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Title: Surveillance and Monitoring Program Corrosion Working Group Meeting March 27, 2014

Author(s): Worl, Laura A.
Narlesky, Joshua E.
Stroud, Mary Ann

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Surveillance and Monitoring Program Corrosion Working Group Meeting March 27, 2014

Table of Contents (LANL Presentations)

Meeting Agenda & List of Attendees	Laura Worl	3
Plan for Determination of the Residual Stresses in the SRS “Hanford” Inner Containers	Mary Ann Stroud	4
Identification of Oxidants and Chloride Species in the ICCWR	Joshua Narlesky	33

Surveillance and Monitoring Program Corrosion Working Group Meeting March 27, 2014 703-41A, Room 136 (Ellenton Room)			
8:00 AM		**Corrosion Working Group Meeting - 1/2 day meeting on special topics**	**CWG**
	Agenda topics include:		**Discussion Leads:**
8:00 AM	2:00	Plans for sectioning containers for residual stress analysis, weld oxide characterization, and future use in SCC shelf-life experiments.	M. Stroud
		SRNL plans for DE lid sectioning, imaging and analysis of ICCWR surfaces: areas examined, properties being measured.	J. Mickalonis
		Use of the above DE results to statistically estimate likelihood of SCC in the inventory. How much sampling and how much surface to examine per container.	E. Kelly
		Plans for archiving DE lids and samples	K. Dunn
10:00 AM	2:00	Discussions of how to identify the oxidants and chloride sources in pitting reactions at the ICCWR.	J. Narlesky
		Discussions of how we will identify crucial characteristics of ICCWR and reproduce the characteristics in surrogates for shelf-life tests.	J. Mickalonis, Kirk Veirs
		Tasks and schedule, with attention to where initiation of some tasks depend on prior completion of others.	J. Berg
		Approval process to start work on tasks.	
12:00 PM		**Meeting Adjourn**	

Plan for Determination of the Residual Stresses in the SRS "Hanford" Inner Containers

Presentation Subtitle

H5098, H5107 and H5117

Mary Ann Stroud, Kirk Veirs, John Mickalonis, John Berg and Laura Worl

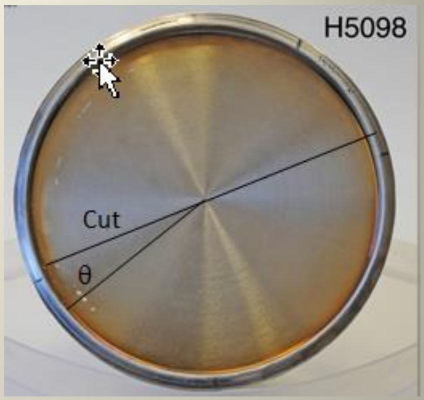
Introduction

- Welded at SRS and sent to Hanford
- SRS welding process representative of Hanford process
- One representative weld (H5107)
- Two with “deliberate” weld defects on or near the weld (H5098, H5117)

Proposed Stress Measurements

	Hoop ($4300/cut)	Axial ($4300/cut)	Radial ($700/hole)
H5107 (Rep.)	Cut in : Half Quarter Eighth (Data on 4 weld regions)	2 - 1/8 sections	2 holes
H5098	Cut in Half (Data on 2 weld regions)		
H5117	Cut in Half (Data on 2 weld regions)	1/8 section (if θ small)	
Totals	8 weld regions 1 weld start/stop 1 weld defect	25% of one can and 12% of second can	2 data points

Goals



- Determine the residual stresses in the container(s)
  - Baseline stresses for realistic samples for corrosion studies
- Use sections of the containers for validation of SCC corrosion study results
  - Maximize the number of sections available
  - Determine θ, the smallest angular subsection

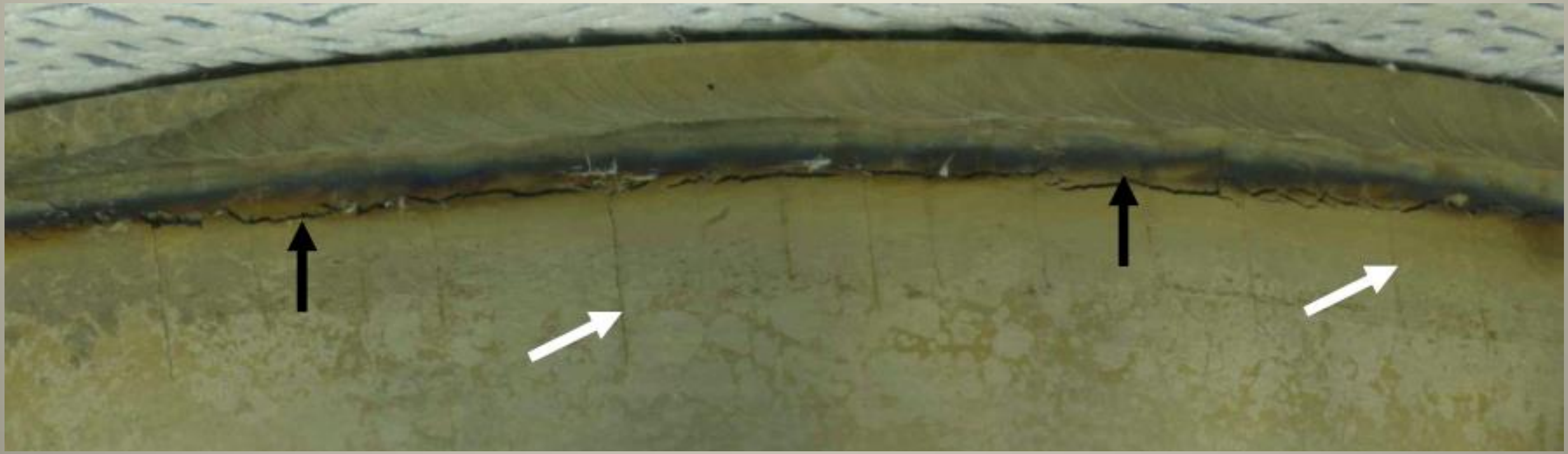
  that retains sufficient stress (95%) so that SCC experiments can be conducted with the subsection with confidence that the results are valid

Criteria for determining lid section height for measurements

- Sufficient to capture entire region with residual stress, altered surface chemistry (weld oxide) and altered microstructure
- Minimal relaxation of residual stress
- More than length of longest SCC from $MgCl_2$ experiments -~ 0.3 "
- Feasible for Hill Engineering

~ 2"

SCC in 3013 inner container weld region exposed to boiling $MgCl_2$



Exterior of one container

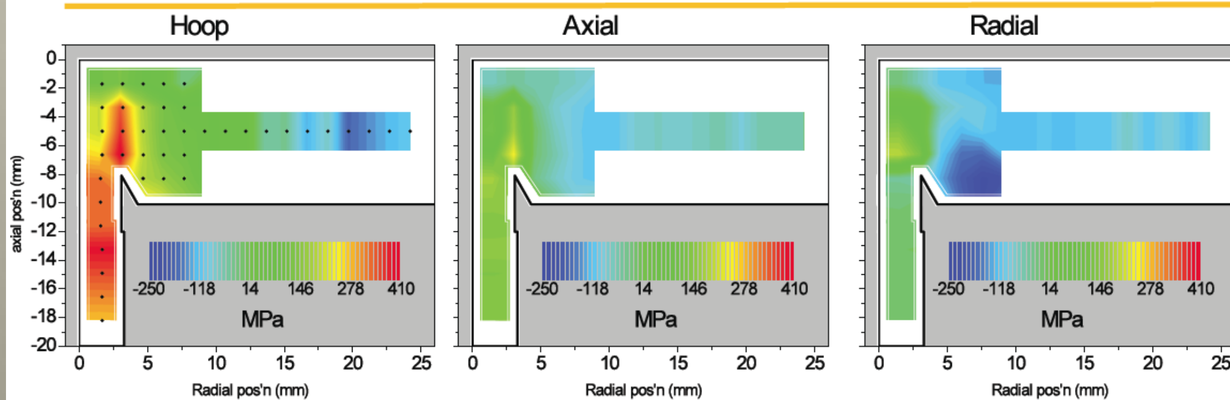
- white arrows - perpendicular cracks (Hoop),
- black arrows - parallel crack (Axial) – 60% of perimeter

Mickalonis and Dunn, SRNL

Which residual stresses should we measure?

