Development of Gas Pressure Cells for Diffraction Experiments: hurdles, headaches and practical considerations

Whitfield, Pamela; Ross, James; Mitchell, Lyndon; Nawaby, Victoria

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Development of Gas Pressure Cells for Diffraction Experiments:

hurdles, headaches and practical considerations

Pamela Whitfield, James Ross, Lyndon Mitchell and Victoria Nawaby

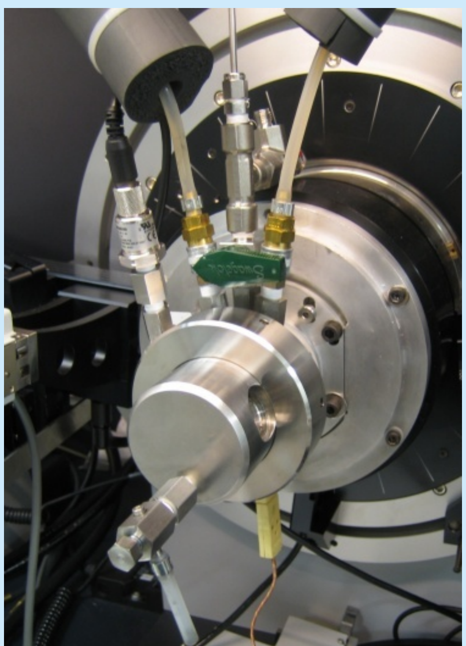
Pressure cells at ICPET the beginning…

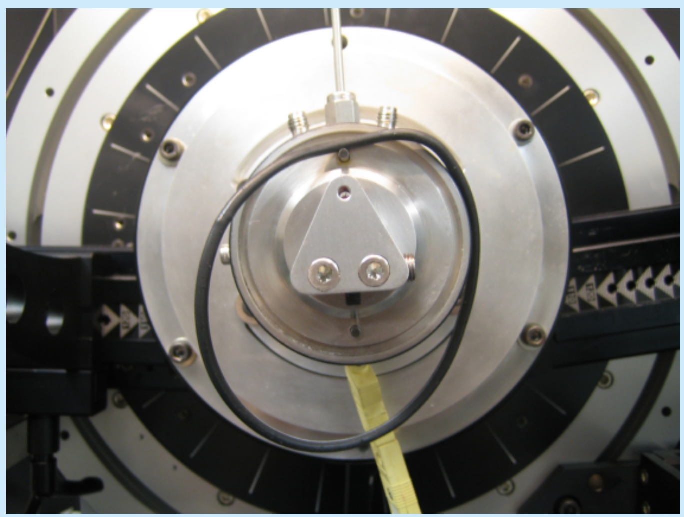
- Polymer researchers were interested in the crystallization behaviour of bio-polymers under sub- and supercritical CO_2.
- Decided to construct a cell for *in-situ* lab XRD
  - rated for 125 bar (1800psi) dry CO_2, 200ºC (recirculating)
  - intended for use with MoKα (17.5 keV) and PSD detector
- Existing literature design re-visited with finite element analysis
  - modifications made for compliance with the ASME pressure code
- 304SS pressure vessel (Nitronic 60 for other parts)
- 1/8” thick coated beryllium windows
- Elastomer seals (started with Viton but changed to Aflas)

Polymer crystallization under CO_2 pressure

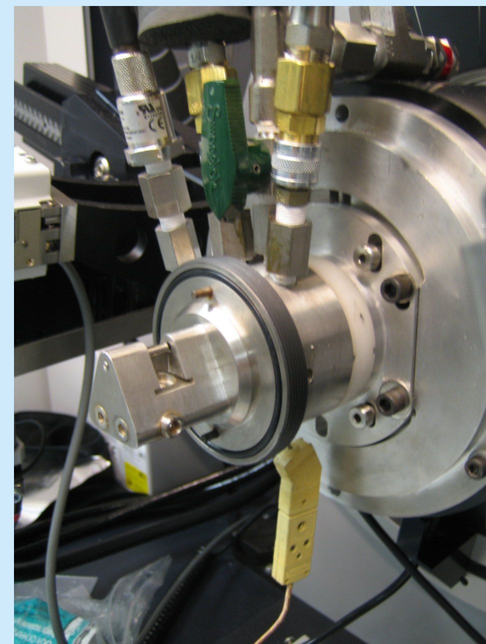
- The cell took ~2 years from concept to delivery
- The cell worked very well but shortly after commissioning the polymer researcher left NRC and the project ended.

The Gen1 stage mounted on a Bruker D8 diffractometer





Viton gets the 'bends' with high pressure CO_2. Aflas resists explosive decompression

