Corrosion Protection Mechanisms of Rare-Earth Compounds Based on Cerium and Praseodymium

Project Number (WP-1618)

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Brief To The Scientific Advisory Board

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Problem Statement

- Corrosion and oxidation cost DoD ~$20 billion annually
  - Cost is >$100,000 per aircraft per year

- Recent OSHA regulations will lead to significant increase in the cost of compliance for application/removal of chromated coatings
  - Cr^{6+} is toxic and carcinogenic

- Rare-earth compounds are proven corrosion inhibitors
  - Compounds used in commercial/DoD products

- Little is known about the protection mechanisms of rare-earths

Technical Objective

To develop mechanistic models for the corrosion protection of metallic substrates by cerium-based conversion coatings and praseodymium-containing epoxy-polyamide primers

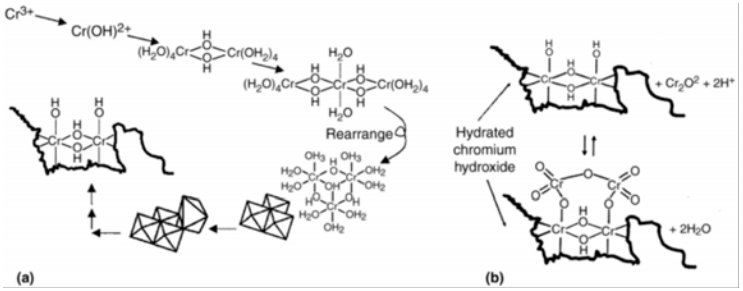
Technical Background

Chromates provide robust corrosion protection

- Protect a variety of metal substrates (Al alloys, steel, zinc, Mg alloys, etc.)
- Several effective coating types (conversion coatings, primers)
- Sensitivity to deposition parameters and environment

Protection mechanism has been studied extensively

a) Cr-hydroxide backbone forms by hydrolysis-polymerization-precipitation
b) Condensation of chromate species onto the backbone



Chromate coatings provide active corrosion protection

L. Xia and R.L. McCreery, J. Electrochem. Soc. 145(9):3083-3089 (1998)

- Cr^{6+} species dissolve from coating and transport to site of attack
- Passivating layer of Cr^{3+} oxide/hydroxide forms

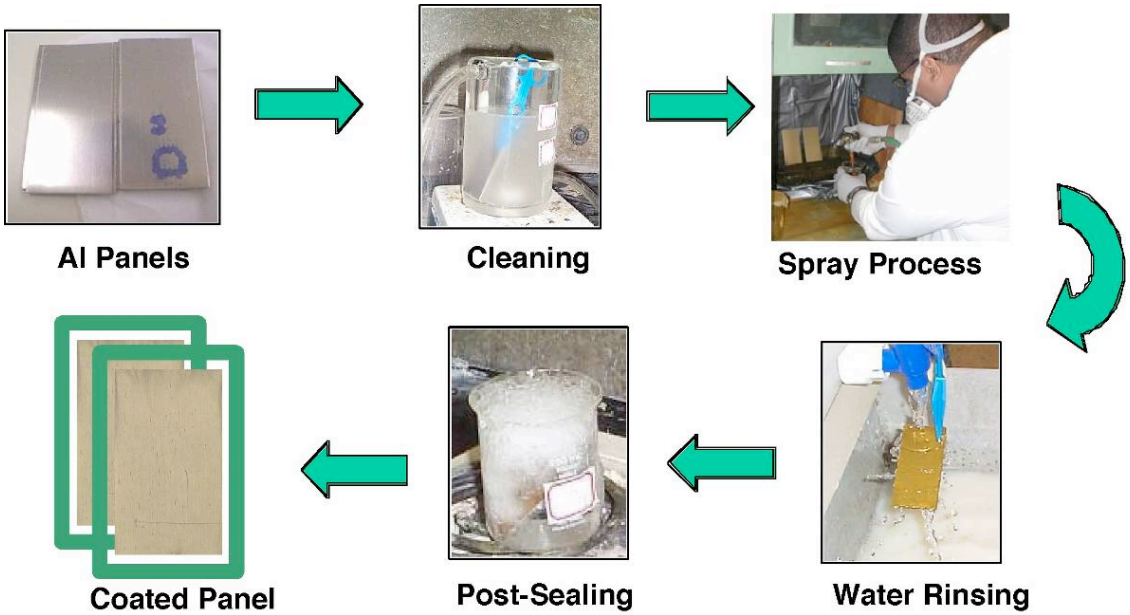
Technical Background

Non-chromate conversion coatings have been developed

- Trivalent chromium pre-treatment (TCP) qualified to MIL-DTL-5541
- Anodizing, oxy-anion analogues, phosphates, permanganates also studied
- Each capable of protecting specific alloys or metals

Rare-earth based conversion coatings have shown promise

- Originally developed by Hinton in the 1980s
- Spray, immersion, and electrolytic processes patented by UMR



UMR CeCC on 2024-T3 after 336 hours salt spray

Technical Background

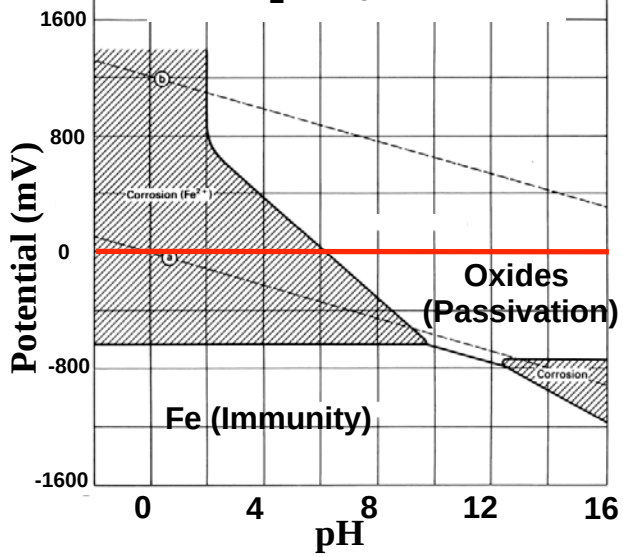
Coating deposition mechanism model has been developed

