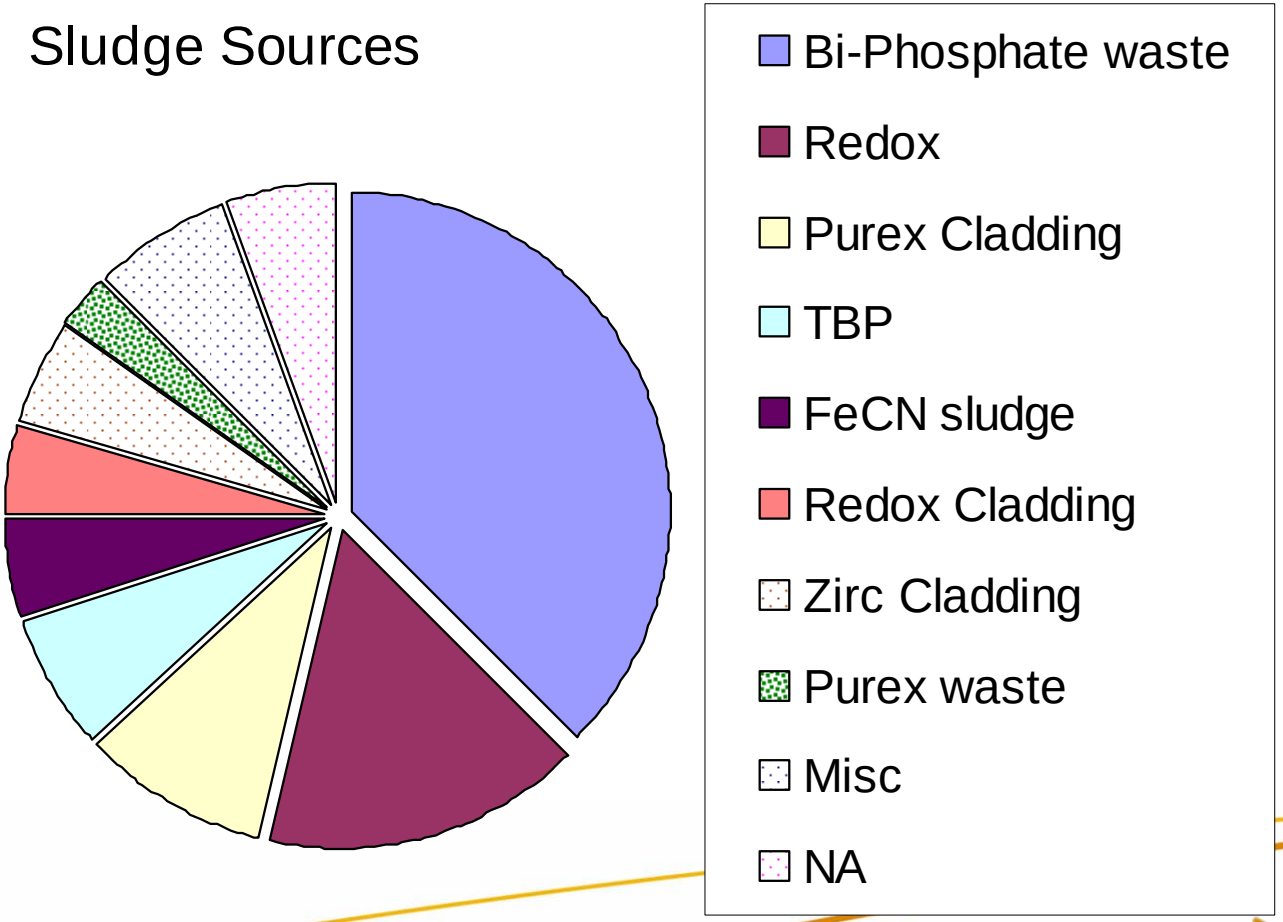
Actual Waste Testing

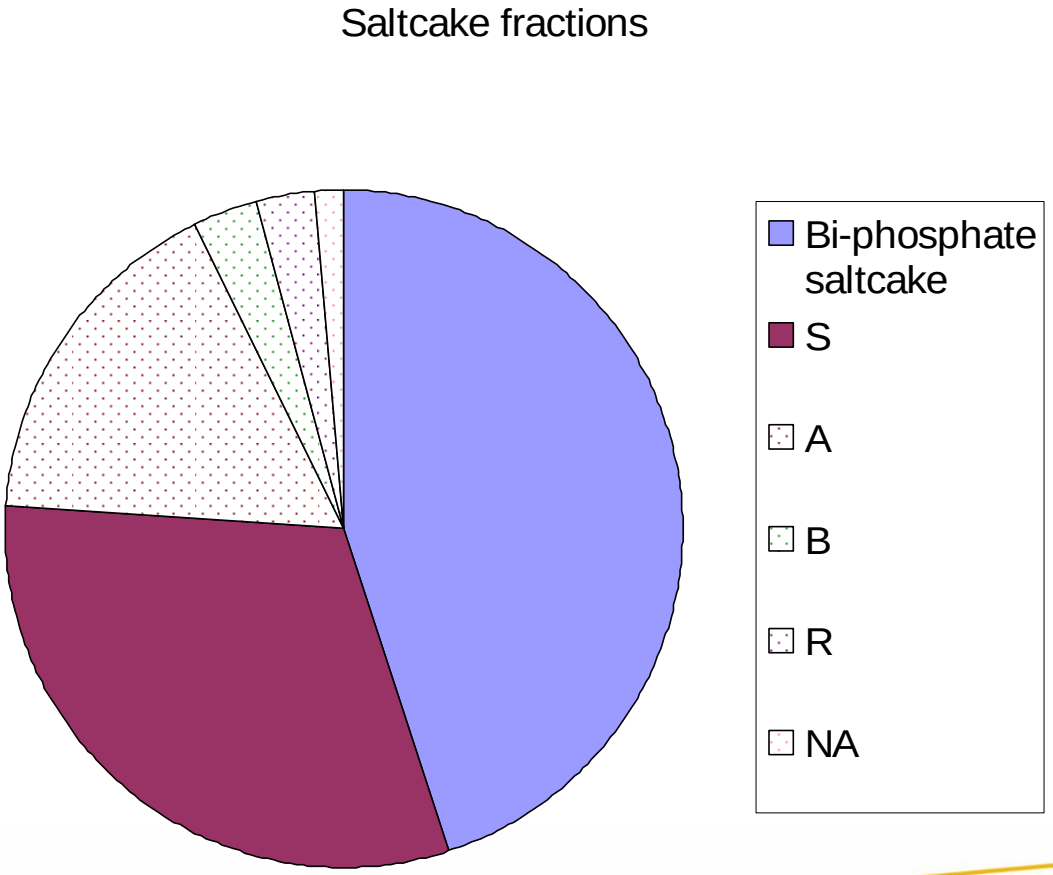
Lanée Snow
Sandra Fiskum
Rick Shimskey
Reid Peterson

Pacific Northwest
NATIONAL LABORATORY

Tested > 75% of sludge waste types



Tested > 75% of saltcake waste types



Tested 8 groups of tank waste types

Group ID	Type	Al	Cr	PO_4^{3-}	Oxalate	Sulfate	Fluoride
1	Bi Phosphate sludge	3%	3%	21%	2%	6%	12%
2	Bi Phosphate saltcake (BY, T)	18%	25%	36%	36%	43%	36%
3	PUREX Cladding Waste sludge	12%	1%	3%	1%	1%	3%
4	REDOX Cladding Waste sludge	8%	1%	0%	0%	0%	2%
5	REDOX sludge	26%	8%	1%	3%	1%	2%
6	S - Saltcake (S)	11%	38%	12%	24%	14%	3%
7	TBP Waste sludge	1%	1%	8%	0%	2%	1%
8	FeCN sludge	2%	1%	4%	1%	1%	1%

- Percentages reflect % of total inventory of species in the tank farm.
- Discussion will focus on those that make up the largest fraction of the Al in the tank farms

Pacific Northwest NATIONAL LABORATORY

Introduction

- What samples are we testing and for what?
  - Group 5 REDOX: Al – boehmite
  - Group 6: S- Salt Cake Cr
  - Group 2: Bi-Phosphate saltcake - Phosphate/Cr
  - Group 1: Bi-Phosphate sludge - Phosphate
  - Group 4: Cladding Waste REDOX - Al – Gibbsite
  - Group 3: Cladding Waste PUREX - Al – Gibbsite
  - Group 7: TBP - Phosphate
  - Group 8: FeCN - No parametric testing

Pacific Northwest
NATIONAL LABORATORY

Batch Testing Protocol

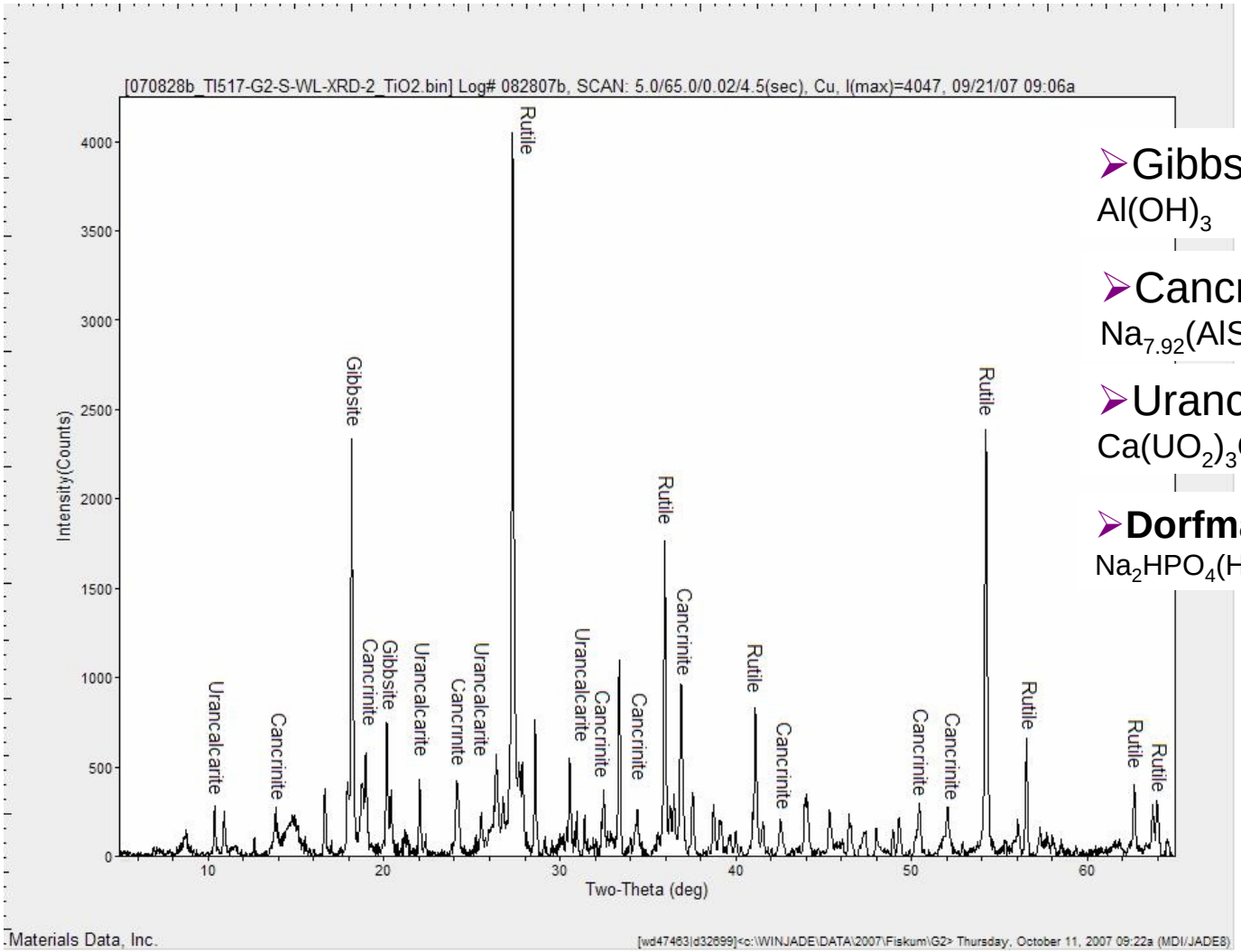
- About 1 g of water insoluble solids in 100 mL in sealed but vented vessel
- Add target amount of sodium hydroxide
- Agitated by shaking
- Temperature maintained by a heating block
- Small – 3 mL – samples removed periodically
- Samples analyzed for metal content
- Residual solids digested and analyzed to complete material balance

