VANDERBILT ELECTROMAGNETICS LABORATORY
DEPARTMENT OF PHYSICS & ASTRONOMY

SQUID Measurements of the Rate of Hidden Corrosion

Vanderbilt University

Corrosion Fatigue and Corrosion Predictive Modeling Technical Interchange Meeting

NCI/USAF, Tinker Air Force Base, Oklahoma City
December 17-19, 1997

Outline

- What is a SQUID magnetometer?
- How can a SQUID image ongoing, hidden corrosion activity within an aircraft lap joint?
- What does a laboratory SQUID system look like?

What is a SQUID Magnetometer?

- **S**uperconducting **QU**antum **I**nterference **D**evice
- RF: A superconducting loop with one Josephson junction and RF bias
- DC: A superconducting loop with two Josephson junctions and DC bias
- Loop impedance is a periodic function of the magnetic flux threading the SQUID
- **A flux-to-voltage converter with unrivaled sensitivity**

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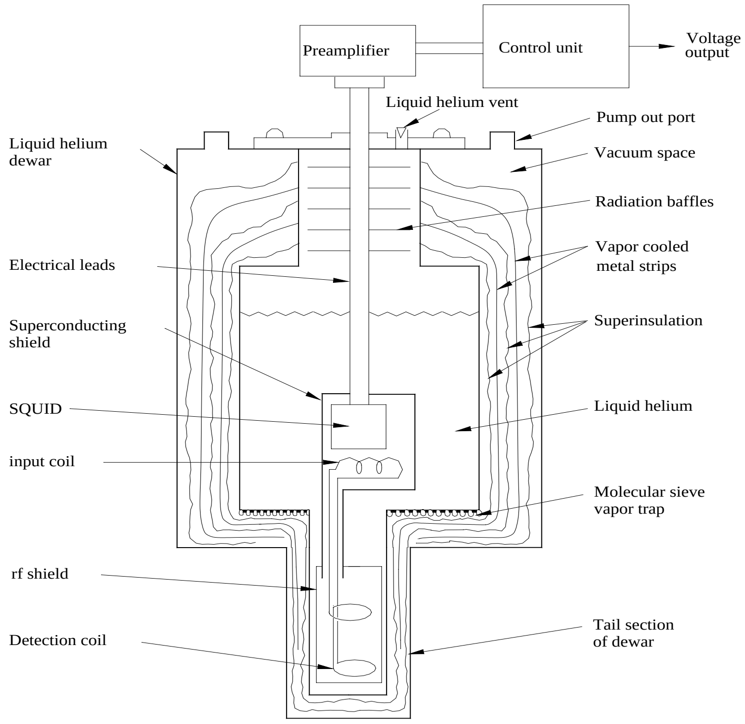
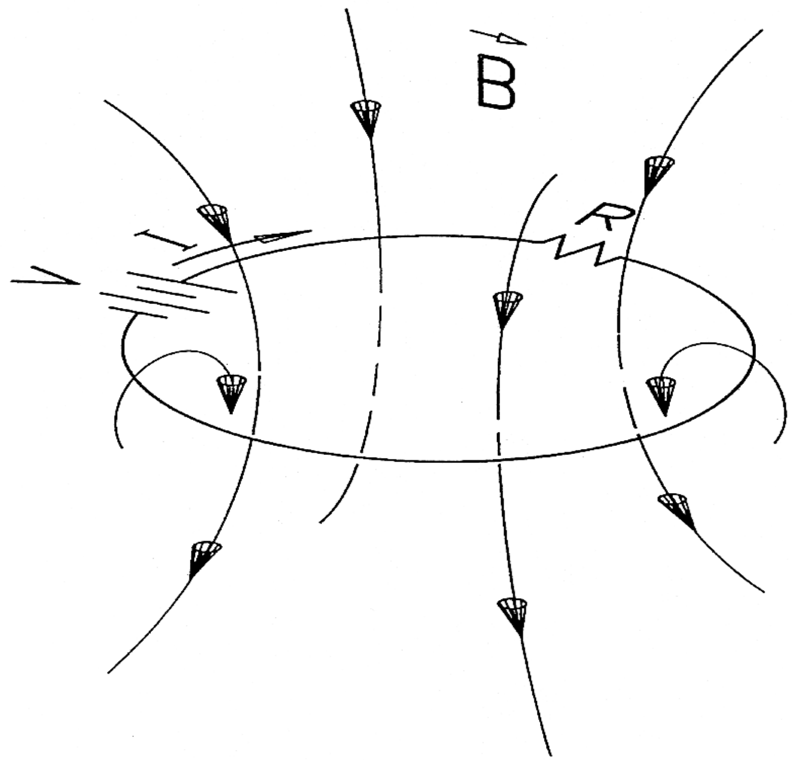
SUPERCONDUCTING QUANTUM INTERFERENCE DEVICE (SQUID) MAGNETOMETERS



Conclusion: Conventional SQUID magnetometers do not have the spatial resolution required to map expanding cardiac wavefronts.

The Law of Biot and Savart

$$\vec{B}(\vec{r}) = \frac{\mu_o I}{4\pi} \oint \frac{d\vec{\ell}\,' \times (\vec{r} - \vec{r}\,')}{|\,\vec{r} - \vec{r}\,'\,|^3}$$



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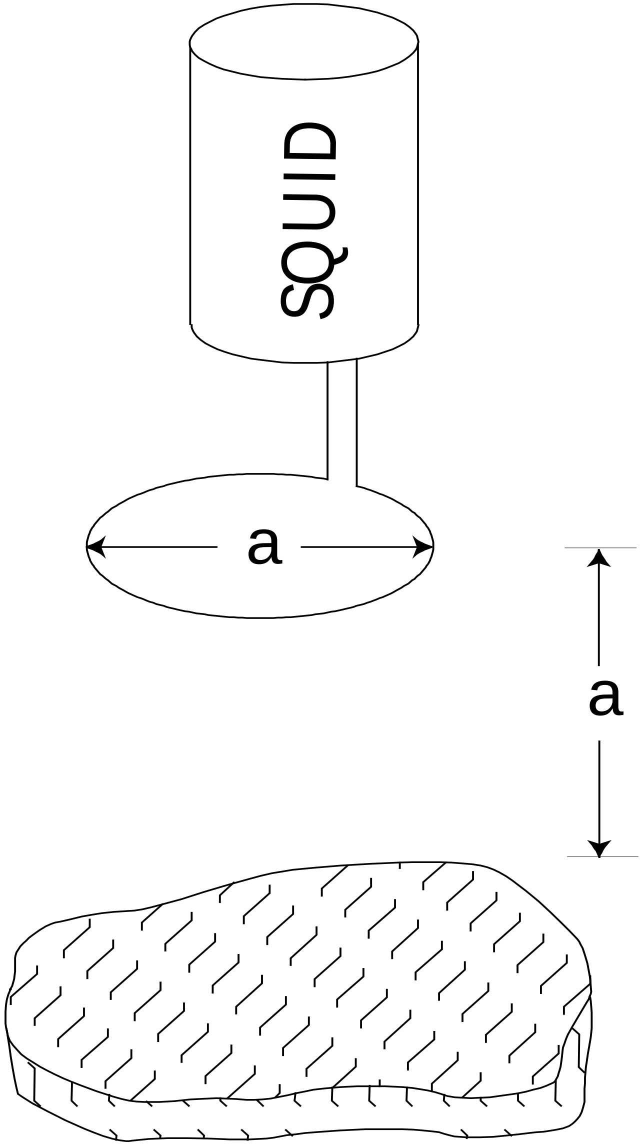
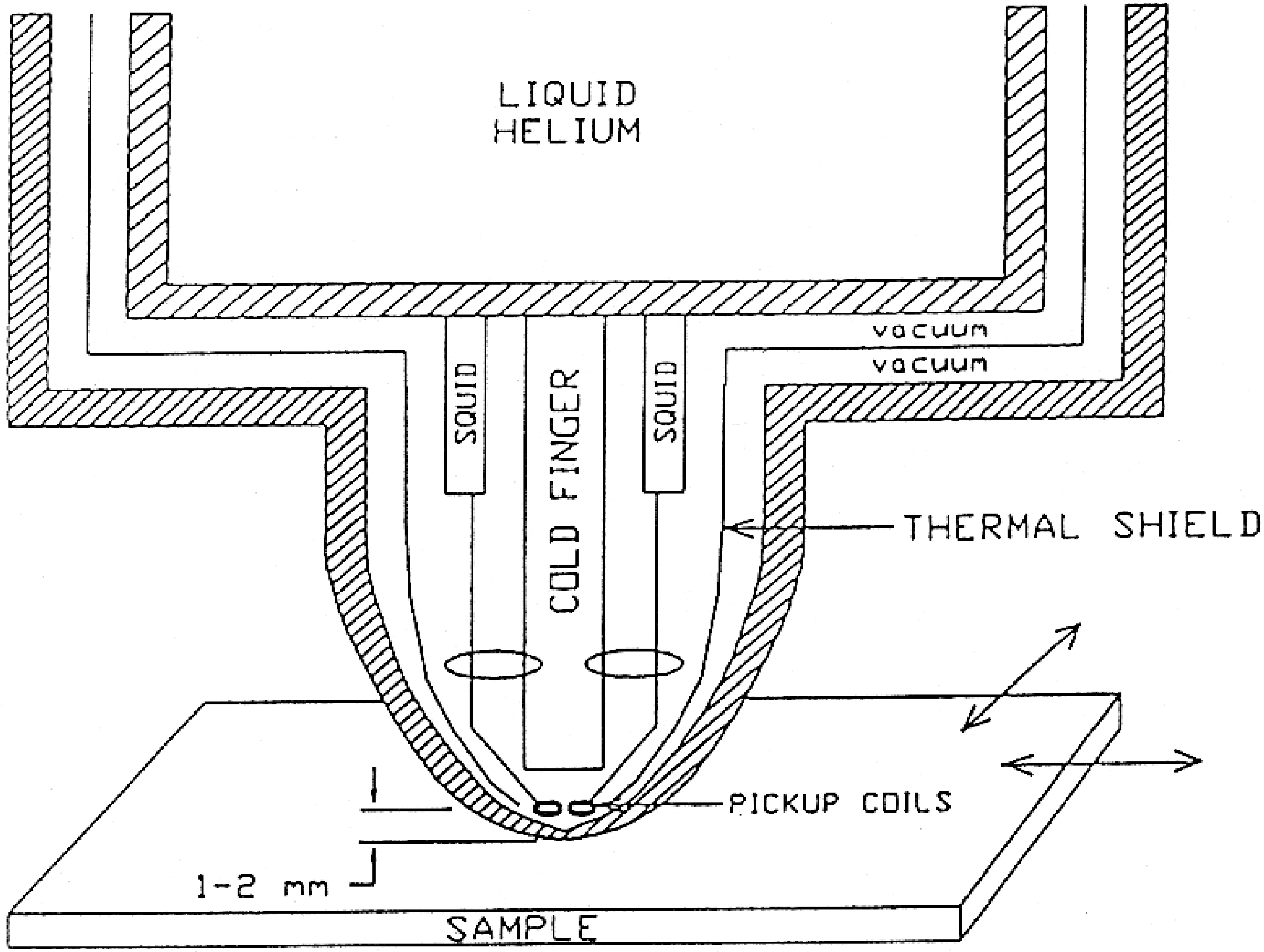
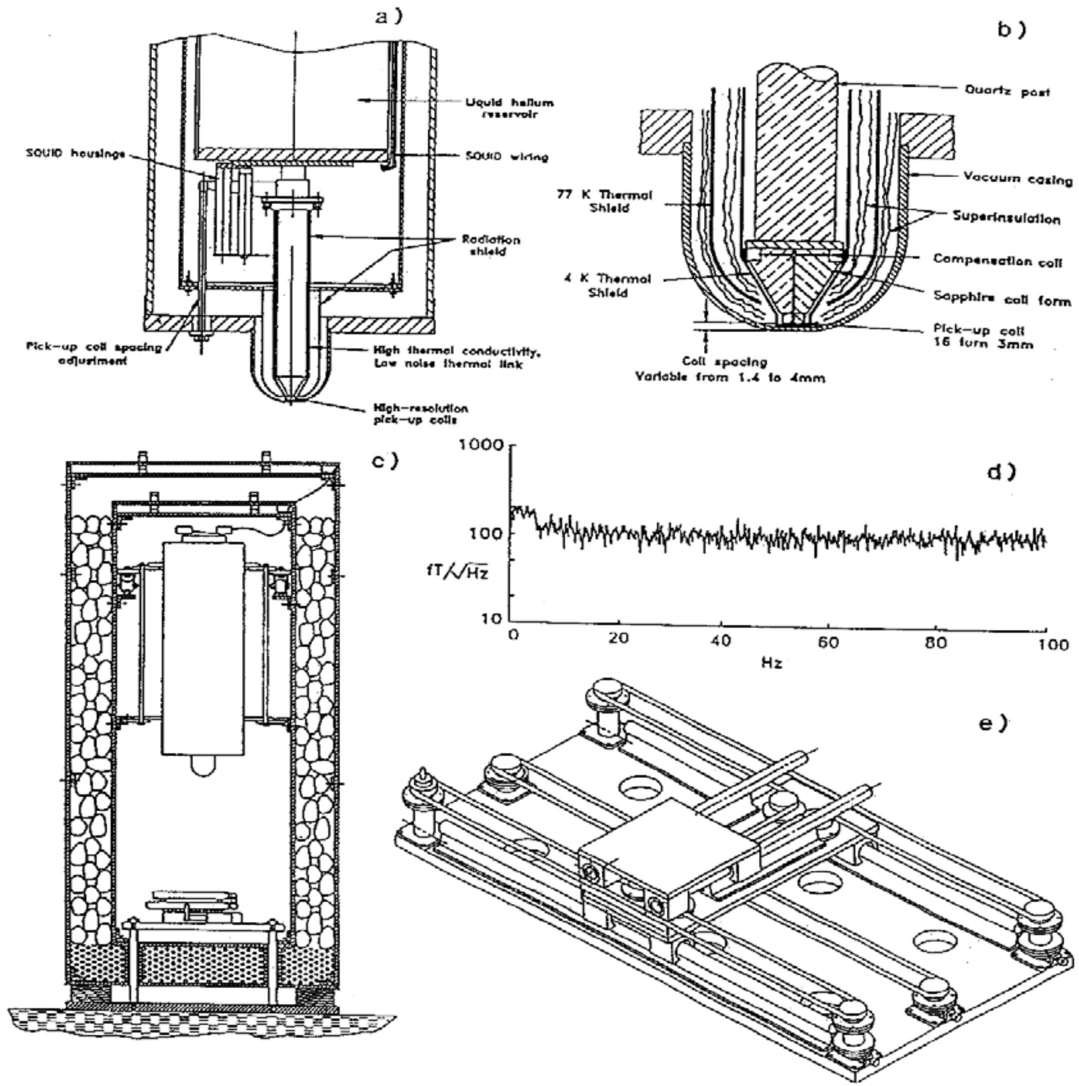
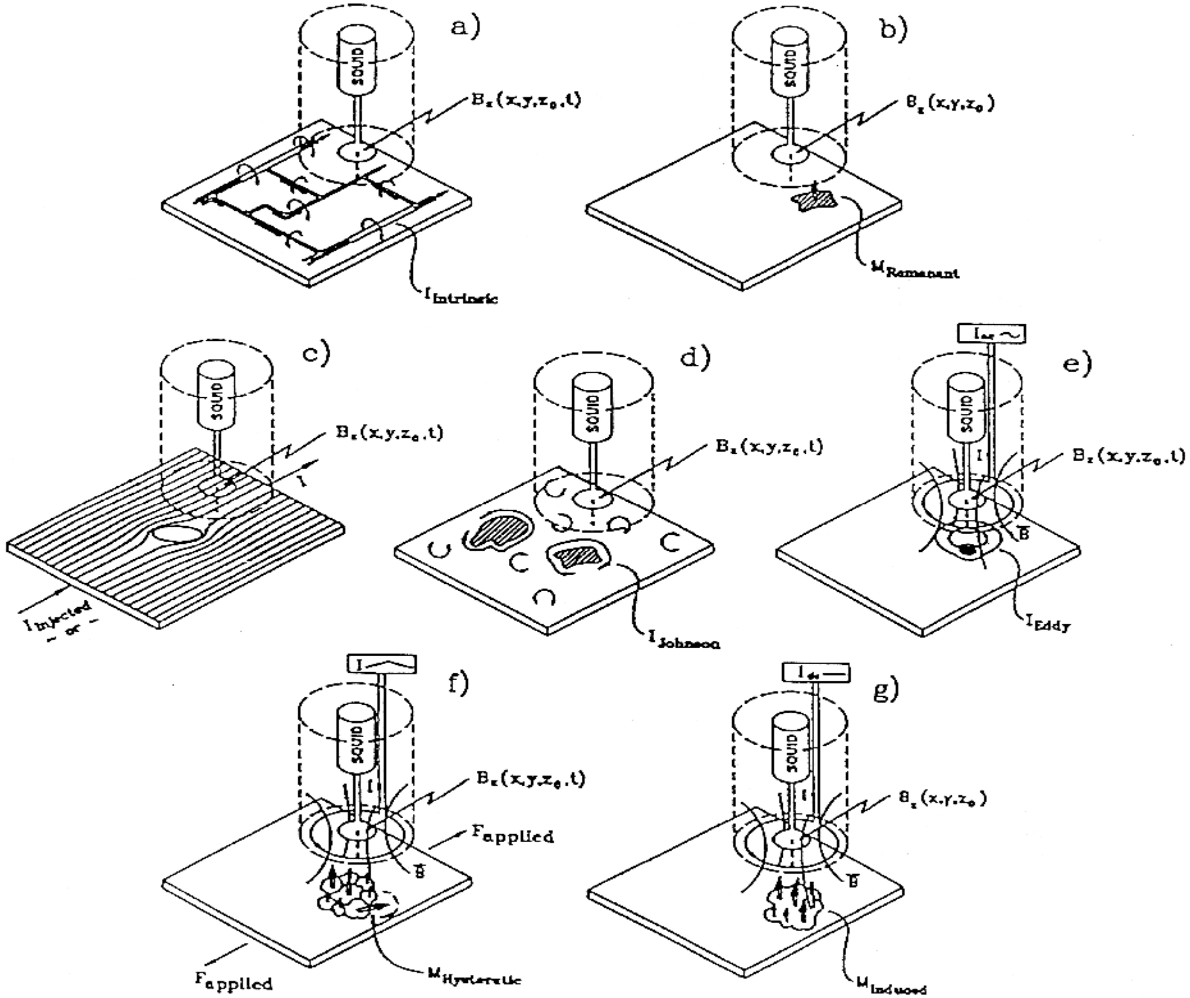
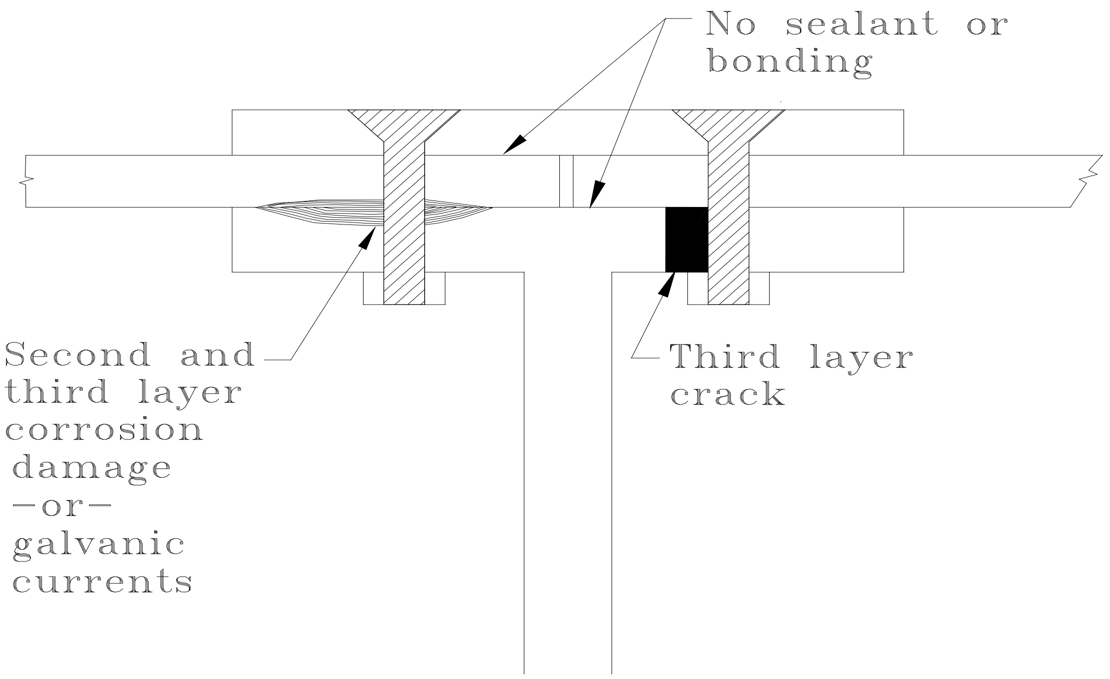