- Hoop and Axial are Key
- Radial for completeness

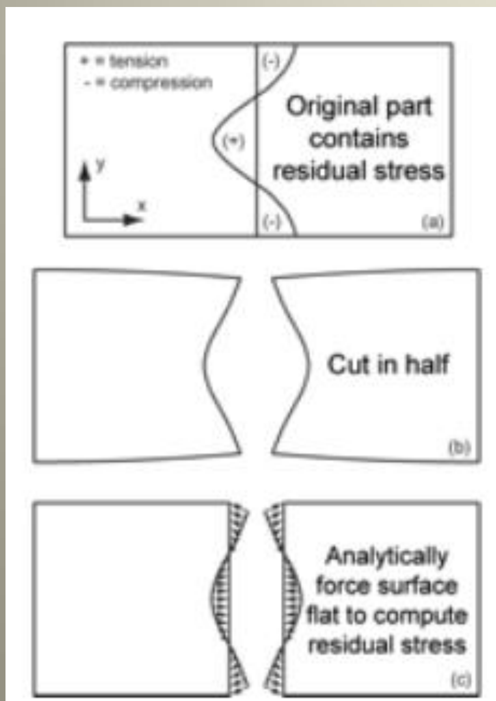
3013 Outer Container – GTAW Lid closure weld in H003085 Neutron stress maps



- **Peak stresses are hoop subsurface in weld**
  - 407 MPa at peak location
  - ~200 MPa at axial location

Mike Prime, LANL

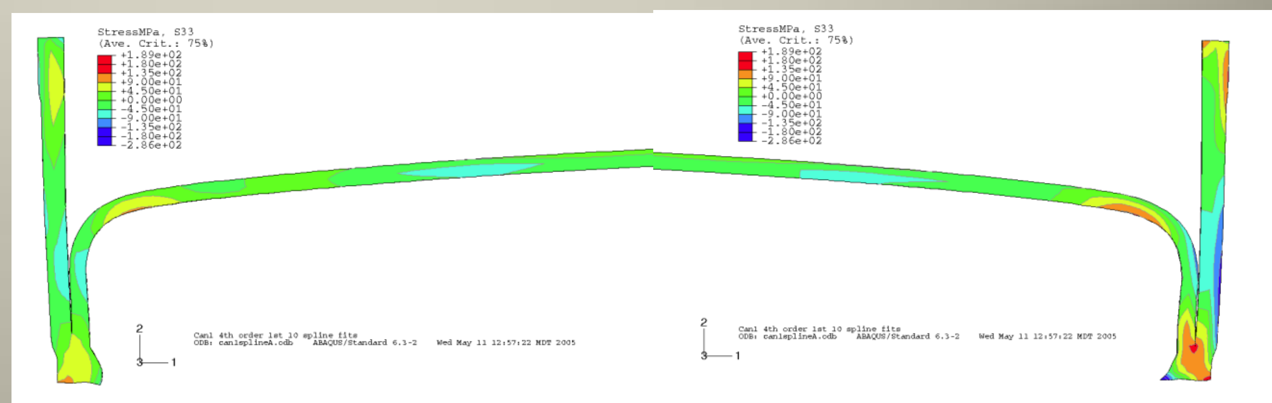
Hoop and Axial measurements
2D Contour



RFETS Inner

- Hoop stress ~ 135 – 180 MPa
- Fairly large uncertainties +45

Mike Prime, LANL

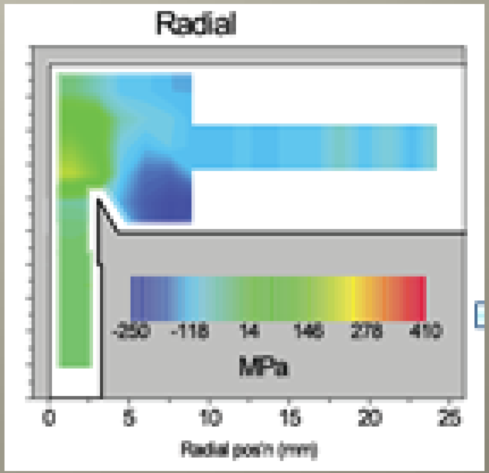


- $4300 per cut
- Thin container makes for challenging measurements.

Radial Measurement

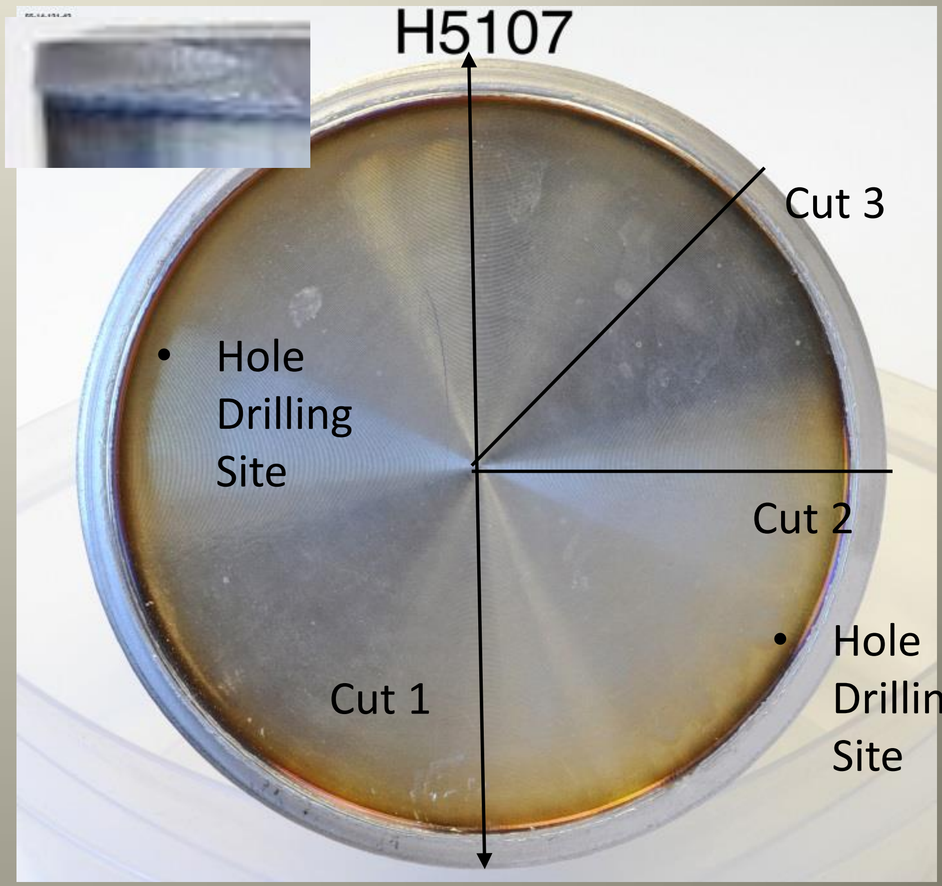
- Hole Drilling (ASTM)
- Less accurate
- $700
- ~ 1mm into surface
- Expect small stress in measurement area
- Small relaxation effect

- Hole Drilling Site



H5107 (Rep.)

