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Title: Pressure Study of Savillex Vessels

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70 YEARS OF CREATING TOMORROW

Los Alamos NATIONAL LABORATORY

Pressure Study of Savillex Vessels

Lisa Colletti, Frank Dickson

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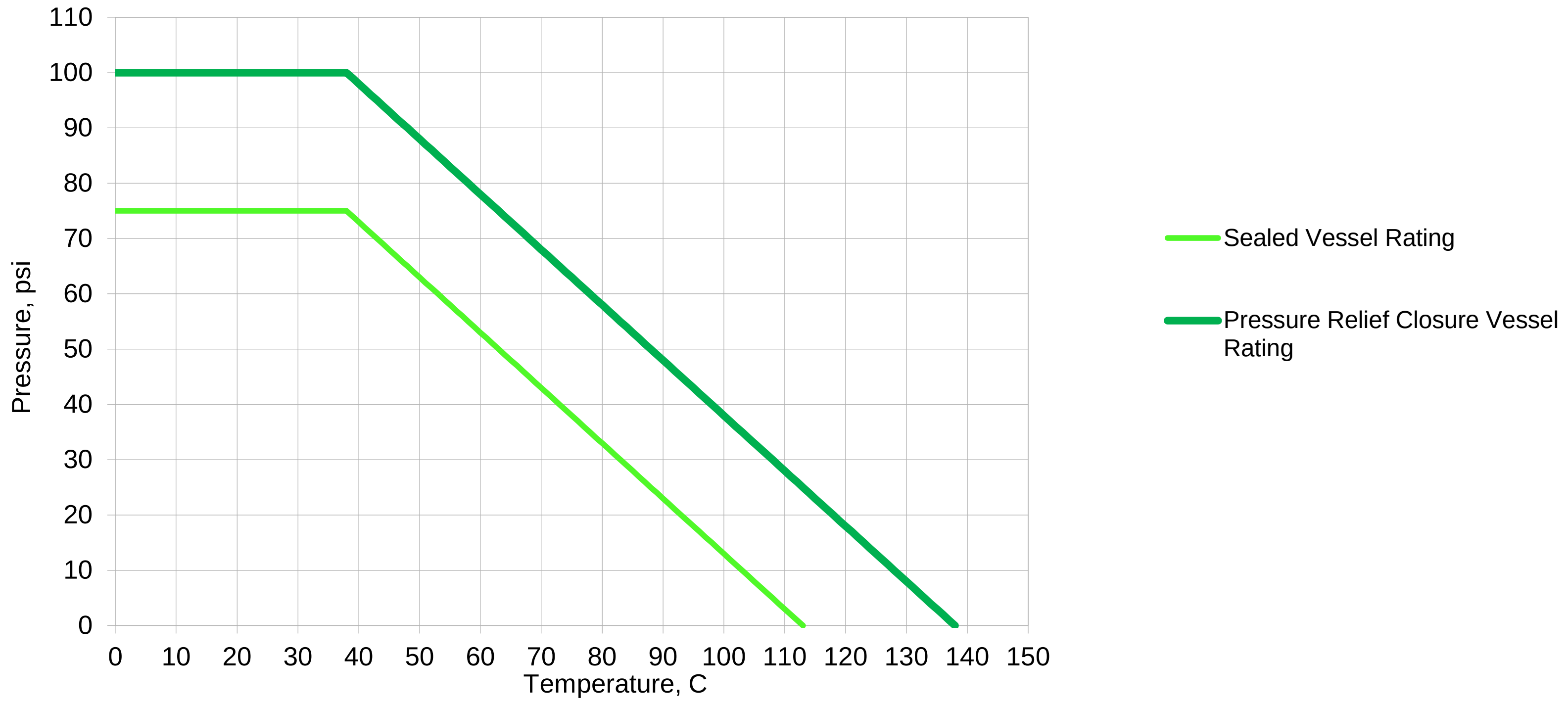
NNSA National Nuclear Security Administration

Why did we decide to test our vessels

- Previous glass vessels under went a violent disintegration in September of 2011, despite the existing process documentation (1972 paper) that indicated only 80 psi was generated. Investigation revealed changes occurring to process over 20 years prior that unknowingly changed safety envelope.
- Wanted a through understanding of our process conditions to prevent conditions that might cause vessel disintegration again (once bitten twice shy).
- A recent conversation with Dave Gallimore indicated that PS had gone with this system solely on the manufacture's specifications of vessels and had not done any independent testing of vessels.
- Manufacture states that the vessels and caps have a 100 psi rating only up to 38 ^{o}C which then drops 1 psi for every degree over that. Dissolution methods are at 120-150 ^{o}C which theoretically drops the pressure rating to 18 psi to less than 0 psi.

