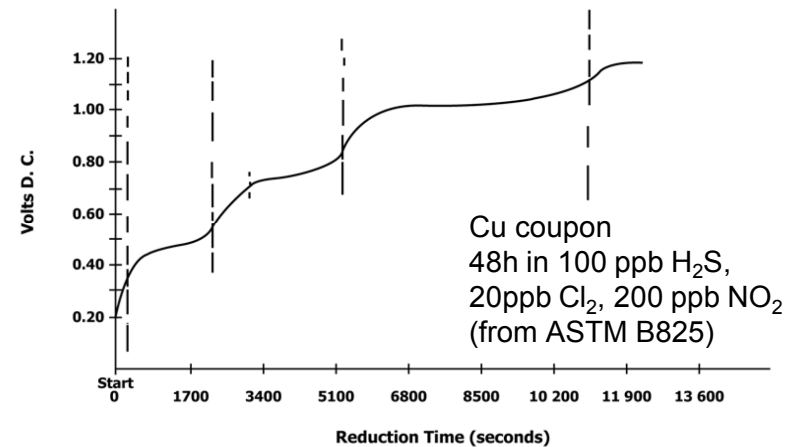
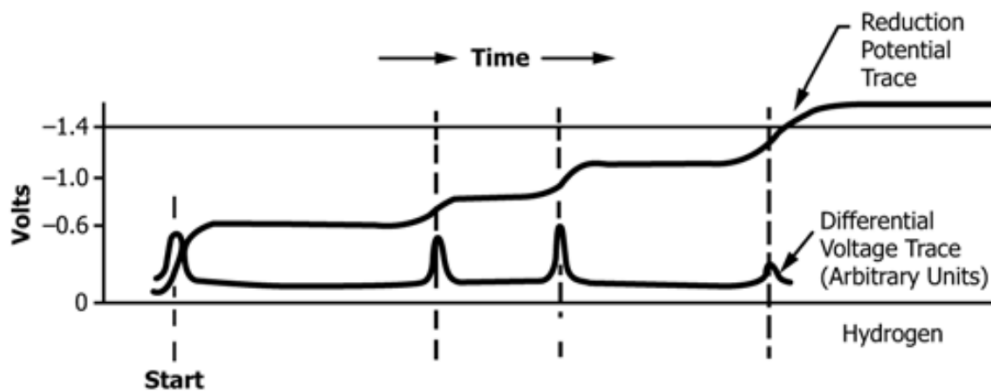
# Analysis of Field Exposed Samples

- Easy to select an environment that accelerates corrosion – want to make sure it is done in a relevant way
- *Field exposed samples tell you what is relevant*
- Analytical techniques as appropriate to quantify properties



# Alternatives to looking at actual hardware

- Sometimes you don't have time to wait and see what the actual corrosion product will be, or you don't have aged specimens from the field
- Witness Coupons (cathodic reduction)
  - ASTM B825 (Coulometric Reduction of Surface Films on Metallic Samples)



# Developing an Accelerated Test Environment

- Desire is for a test that could be run quickly (hours or days) and yield a quantitative assessment of corrosion performance
- Not so easy... IEC 355 (1971)
  - Environments vary widely
  - Changing concentrations from actual could change the mechanism
  - Different materials respond differently to increased aggressiveness
    - Example: In  $\text{H}_2\text{S}$ , corrosion of Ag is accelerated by  $\text{NO}_2$ , but Cu is not
  - Etc.
- Need to be mindful of the pitfalls.