- Cut in half through weld start/stop
  - Hoop stress in 2 weld regions
  - Determine θ
- Cut in quarter then eighth
  - 2 Hoop Stress
  - Quantify circumferential inhomogeneity
- 2 Hole Drilling
  - radial



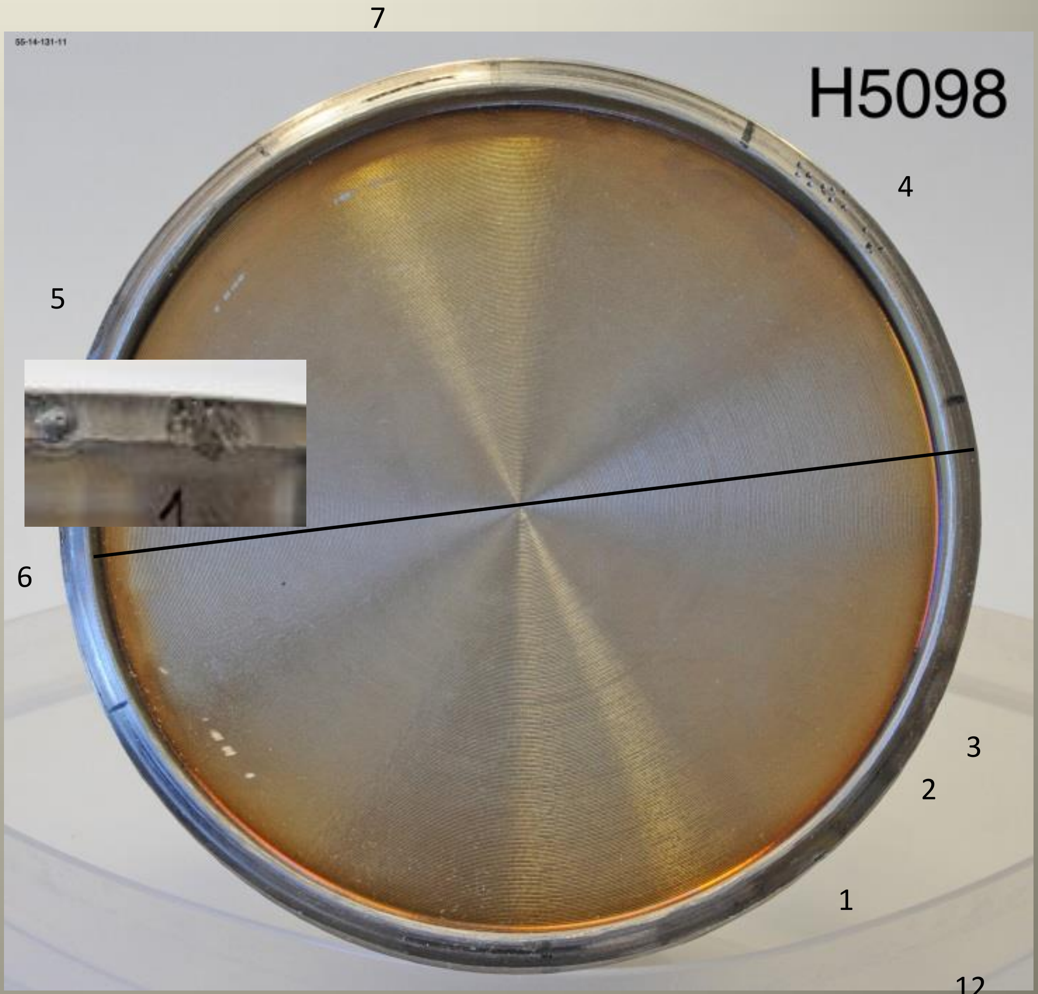
Cuts for Axial stress

- Measure 2 of the 1/8th subsections of lid
  - Weld start/stop
  - Quantify circumferential inhomogeneity
- Section limited use for SCC studies

H5098

- Cut in half
  - Through weld defect
  - Avoid start/stop
- Determine Hoop stress and θ
  - Needed if lid to be used in SCC experiment
- Cut through weld defect to quantify "worst case"

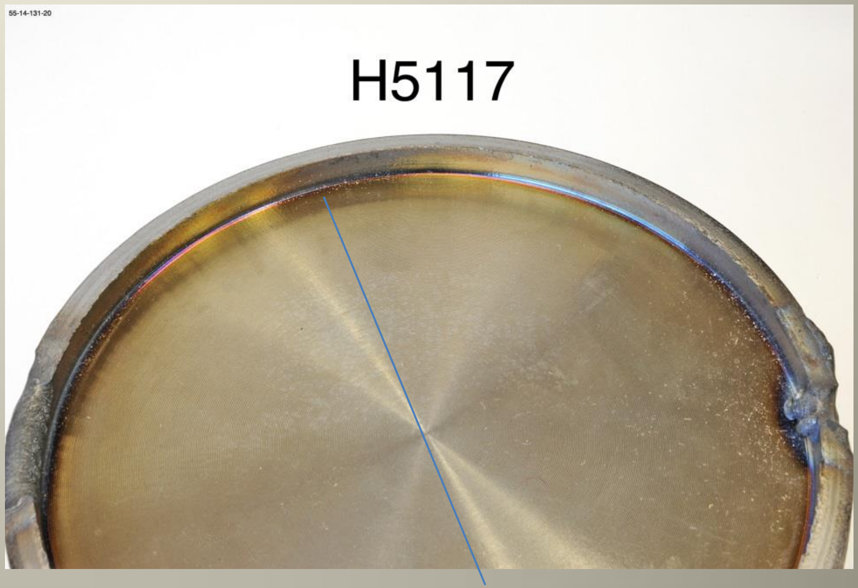
Concern: Are defects sufficiently localized to obtain valid stress data?



H5117

- Cut in half
  - Avoid weld defects
  - Avoid start/stop

- Hoop stress in 2 weld regions
- Determine θ



Proposed Stress Measurements

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Additional slides are extra

Plan for Determination of the Residual Stresses in the SRS "Hanford" Inner Containers