Pacific Northwest
NATIONAL LABORATORY

Experimental Setup

Pacific Northwest NATIONAL LABORATORY

Bi-Phosphate Saltcake 2 XRD



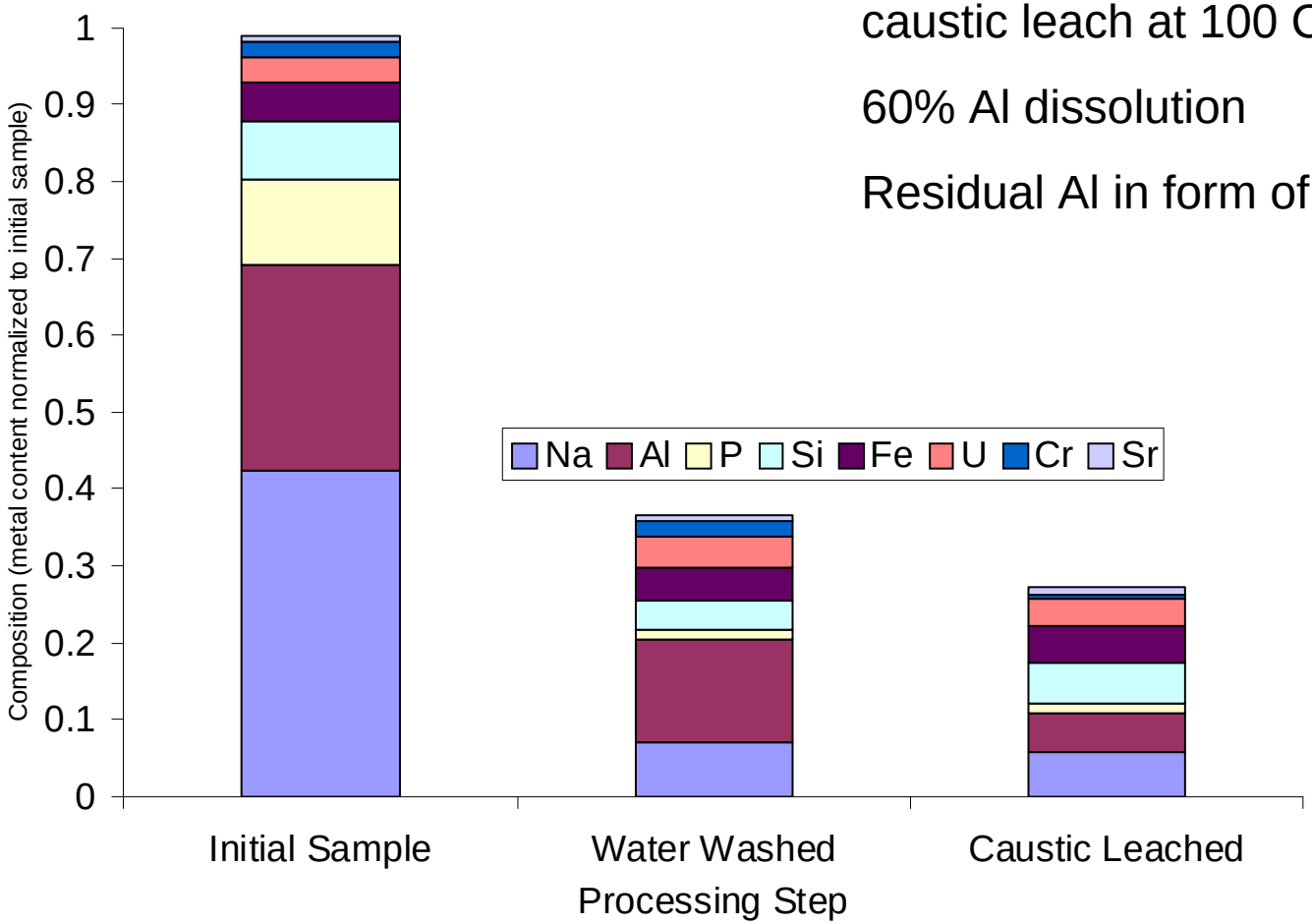
Major Phases:

- Gibbsite
  $Al(OH)_3$
- Cancrinite
  $Na_{7.92}(AlSiO_4)_6(NO_3)_{1.74}(H_2O)_{2.34}$
- Urancalcarite
  $Ca(UO_2)_3CO_3(OH)_6(H_2O)_3$
- **Dorfmanite**
  $Na_2HPO_4(H_2O)_2$

Rutile added as an internal standard

Pacific Northwest NATIONAL LABORATORY

Bi-Phosphate Saltcake Leaching Results



Reaction complete in < 4 hours caustic leach at 100 C

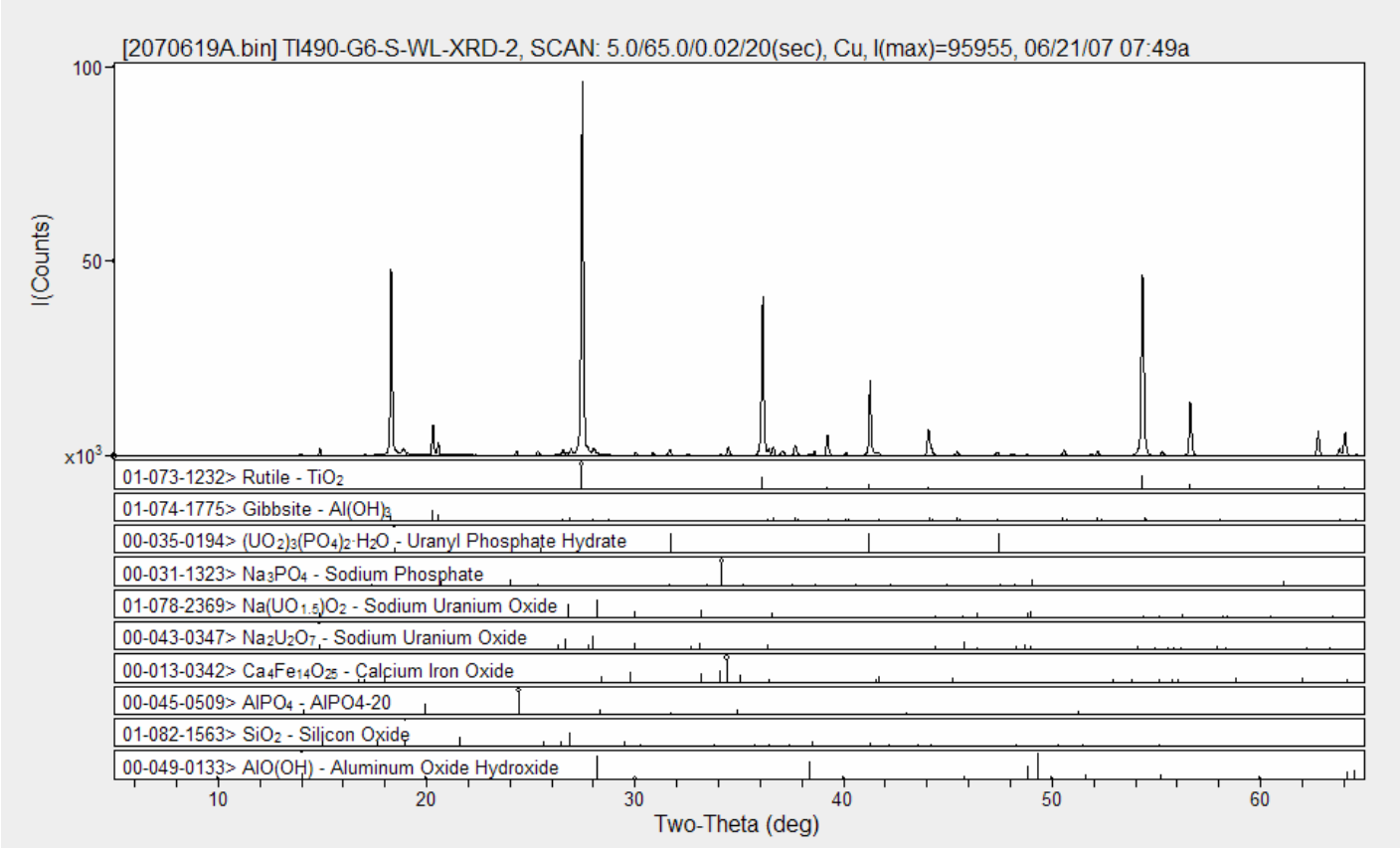
60% Al dissolution

Residual Al in form of cancrinite

Pacific Northwest
NATIONAL LABORATORY

S-Saltcake 6 XRD

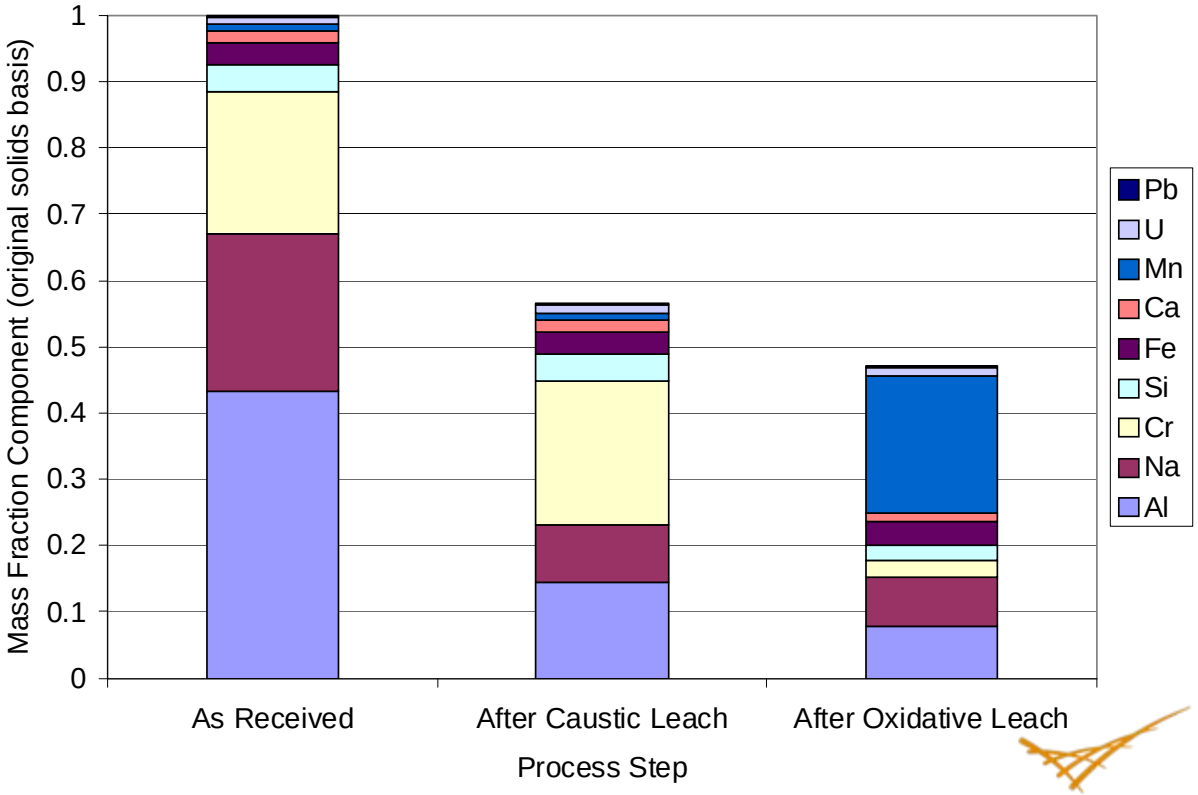
- Group 6 is a mix of Al phases including
  - Gibbsite
  - Aluminum phosphate