- CeCCs form by electrochemically driven precipitation reaction
- Phase stability in Ce-H_2O and Ce-H_2O_2 systems was needed
- E-pH diagram and precipitation studies led to identification of species in solution and forming during precipitation

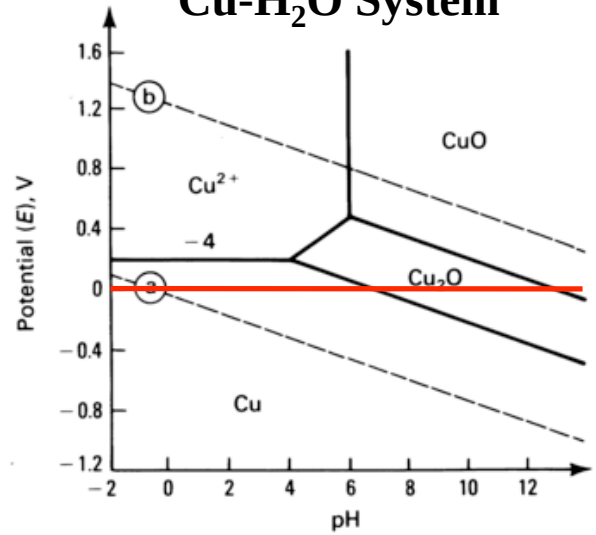
Mechanistic studies require knowledge of phase stability

- E-pH diagrams describe the effects of solution potential (E) and pH
- Also known as Pourbaix diagrams

Fe-H_2O System



Cu-H_2O System

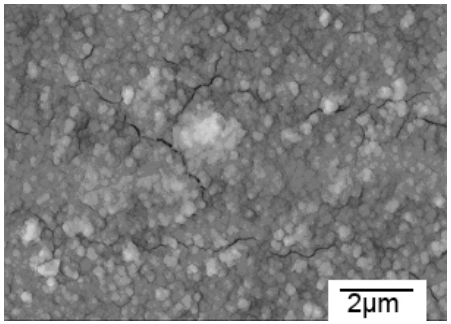


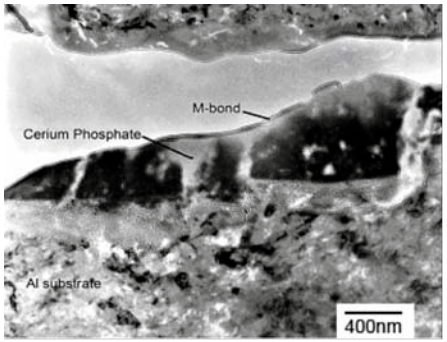
Technical Background

Ce-based conversion coatings can meet military requirements

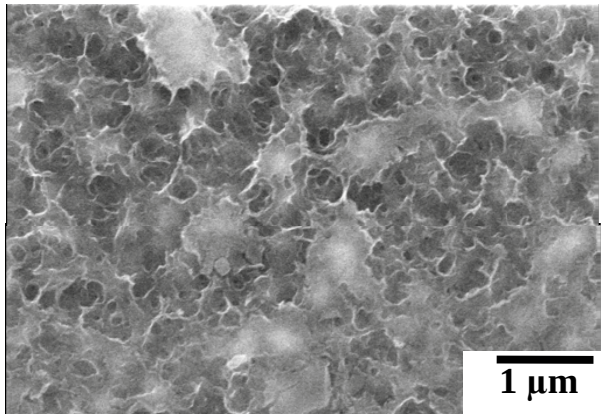
- Previous focus on deposition process
- Corrosion protection mechanism not studied

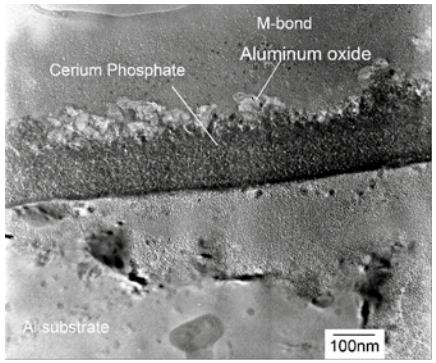
As-sealed CeCC on 2024-T3





CeCC after 336 hours salt spray





Technical Background

Pr-based inhibitors have been developed for primer coatings

- Inhibitor package developed and patented at UMR
- Deft licensed technology and developed/markets commercial products
  - High solids and water reducible formulations
- Deft primers qualified to MIL-PRF-23377 and MIL-PRF-85582
  - Currently used on F-15s (depot) and Apache helicopter (OEM)

F-15 coated with Deft 02GN084 non-chromate primer that uses a Pr-based inhibitor

Technician coating an Apache fuselage with Deft non-chrome primer

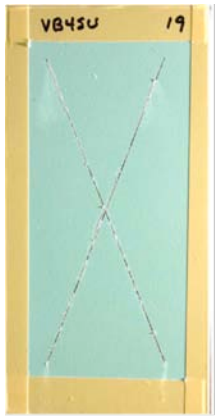
Technical Background

Pr-based primer provides protection equivalent to chromate

- **Best performance on CrCCs; passes 3000 hr salt spray test**
- **Performance poor on CeCC or other non-optimized pre-treatments**

CrCC
Cr^{6+} primer

CrCC
Pr primer



CeCC
Pr primer

Technical Background

Several conclusions can be drawn from previous work

- Rare-earth compounds are not inherently protective
  - Proper phase/compound and appropriate coating type required

- Coatings can provide protection that meets military requirements
  - Barrier protection over large areas
  - Demonstrated ability to protect scribed/damaged areas

- Rare-earth coatings are sensitive to process parameters
  - Substrate preparation, deposition process, post treatment

Successful models must account for the specific features that are critical to performance

- Protection requires proper combination of phase and coating type
- Mechanisms must be studied using phases/coatings that protect
- Process variables must be isolated and controlled