LIQUID
HELIUM
vacuum
vacuum
SQUID
COLD FINGER
SQUID
THERMAL SHIELD
PICKUP COILS
1-2 mm
SAMPLE


a)
Liquid helium reservoir
SQUID housings
SQUID wiring
Radiation shield
Pick-up coil spacing adjustment
High thermal conductivity, Low noise thermal link
High-resolution pick-up coils
b)
Quartz post
Vacuum casing
77 K Thermal Shield
Superinsulation
Compensation coil
4 K Thermal Shield
Sapphire coil form
Pick-up coil 16 turn 3mm
Coil spacing Variable from 1.4 to 4mm
c)
d)
1000
100
10
fT/√Hz
0
20
40
60
80
100
Hz
e)


a)
SQUID
B_z(x,y,z_0,t)
I_Intrinsic
b)
SQUID
B_z(x,y,z_0)
M_Remanent
c)
SQUID
B_z(x,y,z_0,t)
I_injected
d)
SQUID
B_z(x,y,z_0,t)
I_Johnson
e)
SQUID
B_z(x,y,z_0,t)
I_Eddy
f)
SQUID
B_z(x,y,z_0,t)
F_applied
F_applied
M_Hysteretic
g)
SQUID
B_z(x,y,z_0)
M_Induced

WHEN ONE MIGHT USE SQUID NDE ?



Skin depth $\propto \frac{1}{\sqrt{f}}$

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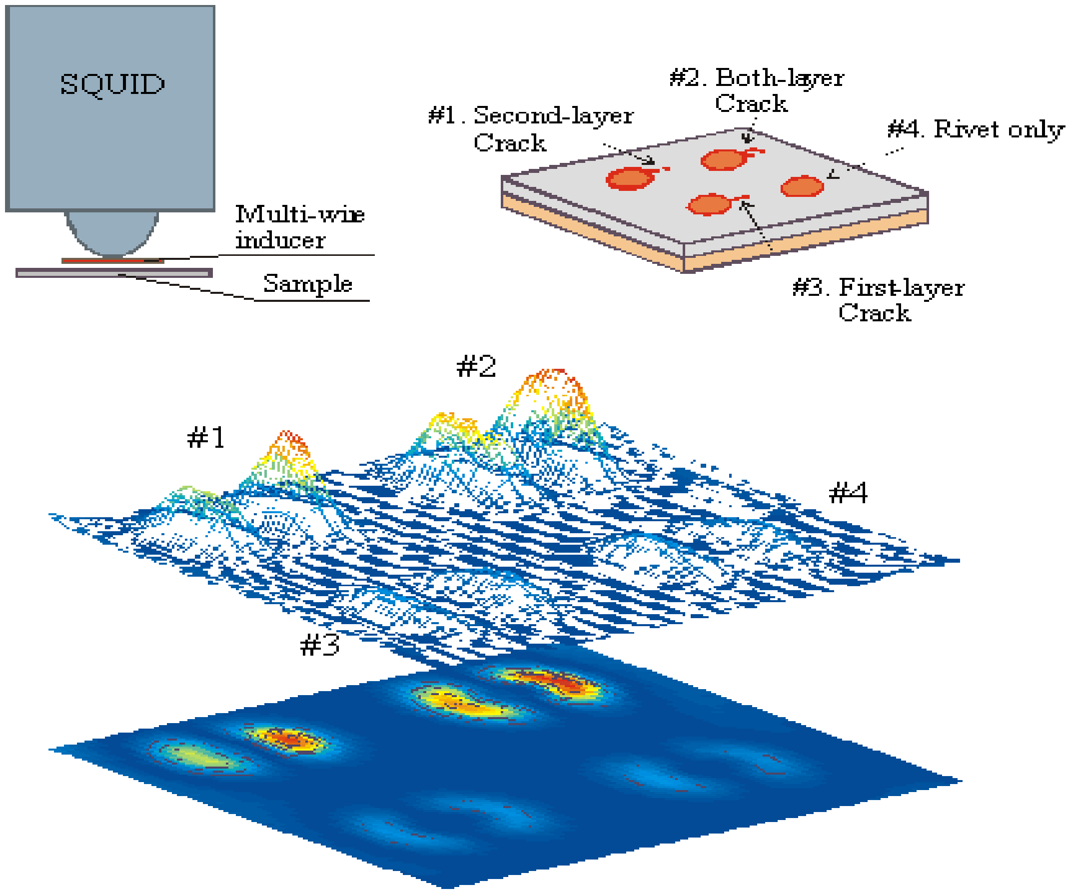
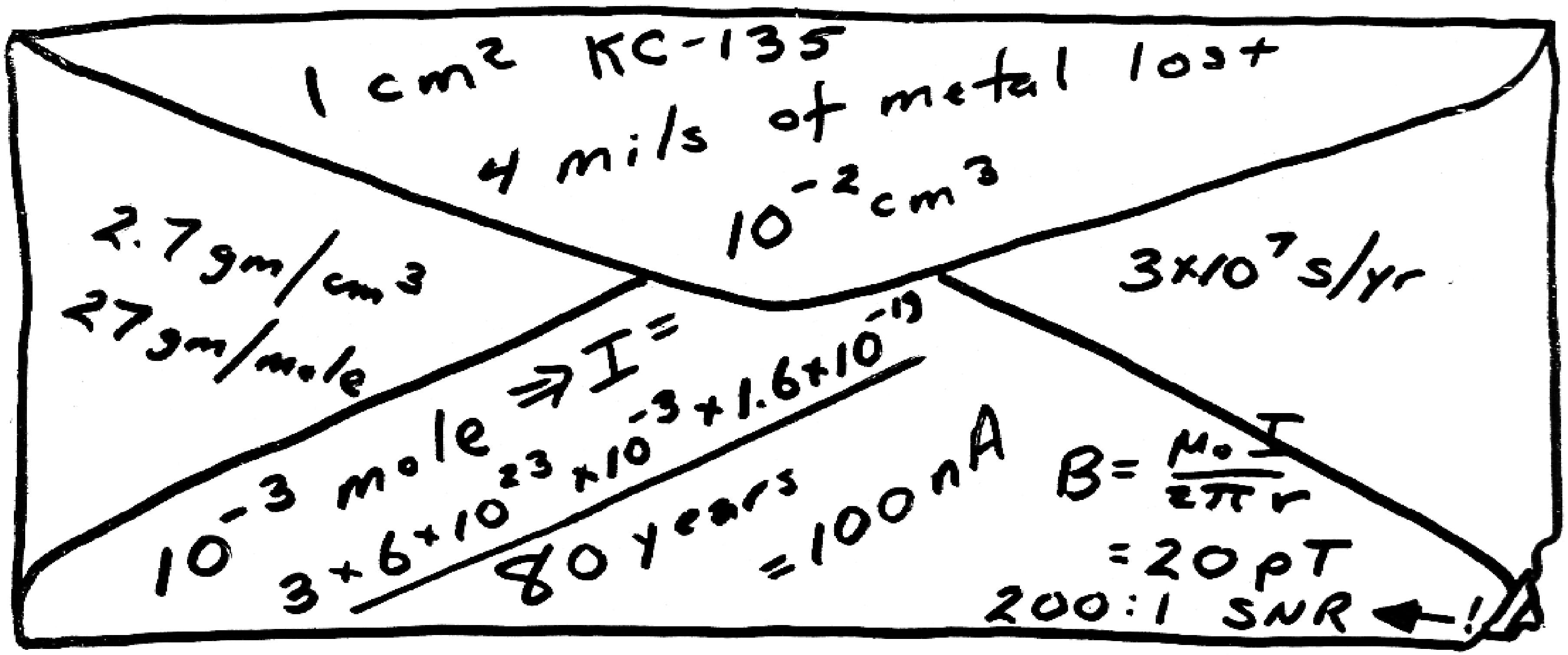
MAGNETIC IMAGE OF CRACKS ADJACENT TO RIVETS

(Using Depth-Selective Technique)




1 cm2 KC-135
4 mils of metal lost
10-2 cm3
2.7 gm/cm3
27 gm/mole
3x107 s/yr
10-3 mole ⇒ I =
3x6x1023 x10-3 x1.6x10-19
80 years
= 100 nA
B = μ0 I / 2π r
= 20 pT
200:1 SNR ←!

SQUID Measurements of Corrosion Activity

- The SQUID images the magnetic field produced by the galvanic currents associated with corrosion
- Bandwidth: DC to 5 kHz
- Sensitivity: 5 f $T/Hz^{1/2}$

Three Types of Corrosion

- **Pitting Corrosion**

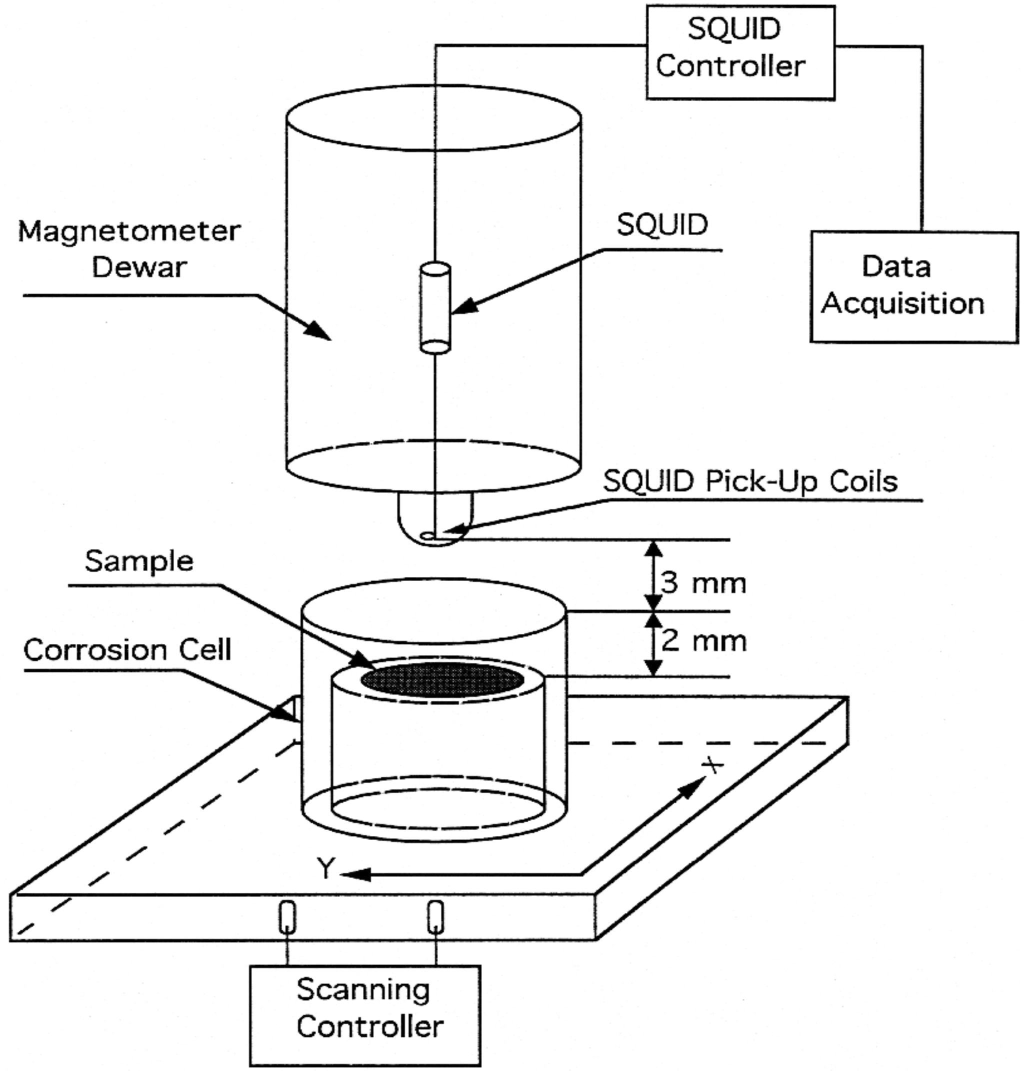
  1.5 mm thick 7075 aluminum alloy
  3.5% NaCl
  Differing Cu^{++} concentrations