Rutile added as an internal standard

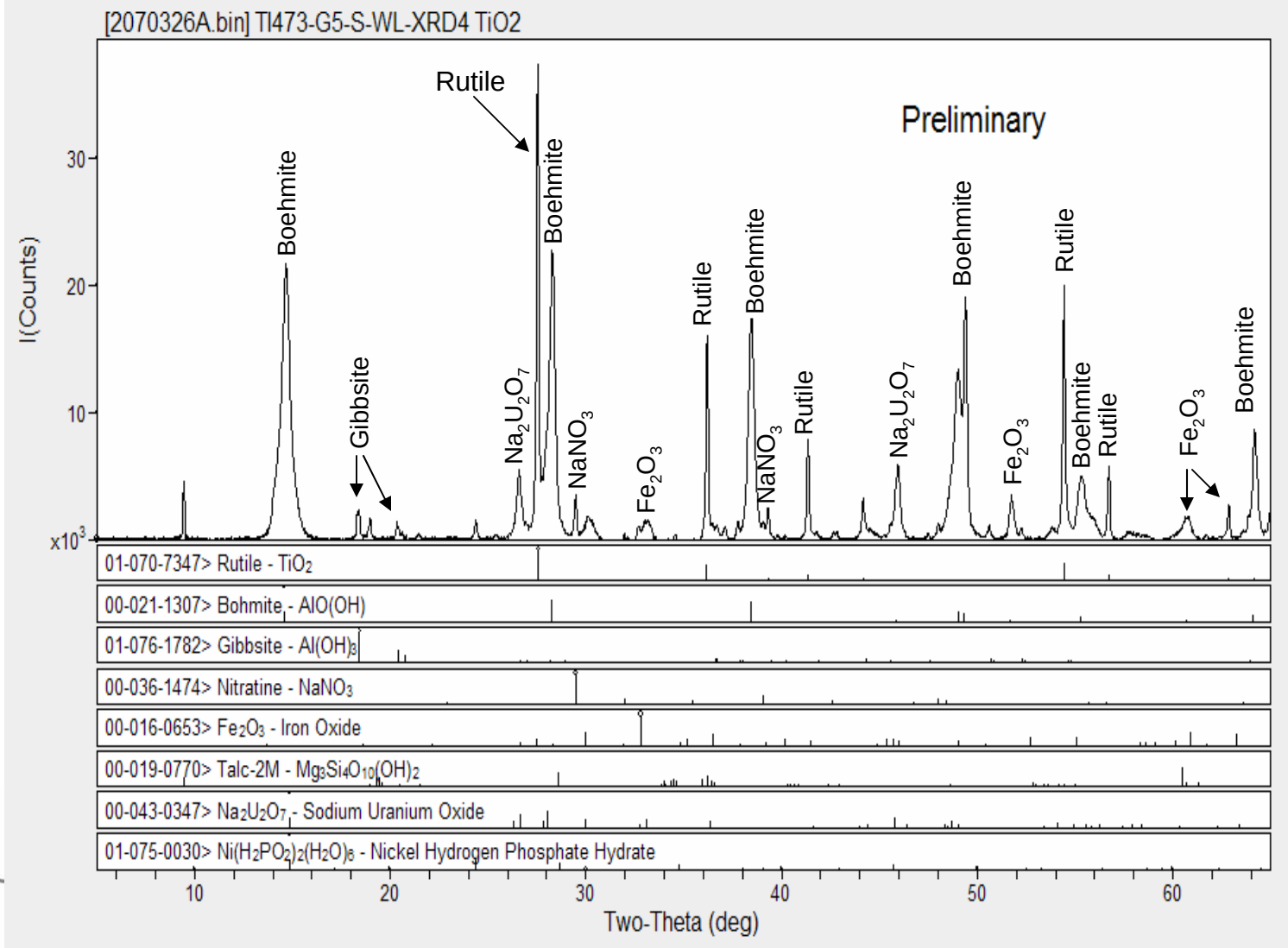
S-Salt Cake Leaching Results

- 86% dissolution of Al from combination of caustic and oxidative leaching
- Residual solids primarily Mn (from oxidative leaching process)

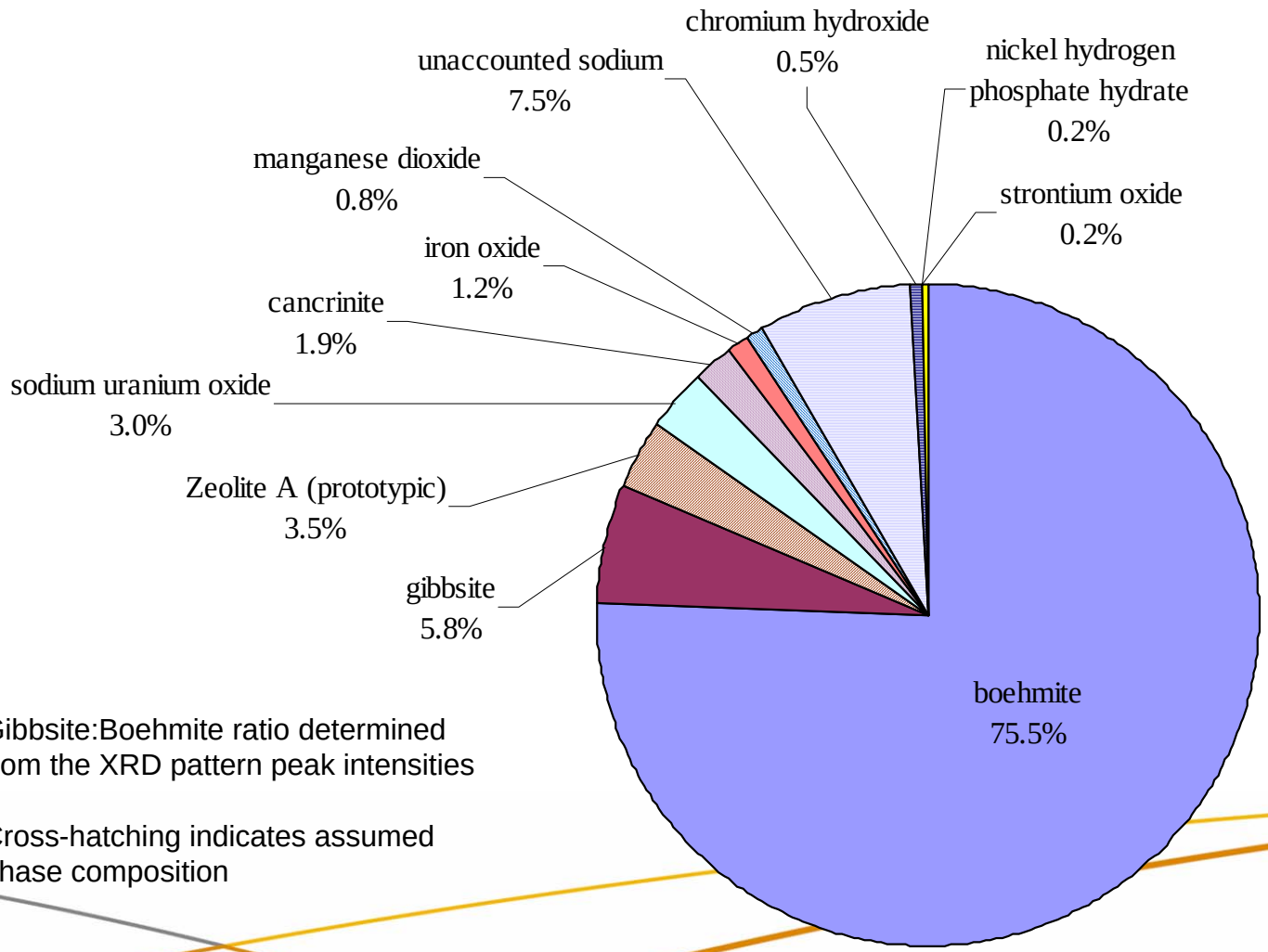


Pacific Northwest NATIONAL LABORATORY

Group 5 REDOX Sludge Water Insoluble Solids XRD



Group 5 REDOX Sludge Water Insoluble Solids



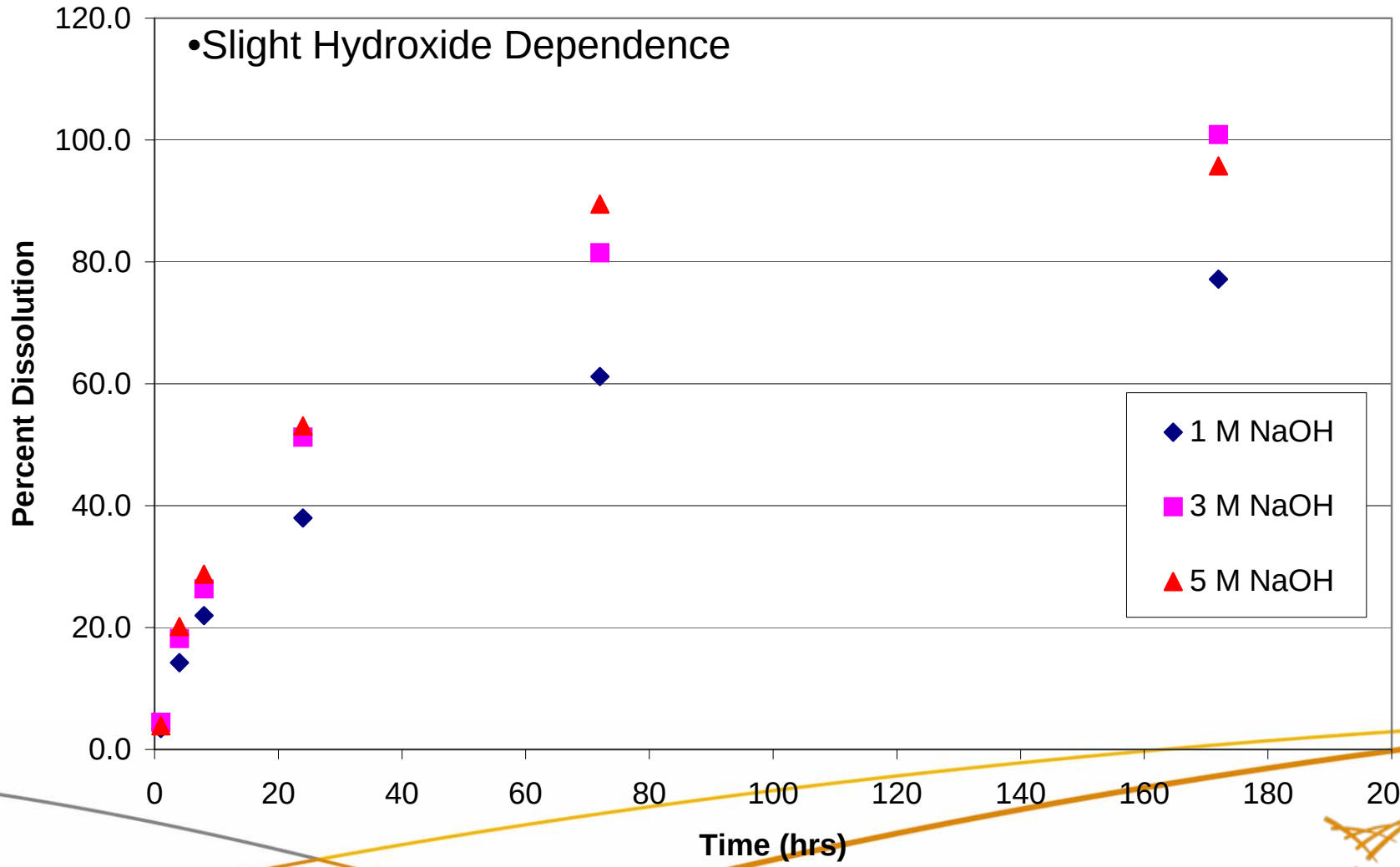
- Gibbsite:Boehmite ratio determined from the XRD pattern peak intensities
- Cross-hatching indicates assumed phase composition