Manufacturer's Specification for Vessel Pressure and Rating vs Temp



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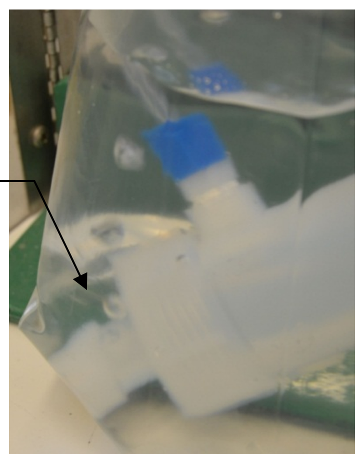
Room temperature testing

Pneumatic Testing

- Vessels pressurized with Argon gas at room temperature leaked at 20 psi and less
- All 3 valves tested leaked

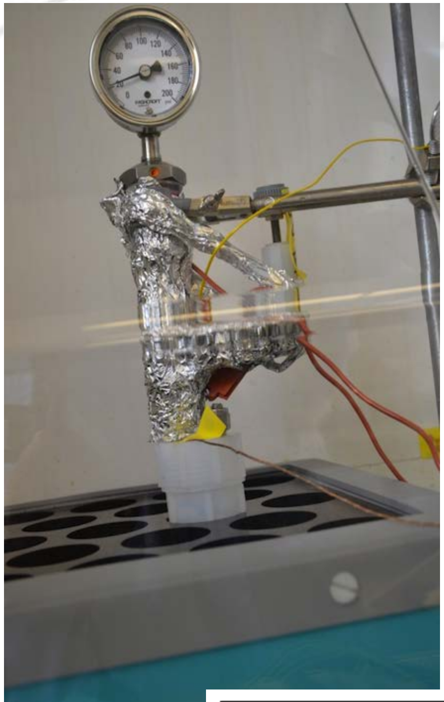
BUBBLES FROM RELIEF PORT AT 20 PSI (ROOM TEMP)



Hydrostatic Testing

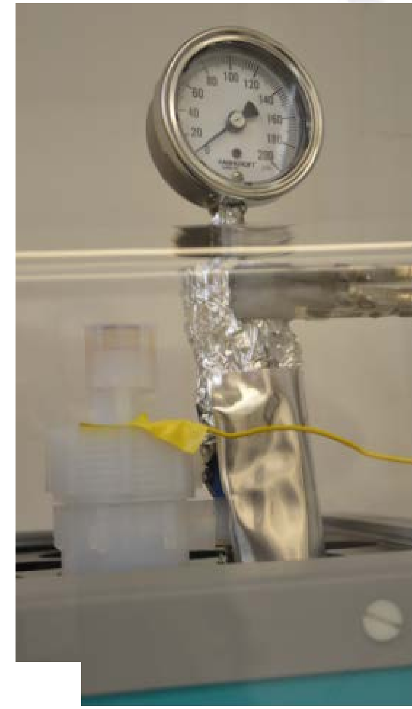
- Vessels filled and pressurized with water
- Bubbles seen at 20 psi and less, as low as 8 psi
- All 6 valves tested leaked