- **Pitting/Intergranular Corrosion**

  1.5 mm thick 2024 aluminum alloy
  3.5% NaCl
  Differing Cu^{++} concentrations

- **Uniform Corrosion**

  1.5 mm thick 2024 aluminum alloy
  2 ml HF, 3 ml HNO_3, 5 ml HCI, 590 ml H_2O


SQUID Controller
Magnetometer Dewar
SQUID
Data Acquisition
SQUID Pick-Up Coils
Sample
3 mm
2 mm
Corrosion Cell
X
Y
Scanning Controller

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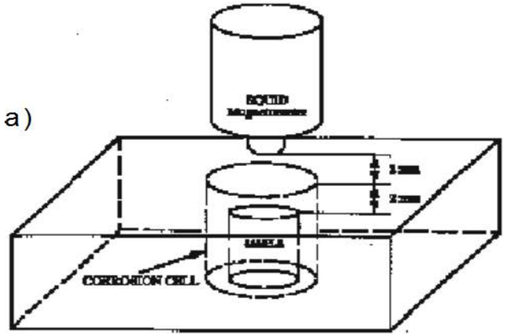
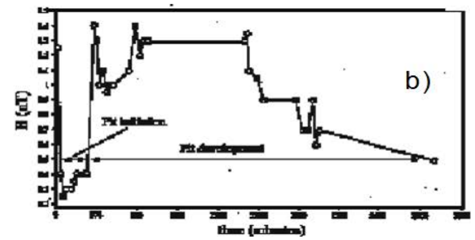
Active Pitting Corrosion

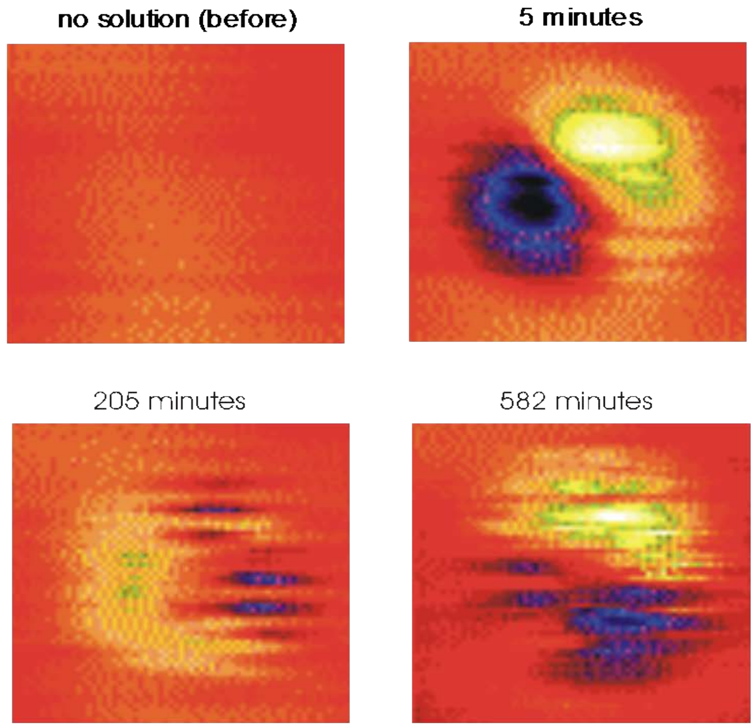
a)



b)



c)



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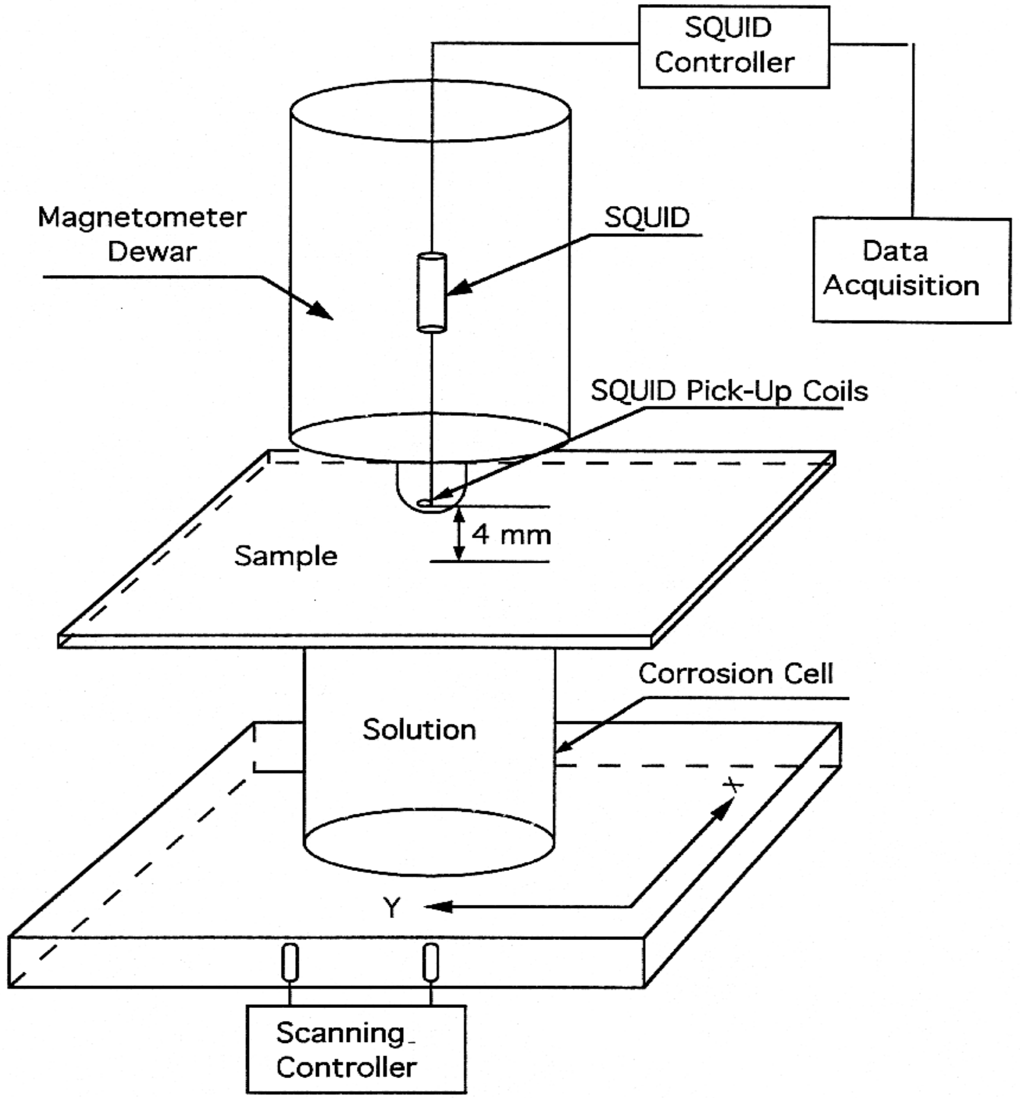

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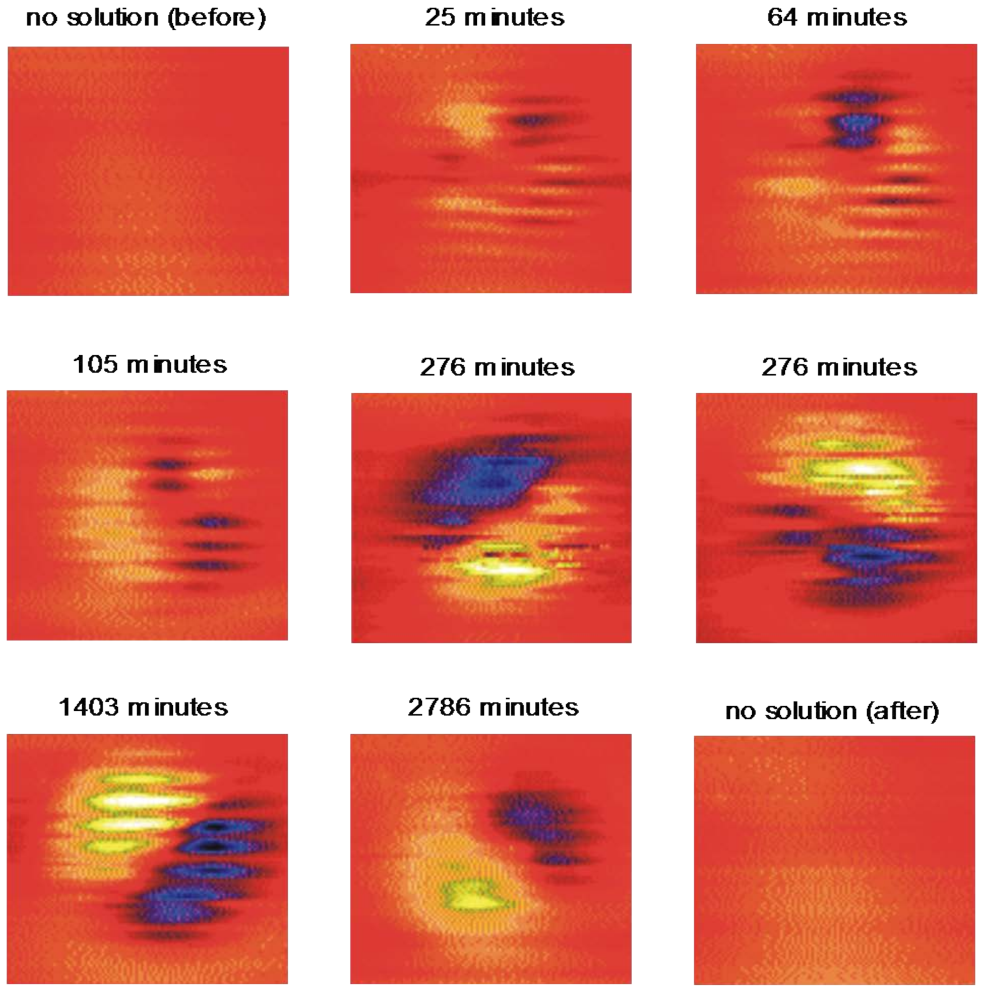
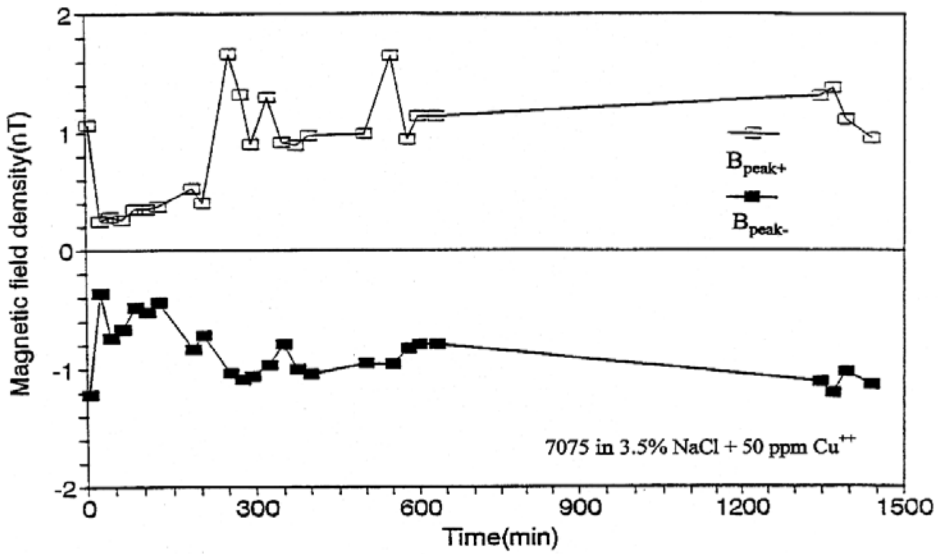
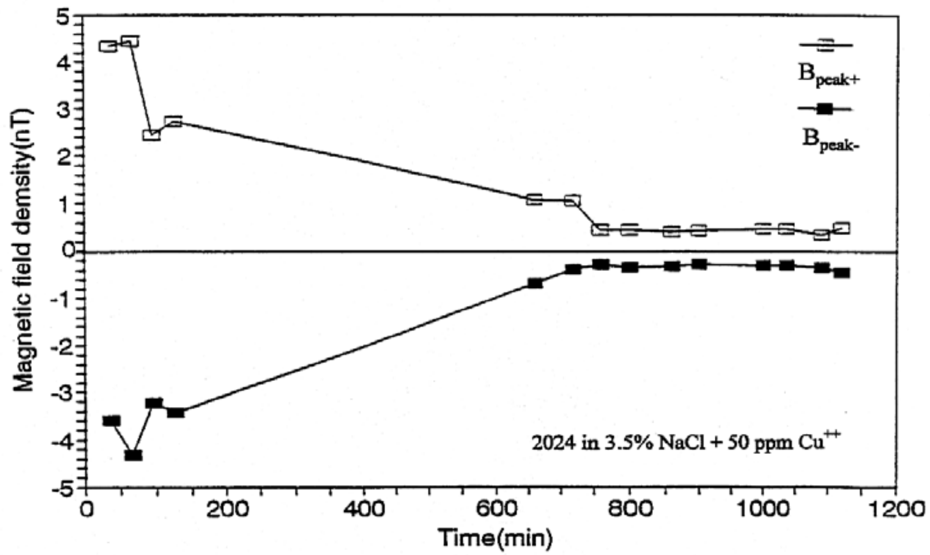
Active Corrosion

(7075 aluminum alloy in 3.5% NaCl + 50 ppm Cu^{++} solution)




Magnetic field demsity(nT)
Time(min)
B_{peak+}
B_{peak-}
7075 in 3.5% NaCl + 50 ppm Cu++


Magnetic field demsity(nT)
Time(min)
B_{peak+}
B_{peak-}
2024 in 3.5% NaCl + 50 ppm Cu++

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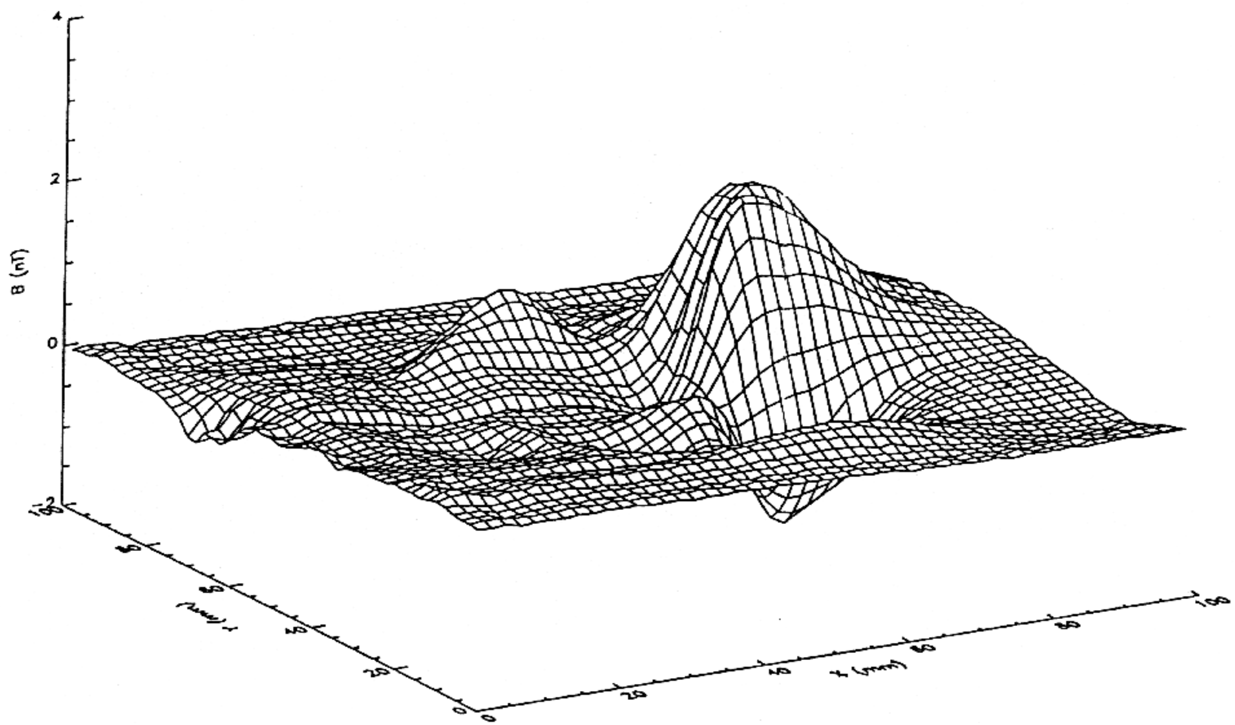
ACTIVE "UNIFORM" CORROSION