Group 5 Test matrix

		Temperature, °C		
[NaOH], M	[$NaNO_3$], M	80	90	100
1	0	1	1	1
3	0	1	3	1
5	0	1	1	1
3	1	0	1	0
3	5	0	1	0

- What you get out of the matrix
  - Activation energy for Al dissolution
  - Hydroxide dependence
  - Enough data for a kinetic model

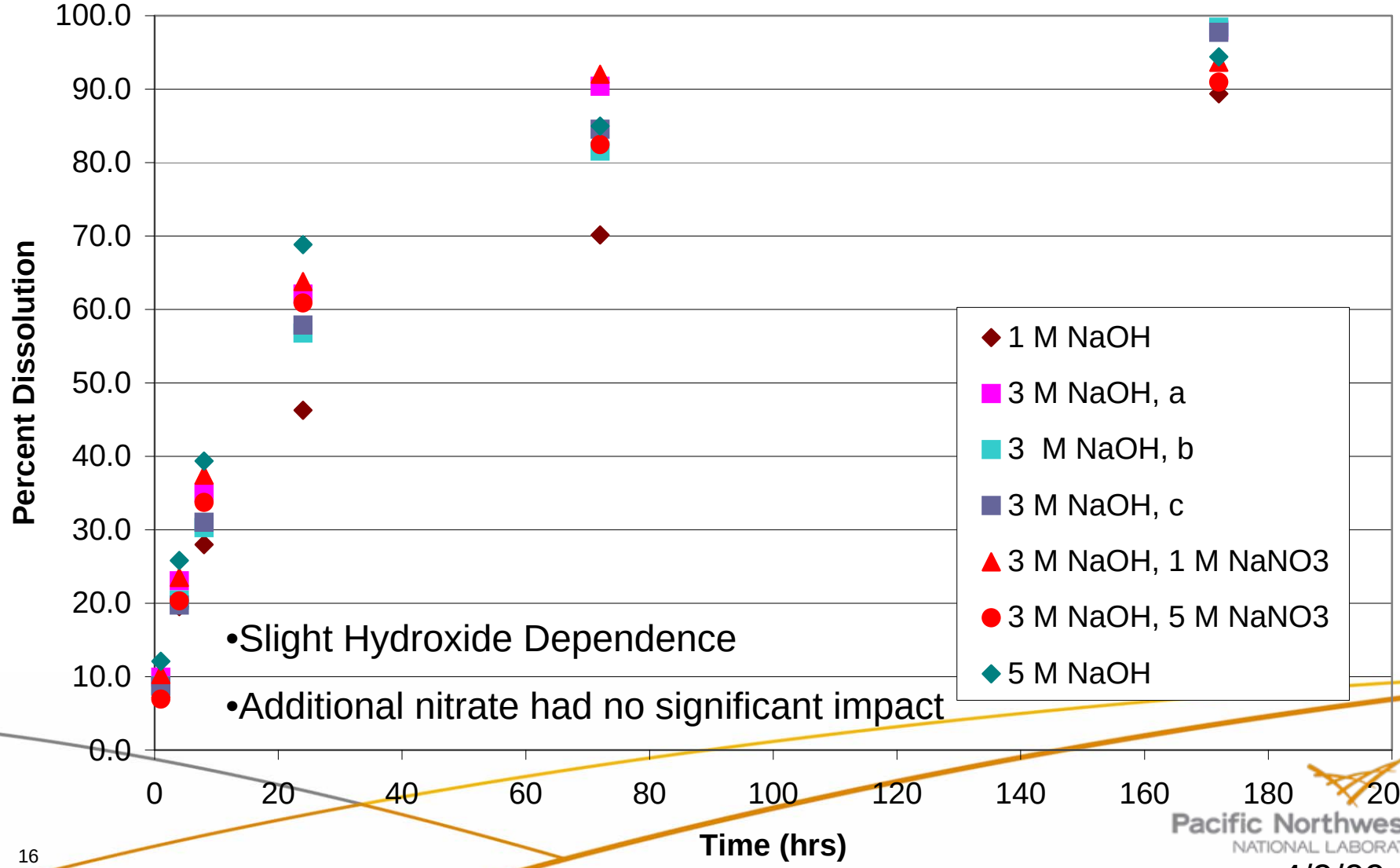
Group 5 Al Dissolution at 80°C



Pacific Northwest NATIONAL LABORATORY

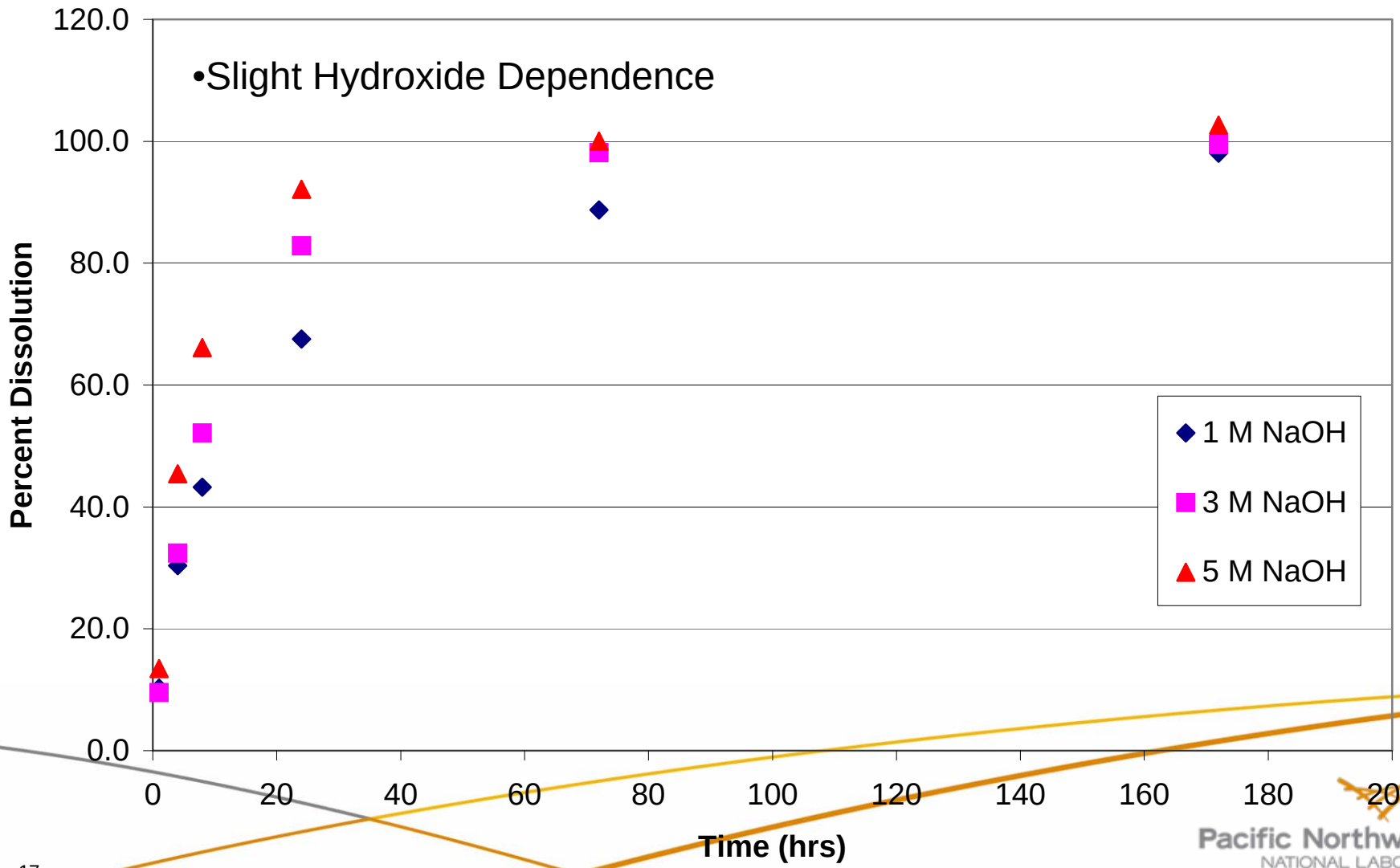
4/9/09

Group 5 Al Dissolution at 90°C



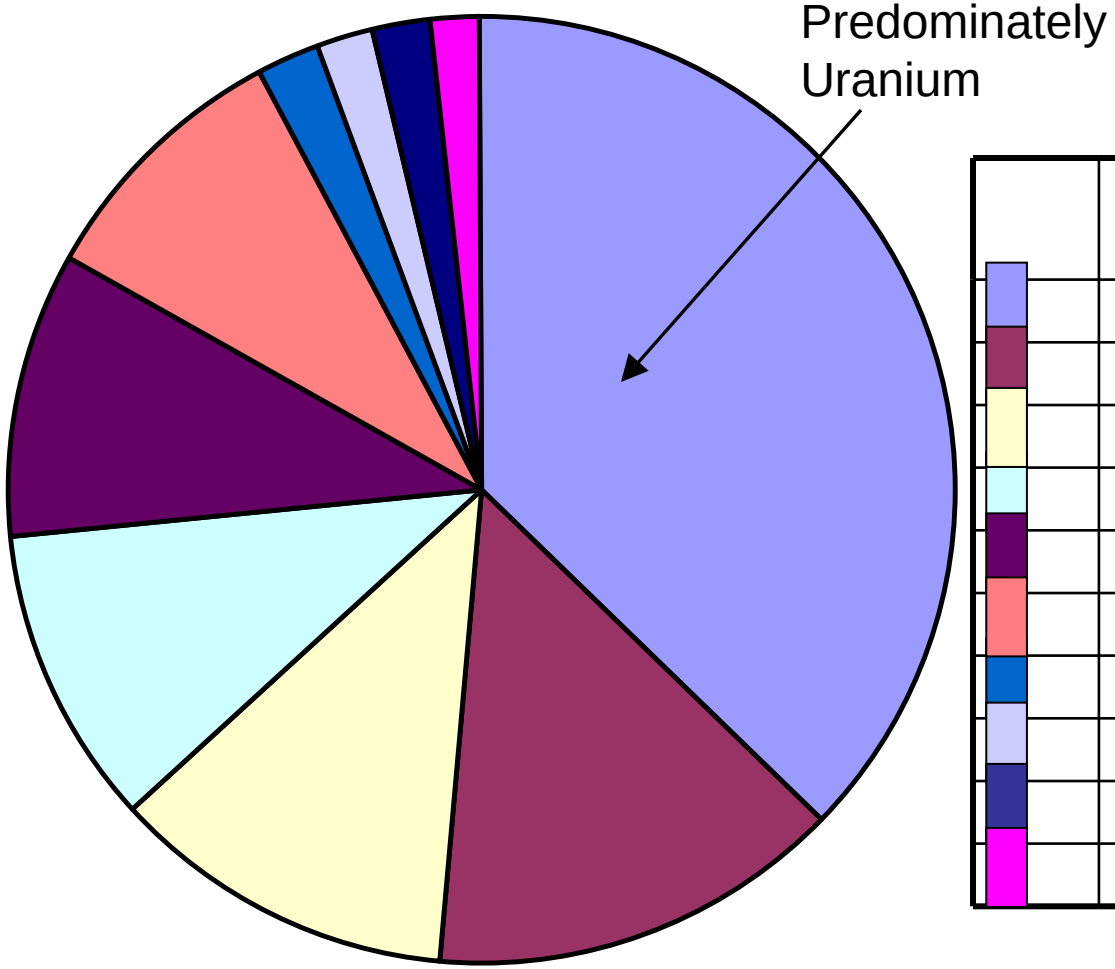
- Slight Hydroxide Dependence
- Additional nitrate had no significant impact

Group 5 Al Dissolution at 100°C



Pacific Northwest NATIONAL LABORATORY

Preliminary Estimate of Group 5 Leached Solids Composition (XRD analysis to confirm)