H5098, H5107 and H5117

Mary Ann Stroud, Kirk Veirs, John Mickalonis,
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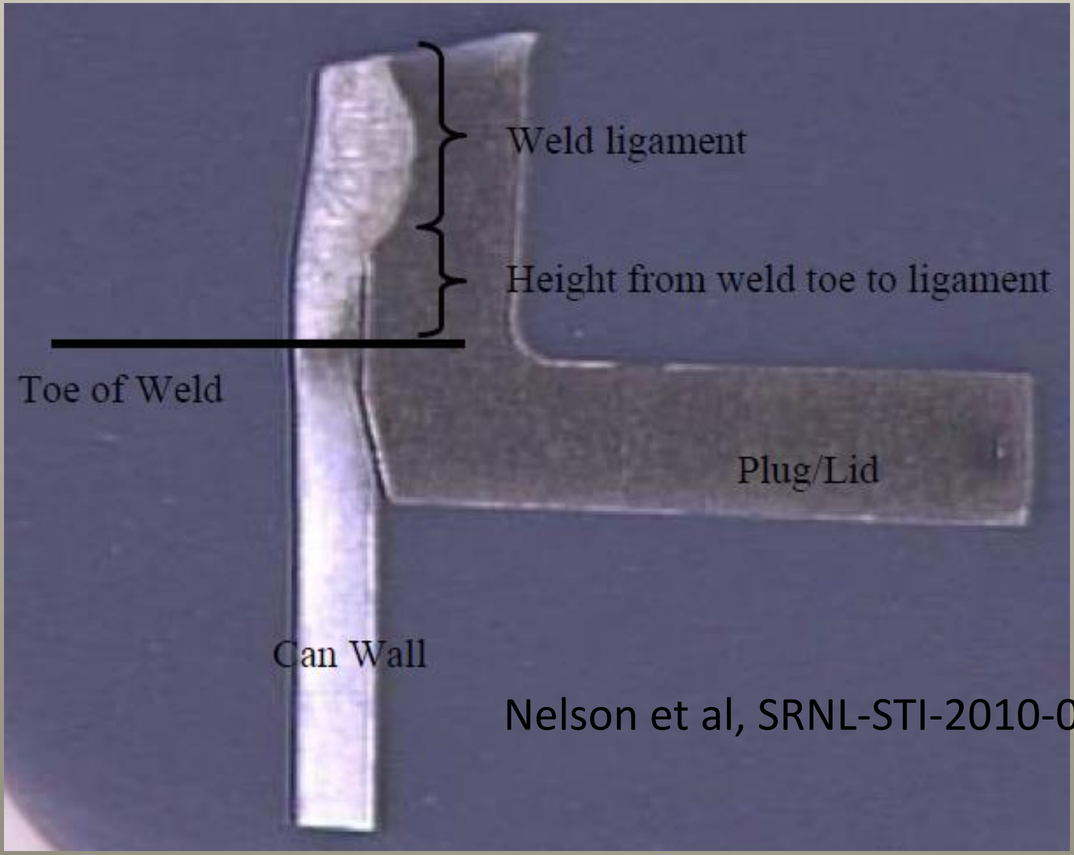
Other measurements?