(<u>BOTTOM</u> surface of 2024 Al plate exposed to solution containing
2 ml HF, 3 ml HNO_3, 5 ml HCl in 590 ml H_20)



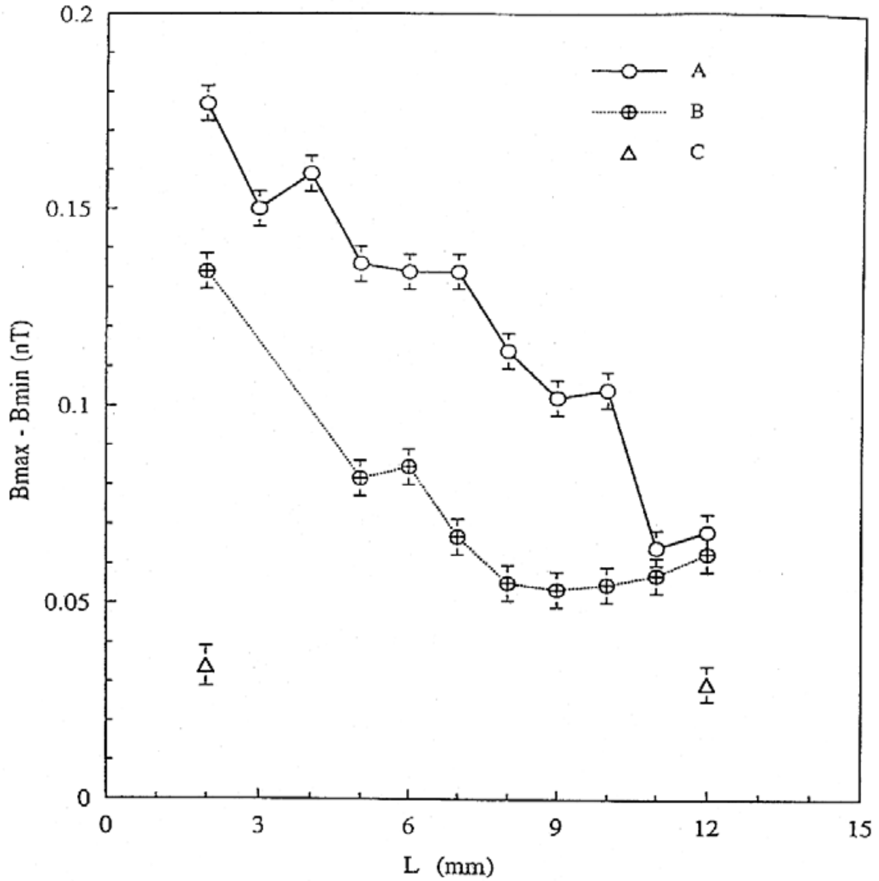


Fig. 3. Magnetic field strength versus L, between the SQUID and the specimen top-surface, for hidden active corrosion of a 3 mm thick, 70×70 mm 2024-T3.125 aluminum alloy plate which has a 50 mm diameter area exposed to 3.5% NaCl solution at the lower surface of the plate, on the side away from the SQUID magnetometer. A) Before the SQUID corrosion measurement, the specimen was exposed to 3.5% NaCl solution for 30 minutes. B) Before the SQUID corrosion measurement, the specimen was exposed to 1 ppm NaCl solution for 36 minutes, 100 ppm NaCl for 27 minutes, 1000 ppm NaCl for 66 minutes, 10000 ppm for 70 minutes, and 35000 ppm (i.e., 3.5%) NaCl for 53 minutes. C) Data obtained after removing the solution following the SQUID corrosion measurement.

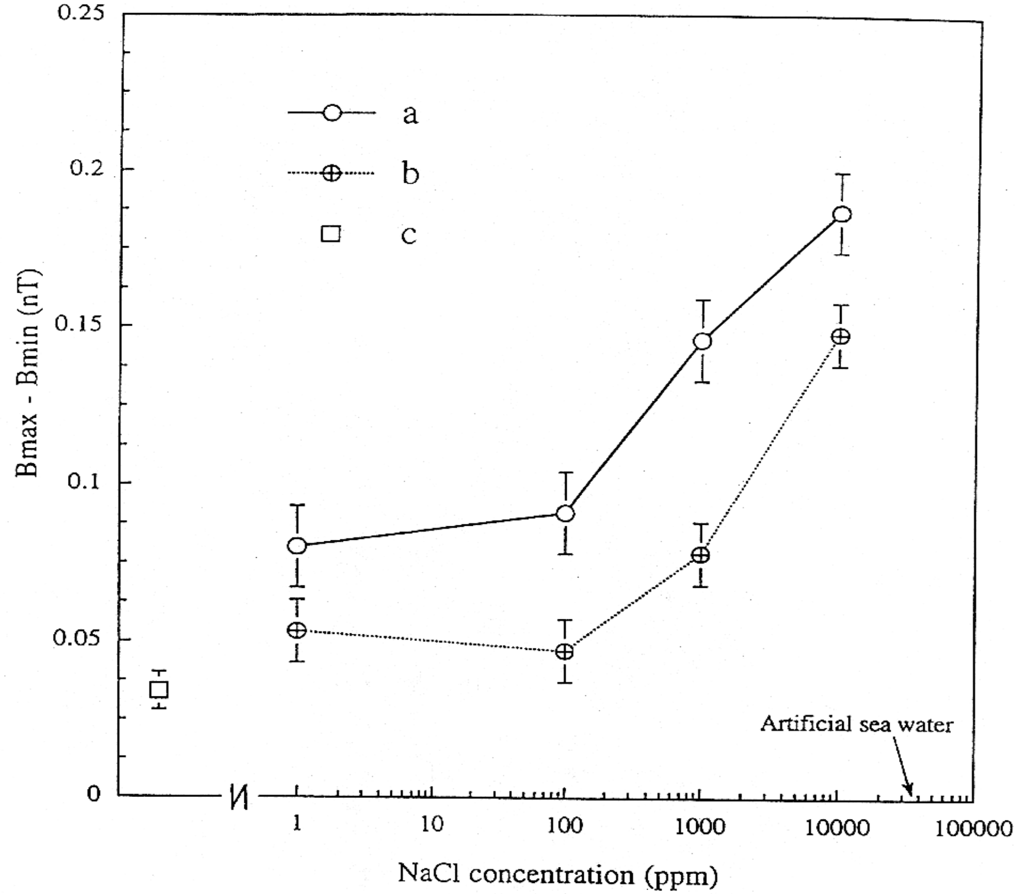


Fig. 2. Magnetic field strength versus NaCl concentration due to hidden active corrosion of a 3 mm thick, 70×70 mm 2024-T3.125 aluminum alloy plate which has a 50 mm diameter area exposed to differing NaCl solution at the lower surface of the plate, on the side away from the SQUID magnetometer. Distance between the SQUID pick-up coils and the specimen top-surface is 2 mm. Data was obtained a) over the period from 0 to 15 minutes, b) over the period from 16 to 30 minutes after the specimen was exposed to the solution, and c) after removing the solution following SQUID corrosion measurement.

Conclusions From Previous Studies

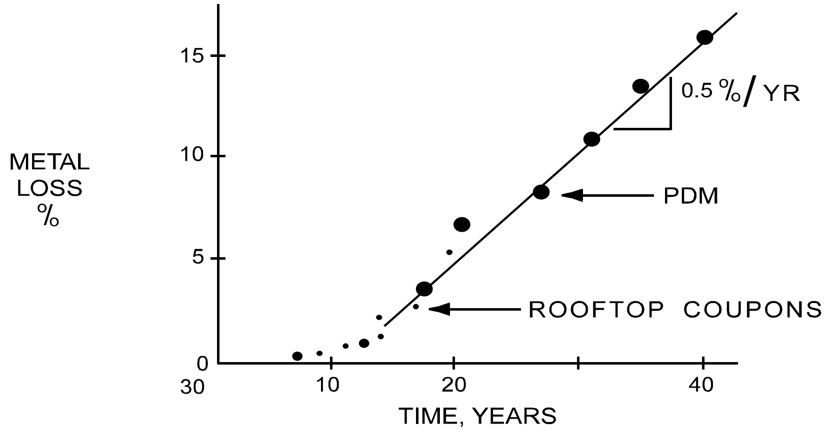
- SQUIDs are ideally-suited for the periodic, non-destructive analysis of corrosion test specimens where the corrosion activity is not directly accessible to a potentiostat, *e.g.*, corrosion that is hidden under a thick coating or one or more layers of metal.
- SQUIDs may be the only technique to detect these hidden currents non-destructively.
- Extending this to intact aircraft on the flight line may be difficult because of the yet-unaddressed problem from the magnetic field from the earth and ferromagnetic fasteners; but laboratory meas- urements should be invaluable for determining corrosion rates.
- SQUID measurements of deep corrosion damage on intact aircraft on the flight line are practical and commercially feasible.

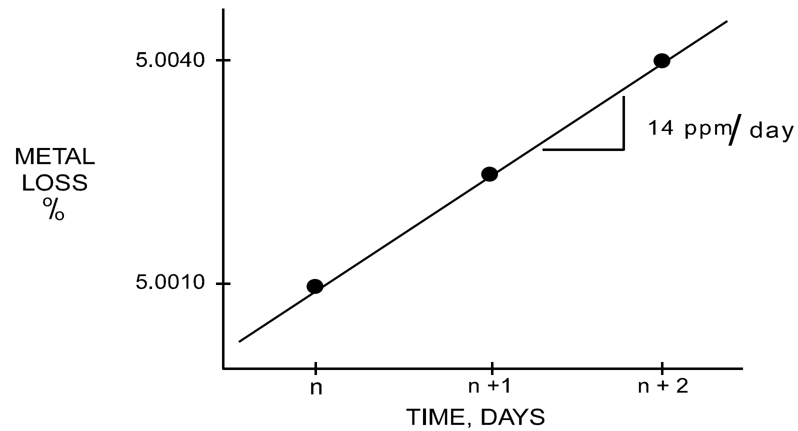
-Question-

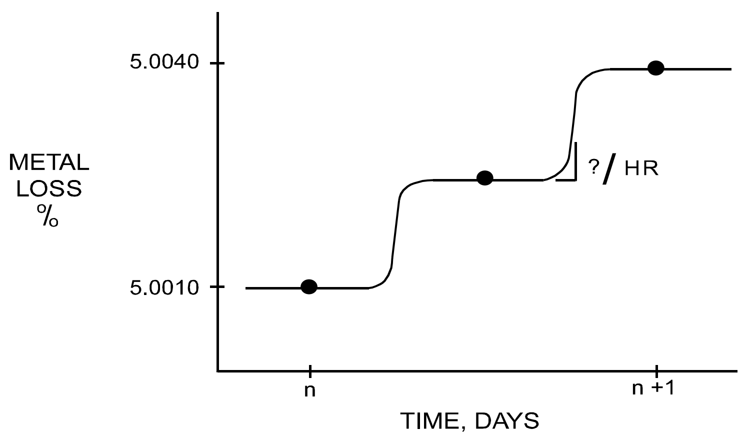
What is the instantaneous rate of corrosion?

How does it depend upon?

- Temperature
- Humidity
- Environment (salt, pollution, etc.)
- Cpc
- Maintenance
- Flight history


METAL LOSS %
15
10
5
0
30
10
20
40
TIME, YEARS
0.5 %/ YR
PDM
ROOFTOP COUPONS


METAL LOSS %
5.0040
5.0010
14 ppm/ day
n
n +1
n + 2
TIME, DAYS


METAL LOSS %
5.0040
5.0010
?/ HR
n
n +1
TIME, DAYS

NCI SQUID System

- Three-axis vector SQUID magnetometer
- Magnetic shield
- Scanning stage
- Computer control system
- Scanning and analysis software