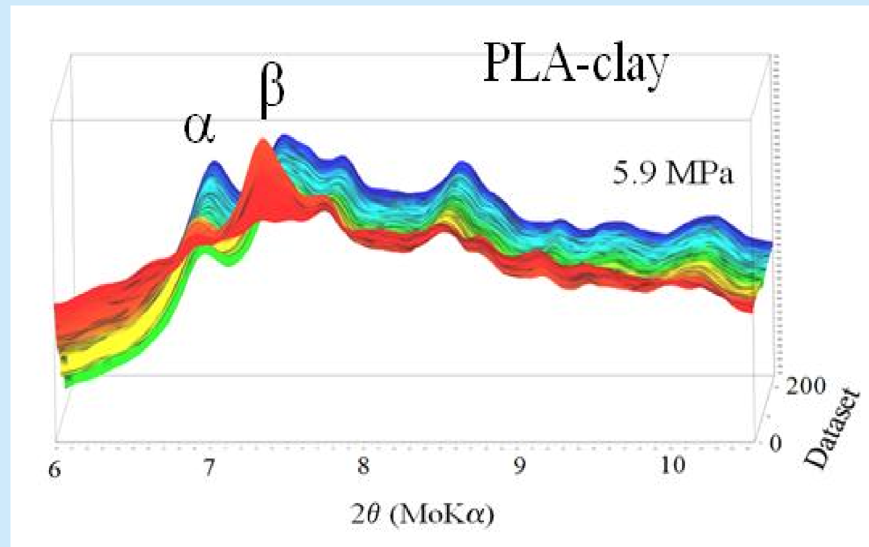


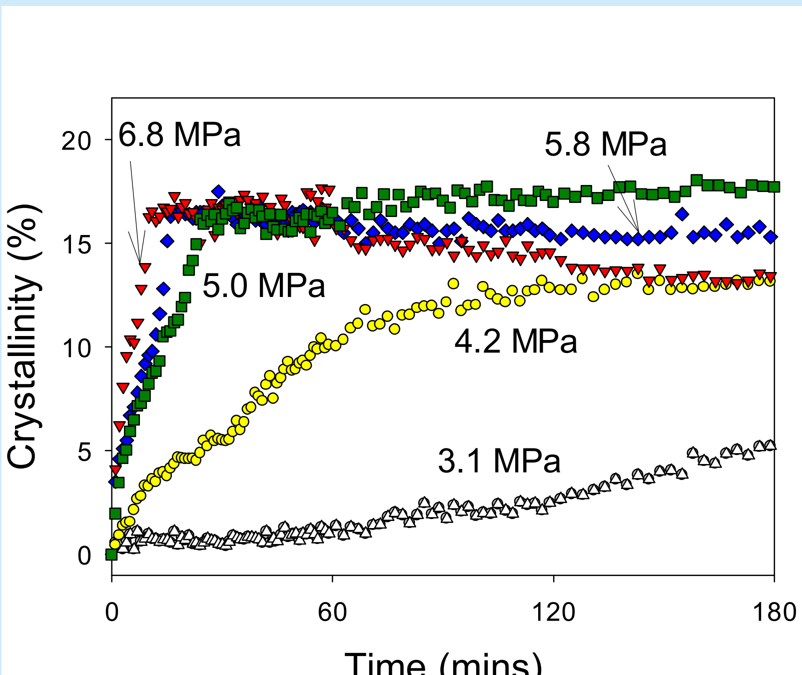
Cover held with a threaded collar

Polylactic Acid

- Crystallization of PLA showed pressure dependence
- Phase changes with some samples…

Crystallization and phase evolution between α and β-PLA in a polylactic acid–clay composite under dry CO_2





Crystallization over a period of 3 hours of PLA-clay composites under dry CO_2

What next?

- Had unique expertise and equipment but needed a new direction…..
- Was suggested that such technology could be useful for studies relating to reaction kinetics in CO_2 sequestration
  - geochemical models rely on reaction kinetics data to make long term predictions on the fate of CO_2 underground
  - however, there is a serious lack of experimental data on possible reaction kinetics under down-hole conditions
- The big question – can a lab pressure cell give us anything useful?

Proof of concept using Gen1 cell

- Gen1 stage very limited
  - not designed for wet experiments – have to improvise
  - 304SS susceptible to corrosion – high purity H_2O needed
- Targets for a proof of concept
  - synthetic calcium silicate hydrate – very reactive
  - wollastonite – reactive and readily available in pure form
  - calcined lizardite – more reactive than raw serpentine
- Samples had to be damp before heating
  - water is necessary for gas transport and reaction
  - limits upper temperature due to evaporation