Technical Approach

CeCC
(fundamental studies are complete)

Pr-based Primer
(all steps needed)

Phase stability

↓

Coating deposition

↓

Characterization before, during, and after corrosion

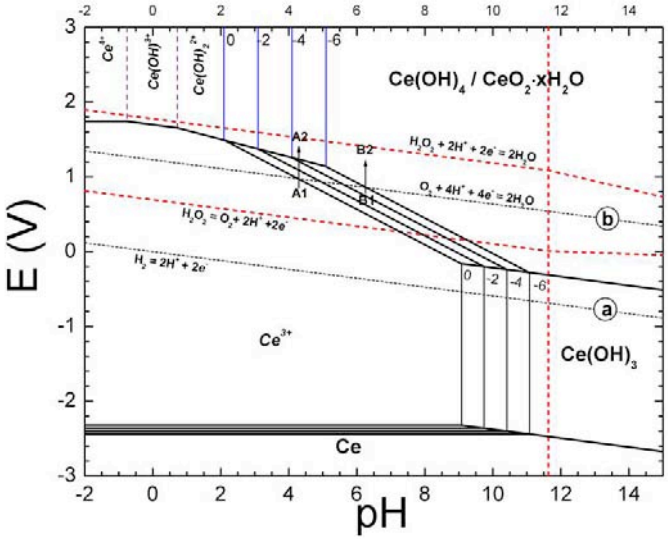
↓

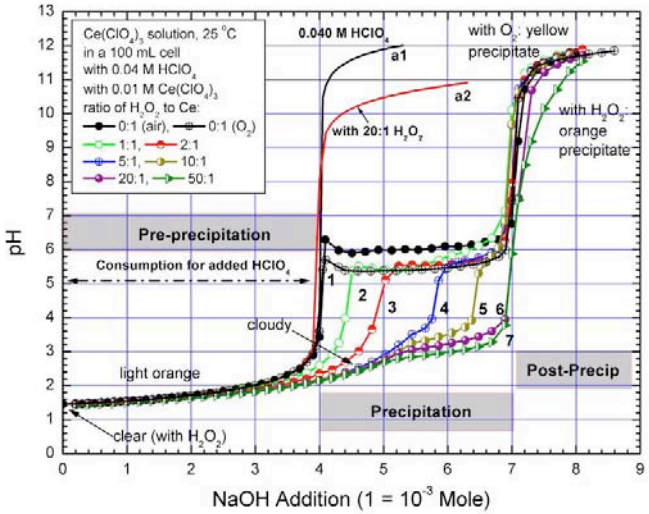
Model development and validation

Technical Approach

Thermodynamics studies will provide the foundation

- **Completed for Ce compounds**
  - **E-pH diagram and precipitation curves**
  - **Deposition mechanism proposed**





- **Fundamental studies needed for Pr system**
  - **Some thermo data in literature, some must be determined**
  - **Focus on effect of pH on stability of solution species and solids**
  - **Precipitation studies in relevant conditions**
    - **Evaluate influence of dissolved sulfate, chloride, etc.**

Technical Approach

Existing coating deposition methods will be used

- **Cerium-based conversion coatings**

  Focus on spray and immersion deposition processes

  Year 1: study 2024-T3 and 7075-T6 substrates

  Years 2 and 3: extend to other Al alloys and metals

Immersion is the same process as spray deposition, except that the coating is deposited during a single immersion (5-15 min) in a coating solution

- **Deft primers with Pr-based inhibitors**

  Evaluate high solids (solvent borne) and water-based formulations

  Deposition done at Deft for consistency

  Year 1: CrCC substrates

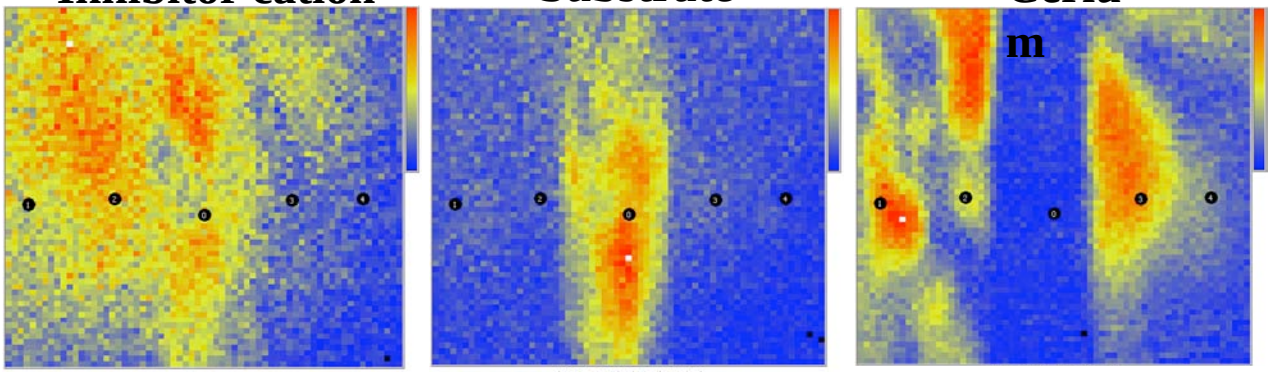
  Years 2 and 3: CeCC substrates and other types of organic coatings

Technical Approach

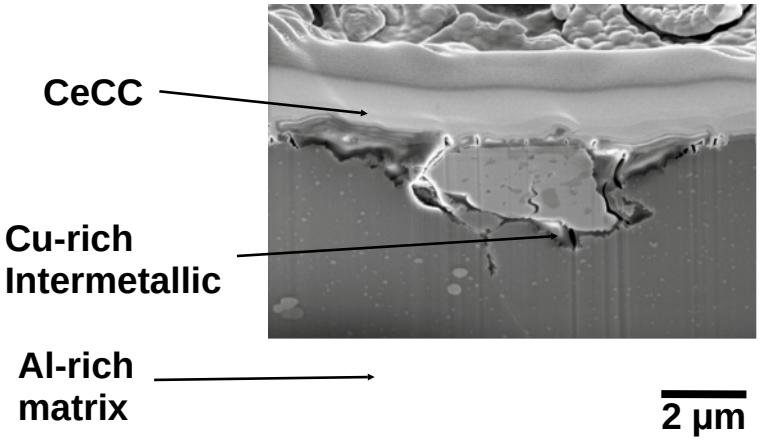
Physical and chemical characterization

- Identify composition, structure, and phases (SEM, TEM, XPS, AES, XRD)
- Before, during, and after corrosive attack