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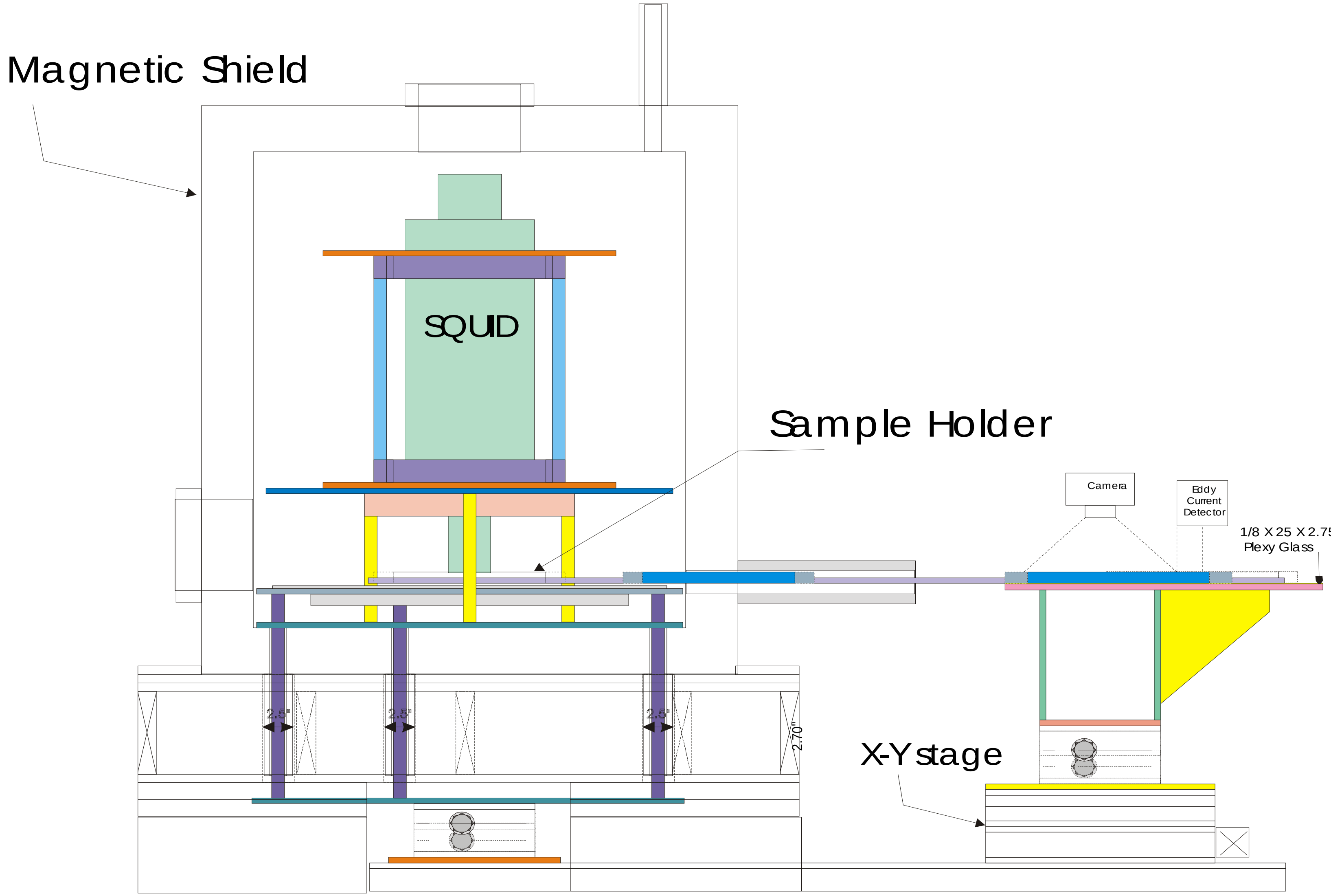
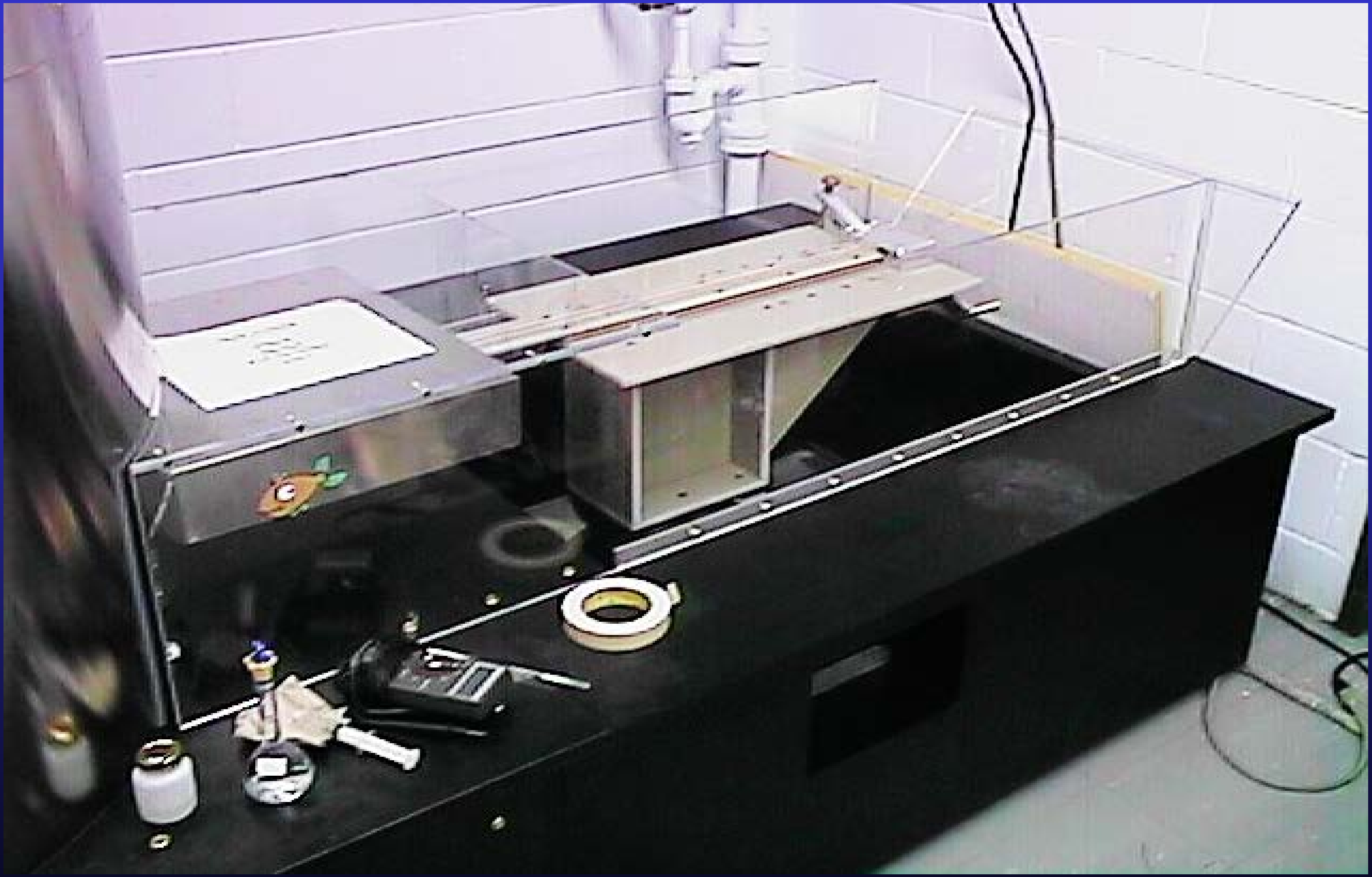
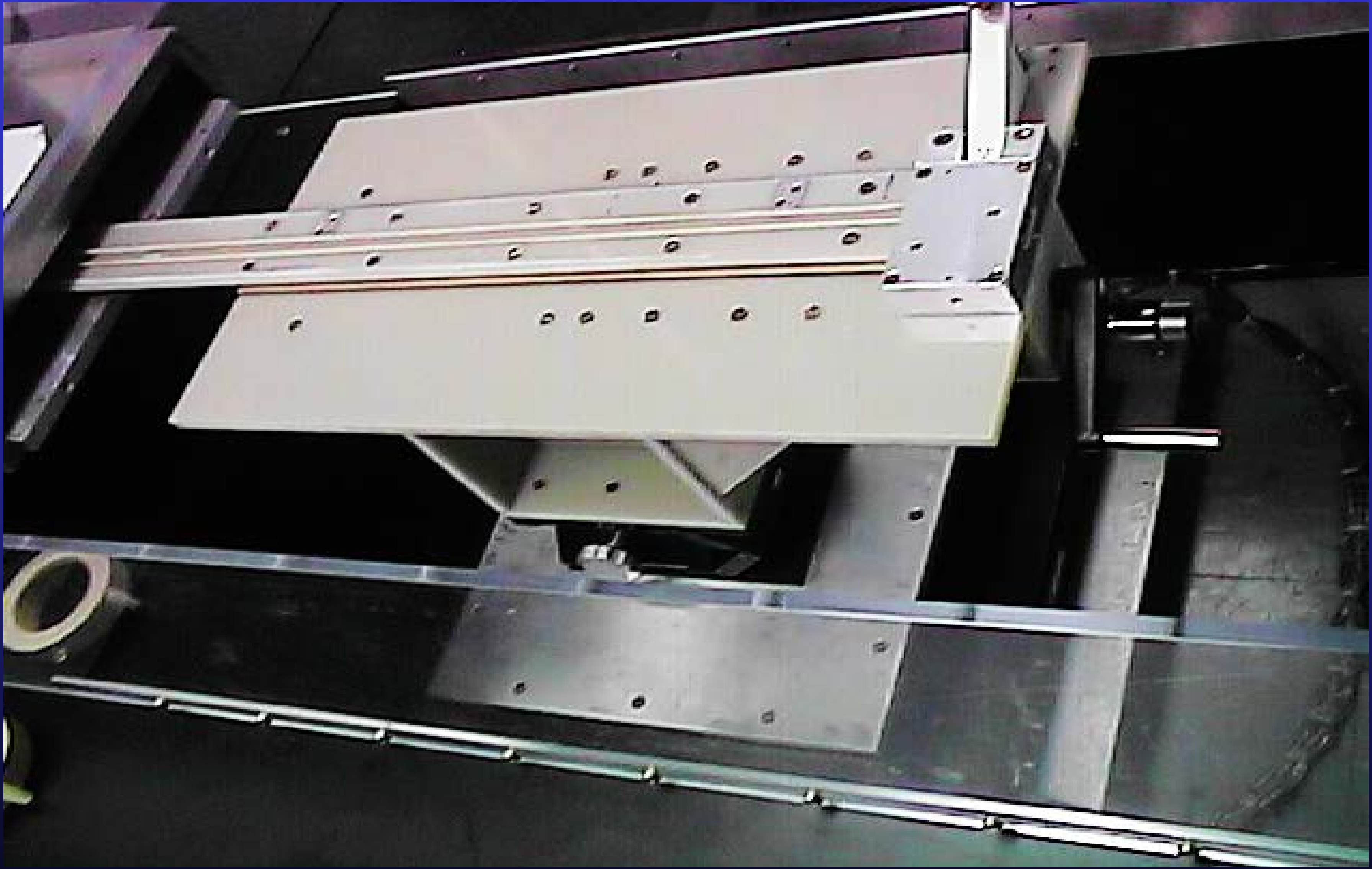
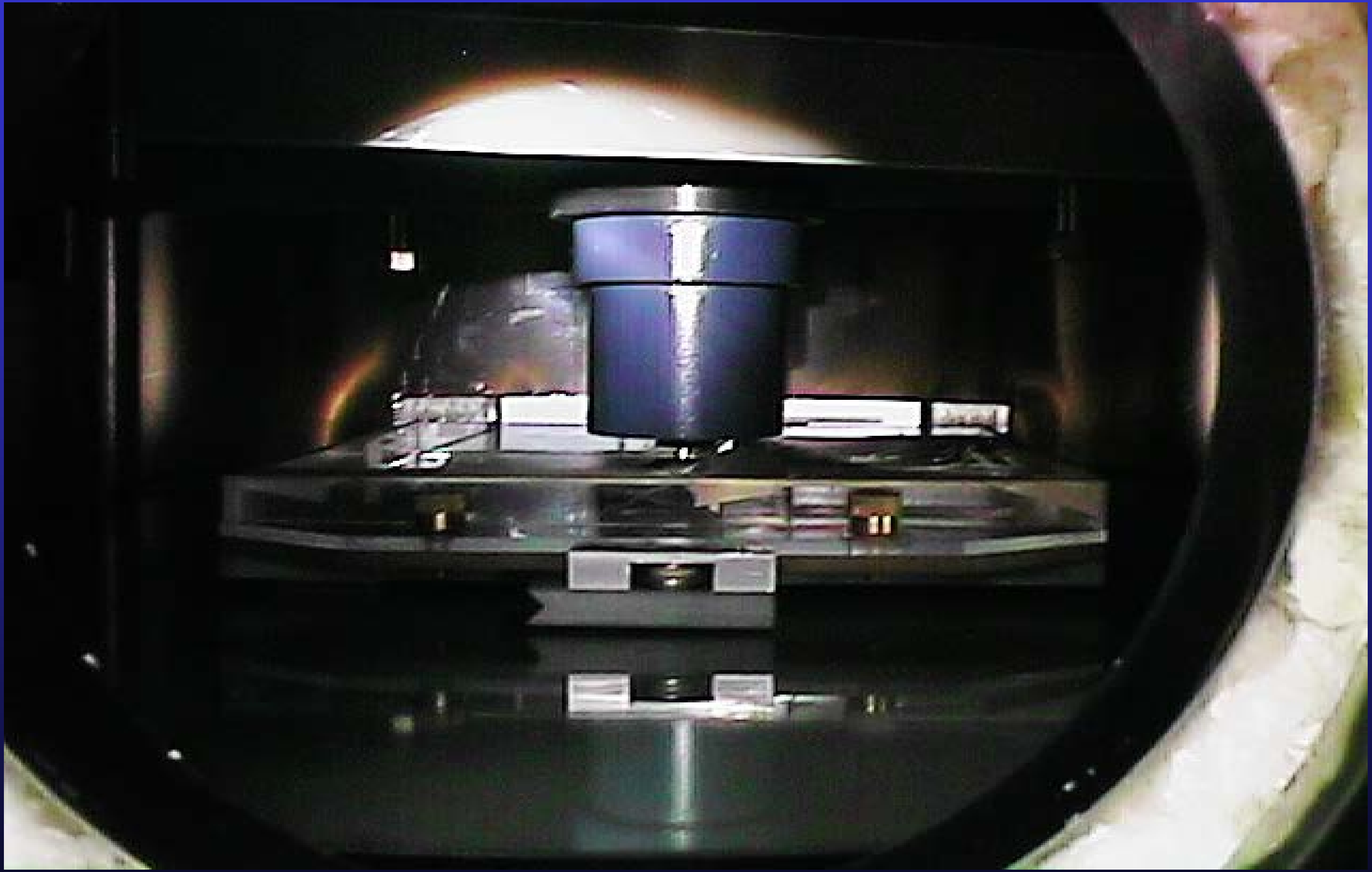
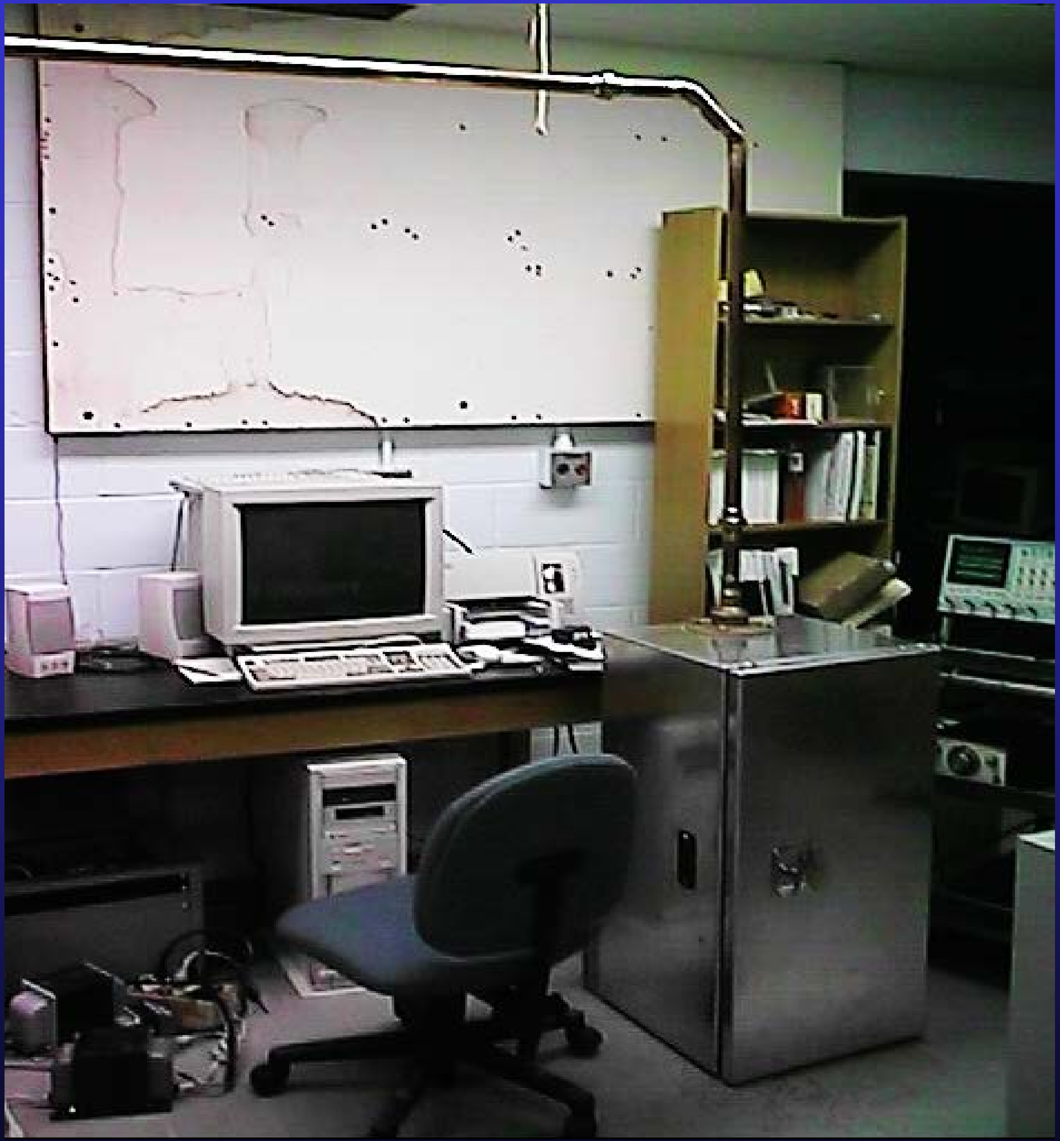