Pressure vessel set up

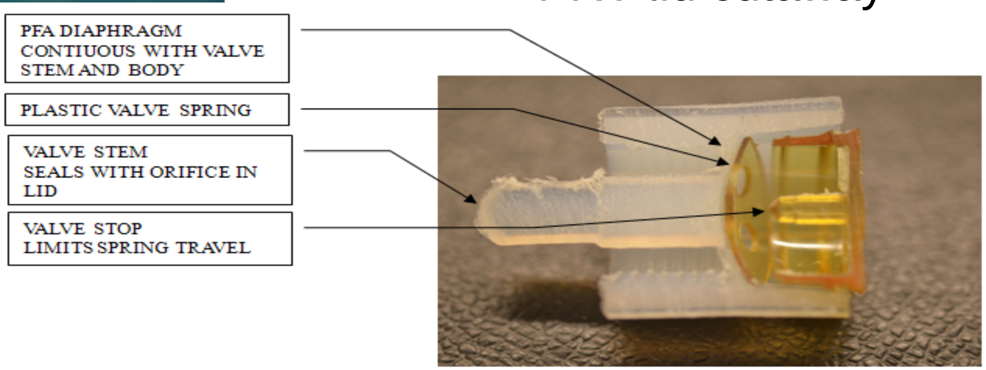


Without PRV lid

With PRV lid



PRV lid cutaway



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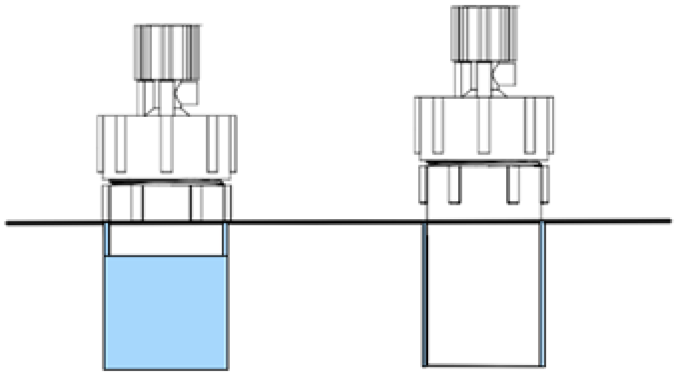
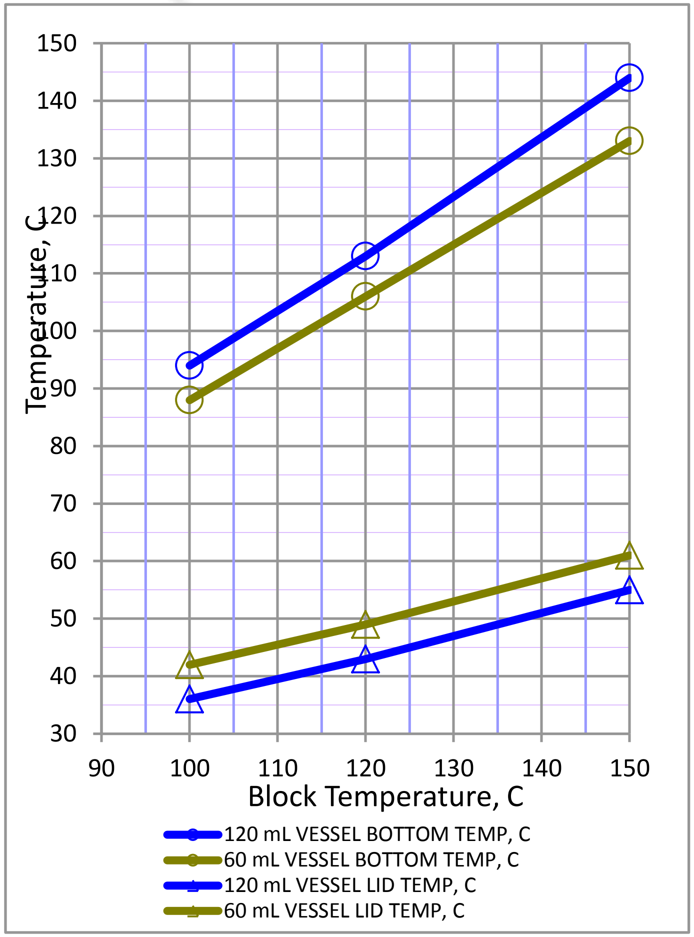
Empty Vessel Heating Characteristics





THERMAL PROPERTIES	Conductivity W/m*K	Specific Heat KJ/Kg*K
Air (20 C)	0.026	1.005
Graphite	400 - 1700	0.71
PFA	0.19	1.17

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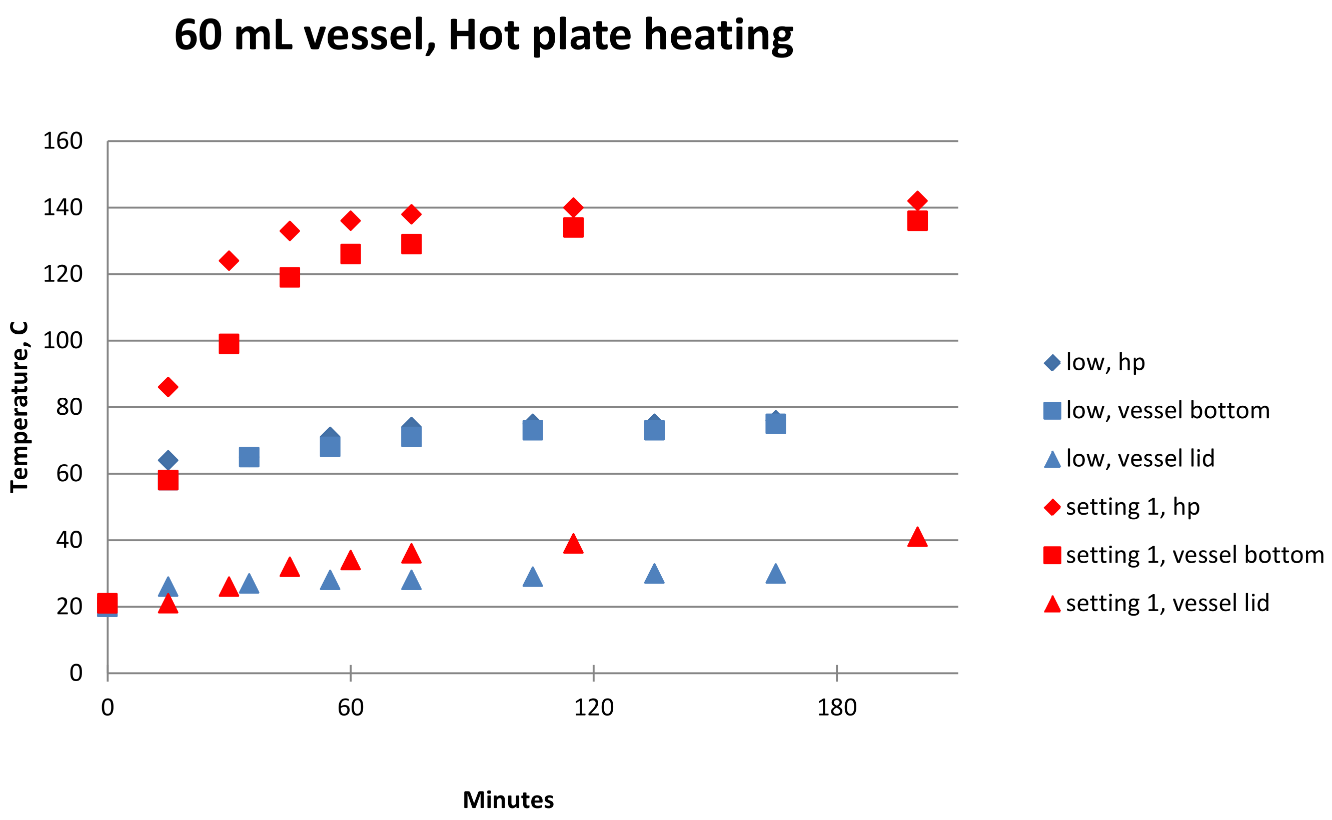
How does the use of a hotplate affect temperature profile?