Inhibitor cation | Substrate | Cerium



Scanning Auger image of Al 2024 with CeCC and UV curable coating after salt spray with coating stripped

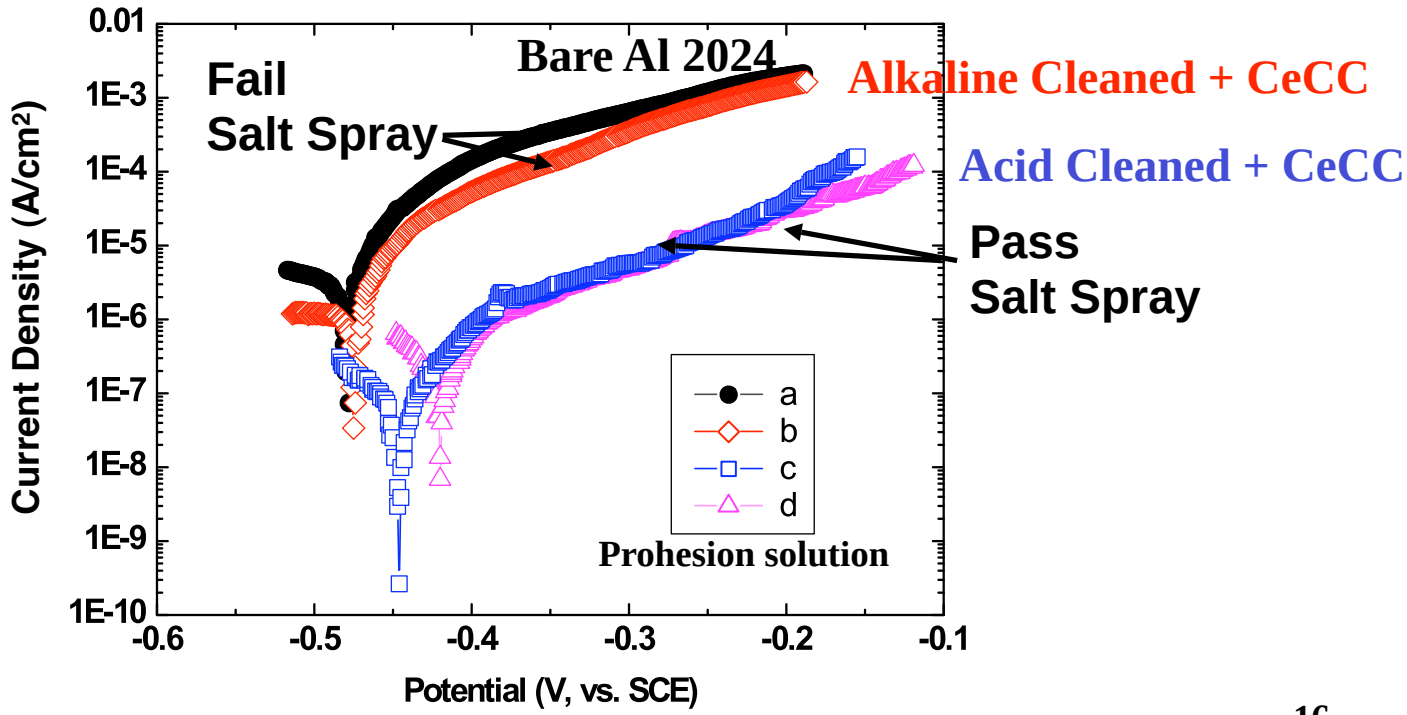


SEM picture of a CeCC sectioned by focused ion beam machining showing corrosion around an intermetallic particle after coating deposition

Technical Approach

Electrochemical characterization

- Focus on transport processes/species in specific environments
  - Solutions (e.g., chloride or chloride + sulfate)
- Conversion coatings
  - Identify species dissolving, transporting, and reacting
  - EIS and polarization to understand response

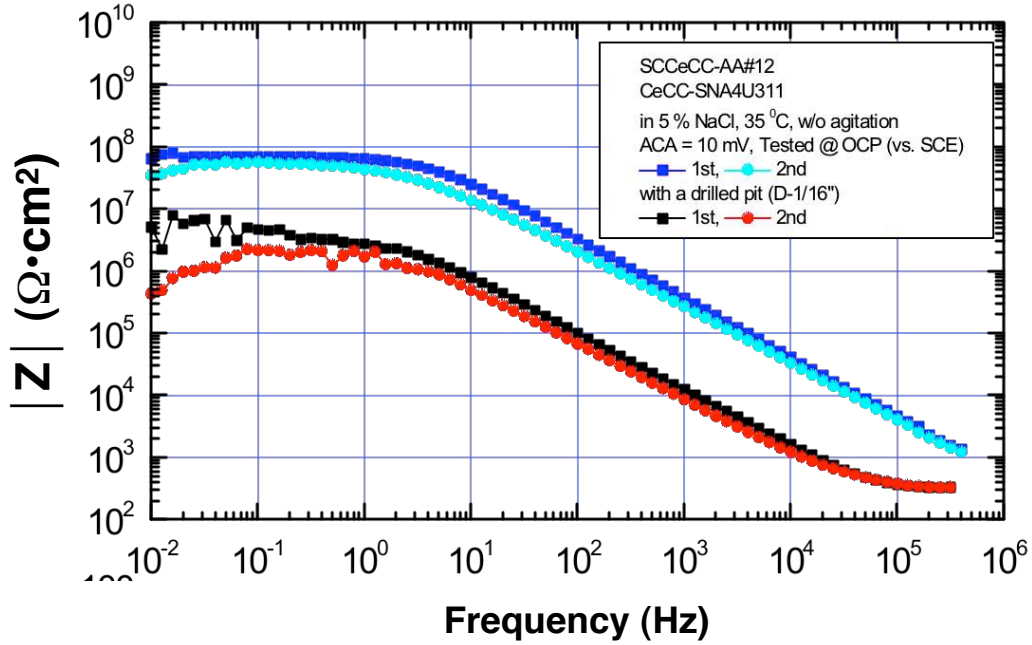


Technical Approach

Electrochemical characterization of primers

- Use "drilled pits" to simulate attack sites
- EIS to monitor changes
  - Degree of protection
  - Characteristics of protective layer
- Analytical characterization of species that form