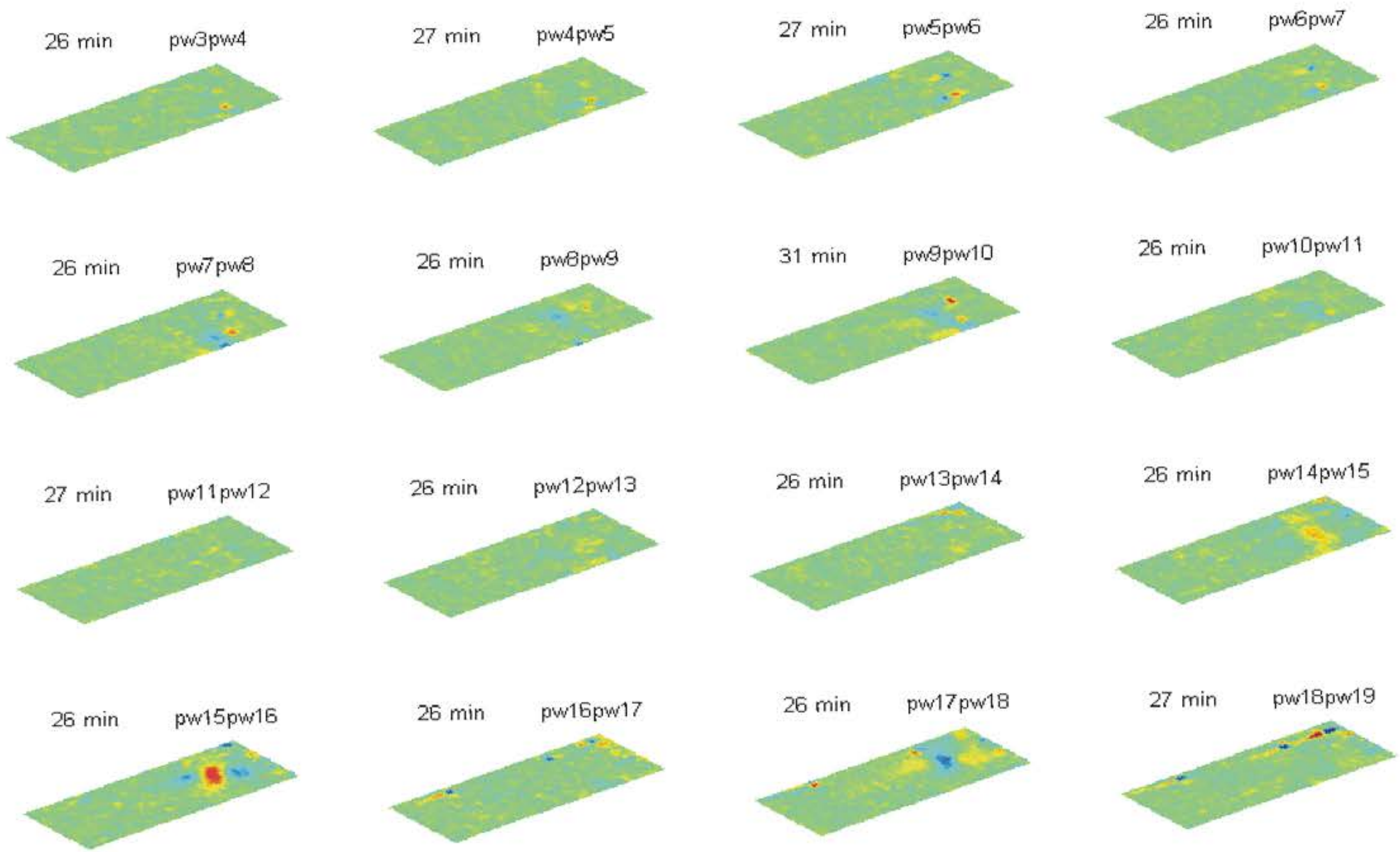




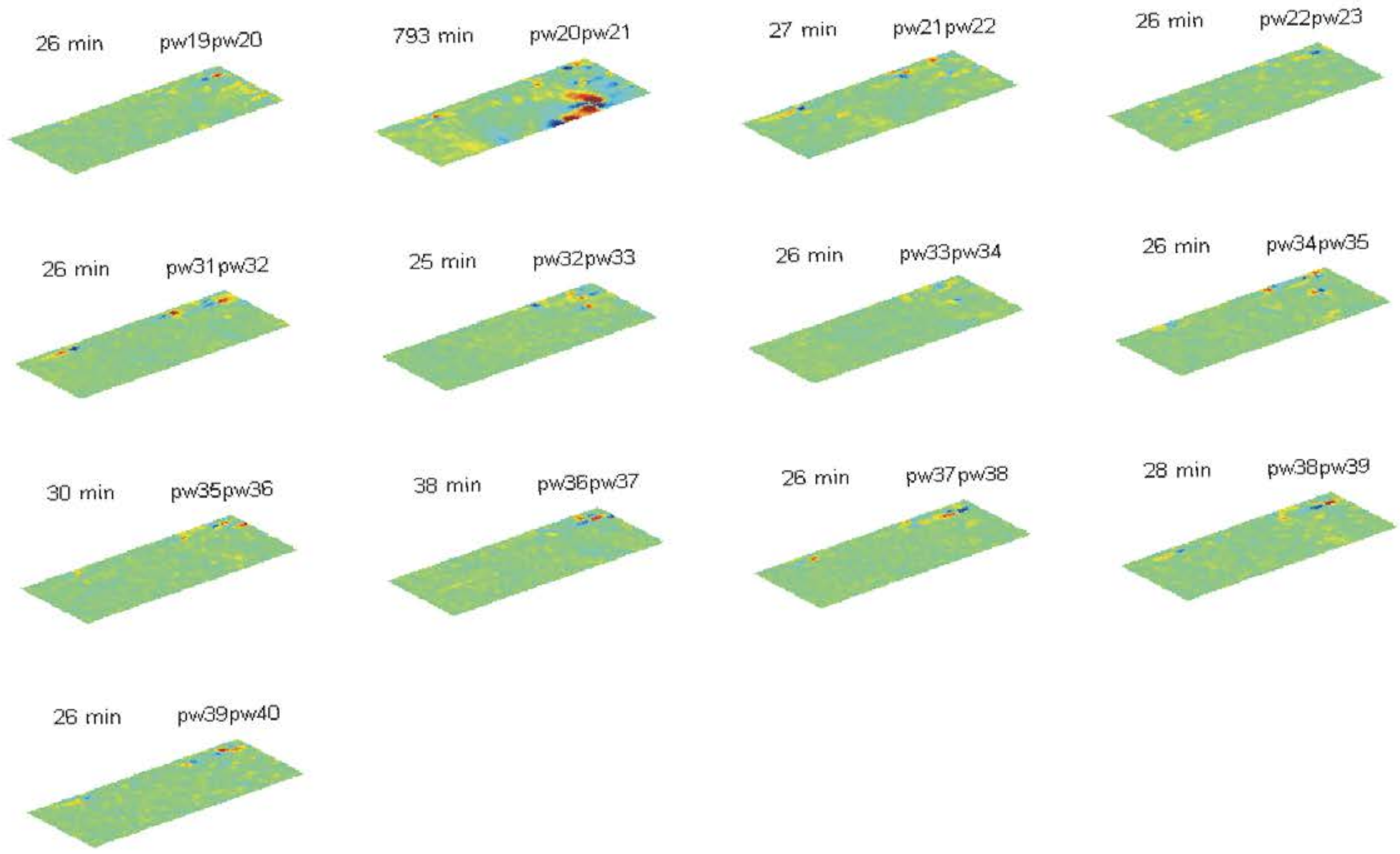


Difference Image 1

Corrosion Change vs. Time



Difference Image 2



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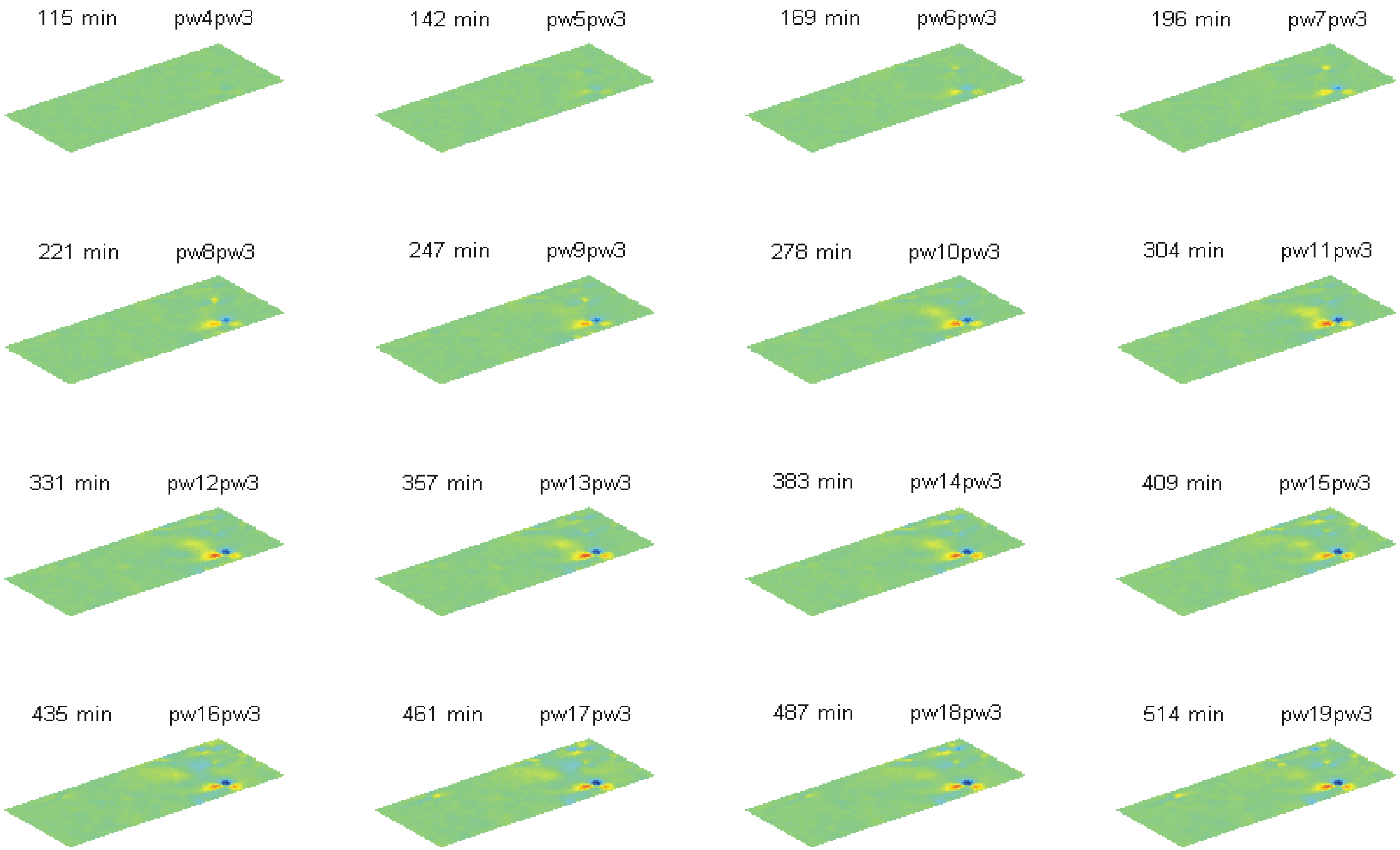
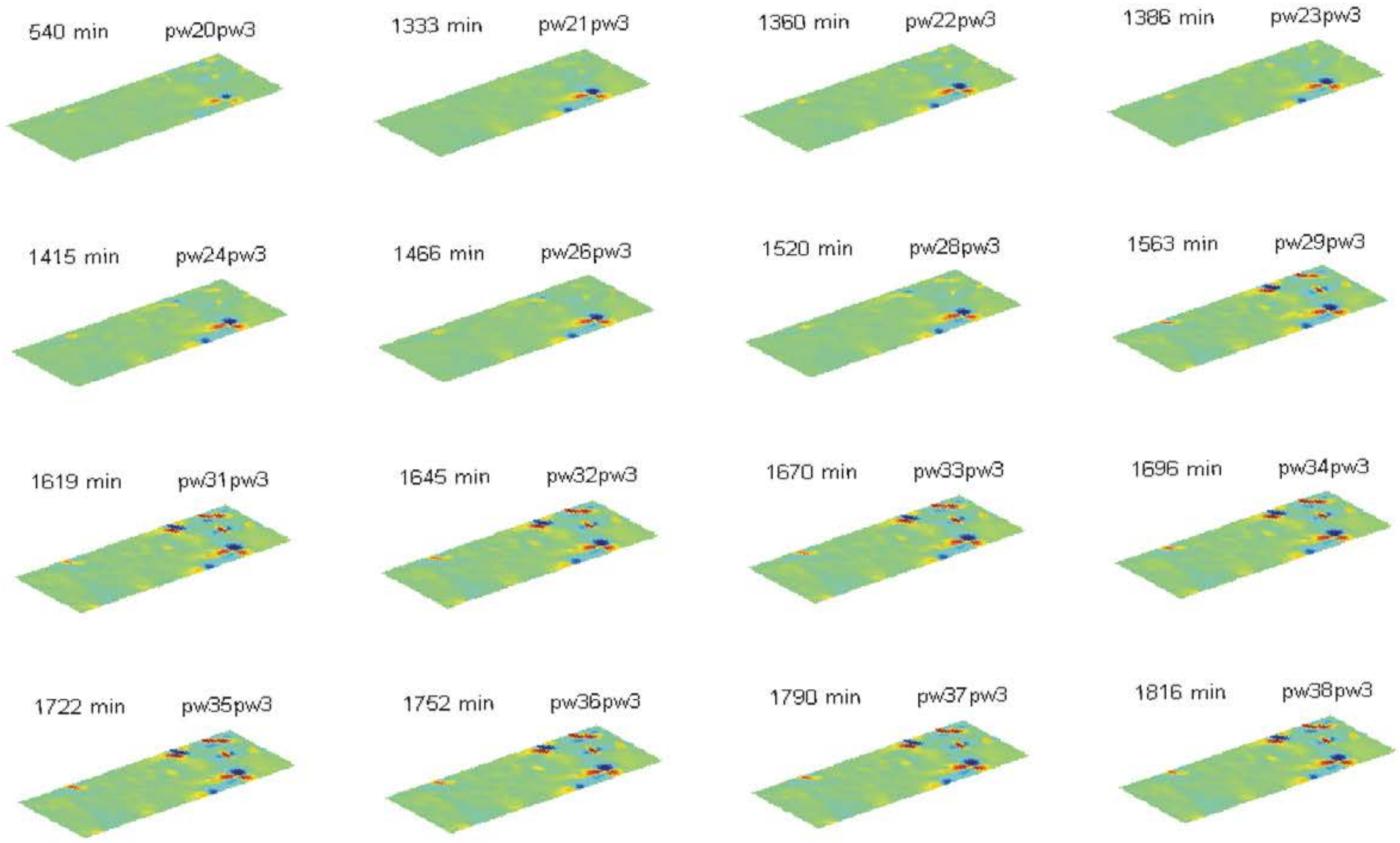
Corrosion Image 1

Corrosion Signal vs. Time



Corrosion Image 2



Corrosion Fatigue and Corrosion Predictive Modeling

Vanderbilt Work Plan

- Assess rate of corrosion in actual lap joints
- Examine the fundamental mechanisms that govern the generation of magnetic fields by corrosion currents

Initial Sample Tests

- **Contamination:** Determine the suitability of fabrication and sealing procedures in terms of magnetic contamination
- **Hydration:** Determine time course needed for the SQUID measurements
  - Weigh, hydrate, weigh, hydrate, weigh ...
  - Evacuate, weigh, evacuate, weigh …

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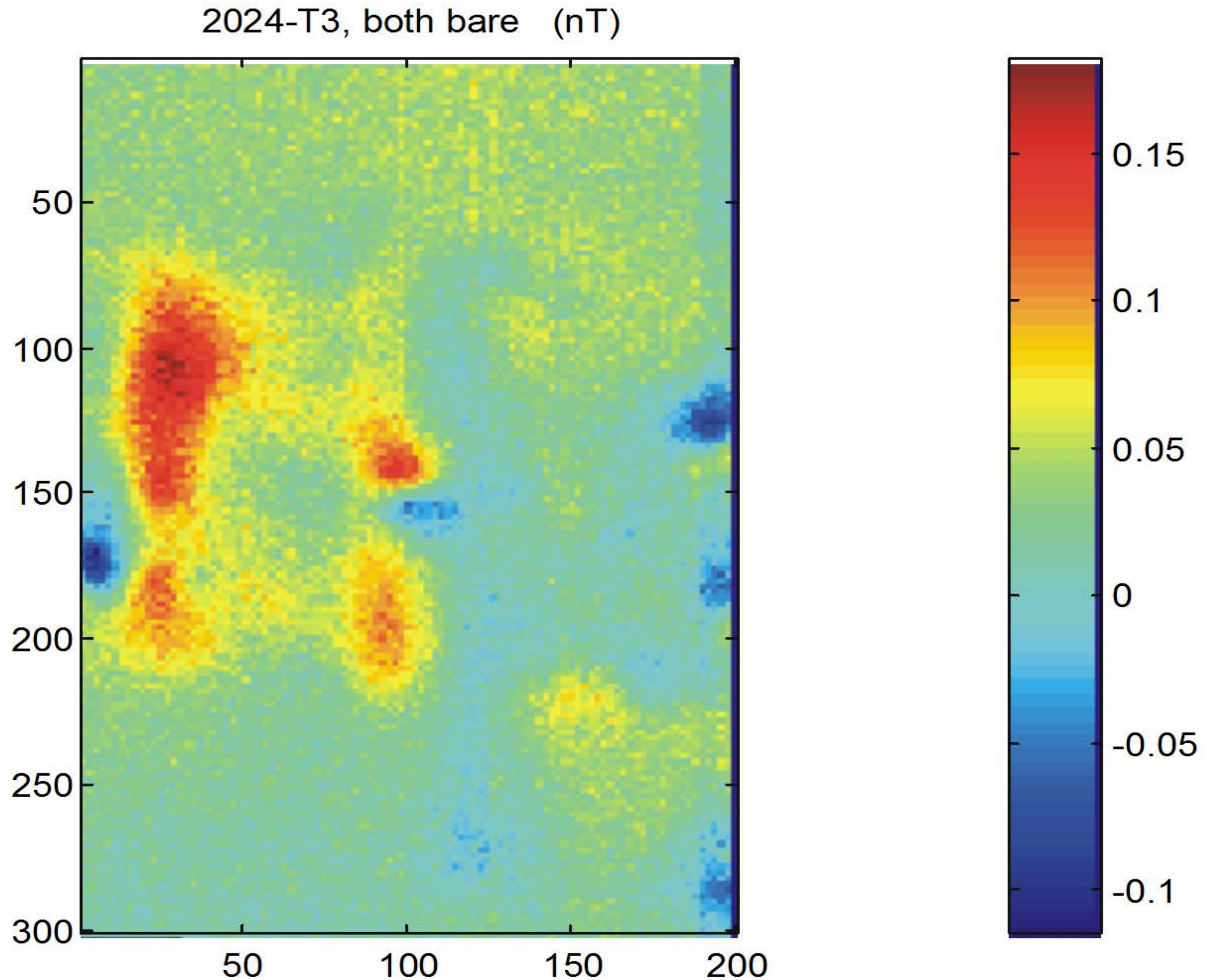