# Mixed Flowing Gas Exposure

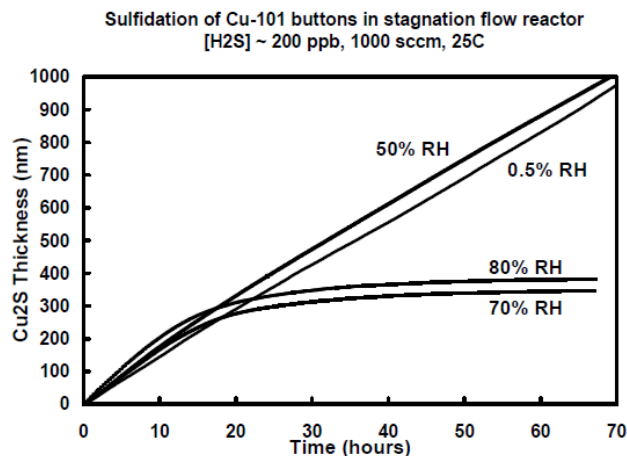
- Accelerate corrosion processes in a manner that is meaningful for the intended application
  - Corrosion mechanism should be accelerated, *not changed*
  - Corrosion product chemical, physical, and electrical properties should be preserved
  - Single component systems generate unrealistic results
  - Accelerated environment is not necessarily simply a more concentrated version of the natural environment
    - Replicate the environmental effects
- Key variables and their role
  - Water
  - Temperature
  - Contaminant gases (NO<sub>2</sub>, H<sub>2</sub>S, SO<sub>2</sub>, Cl<sub>2</sub>, etc.)
    - *There are synergistic effects*
  - Flow velocity

# What do The Environments Described Here Probe?

- Designed to accelerate corrosion of silver, copper, and noble metal plated copper.
- While they may impact other materials, that impact must be probed before it can be effectively interpreted.
- Rate of acceleration may vary from material to material
- Complex geometries/systems can create microenvironments within themselves – hinder usefulness of exposing a device to a MFG environment

# Variable 1: Water Content (Humidity)

- Critical variable in almost all environments used to assess atmospheric corrosion performance for microelectronics
- But is it needed?
  - Is there a critical RH?
  - Sulfidation of copper in  $H_2S$  will go at 0% RH
- Is it a viable accelerant?
  - Increase to 80% RH without changing mechanisms
  - Not a strong impact on corrosion rate



Cu in H<sub>2</sub>S  
Similar rate in 0.5 and 50% RH  
Transition to different mechanism  
faster at higher RH

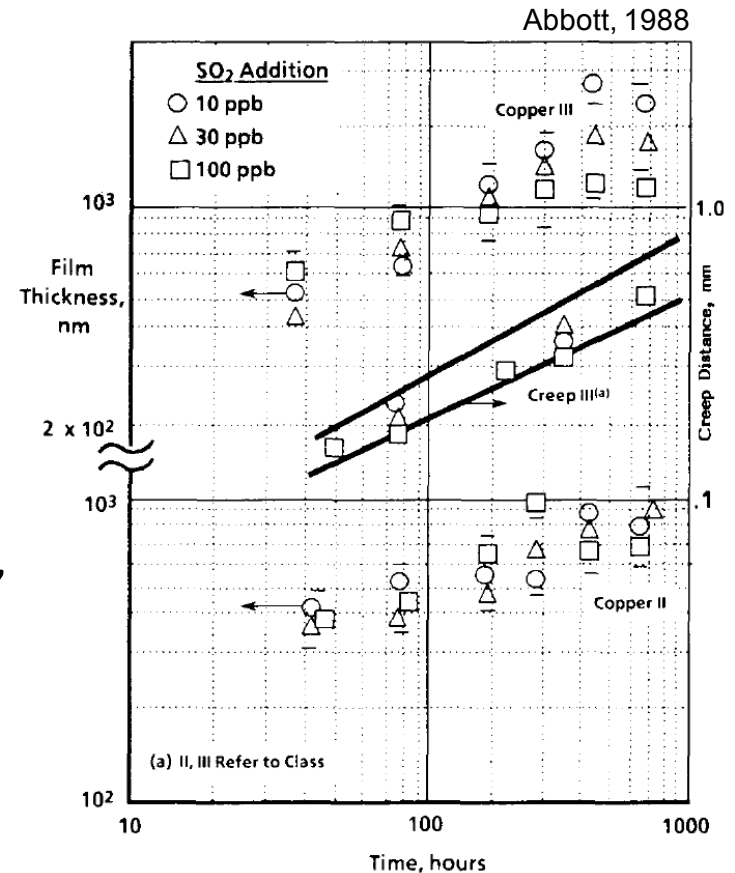
Barbour et al., SAND02-0699

## Variable 2: Temperature

- Critical control in all mixed flowing gas environments
- Most corrosion reactions respond to temperature
- Is it a viable accelerant
  - Activation energy for some key reactions (e.g., sulfidation of copper) are low
  - Experimental issues associated with higher temperature, higher humidity gas streams
    - Condensation issues