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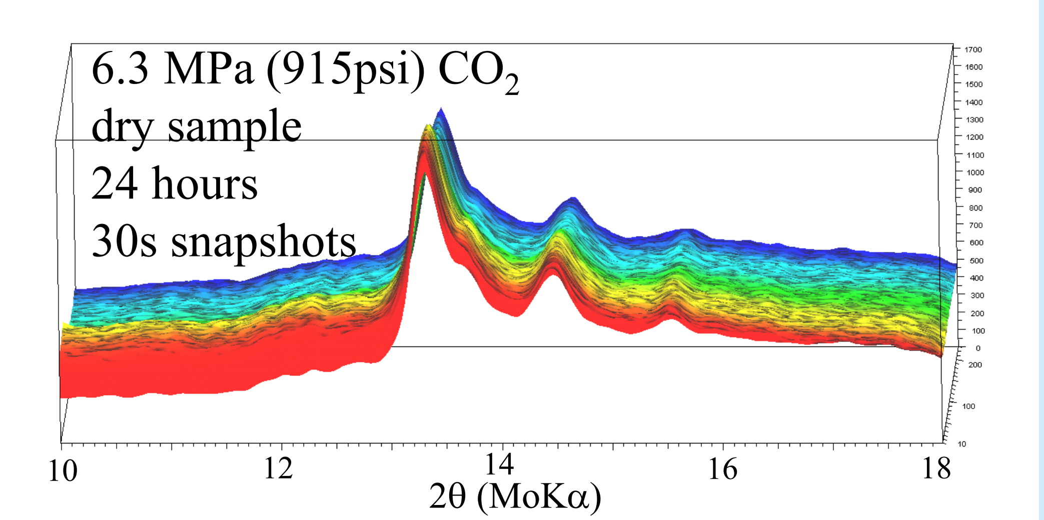
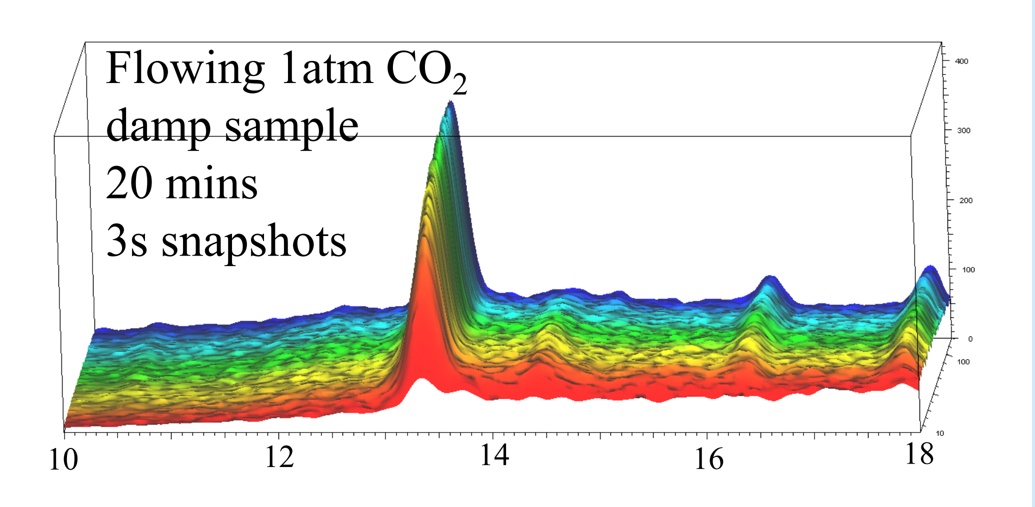
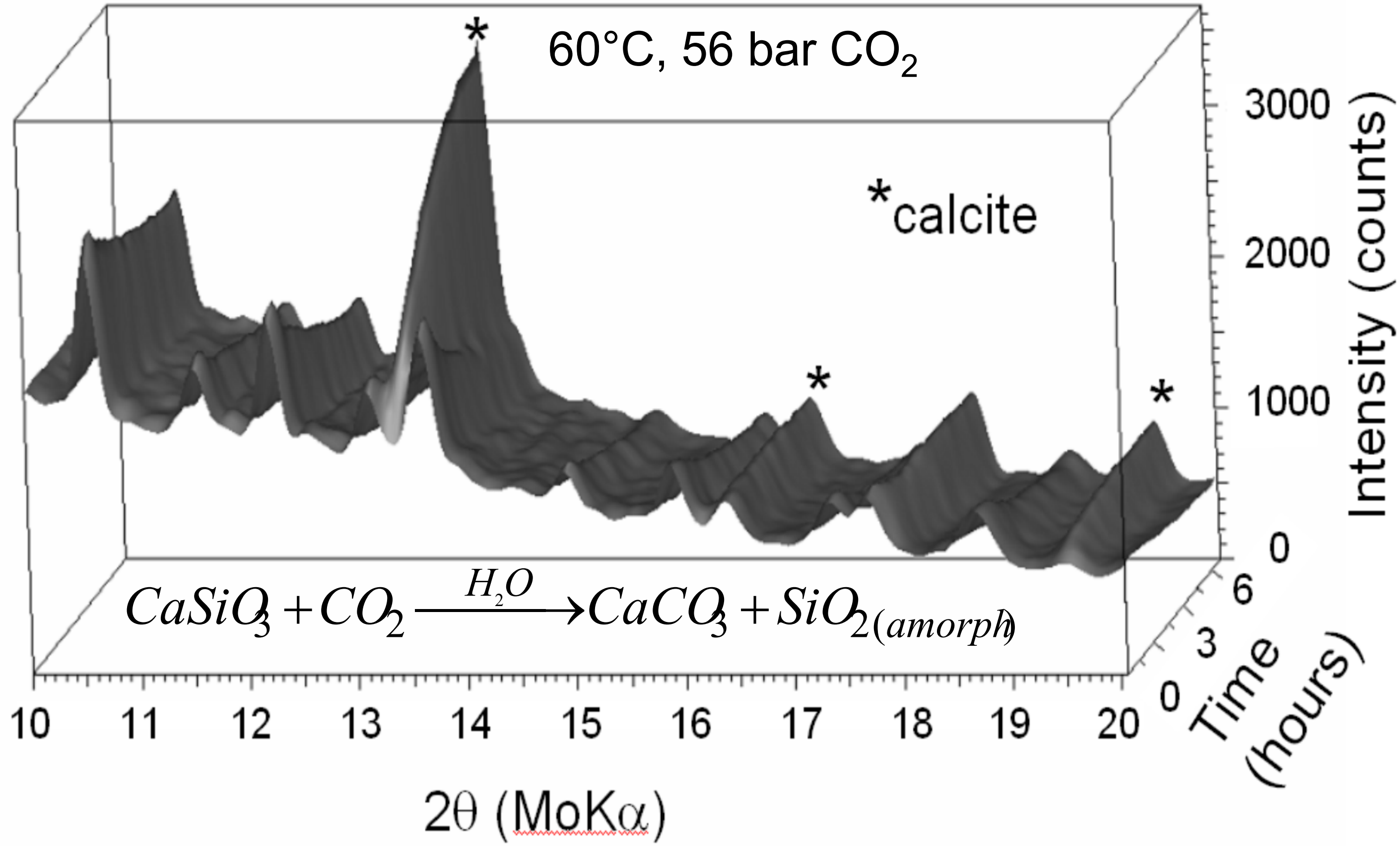
Effect of water – synthetic C-S-H carbonation

- Calcium silicate hydrate (C-S-H) is the main binding phase of cement and very reactive with CO_2
- Without water no reaction at 915psi over a full day
- A couple of drops of water and reaction almost instantaneous with flowing CO_2
  - struggled to get good enough time resolution