1.5 mm diameter drilled pit



Technical Approach

Performance evaluation

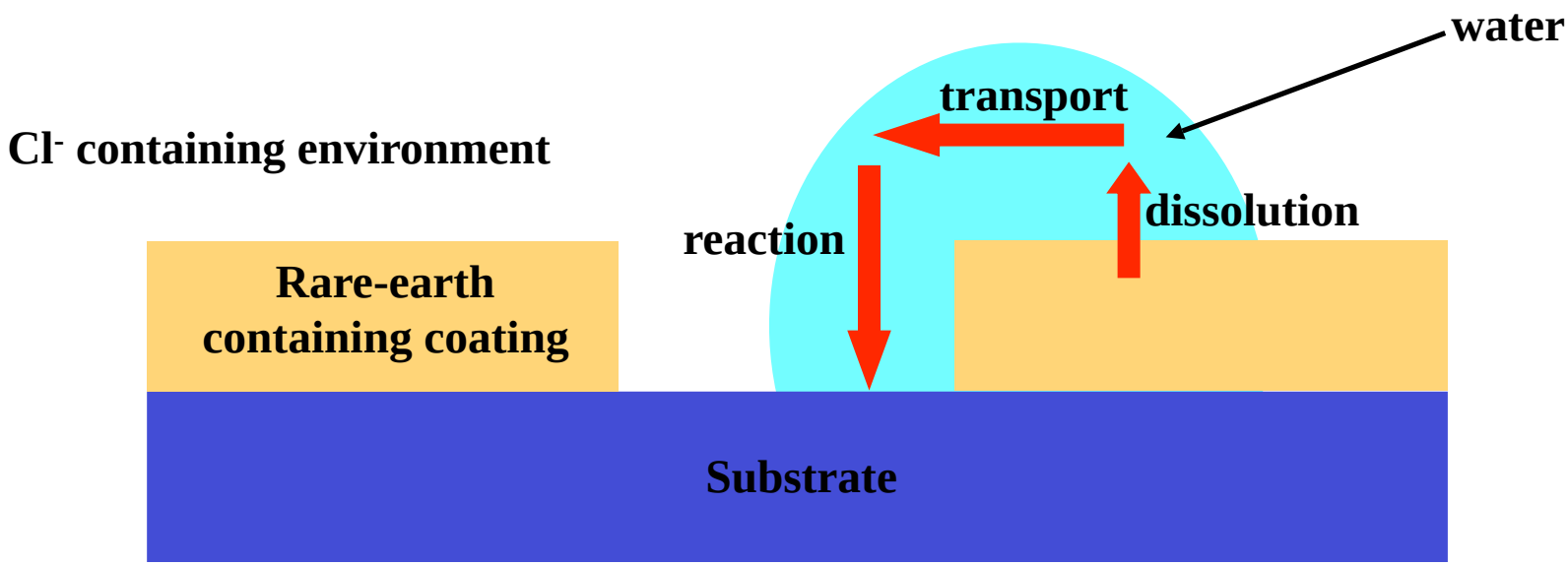
- Salt spray testing to military standards
  - Conversion coatings: 336 hours or 2 weeks
  - Primers: 3000 hours or ~18 weeks

- Polarization and EIS as potential accelerated alternatives to salt spray
  - Predictive of relative failure rates
  - Electrolyte specific tests (chloride vs. combinations of salts)
  - Tests complete in a few hours vs. weeks
  - Initial results are promising
    - Tests will be improved in this project

Technical Approach

Model development

- Rare-earth compounds not inherently protective
- Protection requires proper phase in the right type of coating
- Parallel, but separate models for conversion coating and primer
  - Identify species that dissolve from coatings
  - Characterize transport processes and rates
  - Specify reactions that lead to passivation



Technical Approach

Model validation

- **Targeted studies and tailored coatings**
  - **Isolate and test individual phases in specific coatings**
    - **Draw on fundamental phase stability studies**
  - **Evaluate specific environments**
    - **Chloride as standard**
    - **Need to understand transport with changes in pH, etc.**

- **Example for primer studies**
  - **Pr phase (PrO_2, Pr_2O_3, Pr_6O_{11}, hydrated oxides, hyrdoxides)**
    - **and paint formulation affect dissolution**
  - **Other components of the paint formulation may affect transport**
  - **Local electrochemical environment affects reaction/passivation**
  - **Formulate paints to test specific phases/ components**

Year 1 Project Plan

Cost Breakdown by Task for Year 1:

• Phase stability studies of Pr compounds	$23 K
• Coating deposition	$98 K
• Characterization (physical, electrochemical, performance)	$122 K
• Protection mechanism analysis	$68 K
TOTAL	$311K

Overall Project Plan

Task	Year 1	Year 2	Year 3
1. Review Literature			
2. Phase stability of Pr compounds			
3. Coating deposition			
4. Characterization of corrosion behavior			
4.1 Physical characterization (SEM, TEM, XPS, etc.)			
4.2 Electrochemical characterization (EIS, CV, etc.)			
4.3 Performance evaluation (salt fog, accelerated)			
5. Protection mechanism analysis			
6. Final model development and application			
7. Attend SERDP symposium and IPR			
8. Technical presentations, papers, reports			