# Variable 3 – Gaseous Species – H<sub>2</sub>S and SO<sub>2</sub>

- Sulfur species are of primary importance for atmospheric corrosion of copper and silver
  - Mechanism – limits its ability as an accelerant
  - Kinetics
  - Chemistry
- H<sub>2</sub>S, SO<sub>2</sub> or Both?
  - SO<sub>2</sub> is a primary atmospheric contaminant, but is substantially attenuated for indoor environments (Abbott, 1988)
  - Synergistic effect with some materials, such as nickel (Gore, 1990)
  - No effect on Cu or porous Au
- Is it a viable accelerant?

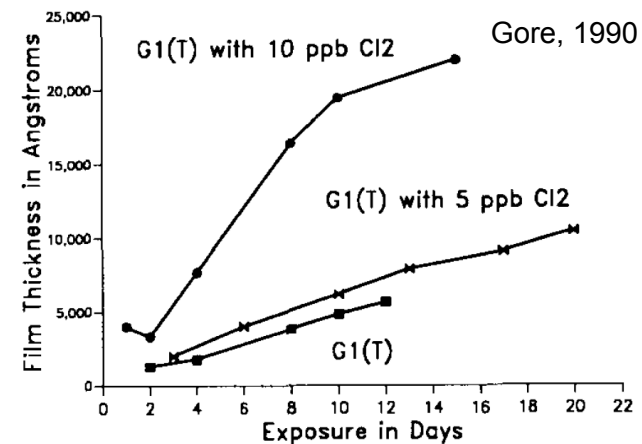
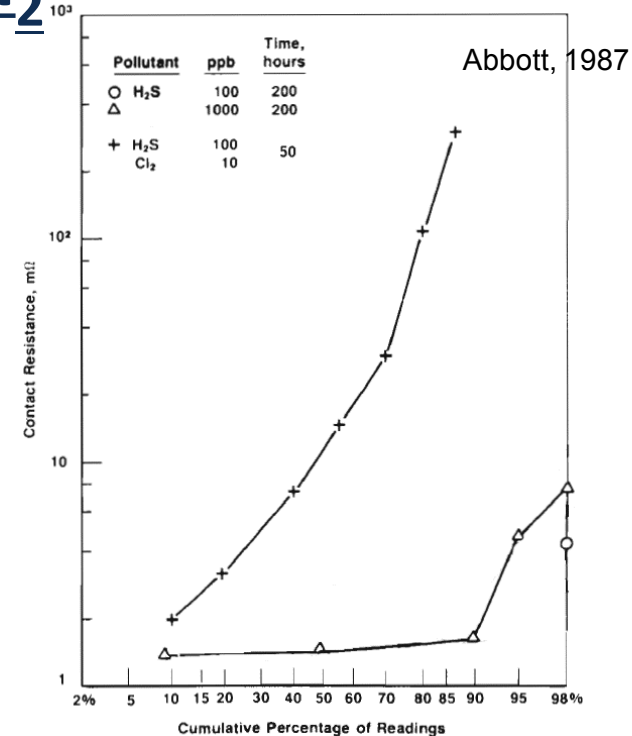


## Variable 3 – Gaseous Species – NO<sub>2</sub>

- Nitrogen dioxide is present in almost all mixed flowing gas systems, but in and of itself, it does not play a direct role
  - Not part of the corrosion product
  - Plays role of an oxidant
    - Other species may replace used to replace it, such as O<sub>3</sub>.
    - Not concentration sensitive (large variations do not impact rates)
- Is it a viable accelerant?
  - No – necessary, but once it's there, more doesn't impact rate (Gore, 1990; Abbott, 1988; Chao, 1991)

# Variable 3 – Gaseous Species – Cl<sub>2</sub>

- Critical constituent of most mixed flowing gas environments
  - Drives chemistries achieved to help produce products similar to observed in the field
  - Does not mean chlorine gas is a dominant specie in real environments
    - Emphasizes criticality of a reactive chloride bearing specie
    - Cl<sub>2</sub> is a convenient way to get there
- Not a viable accelerant
  - Requires precise control – too much results in unrealistic mechanisms and corrosion product