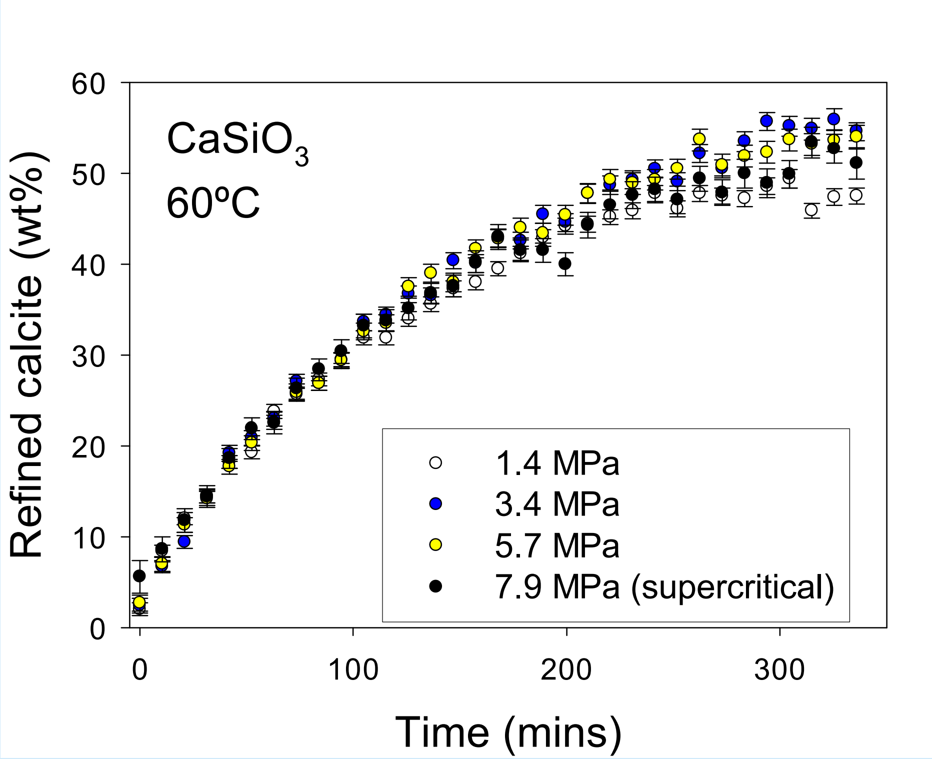
Wollastonite – $CaSiO_3$



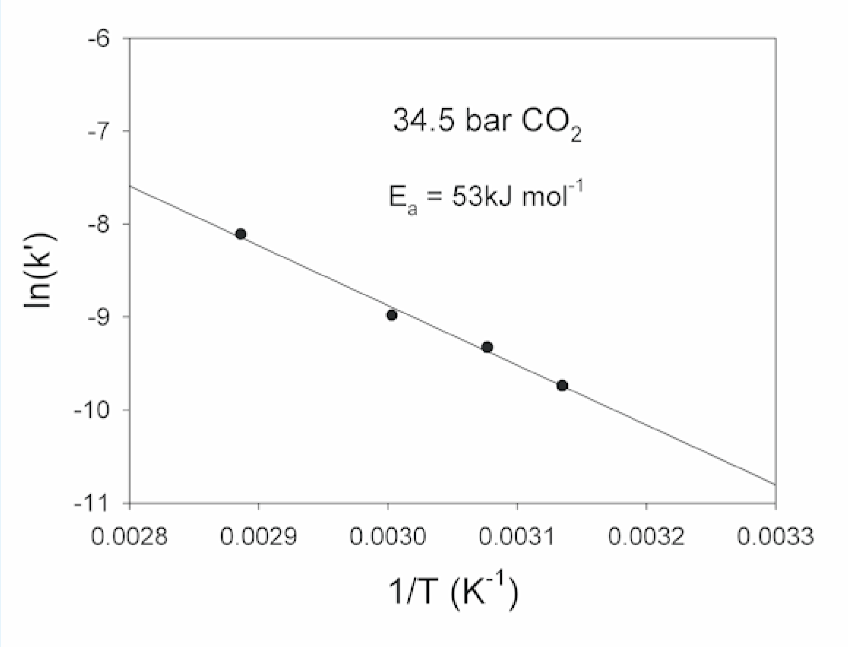
$$CaSiO_3 + CO_2 \xrightarrow{H_2O} CaCO_3 + SiO_{2(amorph)}$$

Time-resolved XRD data showing carbonation of damp wollastonite over 6 hours

Wollastonite – $CaSiO_3$



Carbonation at 60ºC under different CO_2 pressures. Reaction rate not affected when CO_2 supercritical.



Arrhenius plot for carbonation of $CaSiO_3$ to give activation energy for reaction

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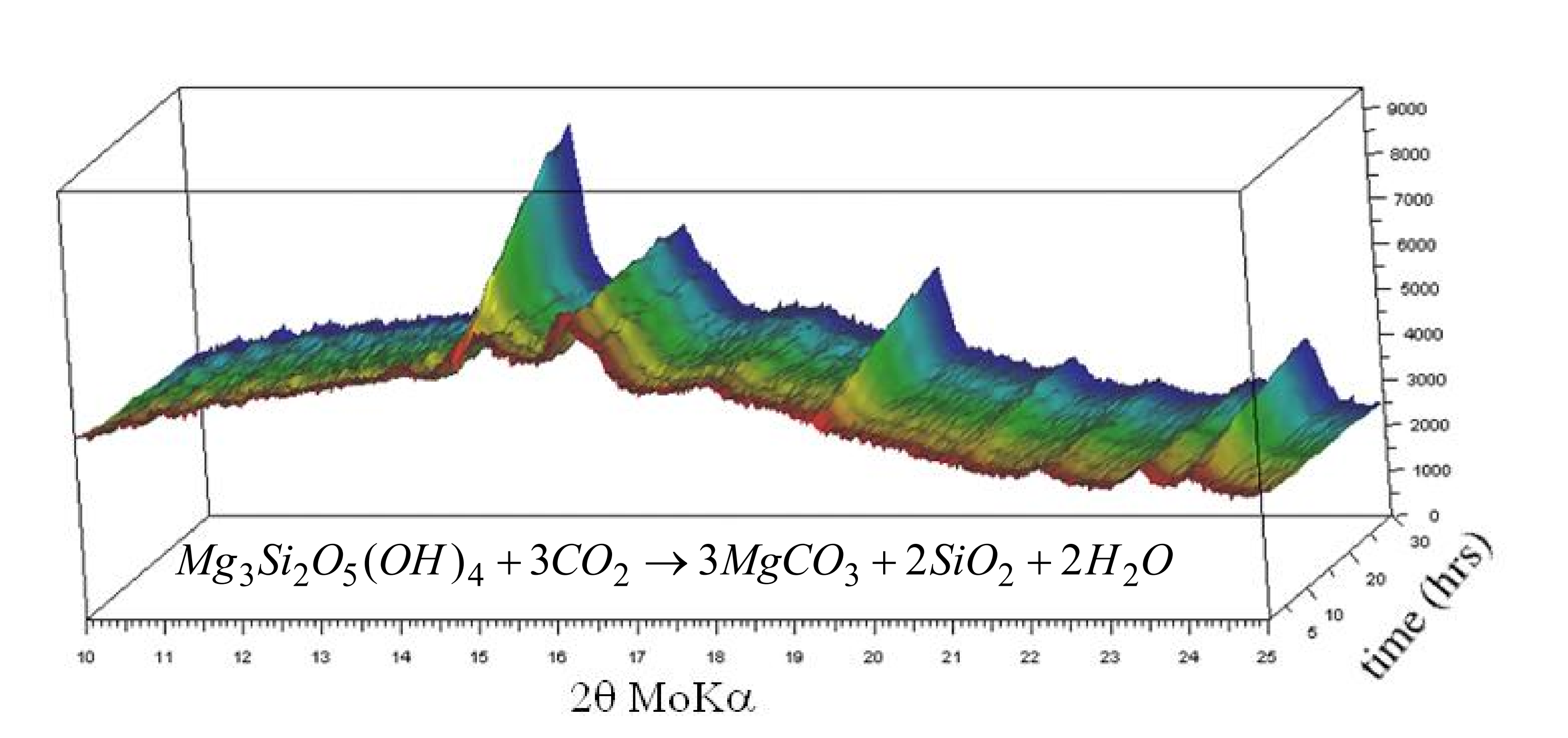
Lizardite (the non-chrysotile serpentine)

- Mg silicates much more sluggish reactions – had to calcine it to get reaction under these conditions