Leached at 90°C for 170 hours in 3 M NaOH

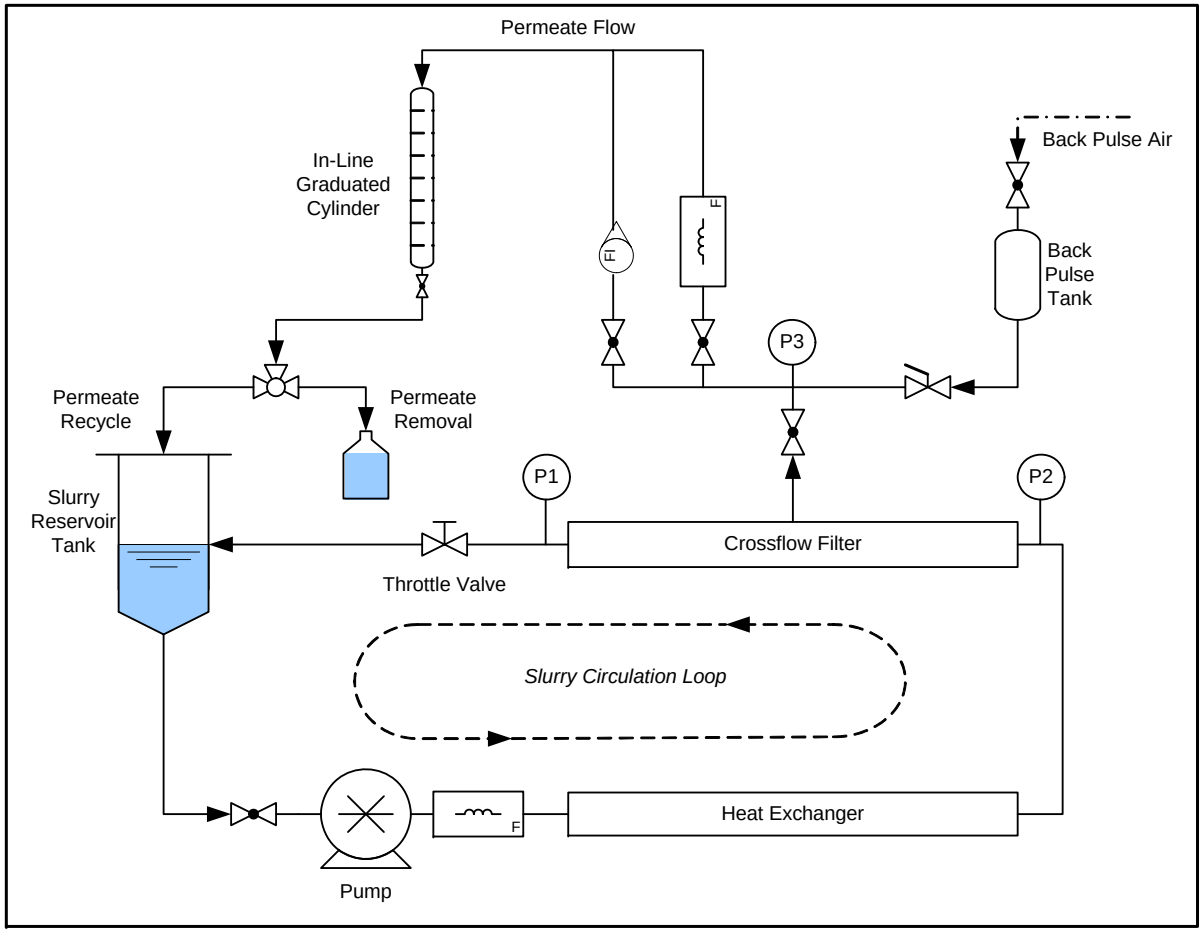
Analyte	Percentage
Na2U2O7	37.2
AlOOH	14.2
$Na_6Ca_2Al_6Si_6O_{24}(CO_3)_2$	11.7
Fe_2O_3	10.2
MnO_2	9.7
$NaNO_3$	9.4
$Ca(OH)_2$	2.1
Na_2SO_4	2.0
$Cr(OH)_3$	1.9
SrO	1.7

CUF Testing Overview

- Low Solids Filter Matrix Results
- Dewatering Behavior
- High Solids Filter Matrix Results
- Leaching Results
- Post-Leach Dewater Behavior
- Wash Dewater Behavior
- Final Filter Matrix Results
- Tests Group 5, Group 5/6 Blend, Group ½ blend and Group ¾ blend

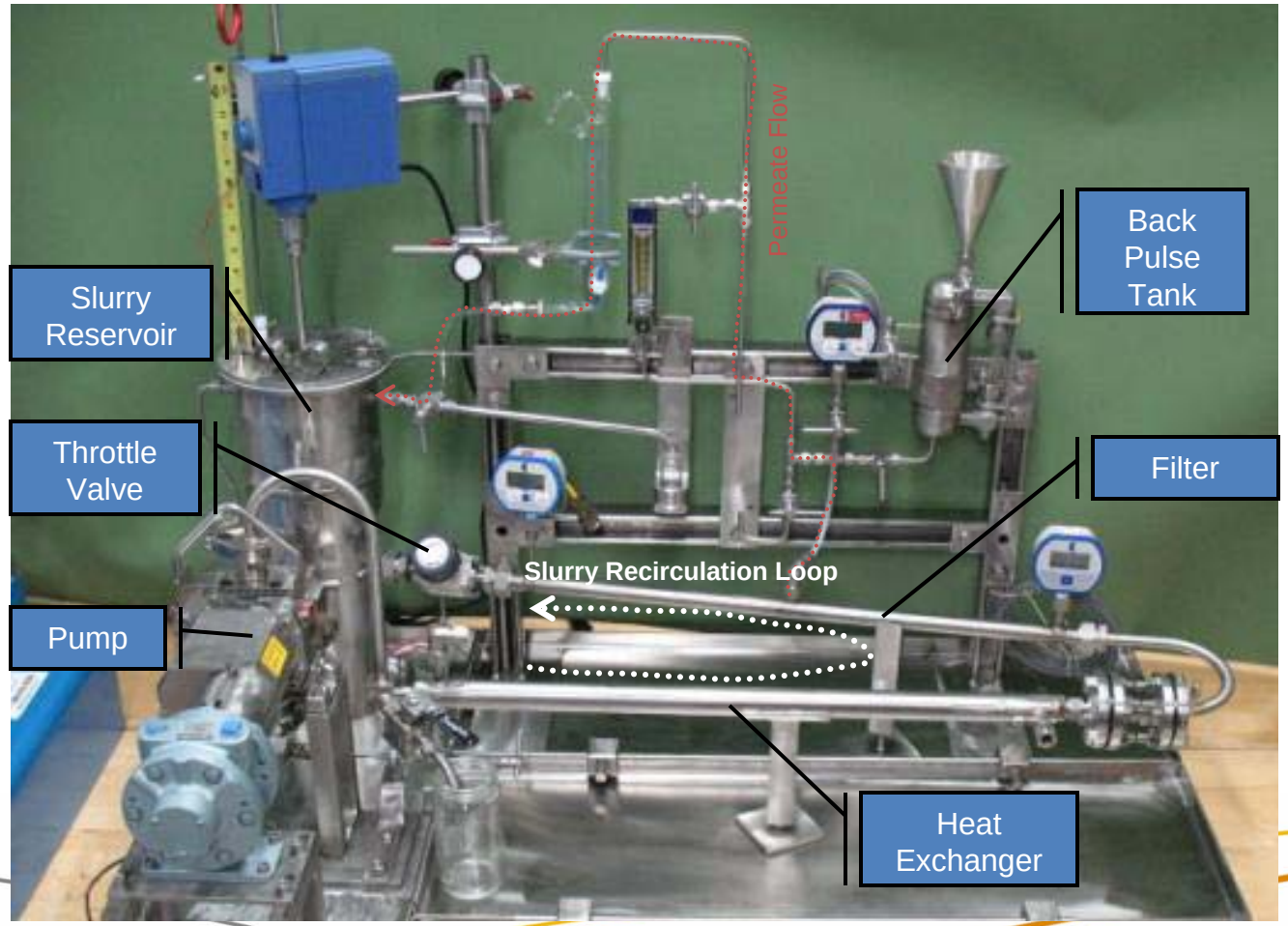
Pacific Northwest
NATIONAL LABORATORY

CUF Piping Diagram



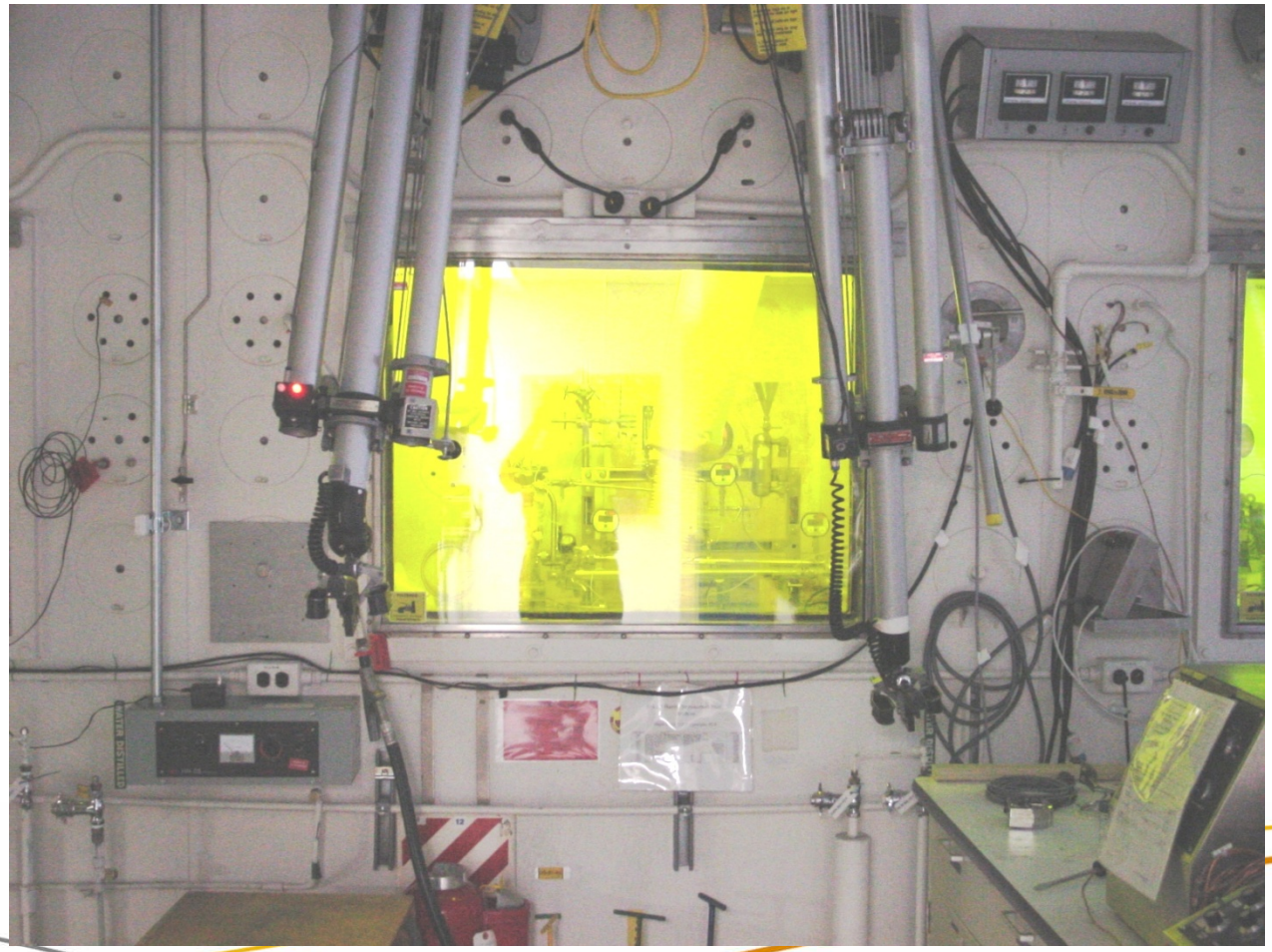
- Closed Loop Recirculation for Slurry
  - Reservoir Tank
  - Pump
  - Heat Exchanger
  - Filter
  - Throttle Valve
  - Magnetic Flow Meter
  - Pressure Gauges
- Permeate Manifold
  - Pressure Gauge
  - Mass Flow Meter
  - Rotameter
  - In-line Granduated Cylinder
  - Back Pulse Chamber