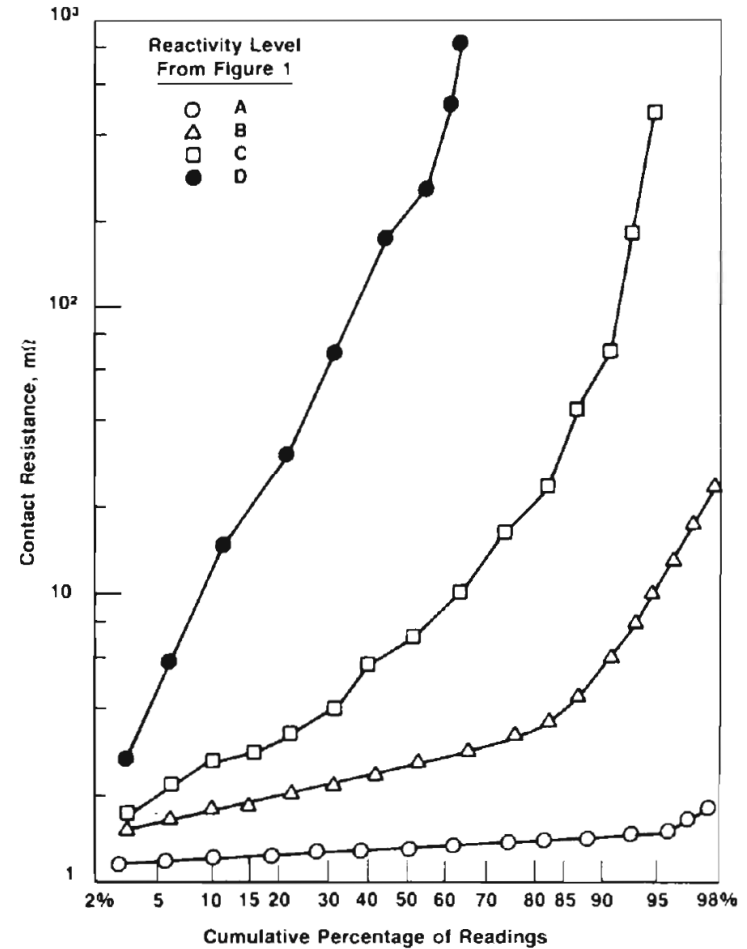
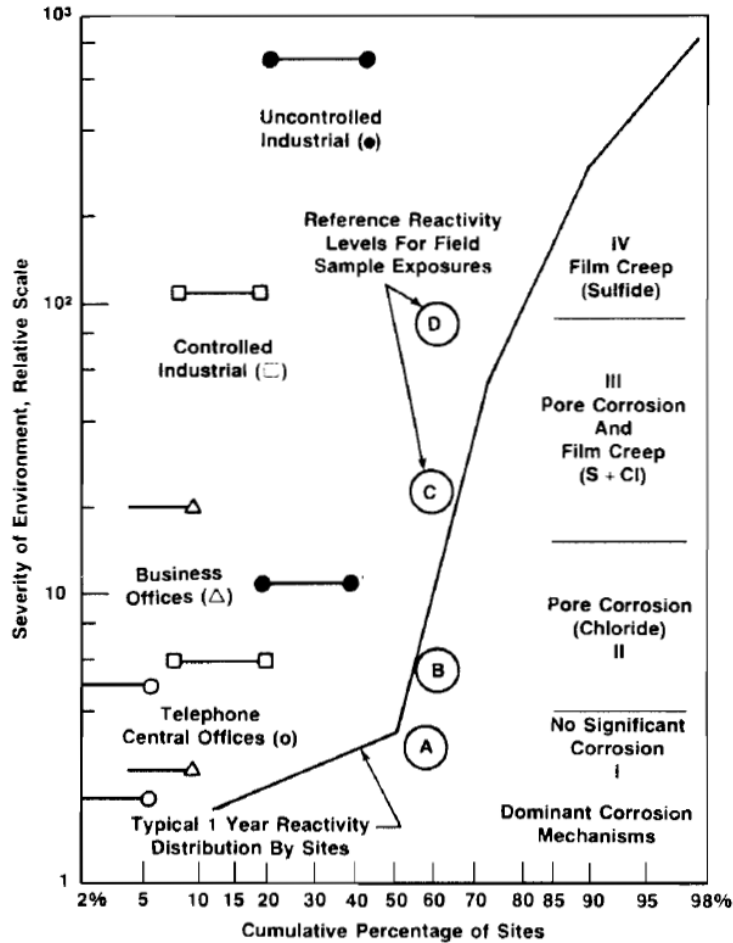