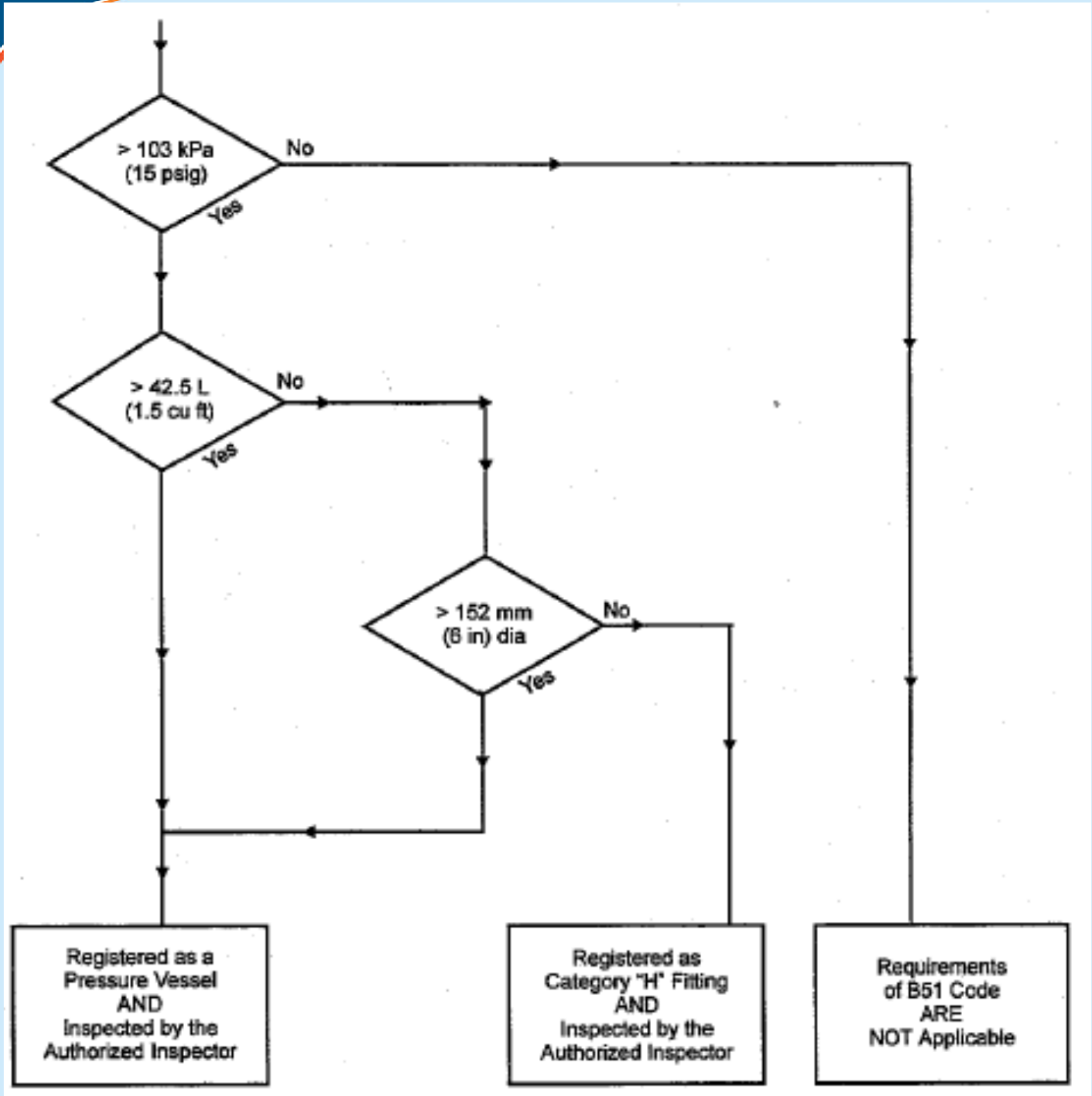
$$Mg_3Si_2O_5(OH)_4 + 3CO_2 \rightarrow 3MgCO_3 + 2SiO_2 + 2H_2O$$

Carbonation of damp, calcined lizardite over 30 hours (4 minute snapshots, 125 ºC, 35 bar CO_2)

The Next Step…

- A custom-designed cell to simulate down-hole conditions
- Would still have to meet CSA regulations and ASME pressure code but working conditions much more severe
  - 300ºC max
  - 300 bar (4350 psi) max
  - concentrated brine (e.g. Salton Sea)
  - acidic conditions (pH3)
  - sour conditions
  - possible impurity gases (e.g. SO_2)
- CO_2, H_2S and CH_4 can be supercritical in this range of conditions

Decision-tree for vessels containing lethal gases under CSA regulations



Due to small size and gas volume the cell classified as a fitting.

Note that in this tree car tires would be classed as pressure vessels! Tires are specifically exempted under the regulations….

Lab & Synchrotron as Complimentary Sources

- High pressure experiments usually done at synchrotrons
  - brightness, tuneable wavelength, detector coverage, resolution…
- Very good for fast reactions
  - e.g. reactions with impurities in the CO_2 stream

- However…..
  - many reactions in proposed CO_2 reservoirs are very sluggish
  - getting kinetic information could take weeks or even longer….
  - synchrotron beamtime isn't available on that timescale

- Lab-based systems are less powerful, slower but….
  - if the reactions are slow then….
  - the X-ray source can be tailored to the problem