CUF Prior to Installation

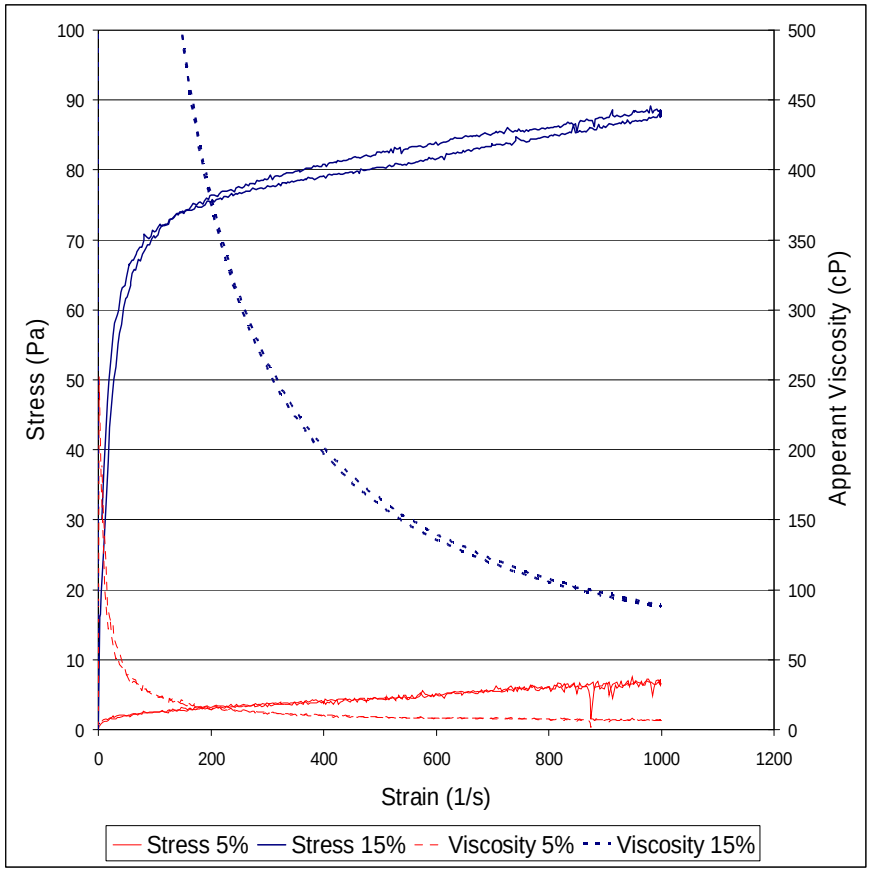


- Filter Length
  - 2 feet
- System Volume
  - Maximum *3.9 Liters*
  - Operating Minimum *1.2 Liters*
  - Startup Minimum *1.5 Liters*
- Pump
  - Rotary Lobe *Up to 12 GPM*
- Instrumentation
  - Pressures *0 -- 100 psig*
  - Temperature *0 – 100°C*
  - Slurry Flow Rate *Up to 15 GPM*
  - Permeate Flow Rate *Up to 180 ml/min*

CUF Inside Cell

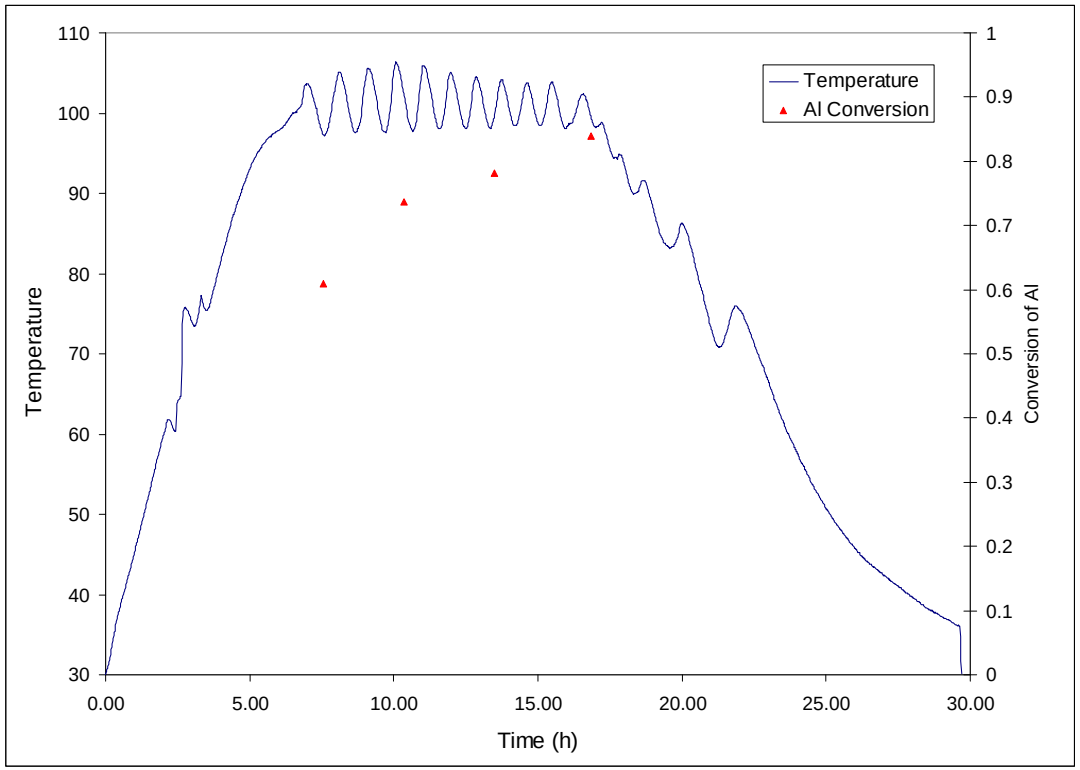


Rheology Comparison of Pre-Leached Waste



- Increase in solids concentration dramatically effects slurry viscosity
- Increase in viscosity correlates with increase in axial pressure increase and change in filter flux behavior.
- However, the filter flux at the high solid concentration was higher that expected, despite the slurry's high viscosity.
- This may be due to the low viscosity of the filter permeate (~1.5 cP).

Leaching Results



- Initial sample taken shows a 60% conversion ~2 hr after heat ramp was completed.
- Final sample has the conversion of aluminum at 84%.
- Final Aluminum/ Caustic ratio may have been above the saturation limit after cooling down.

Leaching Results

- Reasons for Faster Dissolution Rate
  - Material was sheared by processing it in the test skid, breaking agglomerate apart. This increased the surface area to mass ratio of the solid material.
  - Evaporation was significant during testing, with a 30% loss in volume. The increase in caustic concentration also contributed to the increase in the Al dissolution rate.

Pacific Northwest
NATIONAL LABORATORY

Group 3 Initial Solids Characterization

Analyte	µg/g
Al	308,500
Cr	402
Fe	18,400
Mn	1,210
Na	[16,750]
P	[425]
S	--
Si	13,975
Sr	91.5
U	15,825
Zn	[175]
Zr	2,383

Pacific Northwest
NATIONAL LABORATORY

Group 3 Test matrix

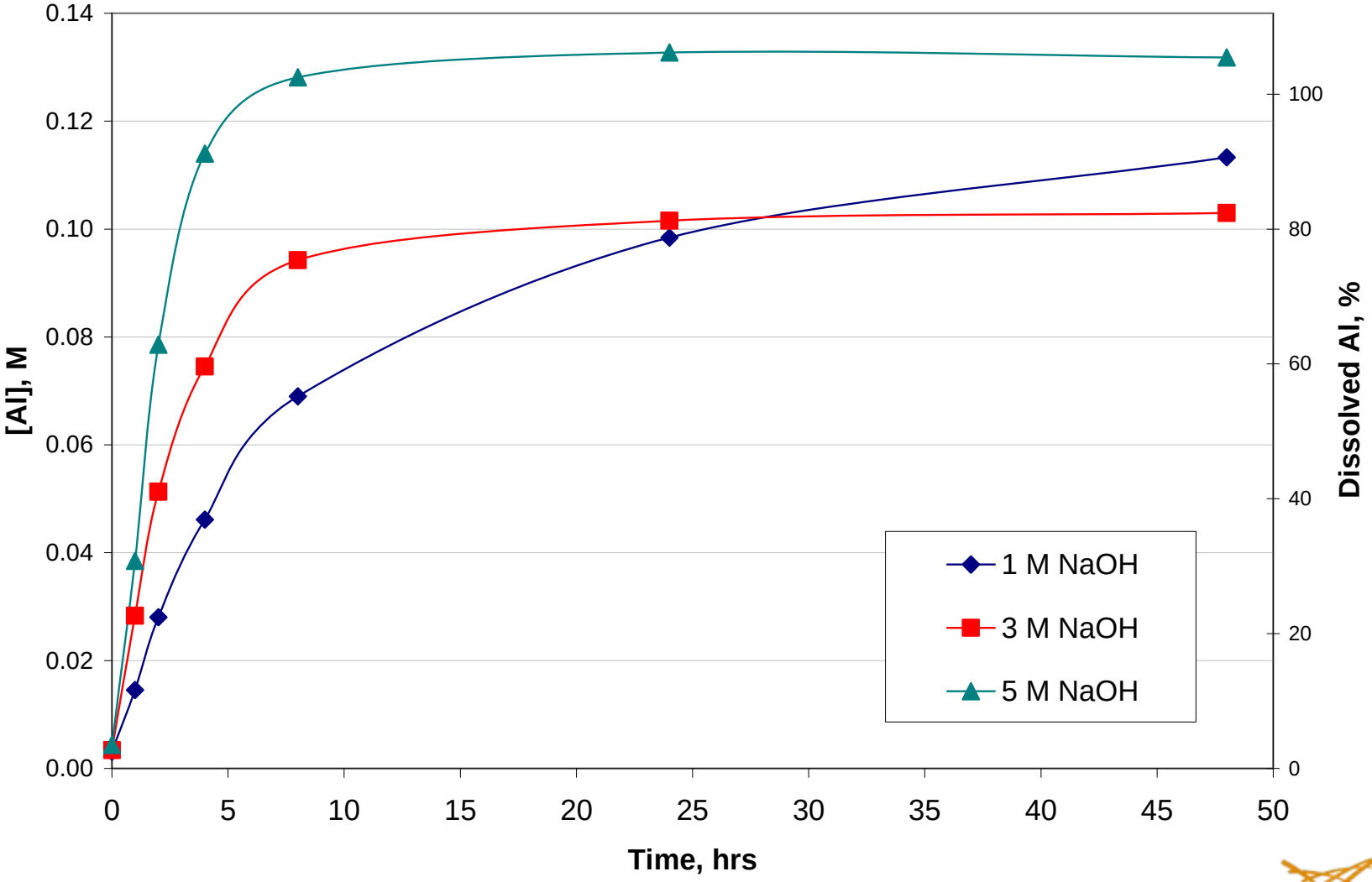
- What you get out of the matrix
  - Hydroxide dependence
  - Temperature dependence