# Existing Test Standards and Their Basis

- **Battelle** (W.H. Abbott)
- **IBM**
- **Telecordia** (formerly Belcore)
- **ISO** (International Organization for Standardization)
- **EIA** (Electronic Components Industry Association)
- **IEC** (International Electrotechnical Commission)
- Note: Just because it's a standard doesn't mean it will meet your need
  - Tweak an existing standard
  - Make something new

# Battelle (W.H. Abbott)

- Four distinct classes (reactivities) of environments



# Battelle (W.H. Abbott)

- Four distinct classes of environments

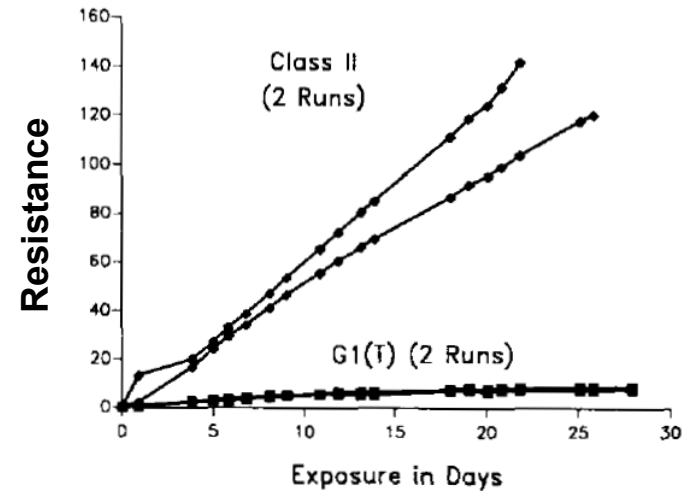
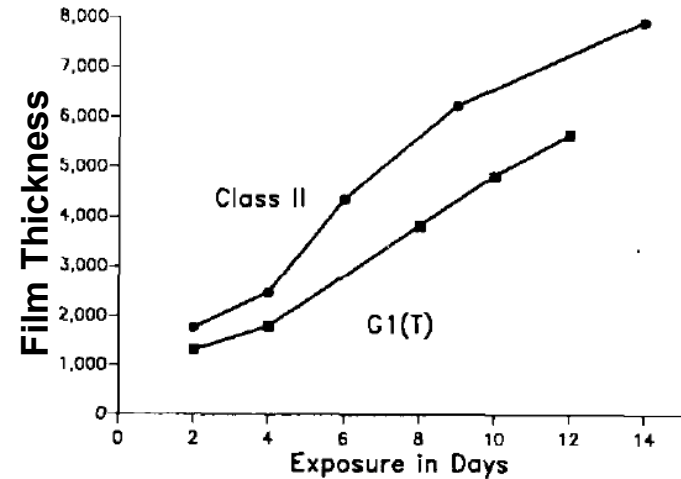
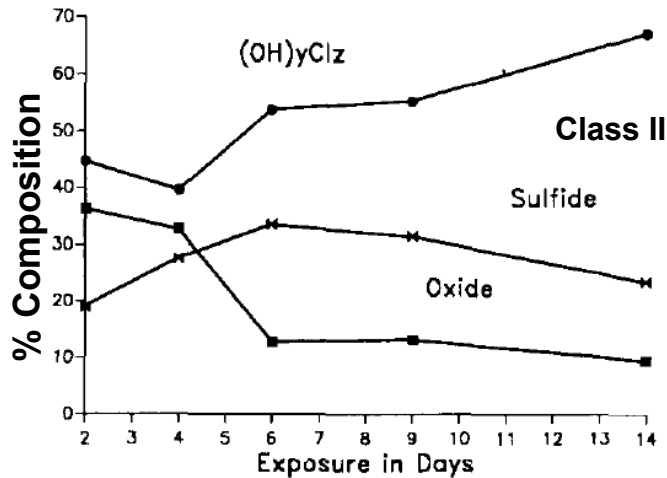
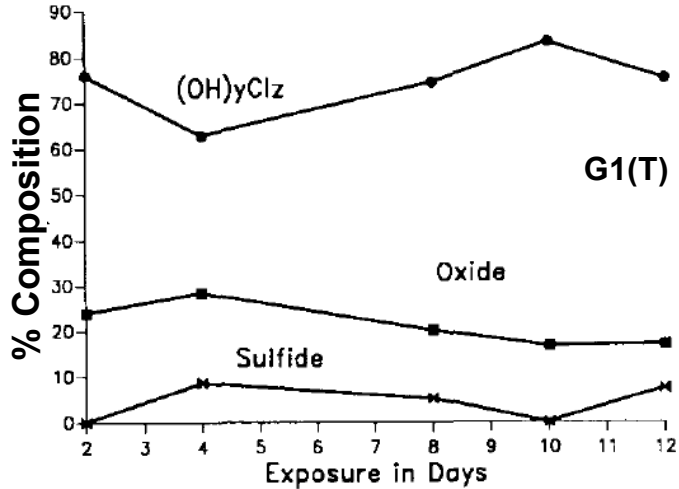
	Mechanism	Corrosion Product Constituents	Copper Corrosion Product
<b>Class I</b>	None	O	Cu <sub>2</sub> O
<b>Class II</b>	Pore	Ni, Cu, Cl, O, S	Cu <sub>2</sub> O, Cu <sub>x</sub> O <sub>y</sub> Cl <sub>z</sub>
<b>Class III</b>	Pore and Creep	Cu, S, Ni, Cl, O	Cu <sub>2</sub> S, Cu <sub>2</sub> O, others
<b>Class IV</b>	Creep	Cu, S, Ni, O, Cl	Cu <sub>2</sub> S, minor Cu <sub>2</sub> O, others