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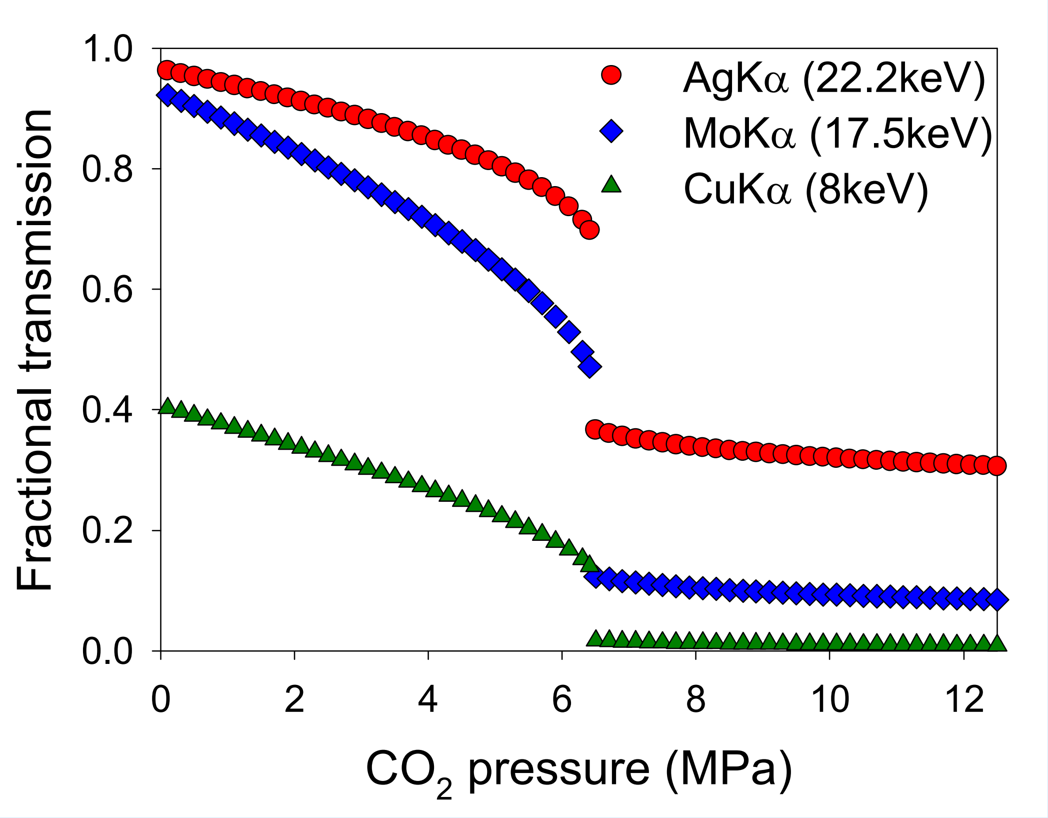
Lab Systems - the energy problem…

- Lab systems are limited by the available X-ray tubes and generators
- Density of CO_2 can approach H_2O at high pressures
- Even MoKα won't punch through – too much attenuation
- Highest practical energy is a silver anode X-ray tube but very rare



Theoretical room temperature X-ray transmission (Gen1) at increasing CO_2 pressure with different X-ray tubes

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Challenges in Building the Gen2 Cell

- Have to satisfy pressure regulations and ASME code
  - ASME boiler and pressure vessel code written for industry
  - materials for a 10 ton boiler not exactly suitable
  - have to get it right first time, on-the-fly modifications not allowed

- Space – we have to make the assembled stage small and light enough to fit on a lab diffractometer θ–θ goniometer
- Design for both reflection and transmission with same cell
- Have to find a TSSA-approved pressure-vessel company willing to work on an all-machined fitting
  - TSSA is the Ontario regulatory body for pressure vessels

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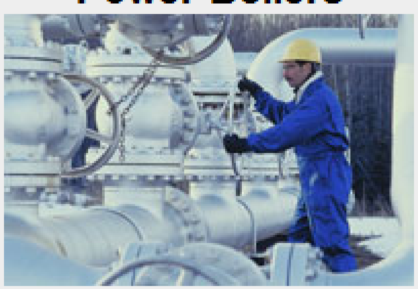
Materials Selection

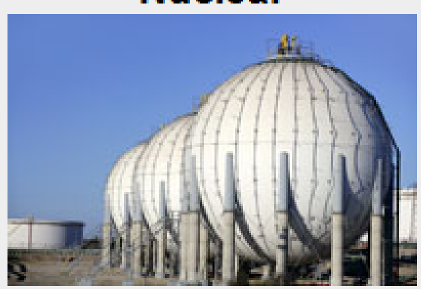
- Materials have to withstand extremely corrosive conditions
  - candidates for vessel were alloys suitable for geothermal wells
  - NACE not enough, had to be ASME compliant
- Grade 20 titanium would be great but its not code-approved
- Settled on C-22 for best corrosion resistance rather than strength
  - bar-stock >4” diameter acceptable under Section VIII, division II ASME but not acceptable under B31.3 piping code
    - had to get a 4” forging made to be code compliant
    - lack of consistency in different sections so gets very complicated…

Power Boilers



Section I, IV

Nuclear



Sections III, XI

Pressure Vessels

Sections VIII, X, XII

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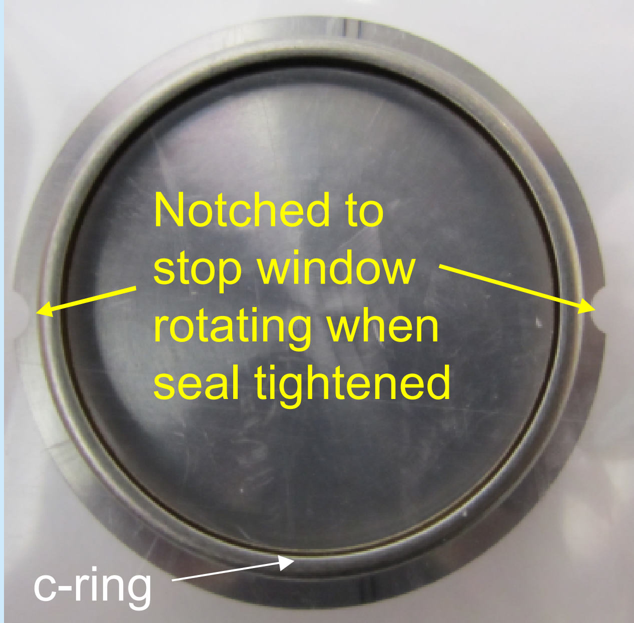
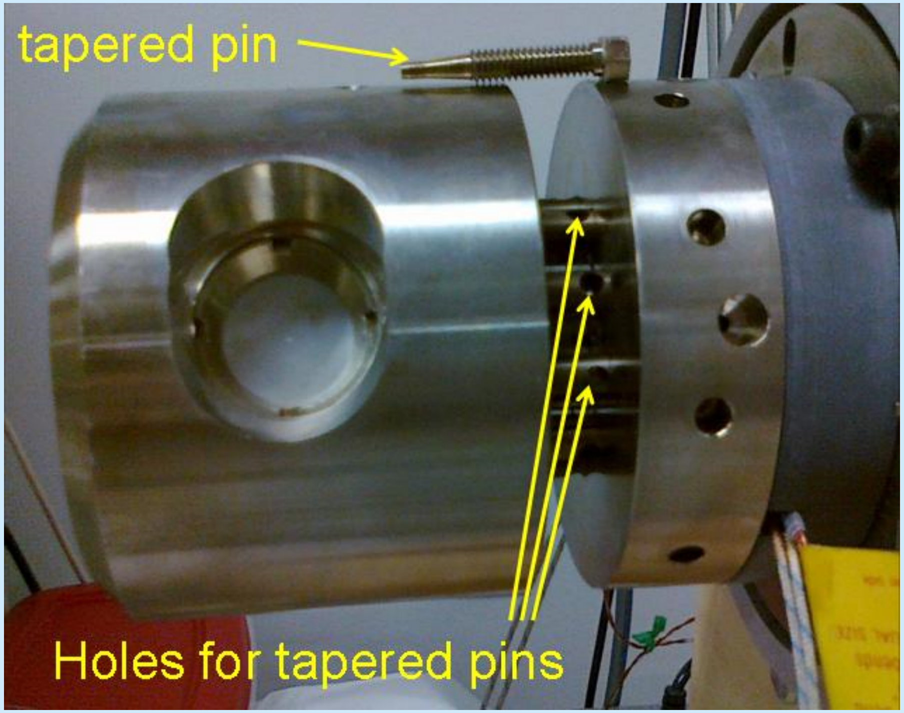
Windows