Project Funding

	SERDP
	$K
Year 1	311
Year 2	309
Year 3	320
Total	940

Deliverables

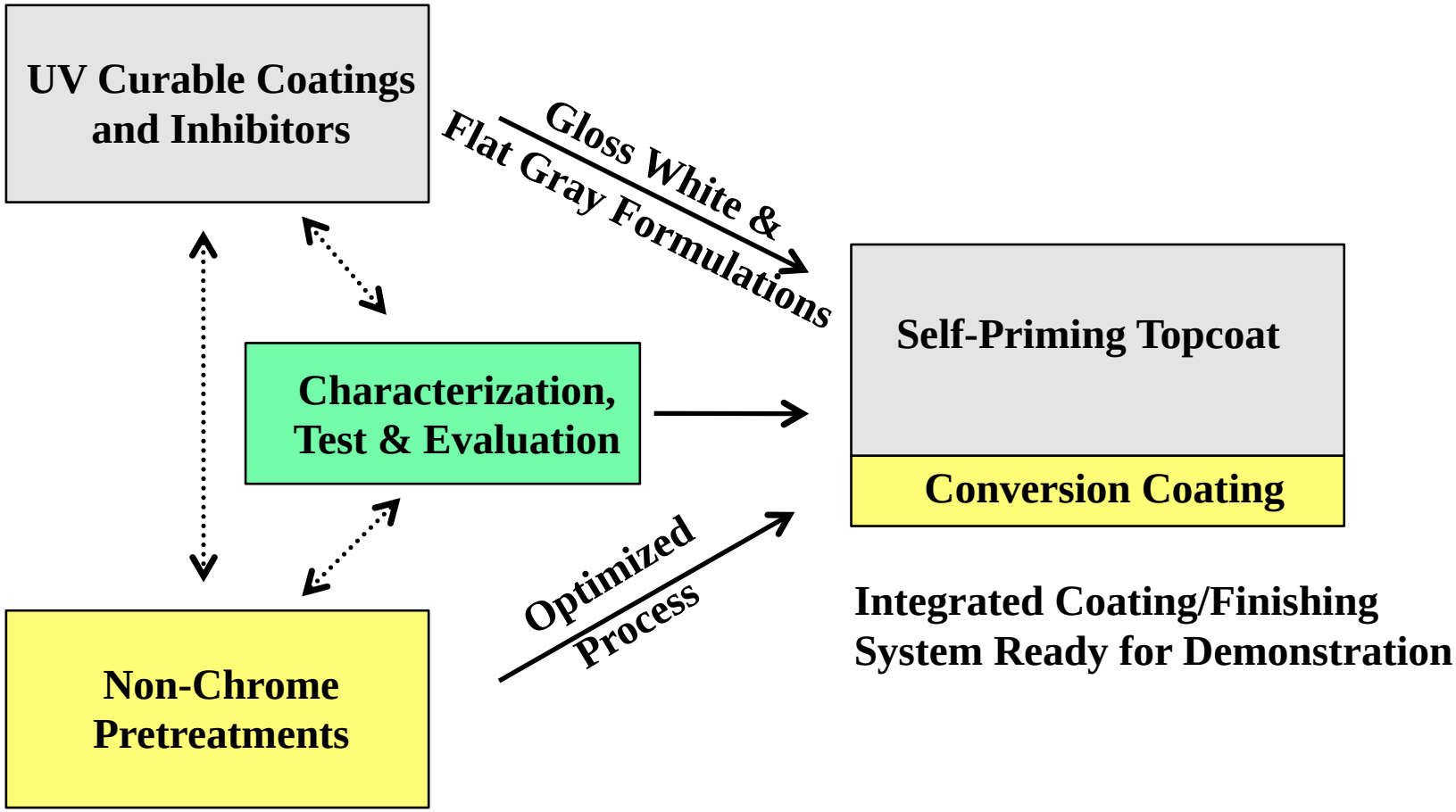
- Mechanistic models for the mechanisms of corrosion protection of rare-earth compounds in CeCCs and Pr-based primer coatings
- Phase stability analysis of Pr compounds including E-pH diagrams and precipitation studies
- Characterization results (physical, electrochemical, and performance)
- Test protocols for accelerated testing of rare-earth coatings
- Conference presentations & proceedings papers (~2 per year per student)
- Peer reviewed journal articles (anticipate ~4 per year)
- 2 PhD students and one research professor/post-doctoral scholar

Backup Slides

Backup Slides

Current SERDP effort focuses on coating development

- Coating system free of VOCs, TRIs, and HAPs
- Conversion coating multi-functional UV-curable self-priming topcoat



Integrated Coating/Finishing System Ready for Demonstration

Backup Slides

The scope of the proposed project should be widened to include a larger range of inhibitor and primers as well as other materials such as galvanized, steel, Mg alloys

The proposed effort is focused on Ce and Pr inhibitors

- **Deft markets a non-chromate primer qualified to military specifications**
  - **Pr-based inhibitor system**

- **UMR has active research on CeCCs**
  - **Spray, immersion, and electrolytic deposition of CeCCs**
  - **Integration of CeCCs into environmentally friendly coating systems**
    - **Zero-VOC, HAP/TRI-free coating system**
  - **Invented Pr-based inhibitor licensed by Deft**

- **The team is uniquely qualified to investigate corrosion protection mechanisms in rare-earth based coatings**

- **The program is focused on coating systems that work**

Backup Slides

The personnel is limited to UMR and Deft

An advisory team will be assembled after final approval

- **Industry and DoD representatives**
- **Prospective members**

Joel Johnson	**AFRL/WPAFB**
Mike Spicer	**AFRL/WPAFB**
John Stephens	**Robins AFB**
Ed Lipnickas	**NAVSEA**
Chris Miller	**ARL**
John Escarsega	**ARL**
Tom Landy	**Army**
Steve Gaydos	**Boeing-St. Louis**
Ramesh Patel	**Boeing-Mesa**