- Analysis of variations in gap between the sidewall and lid



Nelson et al, SRNL-STI-2010-00064

H5107


55-14-131-31
H5107
H5107


55-14-131-35
H5107
I
H5107


55-14-131-34
H5107
H5107
I

H5107


55-14-131-32
H5107
H5107


55-14-131-33
H5107


34
H5107
H5107

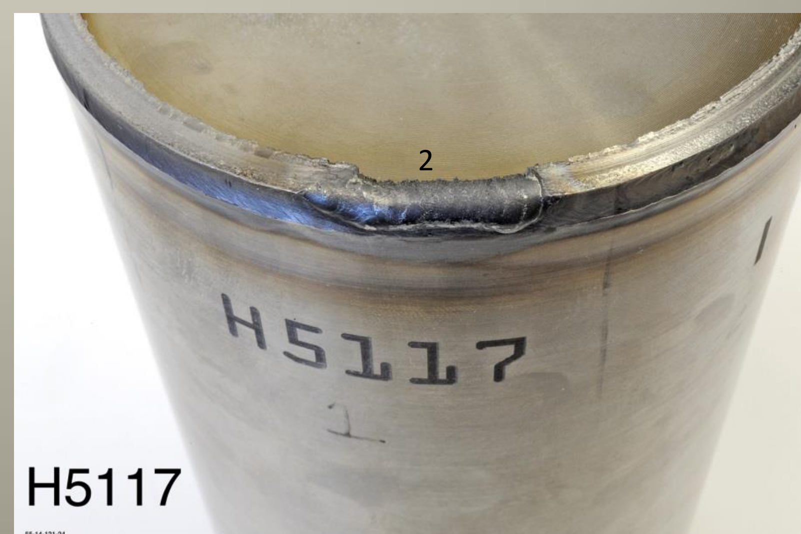

55-14-131-35
H5107
H5107

H5117

H5117

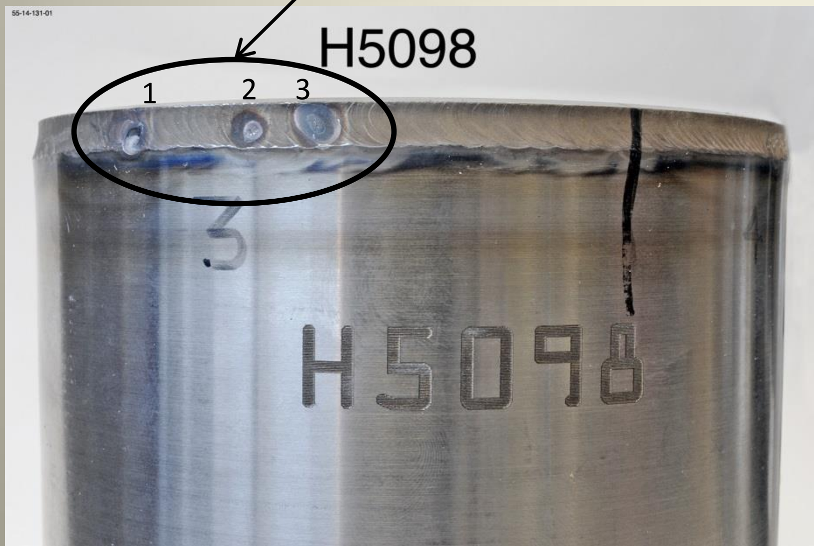
H5117

H5117

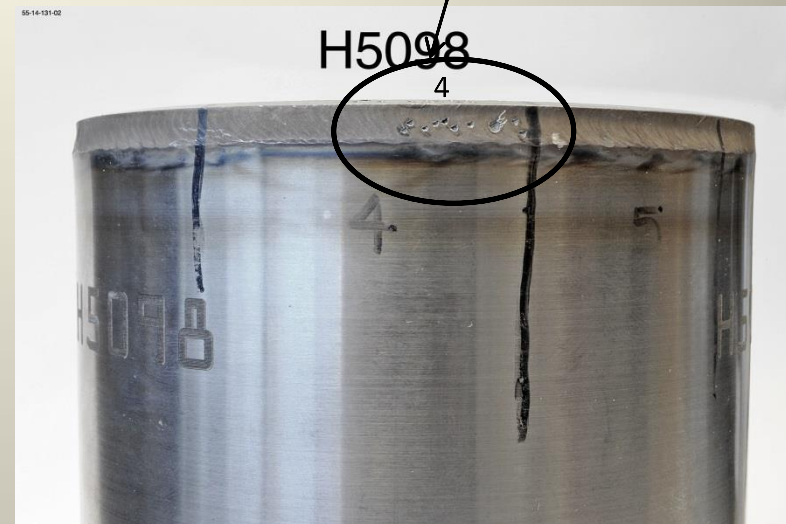


H5098

H5098



Weld defects
55-14-131-01
H5098
1
2
3



Testing
55-14-131-02
H5098
4

55-14-131-03
Testing
4
H5098

55-14-131-04
Weld defects
H5098
5
6

H5098

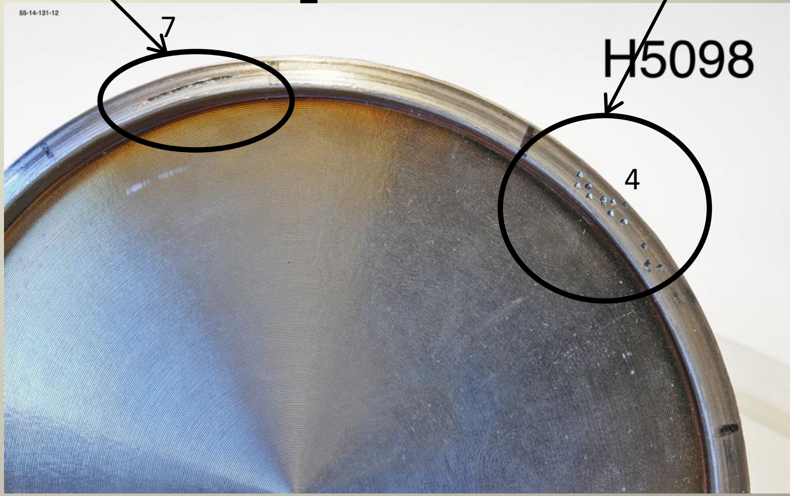

55-14-131-11
H5098
7
4
5
6
3
2
Crevice like feature is artifact of lighting
1

H5098

crevice

1

Testing – same location as on side



Weld defects

Identification of Oxidants and Chloride Species in the ICCWR

Joshua Narlesky & Daniel Rios

March 27, 2014

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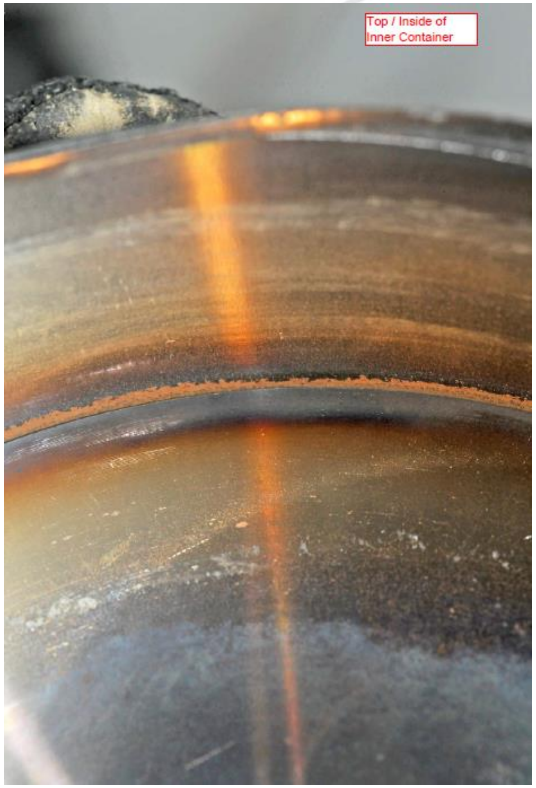
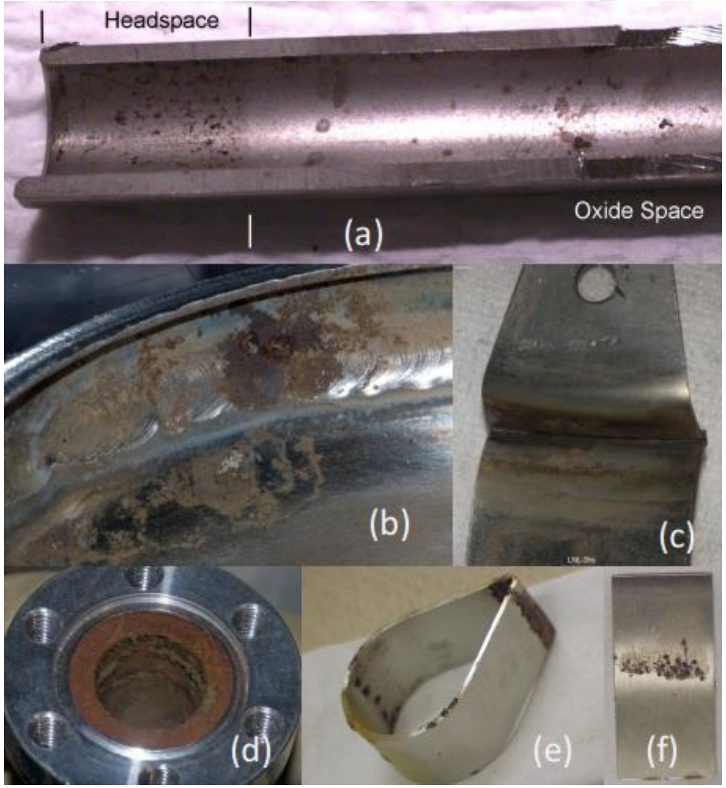
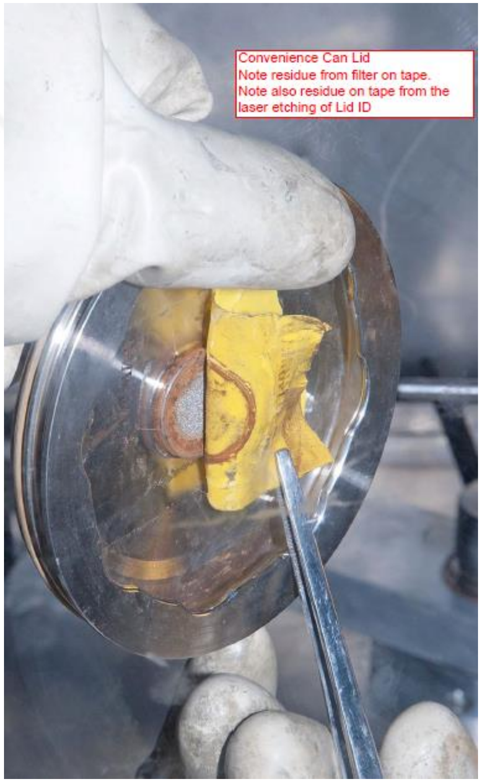
Outline

- What we know about corrosive gases
- Goals of experiment
- Discussion of methods

What we know about corrosive gases







What we know about corrosive gases

- Evidence supports generation of chloride species (Cl_2 or HCl).
  - HCl observed in FTIR at packaging
  - Coatings on 3013 inner containers identified as ammonium chloride.
  - Various examples of corrosion outside of the convenience container (CC).
    - HHMC: corrosion in ICCWR, and outside of CC filter.
    - Other examples of ICCWR corrosion.
  - Known hydrolysis of $MgCl_2$ and $CaCl_2$ produces HCl.
  - Radiolysis may produce HCl and Cl_2 but previous experiments were not capable of detecting these species.
  - pH paper indicates acidic environment in shelf-life studies.

What we know about corrosive gases

- Gaseous chloride species (Cl_2 and HCl) are difficult to detect.
  - Extremely reactive
  - Produced in small quantities
  - Example: HHMC
    - Corrosion observations suggest that corrosive gases were present (but we don't know when).
    - Draeger tube used capture gas at can puncture.
    - No color change observed.
    - Unclear whether HCl was no longer present or whether the quantity and/or sensitivity were to low.

Goals

- Identify test materials (impure Pu oxides).
- Obtain reagent (solid preferred) that will capture corrosive gases and produce a different products based on the corrosive gases it is exposed to.
- Design a test cell such that the corrosive gas preferentially reacts with the reagent rather than the test container.
- Choose a method of detection that can identify and quantify the product(s) produced in the test cell.
- Relate products back to gas phase species present.

Test Container

- Separates test material from reagents
- Has non-reactive surface (want corrosive species to preferentially react with reagents)
- Protects reagents from light
- Leak tight / can be leak checked
- Instrumentation (RH, temperature, etc.)
- Minimize headspace—increase concentration of corrosive gases
- Ability to control initial gas composition

Test Materials

- Representative materials / DE material
  - HHMC material at LANL, ARF-102-85-223, etc.
  - Pros:
    - Sufficient quantify of material
    - Known to produce corrosive gases
  - Cons:
    - Uncertain whether material will exhibit behavior seen previously
- Generate new test materials
  - Add salt(s) to Large Scale base material or pure oxide
  - Pros
    - Can make material with desired composition
  - Cons
    - Not representative of inventory
    - Can be difficult to produce correctly (i.e. hydrolysis can destroy a significant amount of chlorides in material when calcined).