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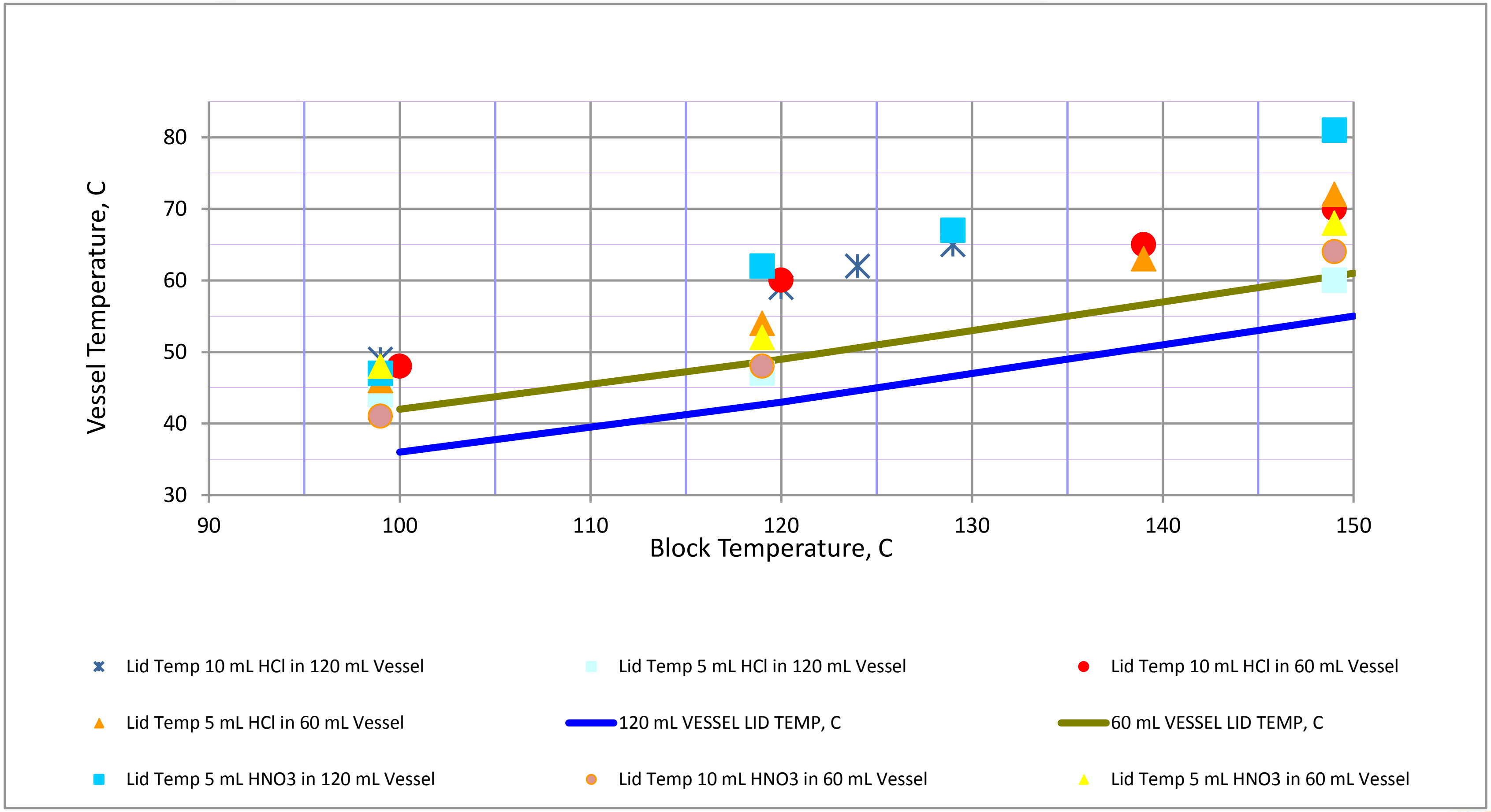
Max Lid temperatures with acids in vessels