Backup Slides

Plan for thermodynamic modeling in phase stability studies

- For Pr system, focus will be on effect of pH, not solution potential
- The goal is to understand solubility and identify soluble/insoluble species
- Four main steps:

1) Collect available thermodynamic data from the literature
   - Solubility and/or free energy of formation
   - Already have some data for hydration of Pr

2) Evaluate the effect of anion additions on solubility/stability
   - Sulfate, carbonate, peroxide, and chloride
   - Possibly some organic salts

3) Experimentally determine precipitation curves
   - Can be used to estimate thermodynamic data

4) Conduct phase identification studies
   - XRD, TEM/SAED, other chemical and structural methods

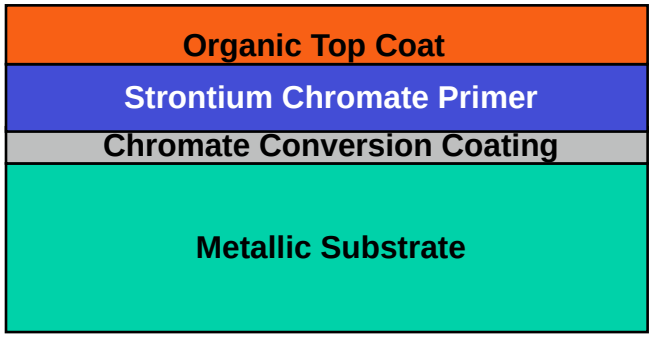
Backup Slides

Military aircraft use a three layer corrosion protection system

- **Conversion coating**
  - Thin inorganic layer usually ~250 nm
  - Provides corrosion protection and paint adhesion
  - Applied by a wet chemical process or reaction with substrate
  - Current practice uses chromate conversion coating

- **Primer**
  - Organic layer on the order of 25 µm thick
  - Majority of the chromate is in the primer
  - Provides long term corrosion protection
  - Chromated primer in most cases with some examples of replacement

- **Outer layer**
  - No chromates/inhibitors
  - Provides visual appearance
  - Washable, fluid resistant, etc.



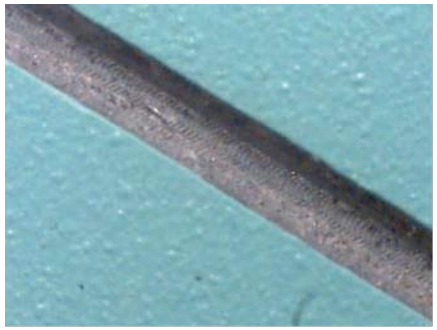
Backup Slides

Pr inhibitors passivate scribes

Scribe in Deft primer darkened, but not salted
Deft primer protects, but mechanism not known