Temp	1 M NaOH	3 M NaOH	5 M NaOH
60	1	1	1
80	1	3*	1
100	1	1	1

* - two extra tests at this condition with 1 M and 5 M $NaNO_3$

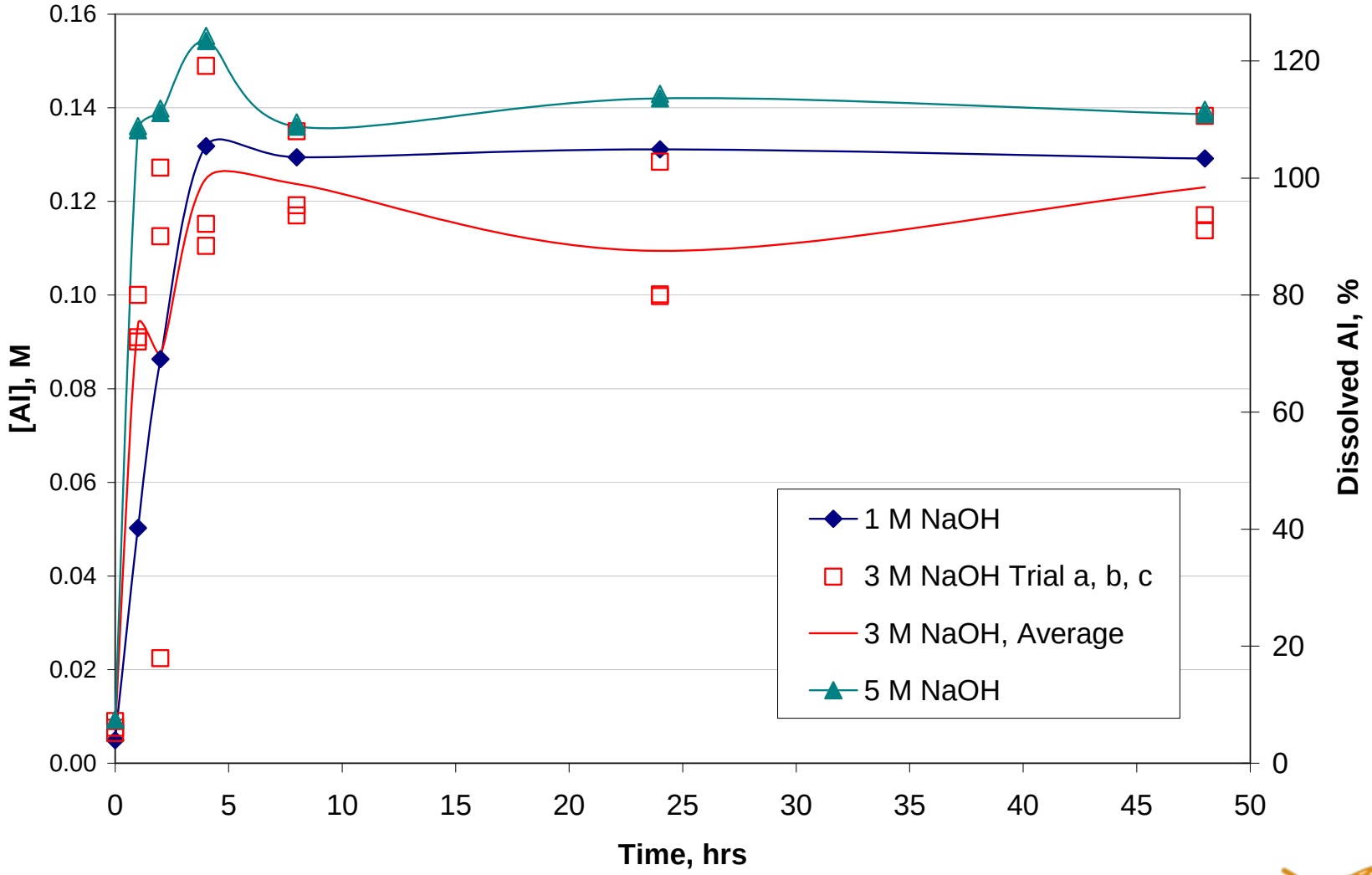
Pacific Northwest
NATIONAL LABORATORY

Group 3 Al Leaching at 60ºC



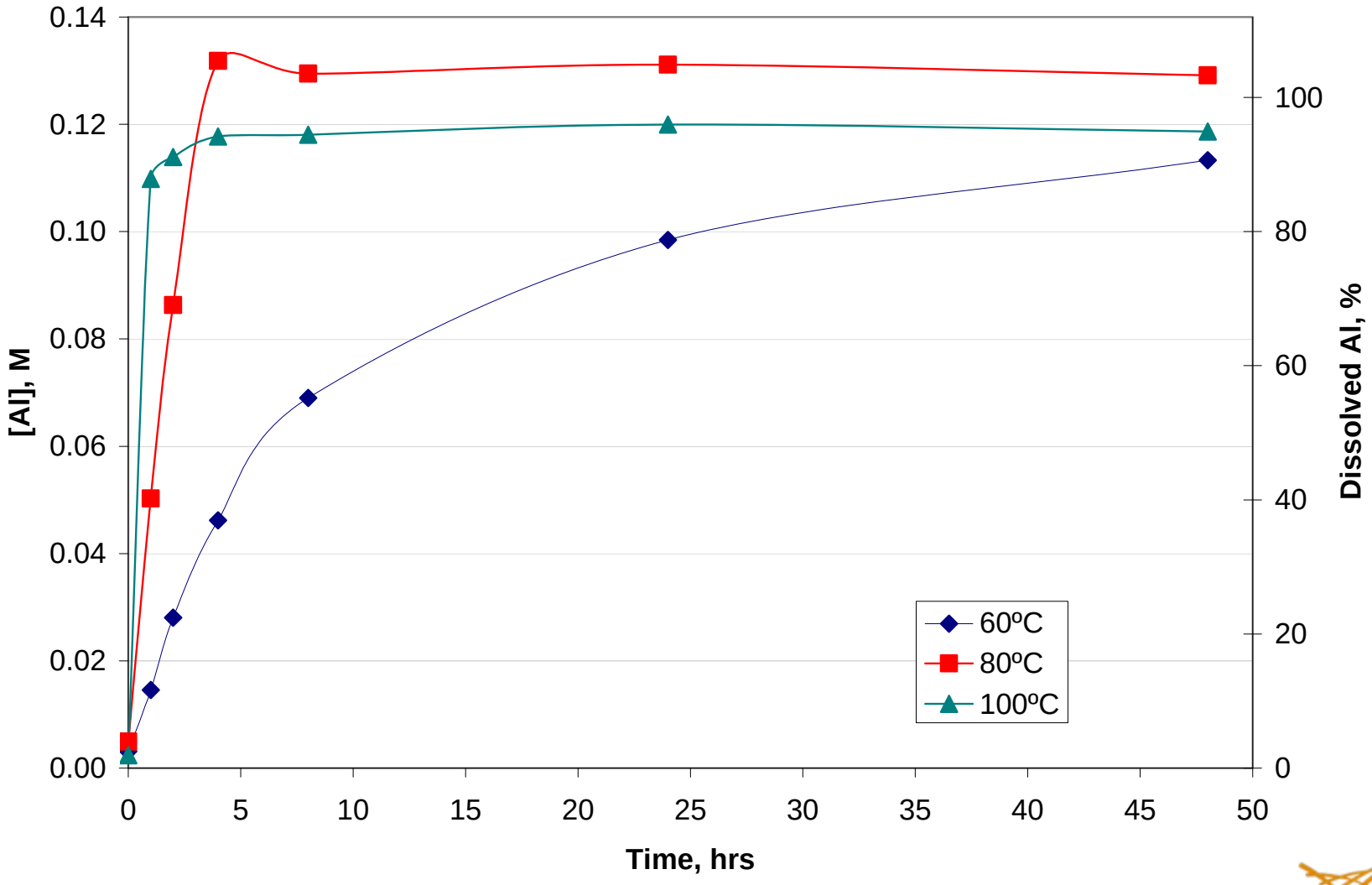
Pacific Northwest
NATIONAL LABORATORY

Group 3 Al Leaching at 80ºC



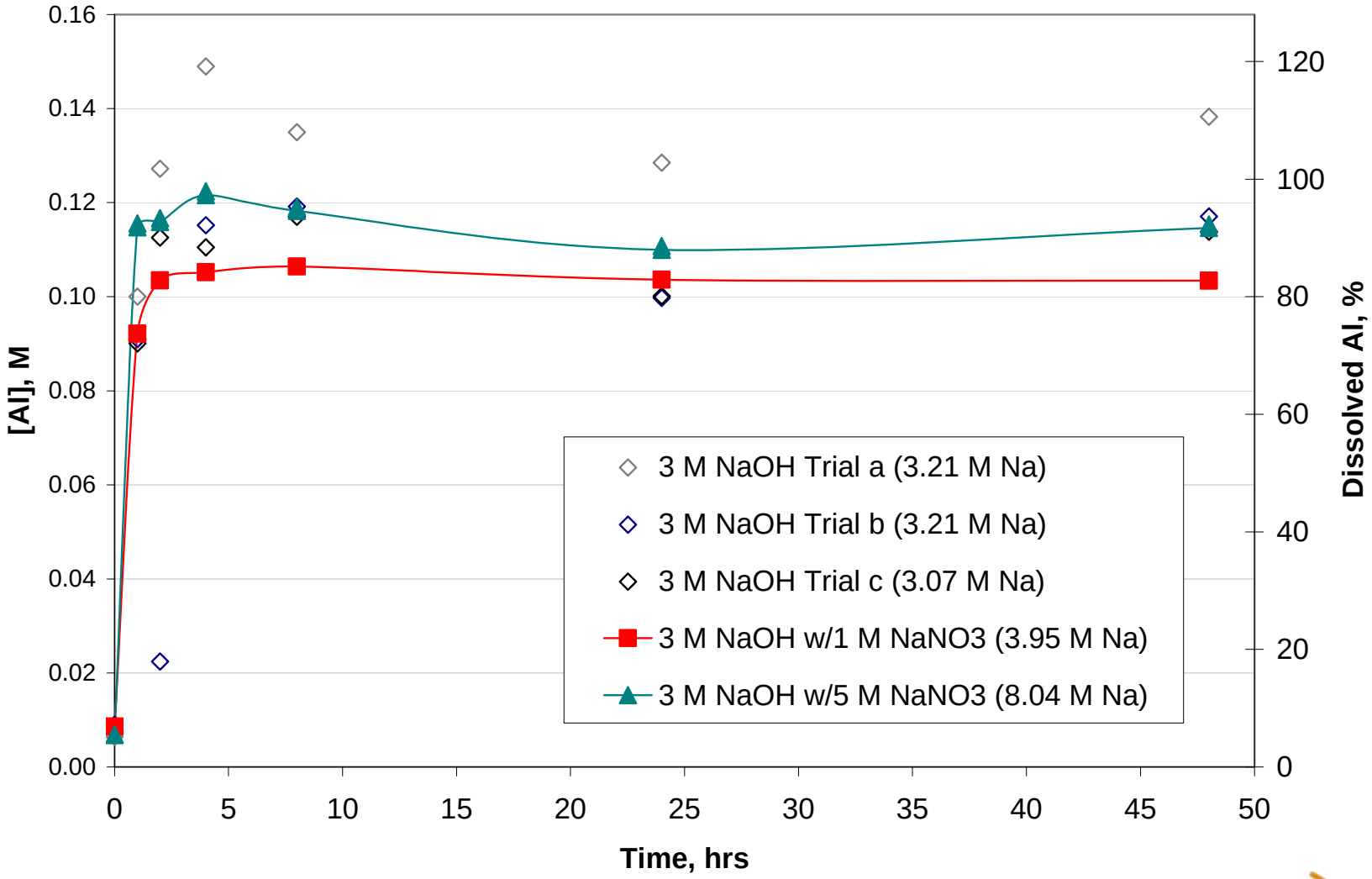
Pacific Northwest
NATIONAL LABORATORY

Group 3 Al Leaching in 1 M NaOH



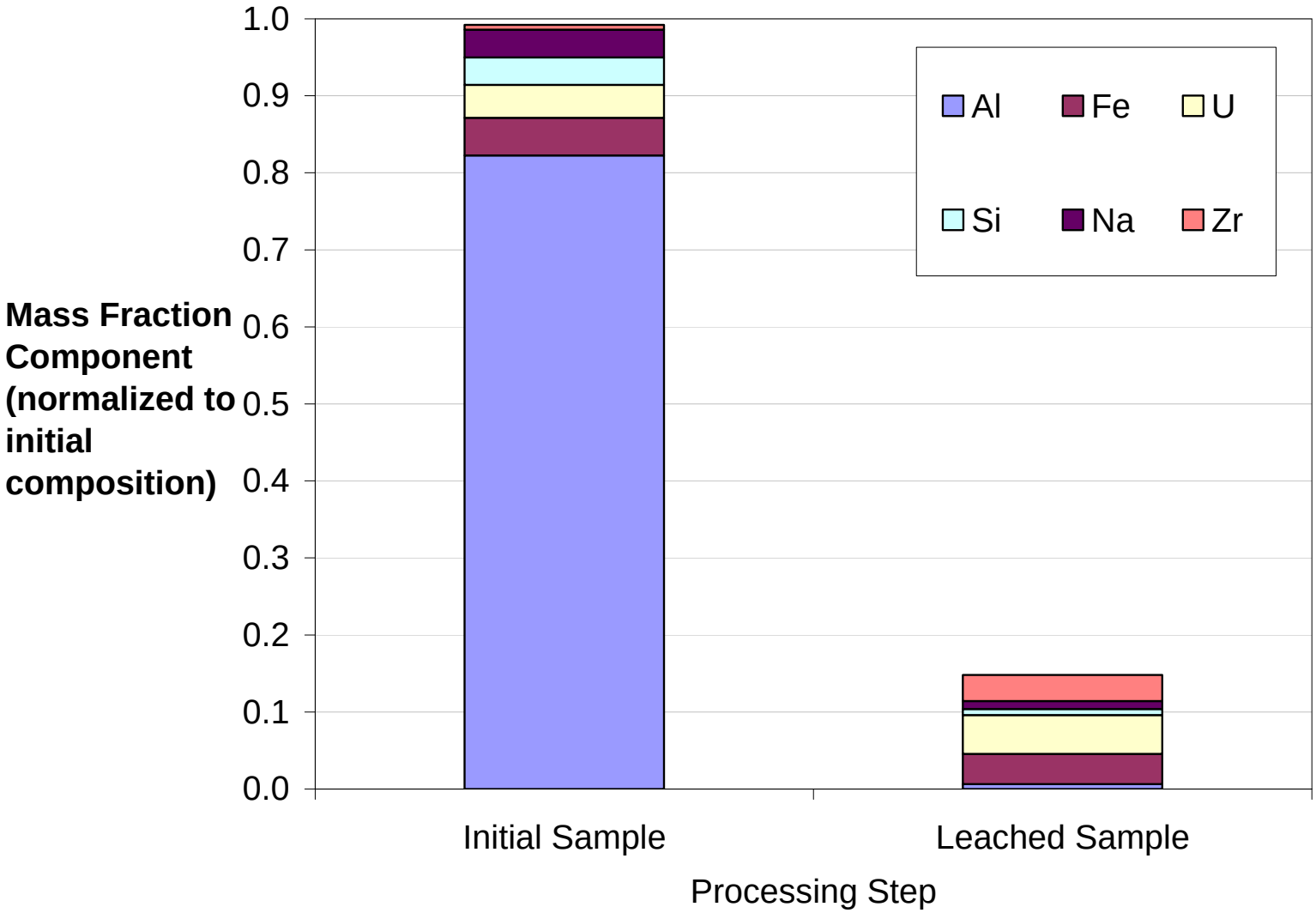
Pacific Northwest
NATIONAL LABORATORY

Group 3: Impact of added nitrate on dissolution rate at 80ºC



Pacific Northwest
NATIONAL LABORATORY