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

- Defined three environmental classes
  - G1 – Business office
  - G2 – Industrial
  - G3 – Harsh Industrial
- Defined the G1(T) environment to mimic G1 conditions

	Gas Concentration (ppb)						
	Cl <sub>2</sub>	SO <sub>2</sub>	NO <sub>2</sub>	H <sub>2</sub> S	% RH	T (°C)	Velocity (ft/min)
<b>G1(T)</b>	3	350	610	40	70	30	100
<i>Class 2</i>	<i>10</i>	<i>--</i>	<i>200</i>	<i>10</i>	<i>70</i>	<i>30</i>	<i>--</i>

## ■ Differences from Battelle Class II



# Telecordia GR-63-CORE

- Section 5.5 – Airborne Contaminants Test Methods
- Two distinct environments defined
  - Indoor (environmentally controlled)
  - Outdoor (not environmentally controlled)

	Gas Composition (ppb)						
	Cl <sub>2</sub>	H <sub>2</sub> S	NO <sub>2</sub>	SO <sub>2</sub>	T (°C)	% RH	
Indoor	10	10	200	100	30	70	Battelle Class II + SO <sub>2</sub>
Outdoor	20	100	200	200	30	70	Battelle Class III + SO <sub>2</sub>

# EIA TP-65B

- Three environmental classes

	Gas Composition (ppbv)					
	H <sub>2</sub> S	Cl <sub>2</sub>	NO <sub>2</sub>	SO <sub>2</sub>	T (°C)	% RH
<b>Class IIA</b>	10	10	200	100	30	70
<b>Class IIIA</b>	100	20	200	200	30	70
<b>Class IV</b>	200	30	200	--	40	75

Key reference: ANSI/EIA-364-65B-2009 “Mixed Flowing Gas Test Procedure for Electrical Connectors, Contacts, and Sockets”

# ISO 10062

	Gas Composition (ppv)				
	SO <sub>2</sub>	H <sub>2</sub> S	Cl <sub>2</sub>	T (°C)	% RH
<b>Method F (1)</b>	500	100	20	25	75
<b>Method F (2)</b>	500	100	20	40	80

Key reference: ISO 10062 “Corrosion Tests in Artificial Atmosphere at Low Concentrations of Polluting Gas(es)”, Second edition.