Reagents

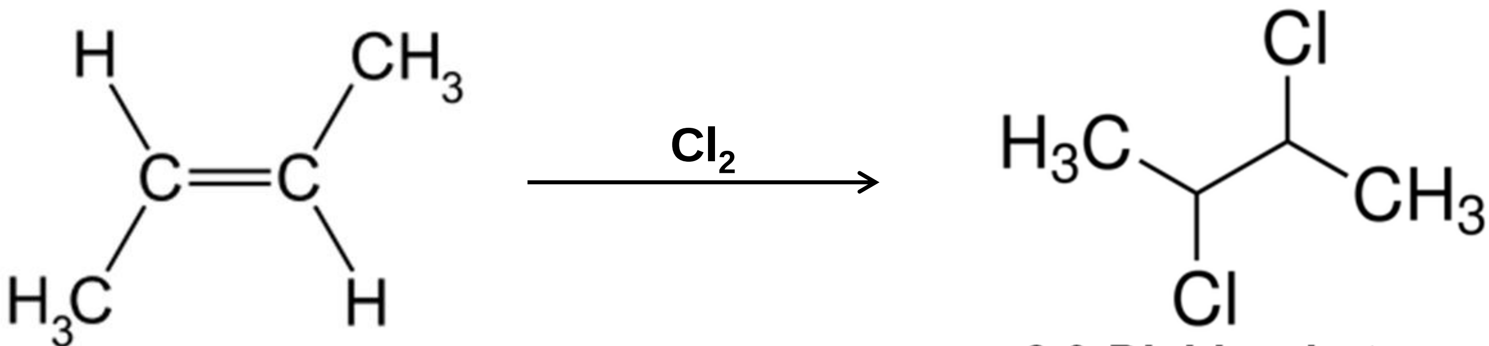
- Capture of chloride species on solid alkenes, alkynes, or on solid organometallic compounds containing appropriate ligands.
  - Method has been used in the literature for bromine (provides yield, reaction time, stability, etc.).
  - Reagents commercially available or we can synthesize specific reagents (complexes tend to be more stable).

Reagents

- Example reactions
  - Basic capture reaction
  - Capture of chloride species on solid alkenes
  - Capture of chloride species on solid organometallic compounds

Reaction of Alkene with Cl_2 and HCl

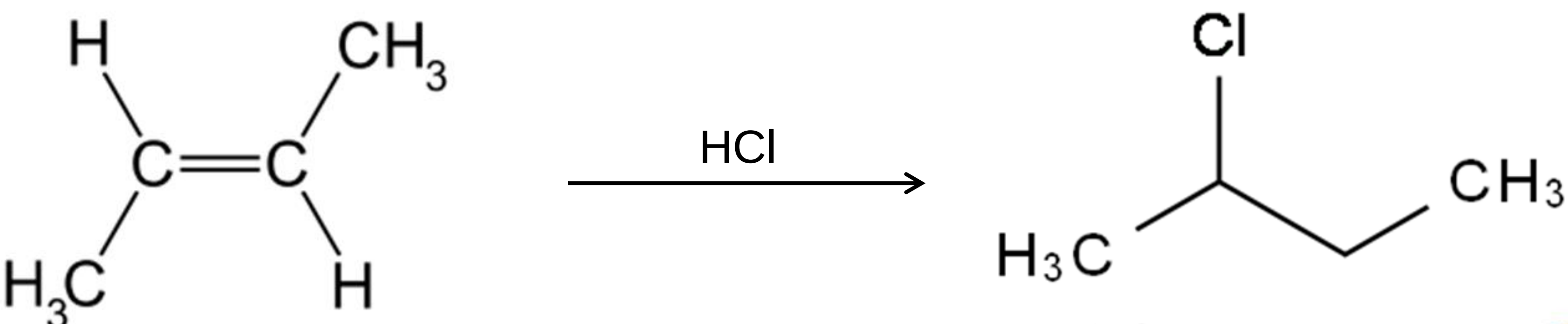
Chlorination



trans-2-butene

2,3-Dichlorobutane

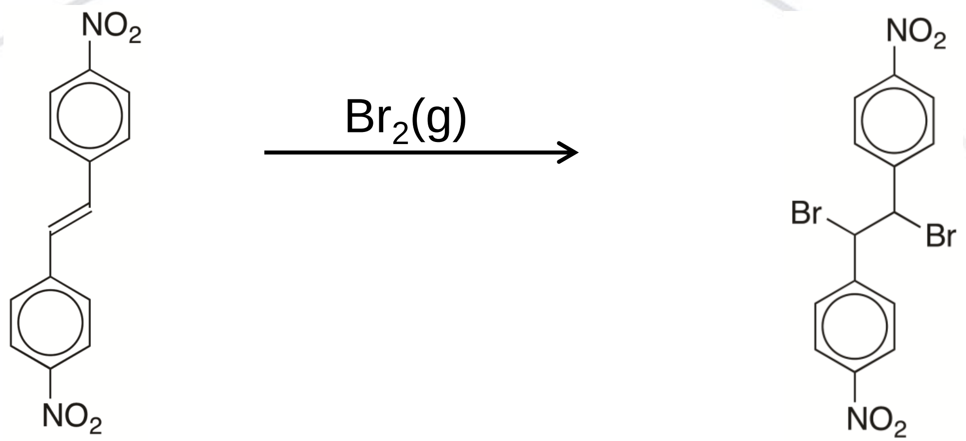
Hydrochlorination



2-Chlorobutane

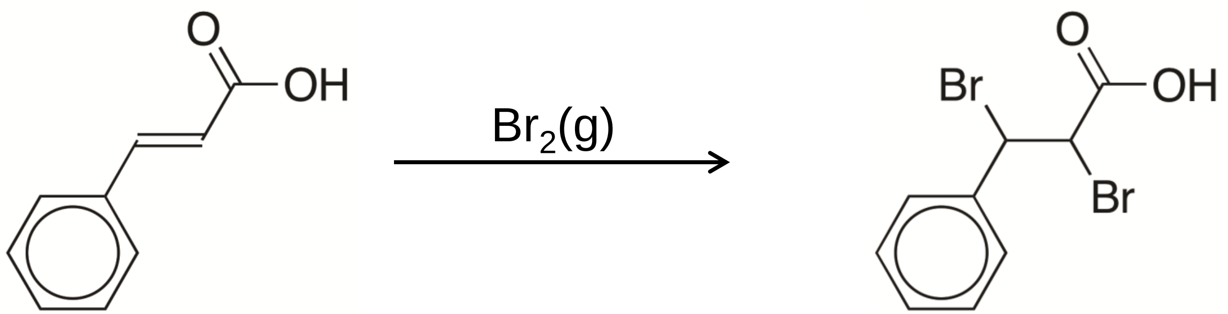
trans-2-butene

Reaction of Solid Alkenes with Br_2 (g)