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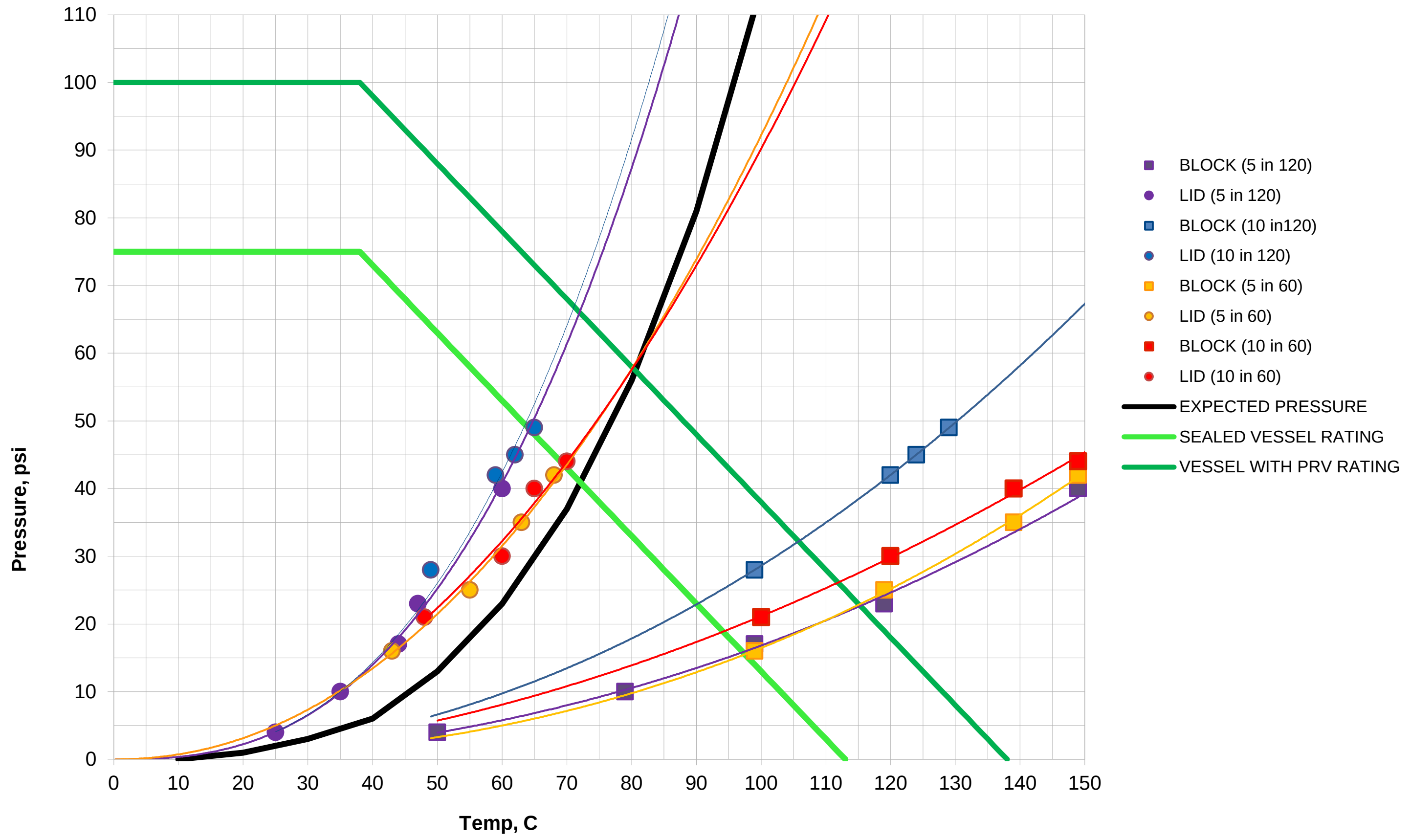
Vessel Pressure vs Temp

5 and 10 mL 33% HCl Acid in 60 and 120 mL Vessel



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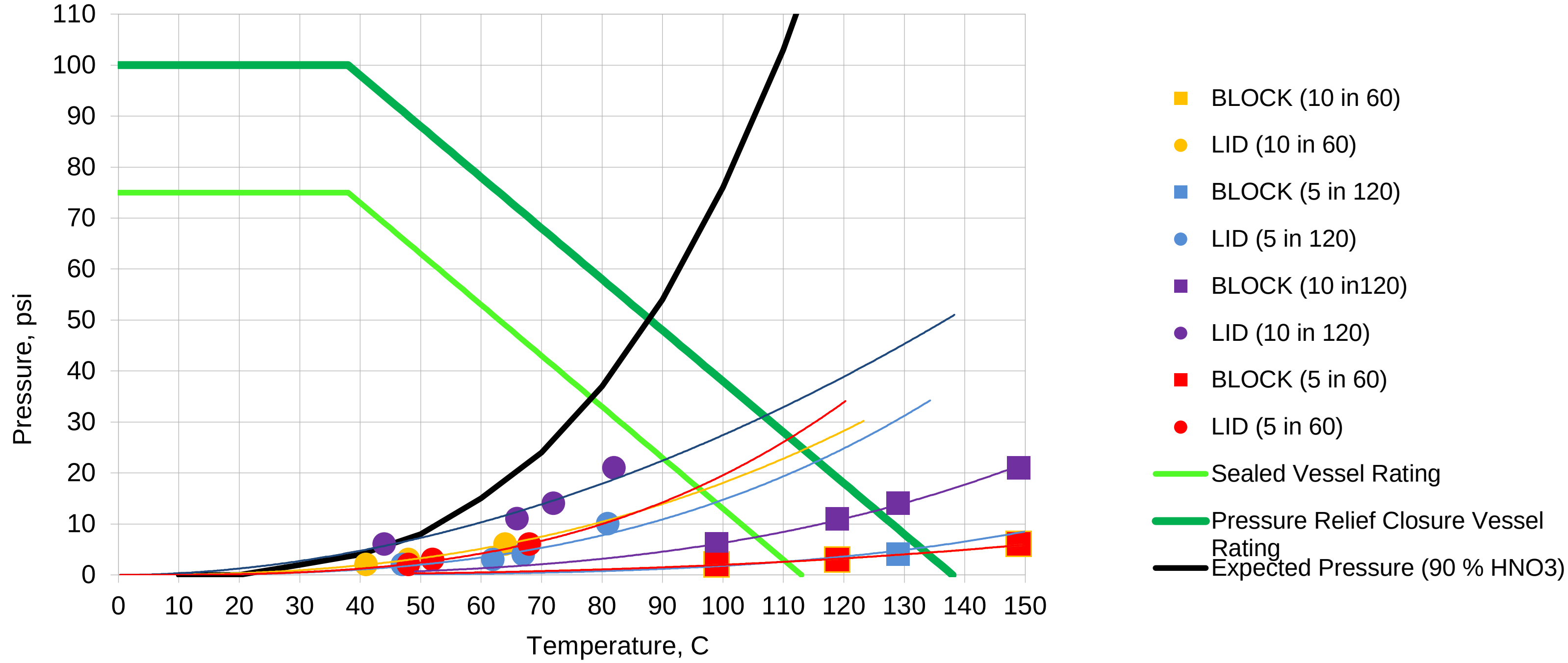
Vessel Pressure vs Temp