# IEC 60512-11-7

	Gas Composition (ppbv)							
	H <sub>2</sub> S	Cl <sub>2</sub>	NO <sub>2</sub>	SO <sub>2</sub>	T (°C)	% RH	V exch/h	
<b>Method 1</b>	100	--	--	500	25	75	3-10	
<b>Method 2</b>	10	10	200	--	30	70	3-10	Class I
<b>Method 3</b>	100	20	200	--	30	75	3-10	Class III
<b>Method 4</b>	10	10	200	200	25	75	3-10	C.II + SO <sub>2</sub>

**Key reference:** IEC 60512-11-7 “Connectors for Electronic Equipment – Tests and Measurements. Test 11g: Flowing Mixed Gas Corrosion Test”

## Other Specifications

- ASTM B845 “Standard Guide for Mixed Flowing Gas (MFG) Tests for Electrical Contacts”
  - 13 environments, including Battelle, IBM, Telecordia, etc. and single gas systems
- MIL-STD-210, MIL-STD-810, MIL-STD-883

# Acceleration Factors

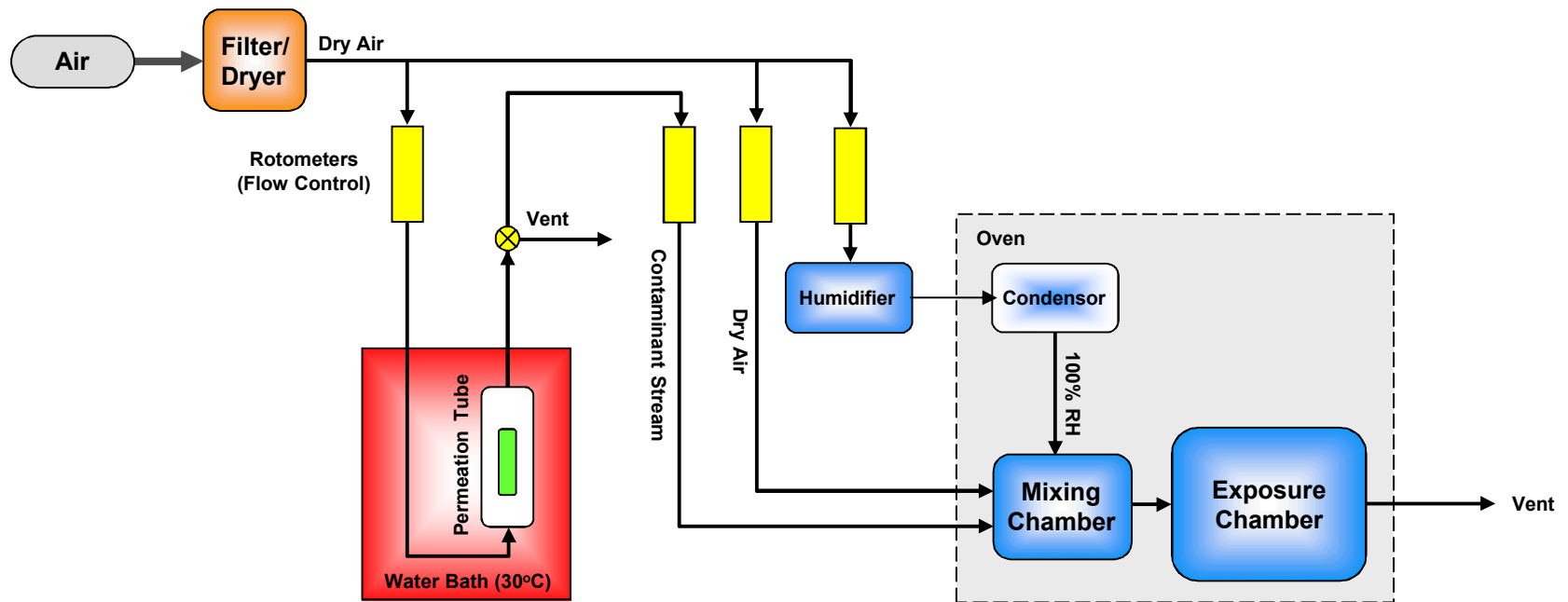
- The acceleration factor is the holy grail for any accelerated test method.
- Can not determine the acceleration factor without having long term data to assess
- Qualitative assessments are more typical
- Beware of “rules of thumb”
  - Williams, 1988 “48 hours of exposure in a laboratory chamber is equivalent to approximately one year of field service”