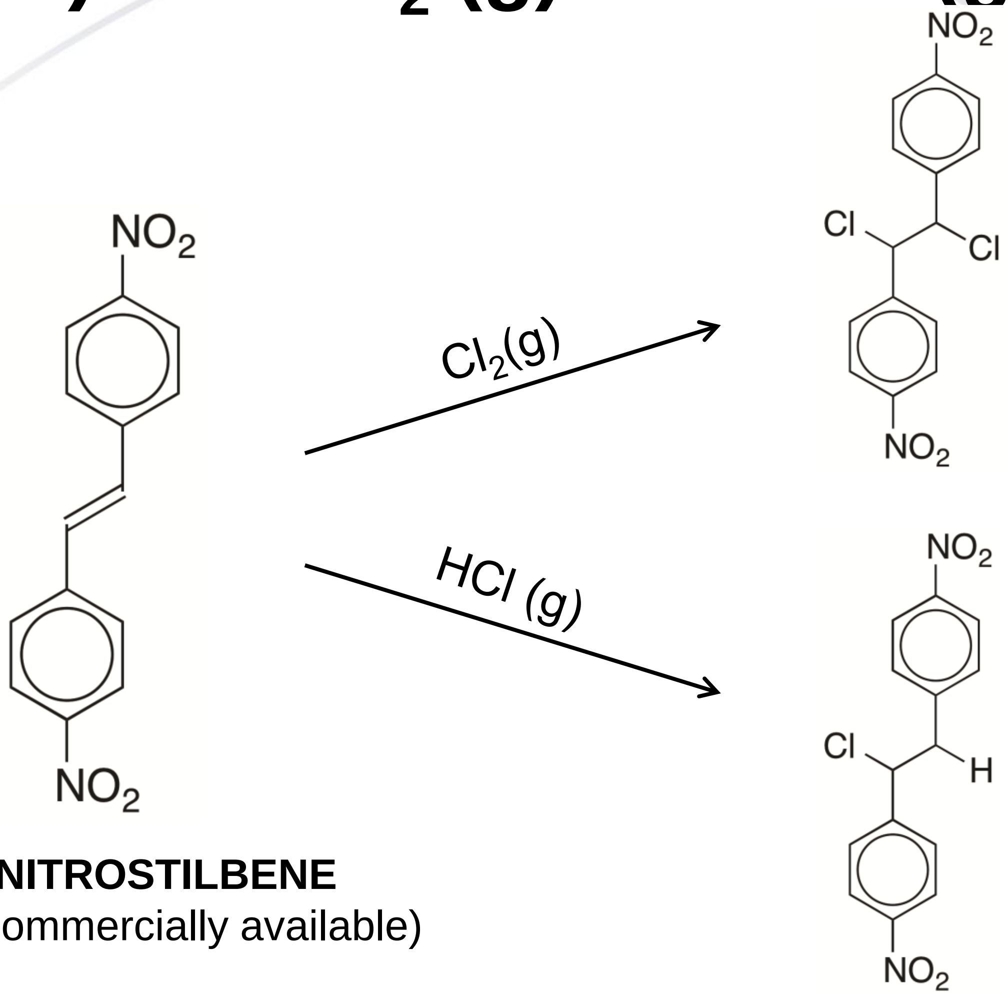
4,4'-DINITROSTILBENE
(solid and commercially available)

J. Am. Chem. Soc., 1950, 72 (6), pp 2494–2496



***trans*-Cinnamic acid**
(solid and commercially available)

Reaction of 4,4'-Dinitrostilbene (solid) with Cl_2 (g) and HCl (g)



4,4'-DINITROSTILBENE
(solid and commercially available)

- 5 different carbon signals
- 3 different proton signals
- MW : 341.14 g/mol

- 10 different carbon signals
- 6 different proton signals
- MW : 306.70g/mol

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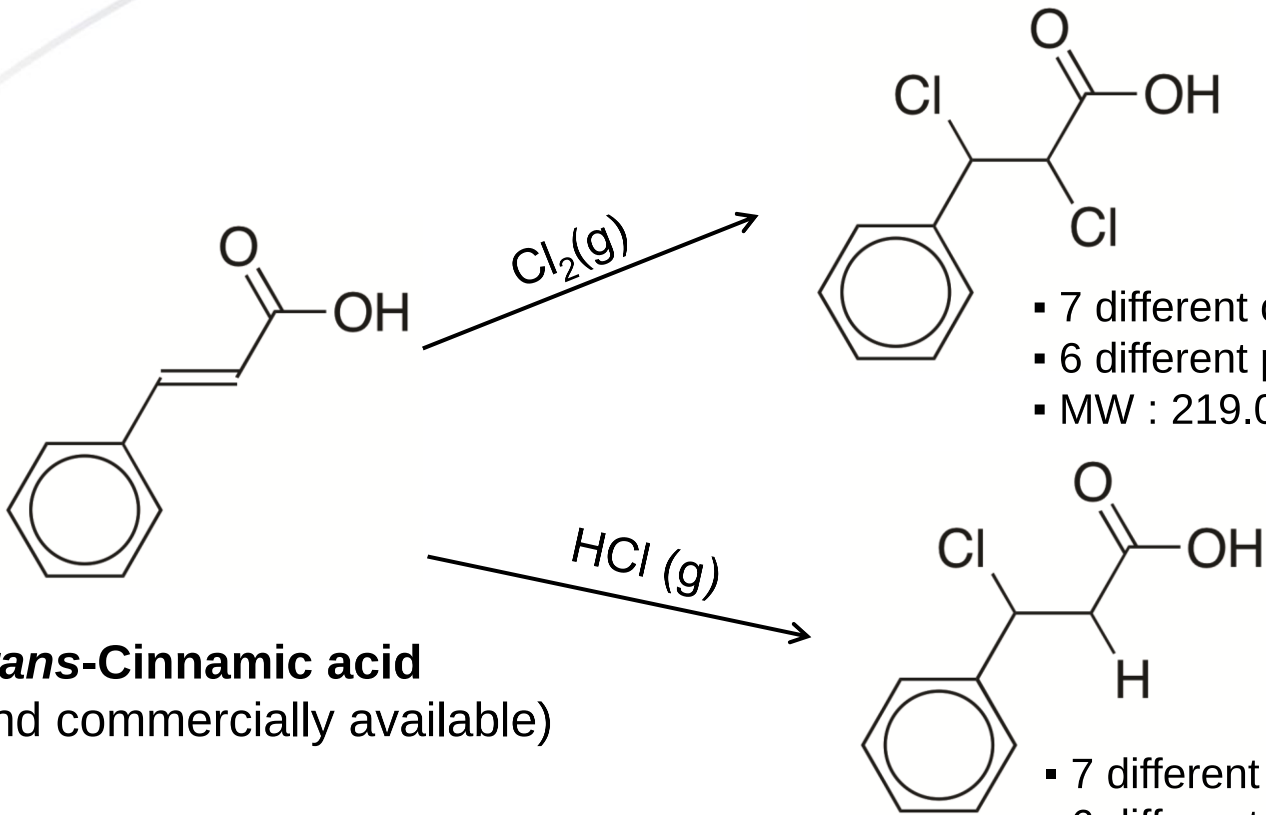
Reaction of Solid trans-Cinnamic acid with Cl_2 (g) and HCl (g)



- 7 different carbon signals
- 6 different proton signals
- MW : 219.06 g/mol

***trans*-Cinnamic acid**
(solid and commercially available)

- 7 different carbon signals
- 6 different proton signals
- MW : 184.62 g/mol

- Same number of carbon and proton signals but their coupling and positions on the spectrum are different