5 and 10 mL OPTIMA (69%) HNO3 in 60 and 120 mL Sealed Vessel



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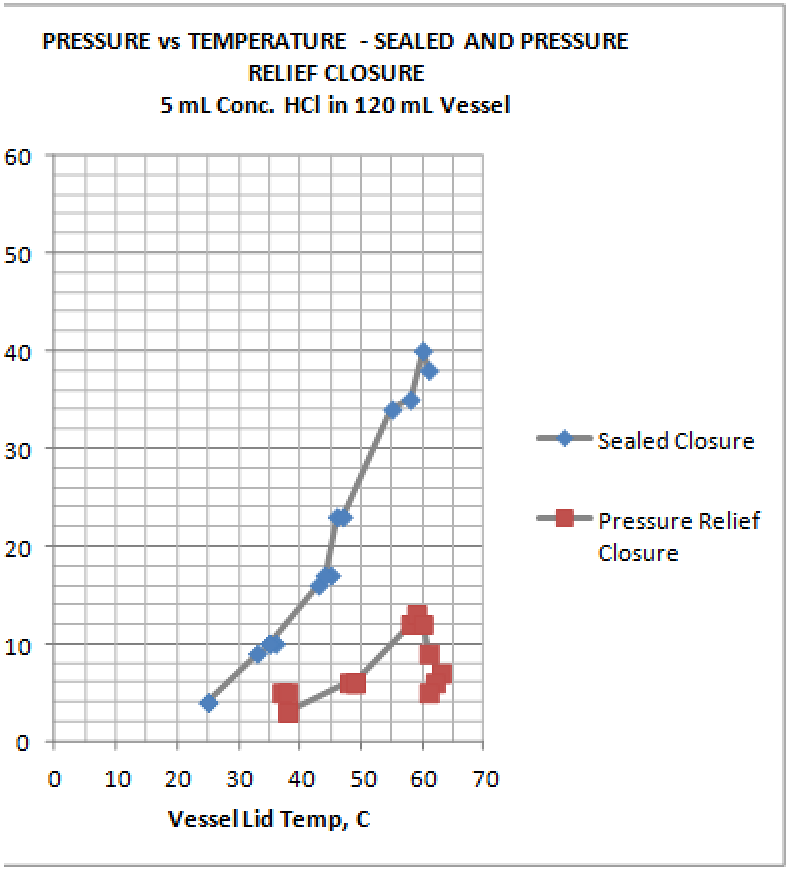
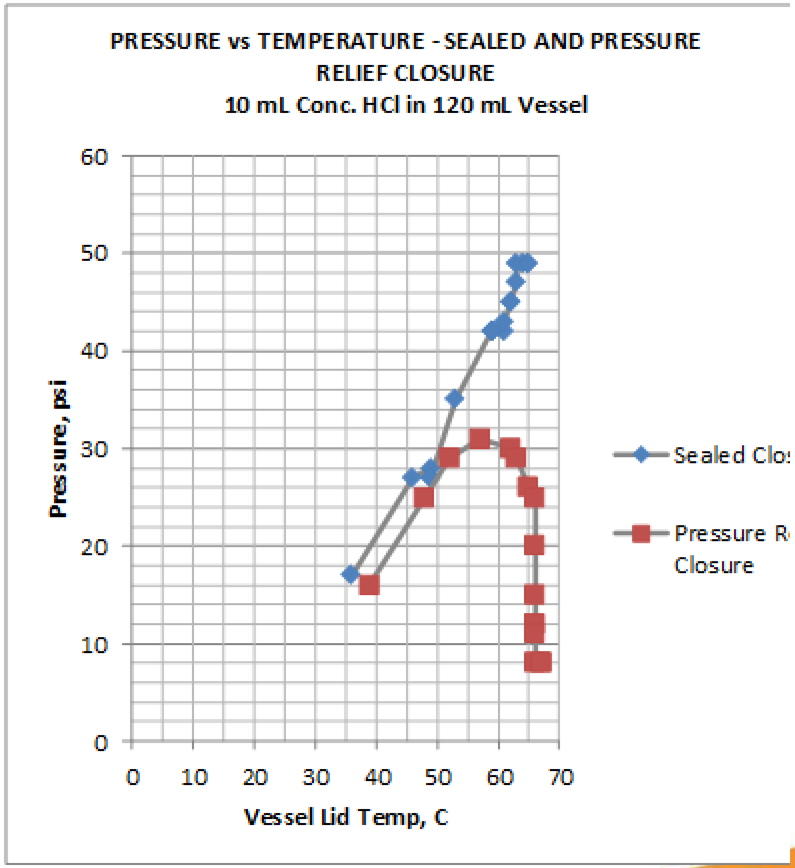
Comparison of sealed vs PRC