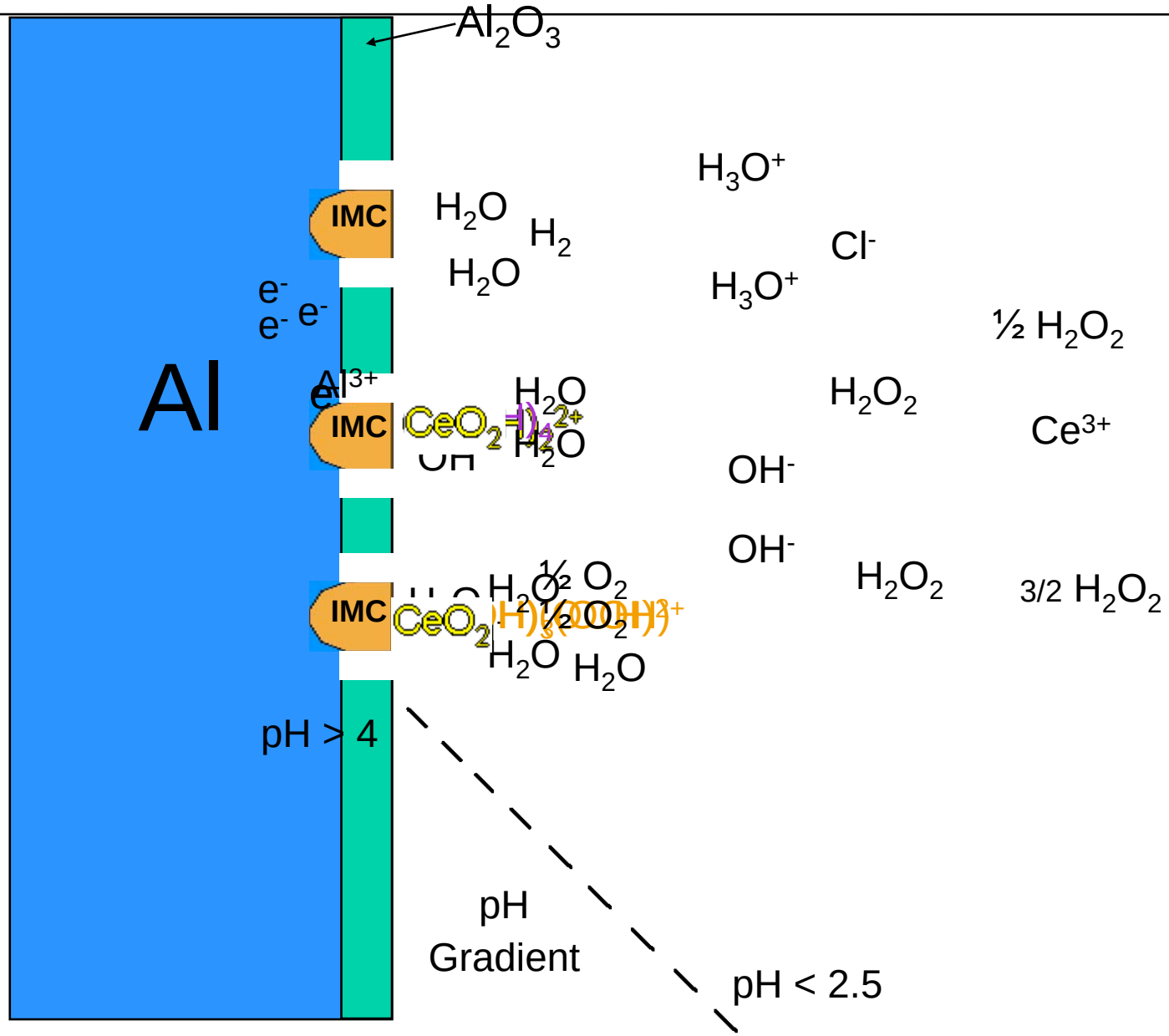
Chromated primer

Deft primer



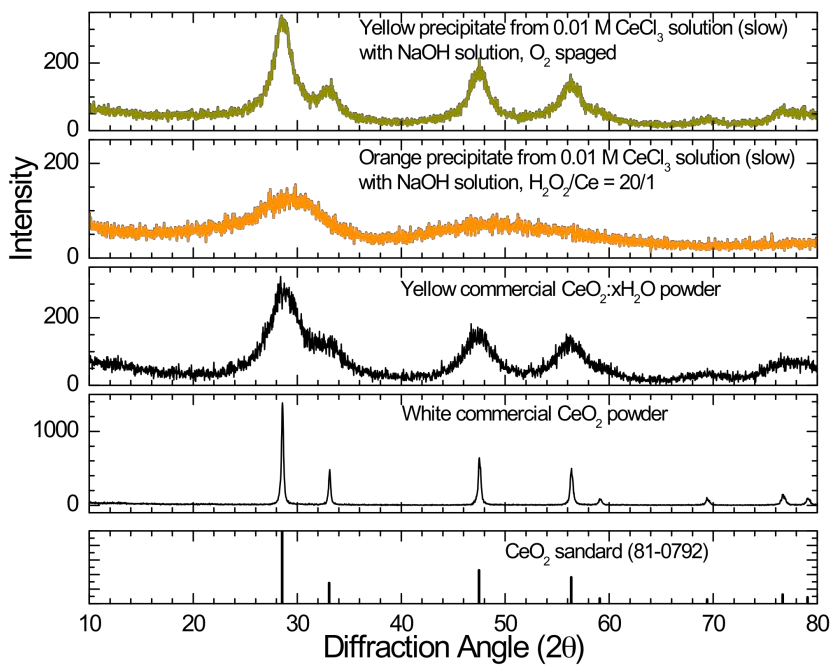
Al 2024-T3 panels with CrCCs and primers after 3000 hours in ASTM B117 salt spray testing. Both inhibited corrosion for the duration of the test.

Backup Slides



Backup Slides

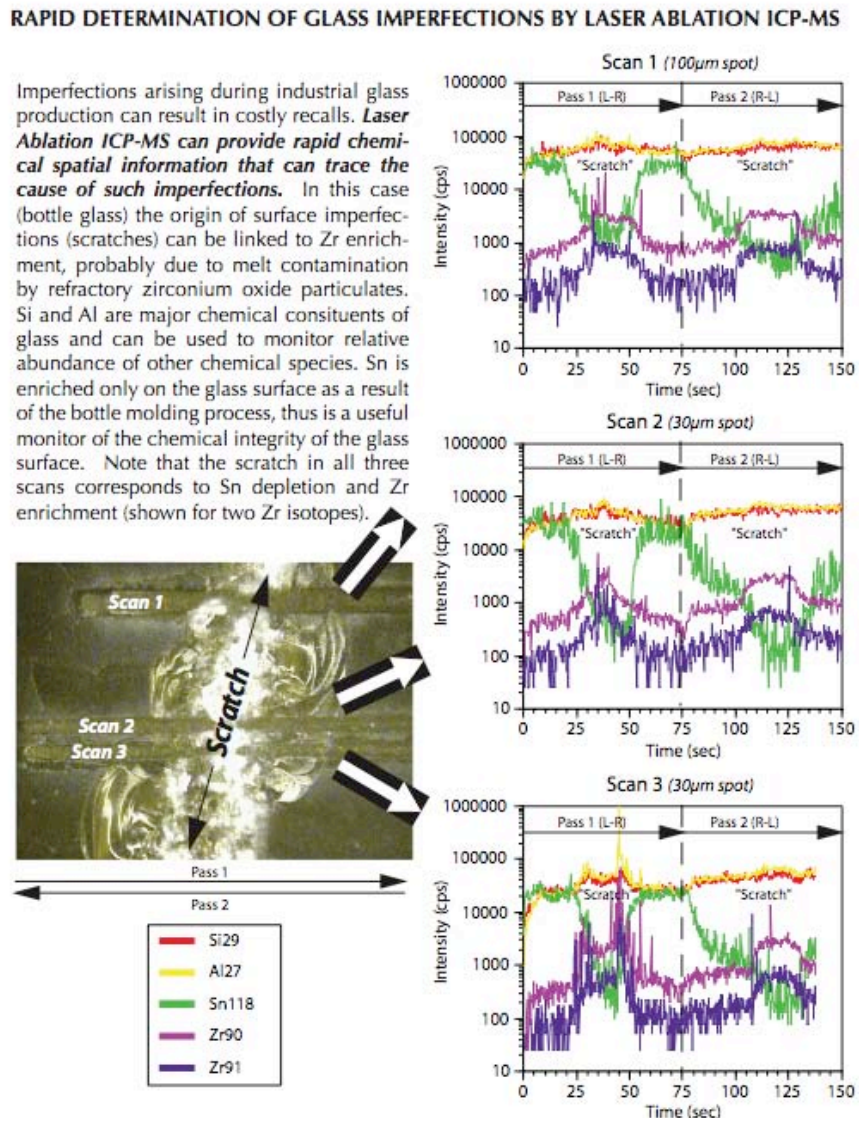
Precipitation tests are a key method to evaluate phase stability



Different species can be precipitated from a Ce^{4+} solution depending on the Ce to H_2O_2 molar ratio

Parallel studies are needed to understand the stability of Pr phases as a function of anion concentration and pH

Backup Slides

Additional characterization techniques available at UMR

Laser ablation ICP-MS
FIB SEM