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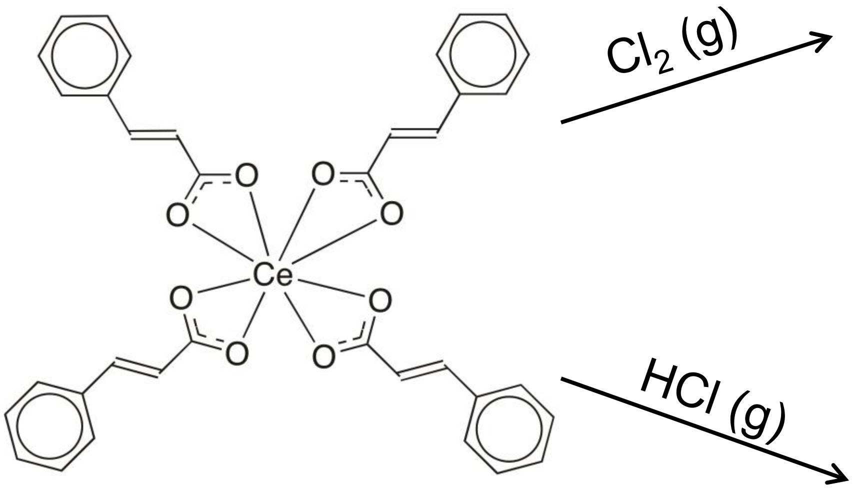
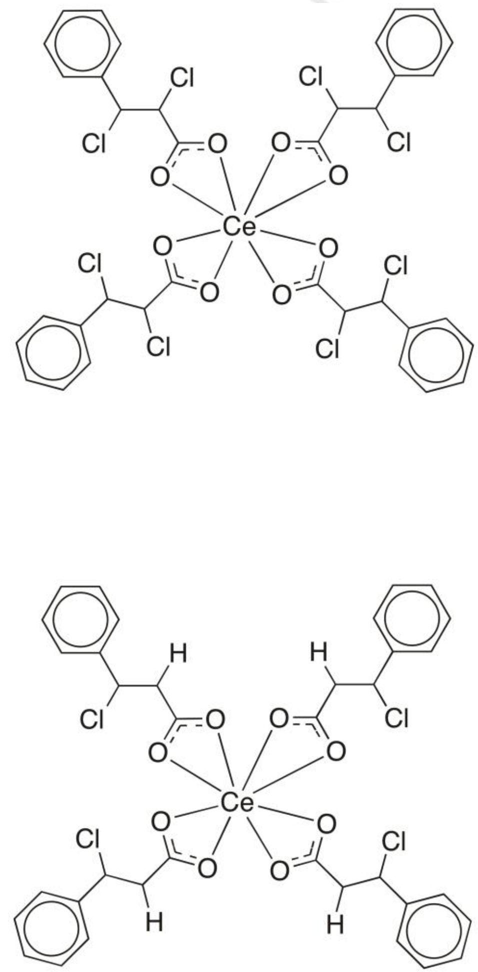
Reaction of $[Ce^{IV}(OOCCH{=}CHPh)_4]$ (solid) with Cl_2 (g) and HCl (g)

- Each ligand has the same number of carbon and proton signals but their coupling and positions on the spectrum are different



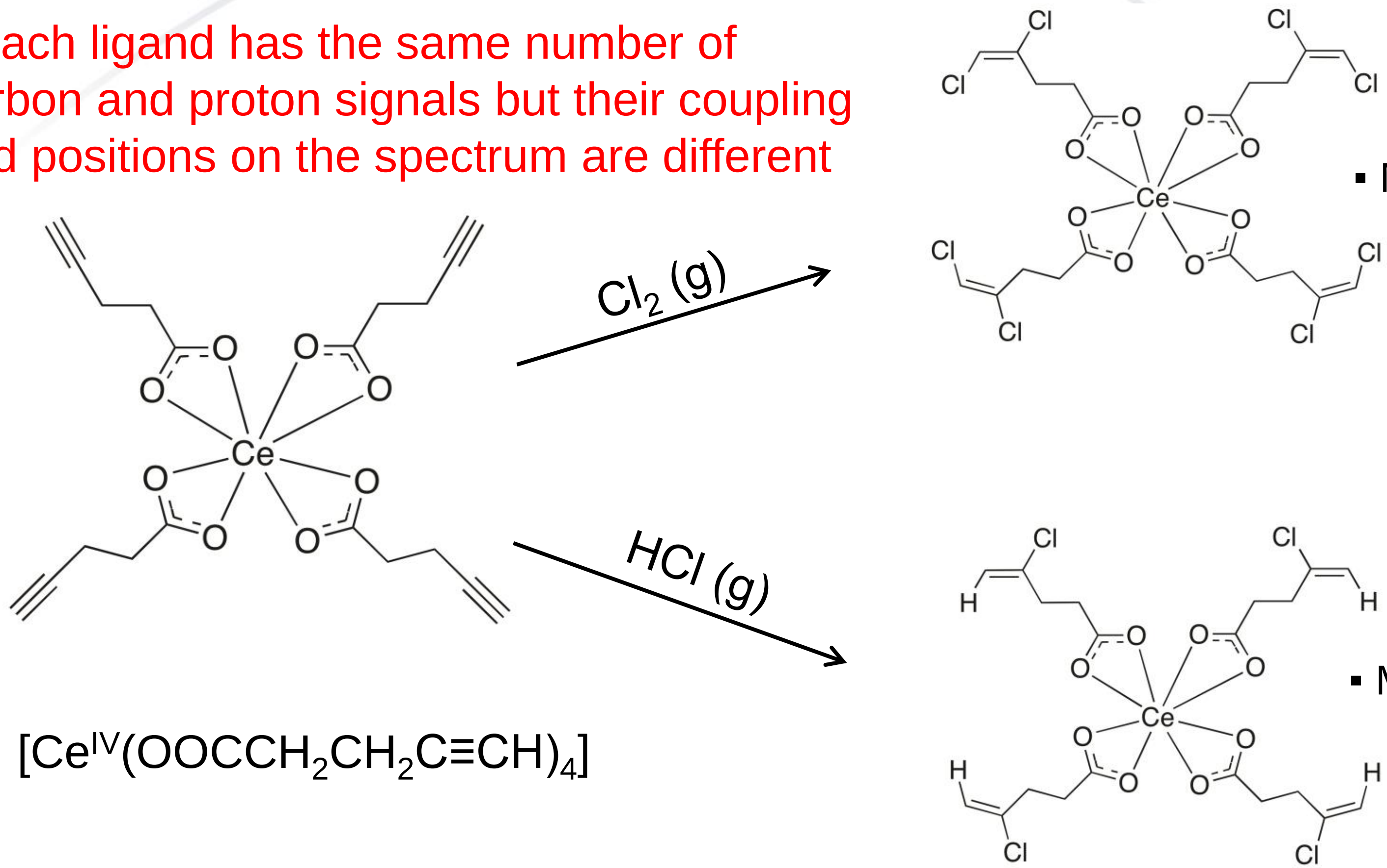
$[Ce^{IV}(OOCCH{=}CHPh)_4]$



- MW : 1012.31 g/mol
- MW : 875.35 g/mol

Reaction of [$Ce^{IV}(OOCCH_2CH_2C{\equiv}CH)_4$] (solid) with Cl_2 (g) and HCl (g)

- Each ligand has the same number of carbon and proton signals but their coupling and positions on the spectrum are different



[$Ce^{IV}(OOCCH_2CH_2C{\equiv}CH)_4$]

- MW : 811.83 g/mol

- MW : 673.83 g/mol

Methods to Detect Products

- Ability to distinguish between products
- Ability to handle Pu-contaminated samples
- Fast and reliable
- Examples
  - Mass Spectrometry (MS)
  - Nuclear Magnetic Resonance (NMR)
    - May be less sensitive
    - Analysis requires < 1 day
    - Difficulty: transfer of sample
    - Capability exists at radiological facility at LANL

Discussion