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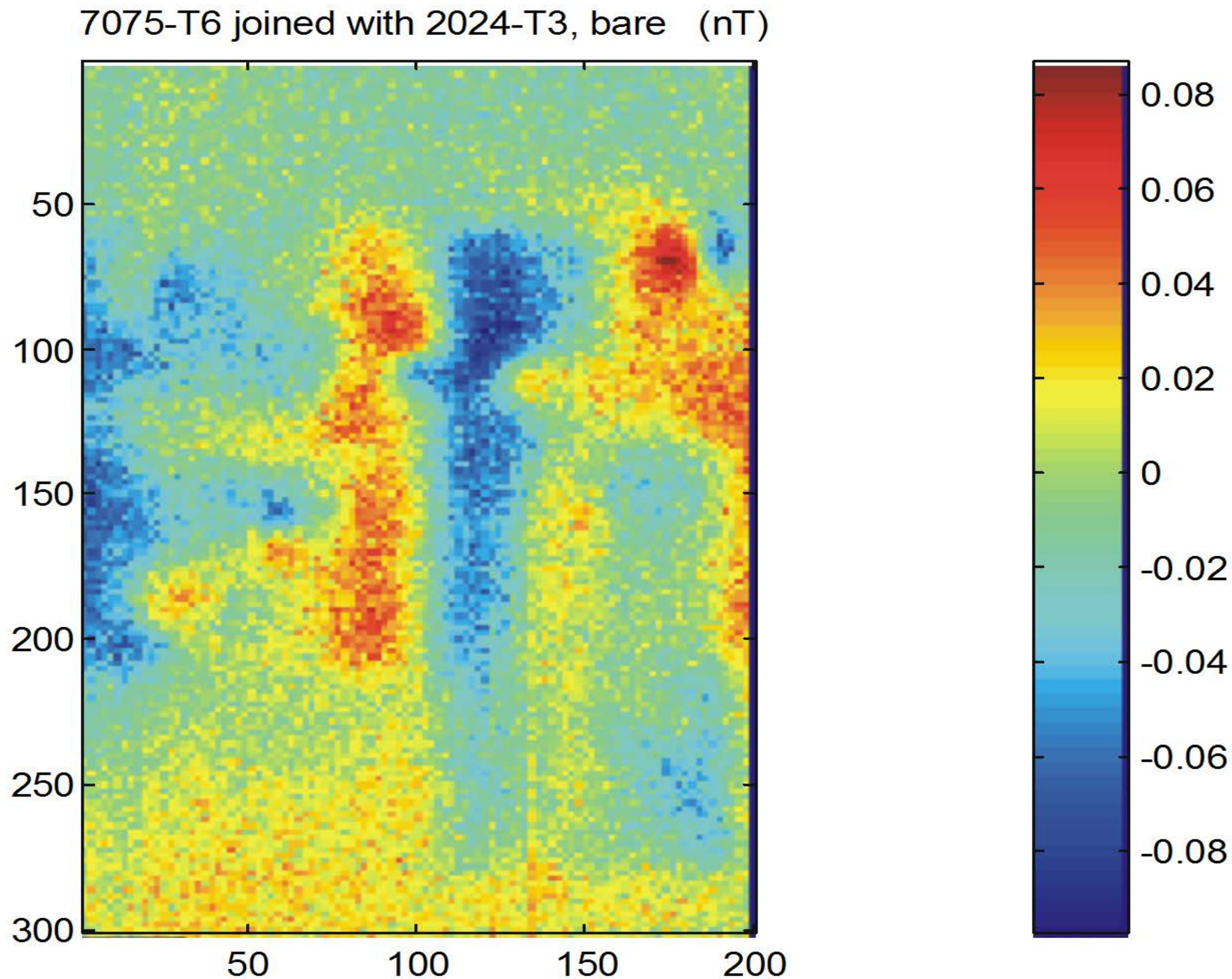

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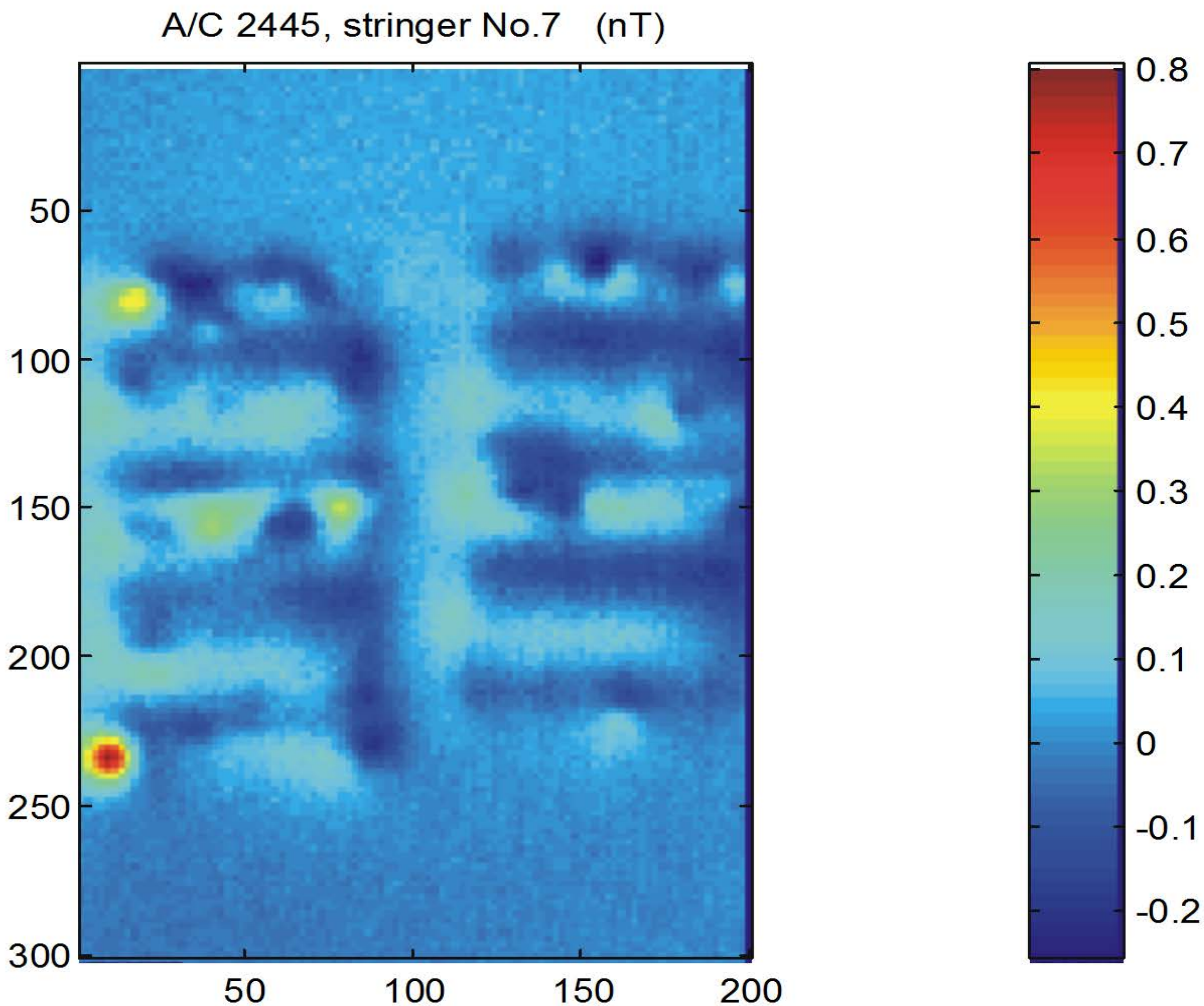


Calibration of Magnetic Signals:

Correlation of SQUID and Mass Loss

- The spatio-temporal correspondence between SQUID measurements and corrosion damage is unknown.
  - a) Accelerate corrosion
  - b) Image with SQUID
  - c) Weigh
  - d) Repeat (a)
  - e) Disassemble and quantify corrosion

Action: Devise protocol for accelerated corrosion

SQUID Testing for Precorroded Joints

- Evacuate samples of 24 hrs at 125 F
- Weigh
- Baseline SQUID measurements
- Rehydrate for 24 hours with H_2O
- Reweigh
- Retest with SQUID …. repeat

Action: Choose other solutions to study effect of atmospheric conditions

Corrosion Versus Temperature

- Corrosion will be observed in selected samples at a variety of temperatures.
  Action: Determine range of temperatures

- Freeze sample to halt corrosion and identify magnetic contamination

Calibration of Magnetic Signals:

Spatial effects in signal production

- If the source is random dipoles, then the fields of each dipole will partially cancel

$$B(z) = \mathrm{A}\ z^{n}\,\mathrm{e}^{-k/z}$$

- Use corrosion patterns on polycrystalline aluminum samples to control *k*
  - Copper surface patterns (dots, lines)
  - Different durations of heat treatment
- Differing sample thicknesses

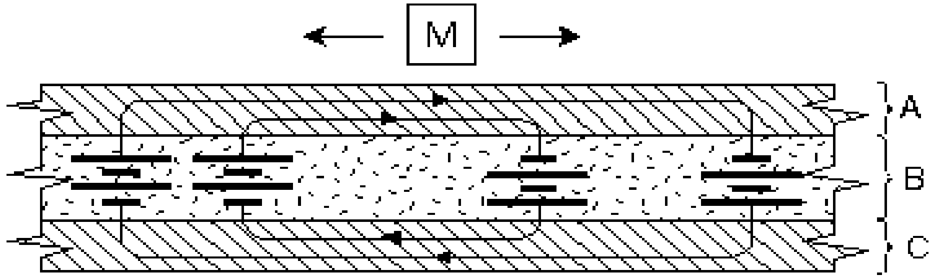
Calibration of Magnetic Signals:

Mechanism of signal production

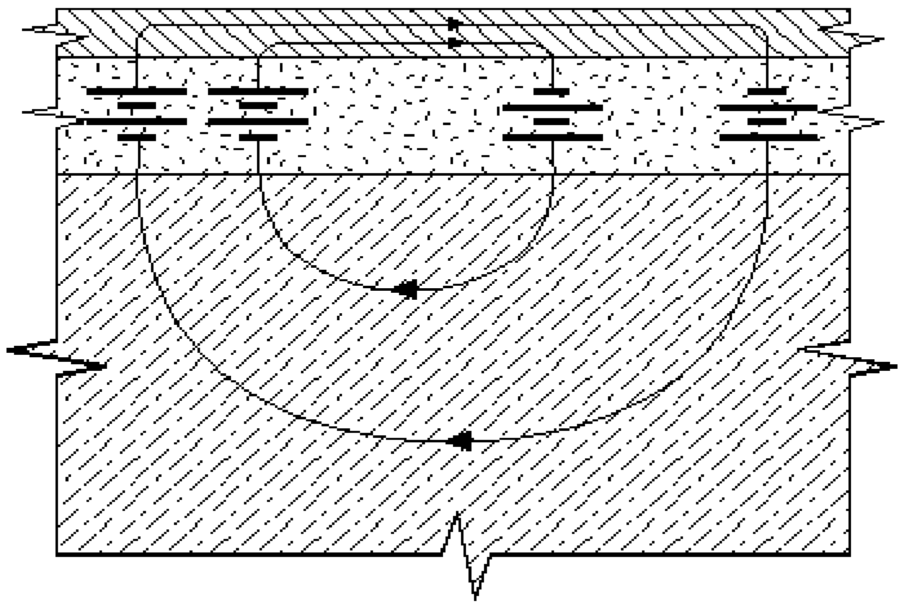
- In the simplest theory/model, an unbounded corroding lap joint is magnetically silent.
- We see clear magnetic signals that vary over space and time.
- The simplest theory/model is therefore wrong.
- What is the correct theory/model?

THE SIMPLEST MODEL

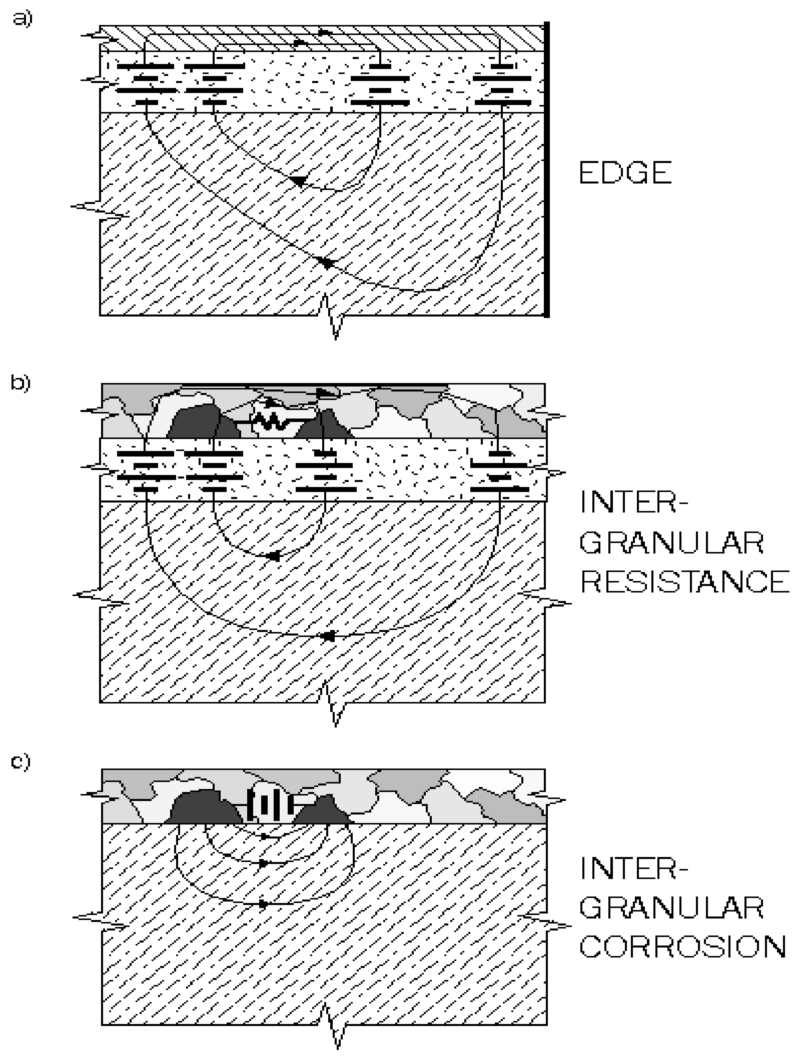
a)



b)



MORE REALISTIC MODELS



Summary

- SQUIDS can map the rate of corrosion inside a lap joint sample.
- The signals are not yet calibrated in terms of rate of mass loss.
- Calibration procedure designed
- Uncalibrated signals can still elucidate factors that affect rate.
-  