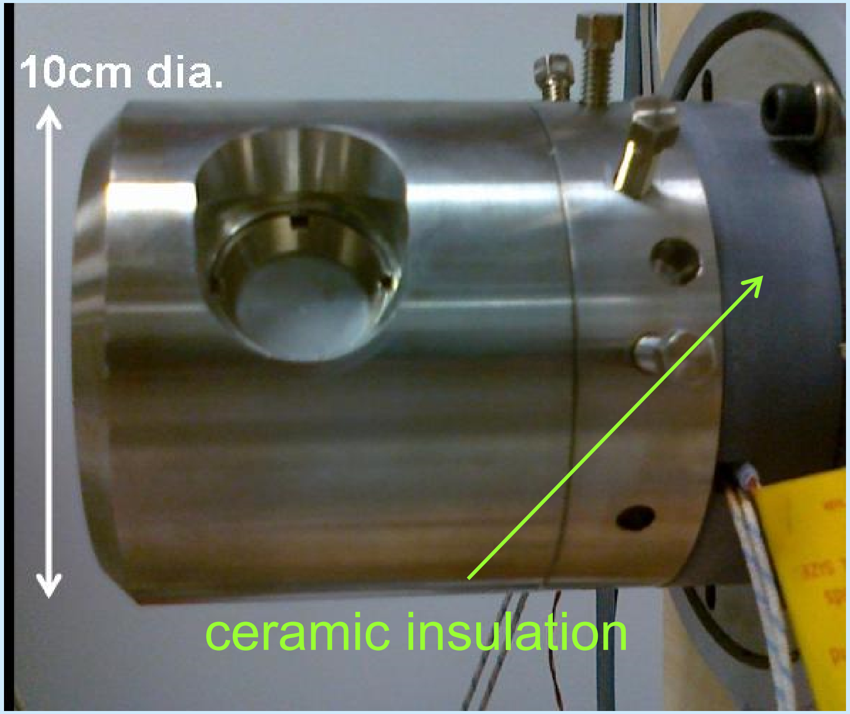
- The windows were the biggest problem…
  - Beryllium very sensitive to chloride corrosion but can get certified stress-strain behaviour for structural grade Be
- Would be great to use thinner diamond of sapphire windows but
  - materials properties not certified so can’t use them
  - tests to failure on windows not good enough…
- Brush-Wellman recommended Ta coating
  - AgKα can get through it
  - window assembly designed to avoid damaging this coating
  - each window ¼” thick and costs $2500!
- Nickel alloy c-rings used for window and cover seals
  - The seal with c-rings actually improves with pressure



What it looks like…

- Complete redesign from the ground up
  - little in common with Gen1 design

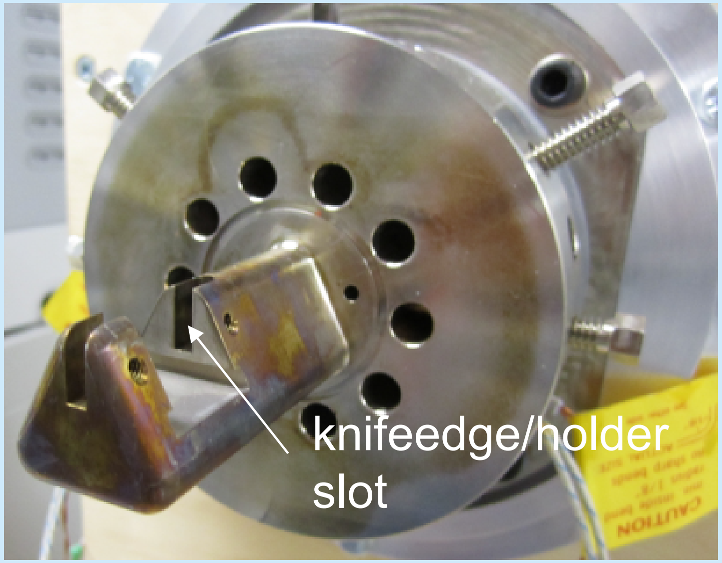




Cover held by 12 tapered pins seating into retaining bolts. The Gen1 design using a locking collar warped during FEA analysis under the stress of Gen2 conditions.