# Implementation

- Significant hazards associated with constituents
- Consider active surface area -> chamber size, flow rate
- Consider information needed -> chamber complexity
- Consider chamber geometry -> stratification, dead zones
- Consider chamber materials -> consumption
- Validation is critical
  - Witness coupons

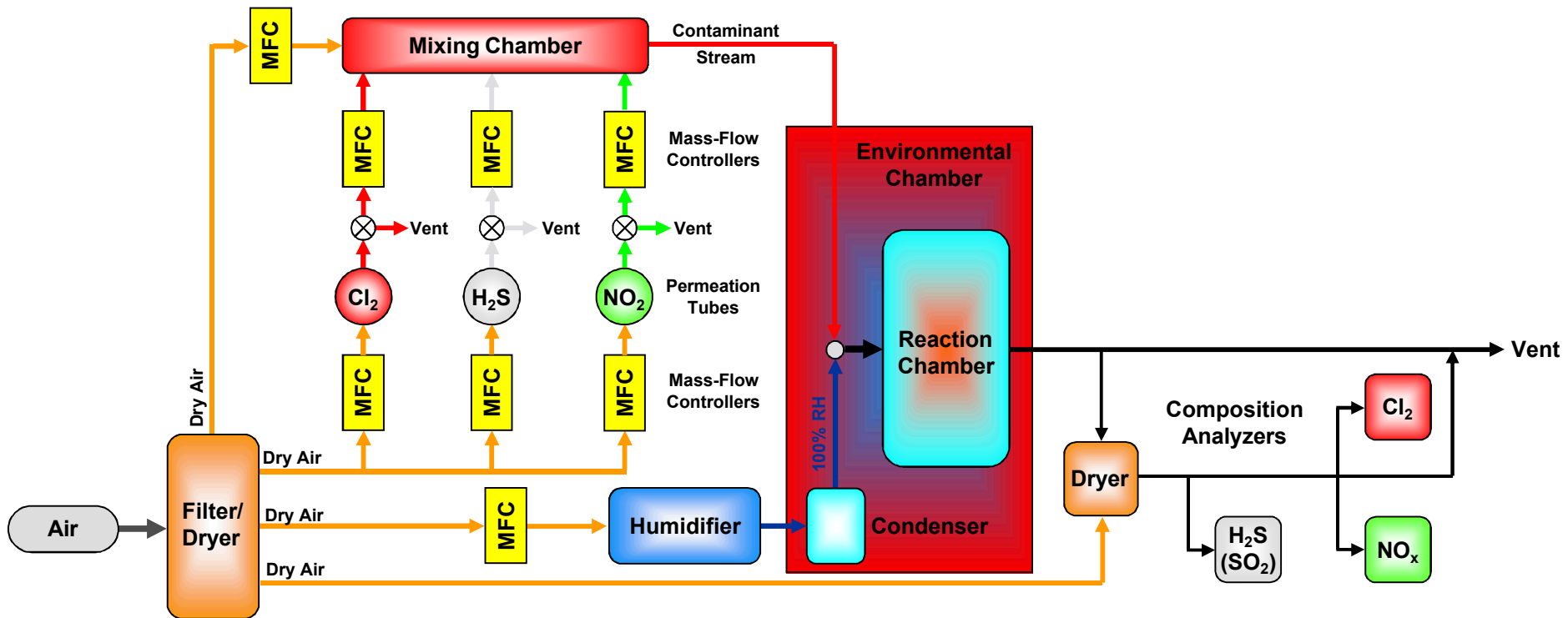
# Example 1 – A Manual System (Rotometers)

- Issues to consider – consumption and source integrity



# Example 2 – Active Control (Feedback)

- Issues to consider – sensitivity, stratification



# Summary

- Mixed flowing gas environments can allow acceleration of atmospheric corrosion reactions in a relevant way.
- Absolutely critical that you know what is important for your application.
- Pioneering work of W.H. Abbott (Battelle Labs) and IBM led to the basis of many of the current MFG specifications.
- Implementation is not trivial.