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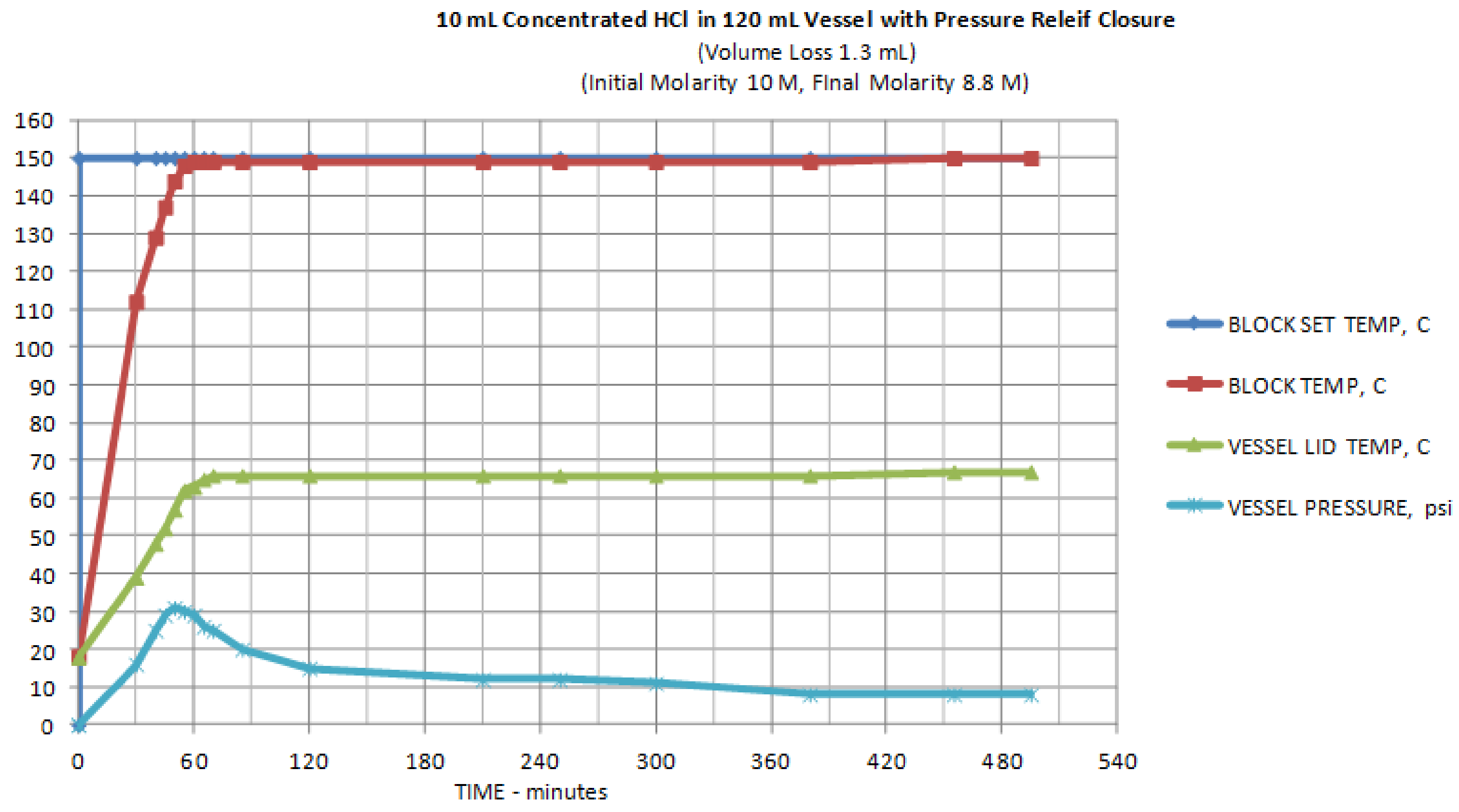
What a full run looked like