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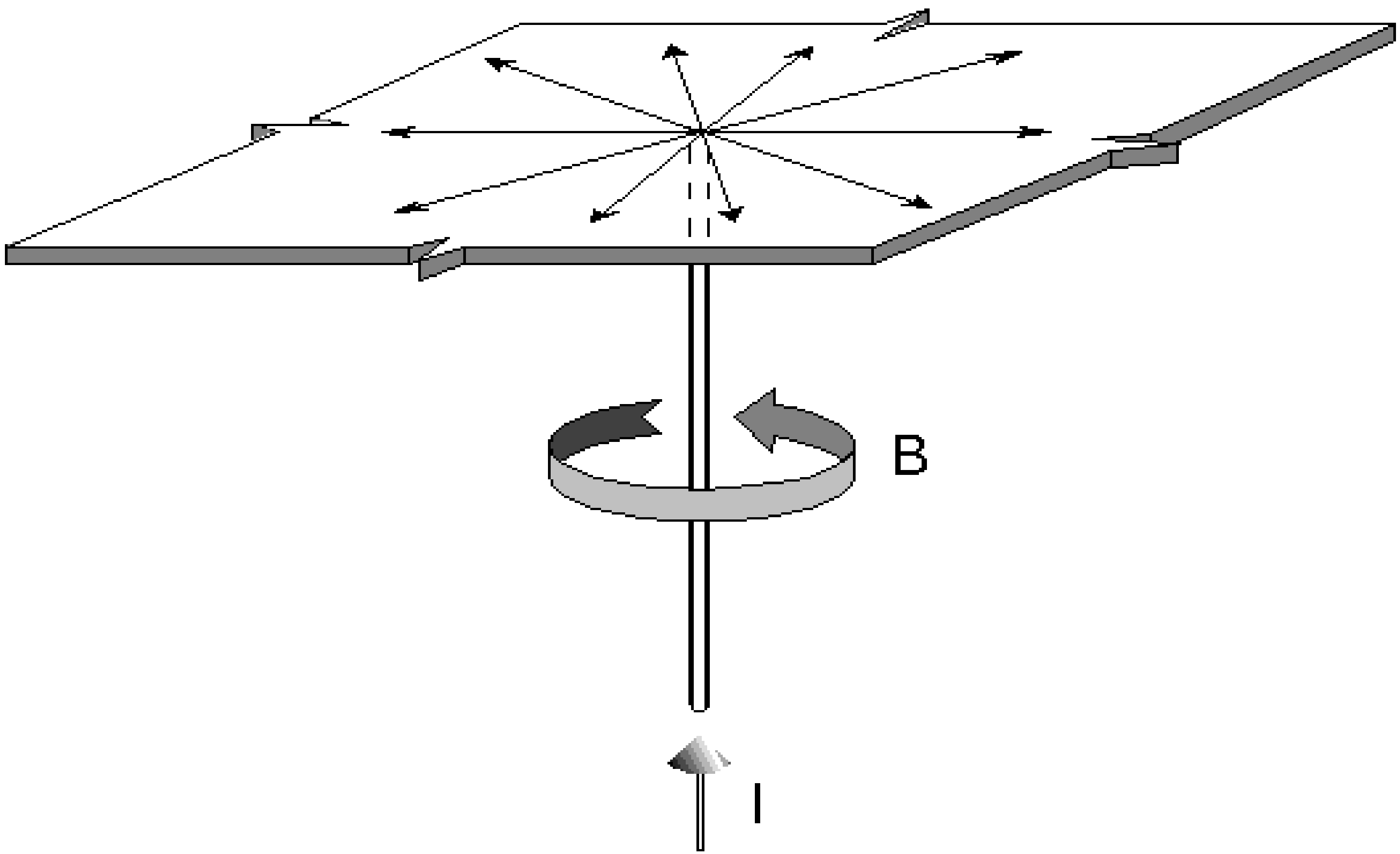

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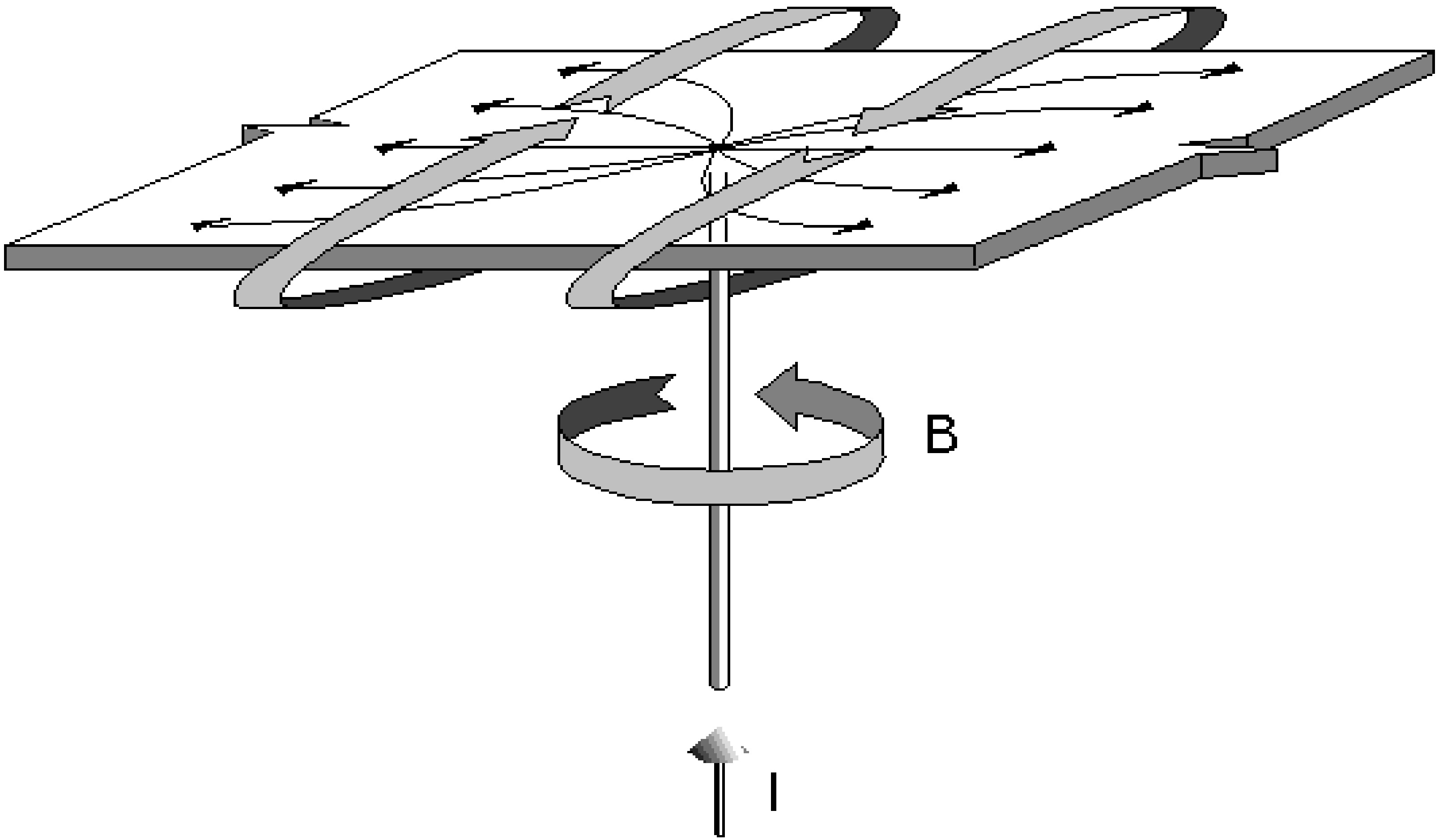

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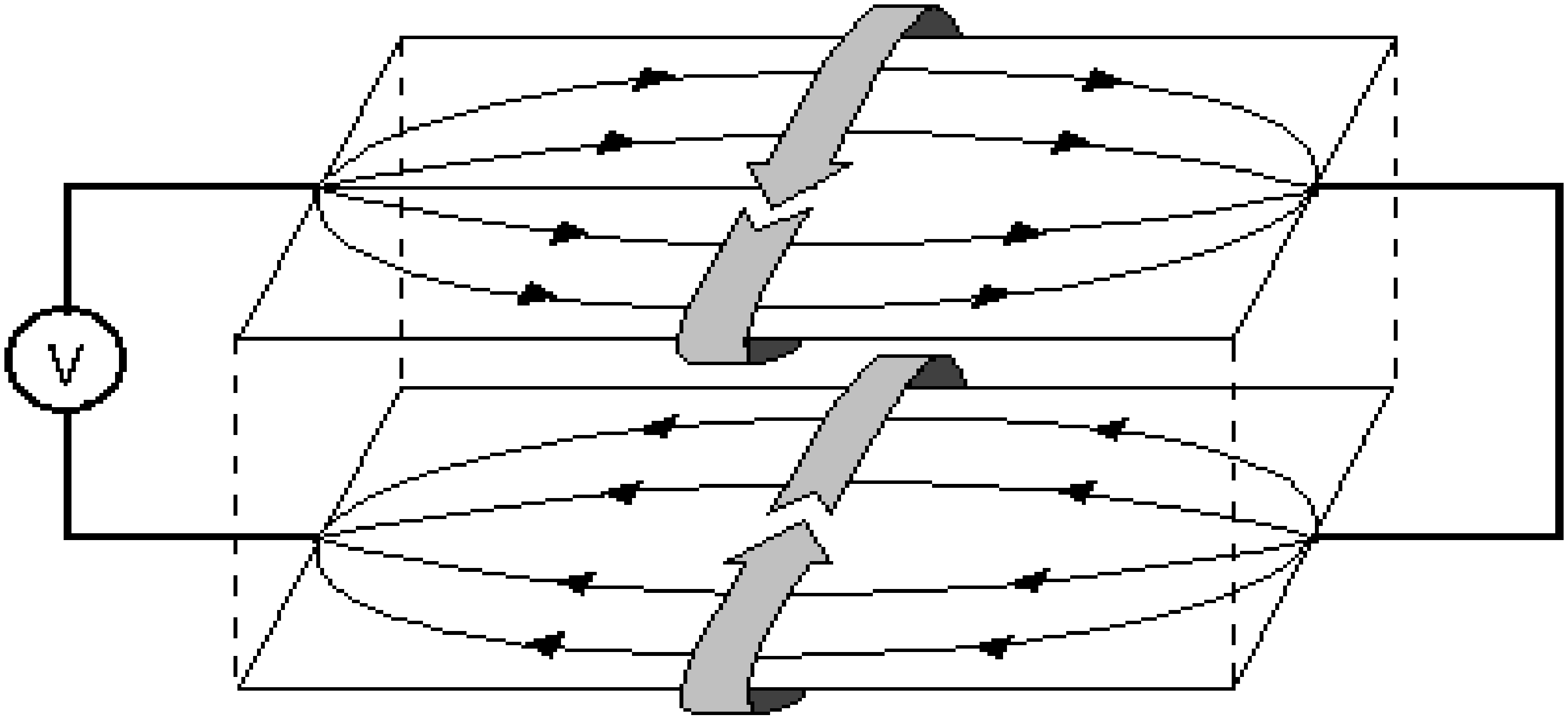

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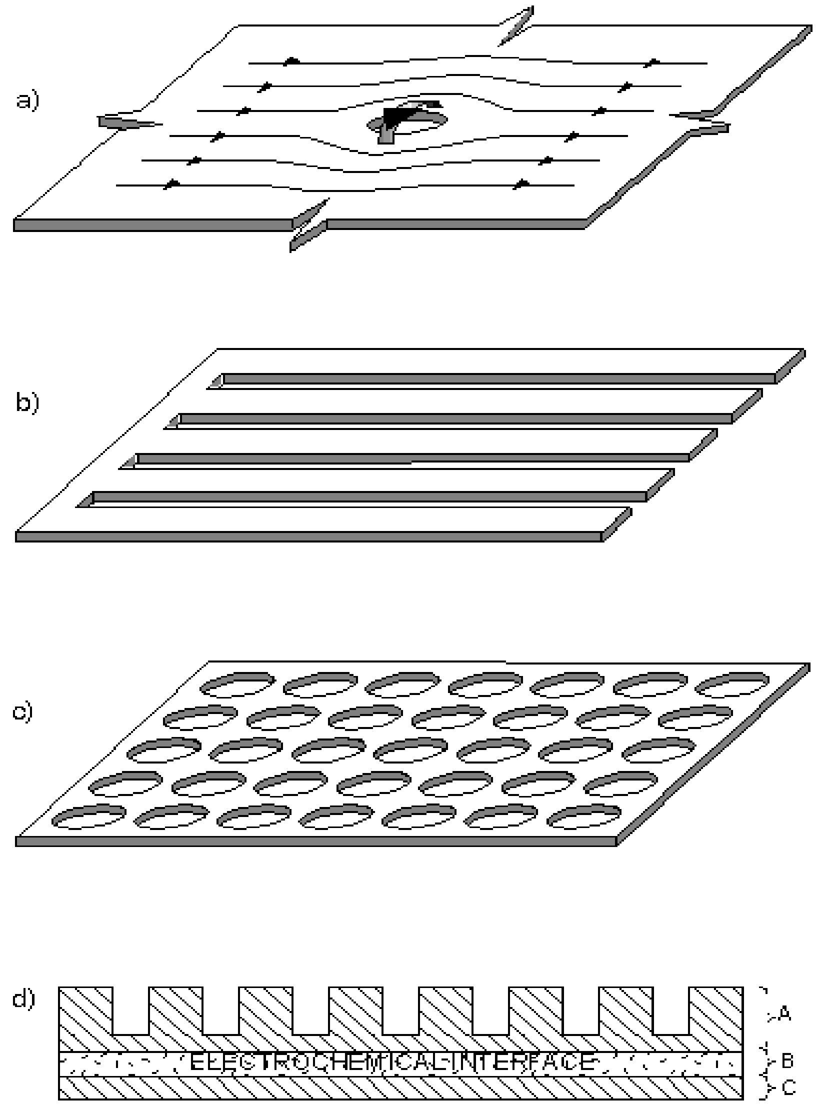
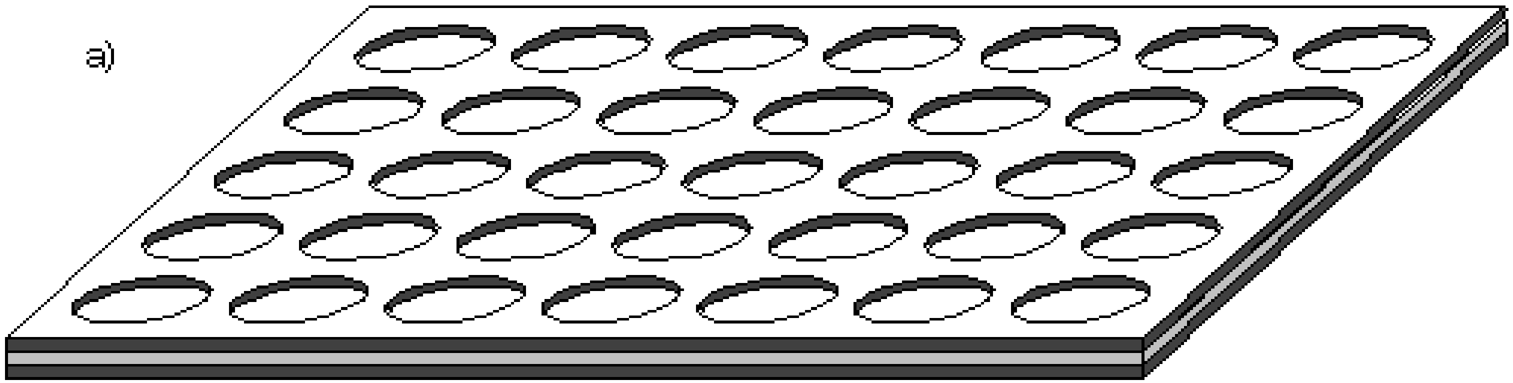
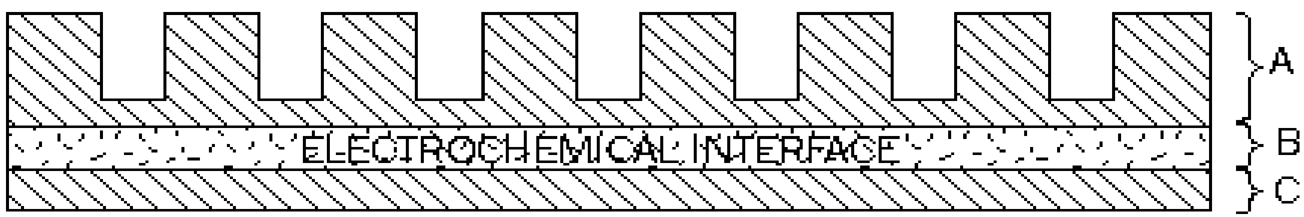


a)



b)



Calibration of Magnetic Signals:

Effects of Inhomogeneities on Signal Generation

- Machined inhomogeneities
- Correlation of SQUID results with scanning impedance bridge
- Mathematical model of magnetic fields from corrosion

Hardware Development

- Sample Chambers
  - Water-jacketed, temperature-controlled
  - Instrumentation: thermistor, hygrometer
  - Vacuum drying?
- Sample Design
  - Kinematic for accurate repositioning; no additional corrosion sites.
- Scanning Stage