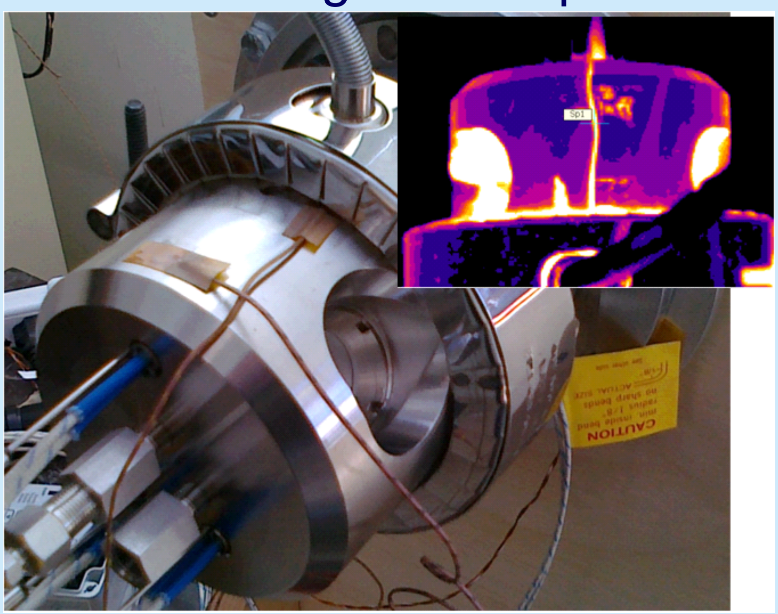
Other features

- Electrically heated
  - 3 sets independently controlled for a more even temperature (reduce stress)
- Multipurpose internal slot
  - integrated Ta knife-edge for reflection
  - sample holder for transmission experiments



The design process

- Basic design done at the NRC design and Fabrication Services – including full FEA and thermal modelling
  - done to ASME section VIII division 2 (design by analysis)
  - certified as process piping under ASME B31.3 (small volume)
- A prototype was built to test thermal behaviour of the cell
  - checking for hot spots that would increase local stresses



Instrumented mock-up of the Gen2 stage made for testing thermal behaviour. Inset is a infra-red image of the stage at an internal temperature of 300°C.

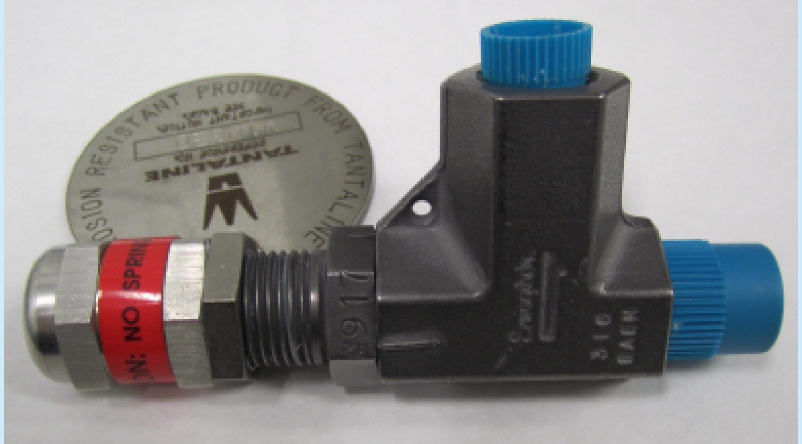
More Regulatory Headaches….

- As per Ontario regulations the design had to be fully reviewed, reanalyzed and signed off by professional engineers (in this case All-Weld)
- The design was then submitted to the Ontario regulator for yet another review (third time..) and final design registration
- Now All-Weld can go ahead and make one……
- Before delivery has to be hydrostatically tested to 1.5x maximum working pressure – 450 bar (6500 psi)

You have the cell… Now what?

- The cell has to be part of an integrated system to get results
- Siemens don't make silver anode X-ray tubes any more
  - special order (Bruker persuaded them to make a small batch)
- Standard high speed detectors for lab systems don't work with AgKα – need good efficiency make most of the weak signal
  - special custom Si-strip detector required
  - for transmission work a custom AgKα focussing mirror is needed
- High pressure CO_2 syringe pump
- Corrosion-resistant valves/fittings

The most expensive Swagelok relief valve you'll ever see…
Ta-coated, special Kalrez o-ring for valve seating



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Timeline

- The whole process has taken over 2 years from design concept to finish……. again
- All-Weld due to complete construction by mid-March
- After testing delivery is expected end of March
- Commissioning and testing to follow on lab diffractometer
- Then we're open for business!
- Integration of cell on a NSLS beamline will follow….

Conclusions

- The whole process is one very big headache
- Pressure regulations make life very difficult and ironically can be less safe with necessary compromises on materials
- Canada has the toughest pressure vessel regulations in the world
  - the US is actually a bit easier…
- For CO_2 sequestration work both synchrotron and lab-based studies will play a role
  - some reactions are too slow for synchrotrons unless you have your own beamline to play with….

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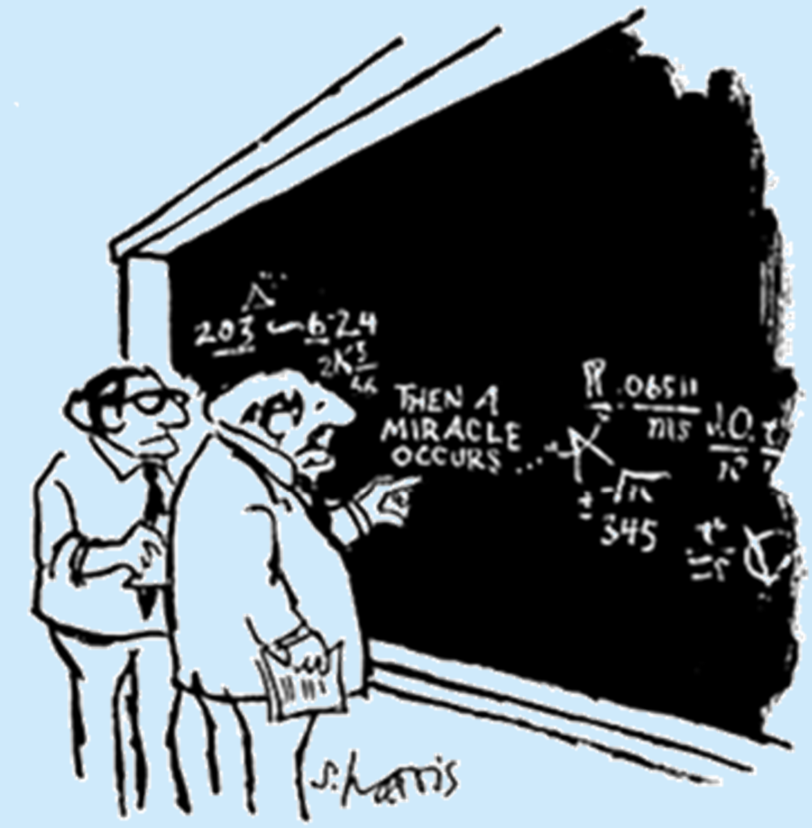
Questions?



"I think you should be more explicit here in step two."