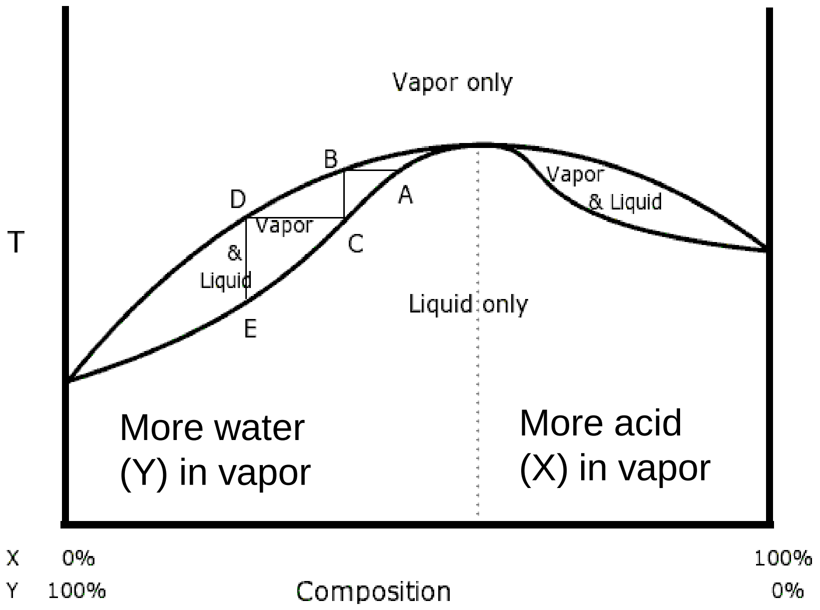


Acid loss summary

Acid	Acid	Vessel	Filler	Time	Temp	Diff. in Acid Weight	Concentration, M		
	mL	mL	Block	hr	C	g	Initial	Final	Diff
Conc. HCl	5	60	Yes	5-Apr	150	0.75	10.3	8.7	1.6
Conc. HCl	5	60	No	5-Apr	150	0.49	10.3	9.5	0.8
Conc. HCl	5	60	Yes	5-Apr	100	0.46	10.3	10.3	0
Conc. HCl	5	60	No	5-Apr	100	0.33	10.3	10.3	0
Optima HNO3	5	60	No	5-Apr	150	0.04			
Optima HNO3	5	60	Yes	5-Apr	150	0.14	15.3	15.3	0
Optima HNO3	5	120	NA	5-Apr	150	0.26	15.3	15.3	0
Optima HNO3	10	120	NA	5-Apr	150	0.08	15.3	15.3	0
Optima HNO3	5	60	No	5-Apr	100	0.04			

HNO3, HCL, HF are all negative azeotropes

- Azeotropic point: The solution composition exactly matches the composition of vapor phase. You cannot separate the two components by basic distillation processes.
- for a system pressure of 1 bar
  - HNO_3: BP = 120.5°C, and a HNO_3 concentration of 68 wt%, (15.2M)
  - HCl: BP = 108.6°C, a HCl concentration of 20.2 wt% (6.15M).
  - HF BP = 120 °C , HF concentration of 35.35% (20M).



- *By starting at 12 M HNO_3, PS is potentially distilling out water shifting concentration towards azeotropic point.*
- *By starting with 15.3 M HNO_3 in PA, concentration never changes even with solution loss.*
- *By starting with 12M HCl in PA, we distill out HCl lowering the HCl concentration in solution towards azeotropic point.*

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Is solution loss a problem… YES!

- Some materials are volatile (SiF_4, $GaCl_3$, etc.) which would affect analyses of trace elements.
- Solution chemistry is critical during the dissolution of PuO_2
  - Use of HCl allows higher HF concentrations, a critical factor in dissolution of high fired materials or materials with large amounts of refractory materials.
  - Loss of HCl affects the solution chemistry by lowering acidity values and increasing free F^- concentrations.
  - Loss of either HCl/HNO_3 will lower the volume and increase HF and F^- concentrations
  - Both of previous effects can drive formation of PuF_4, an insoluble precipitate
  - Prevents true understanding of the dissolution process as the dissolution conditions change during the experiments.
- Loss of acid changes the matrix of the material being analyzed which is critical in
  - Separations
  - Matrix matching for spectrophotometric methods

Can we just use HNO_3? Not desired…

- Though we can just use HNO_3, this would cause massive disruptions to existing processes.
- The required changes to PA methods would cause significant increase in sample prep time and increased uncertainties.
  - We've seen this in our 238 spectroscopy system. A rough doubling of uncertainty has been seen since switching to HNO_3 for dissolution. On going work to reduce back to past levels.

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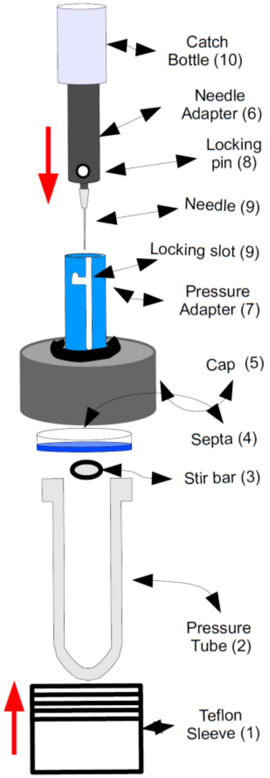
Options Going Forward

- Could potentially change to hotplate to have lower overall temperature on lid.
- Could find alternate vessels.
  - Q-tube disposable glass vessel
  - Pressure release at 200 psi, tube rated to 500 psi.
- Carry on with current method, but..
  - Some elements may be lost.
  - May require dissolution spikes.
  - May have reruns due to precipitation of PuF_4.



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