Group 3 Residual Solids



Pacific Northwest NATIONAL LABORATORY

Group 4 Initial Solids Characterization

Analyte	µg/g
Al	332,500
Bi	2,310
Cr	6,100
Fe	16,200
Mn	5,195
Na	[37,000]
P	4,480
S	[1,200]
Si	[15,050]
Sr	76.8
U	13,000
Zn	1,065

Pacific Northwest
NATIONAL LABORATORY

Group 4 Test matrix

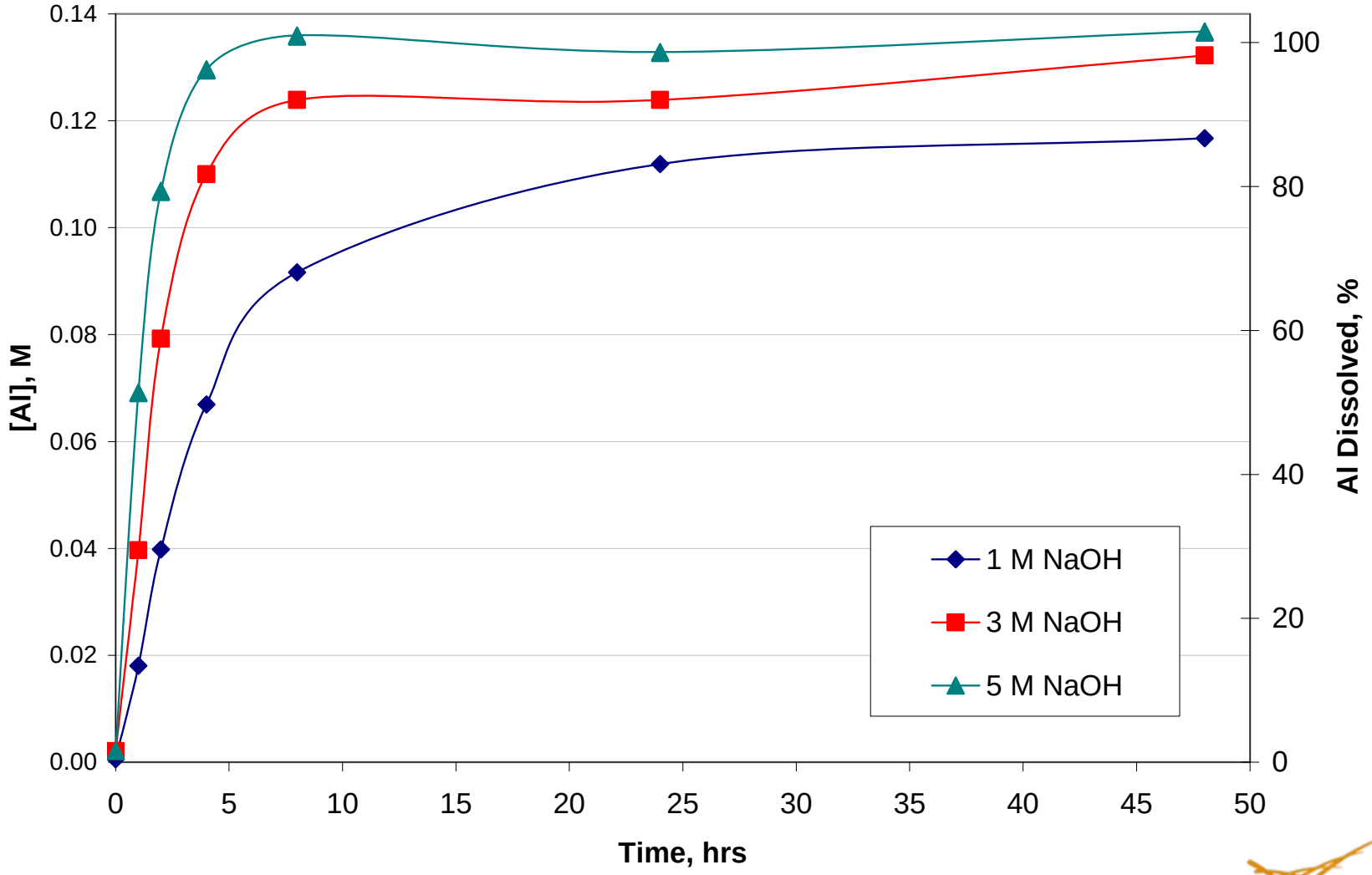
- What you get out of the matrix
  - Hydroxide dependence
  - Temperature dependence

Temp	1 M NaOH	3 M NaOH	5 M NaOH
60	1	1	1
80	1	3*	1
100	1	1	1

* - two extra tests at this condition with 1 M and 5 M $NaNO_3$

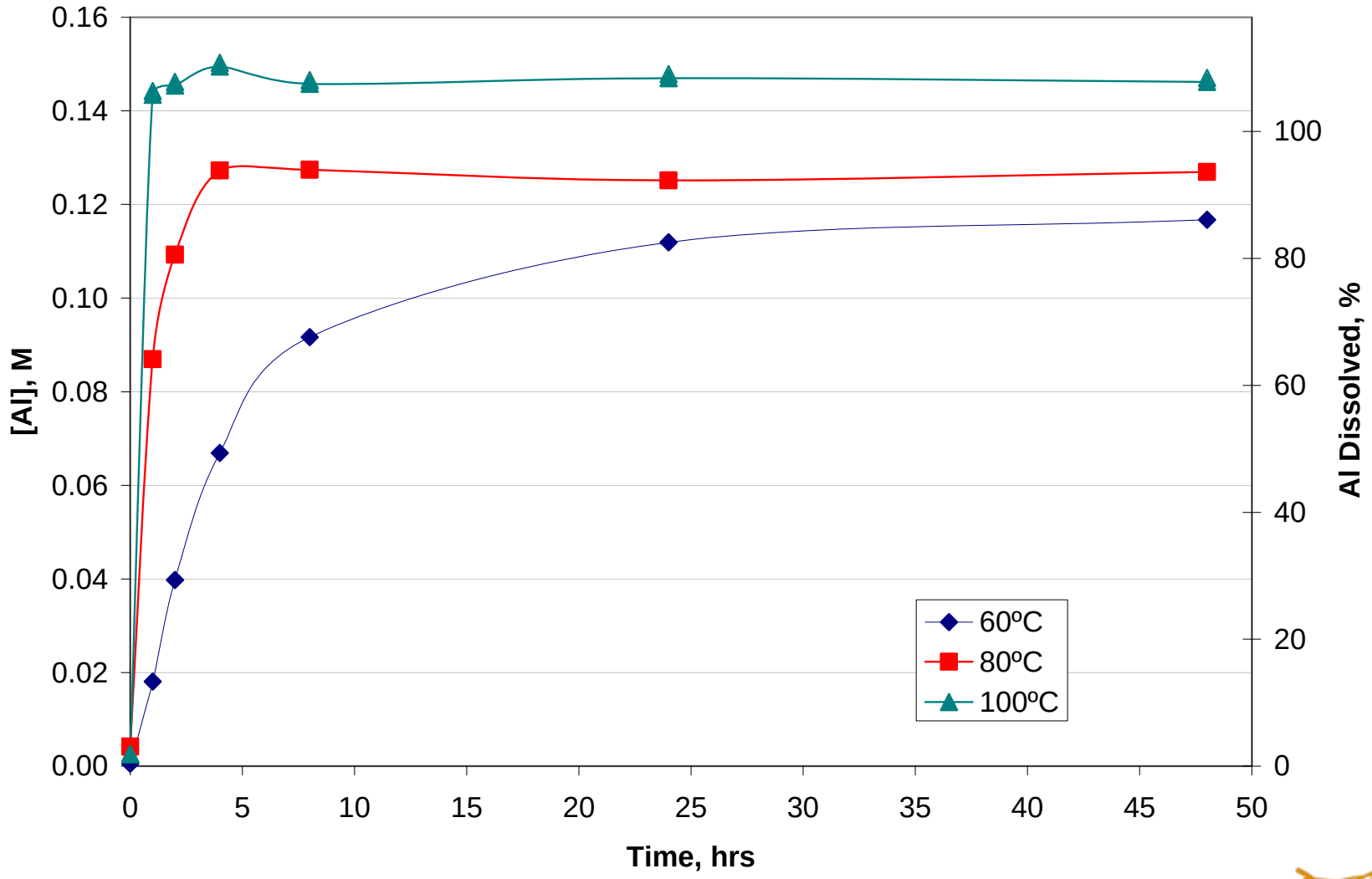
Pacific Northwest NATIONAL LABORATORY

Group 4 Al Leaching at 60ºC



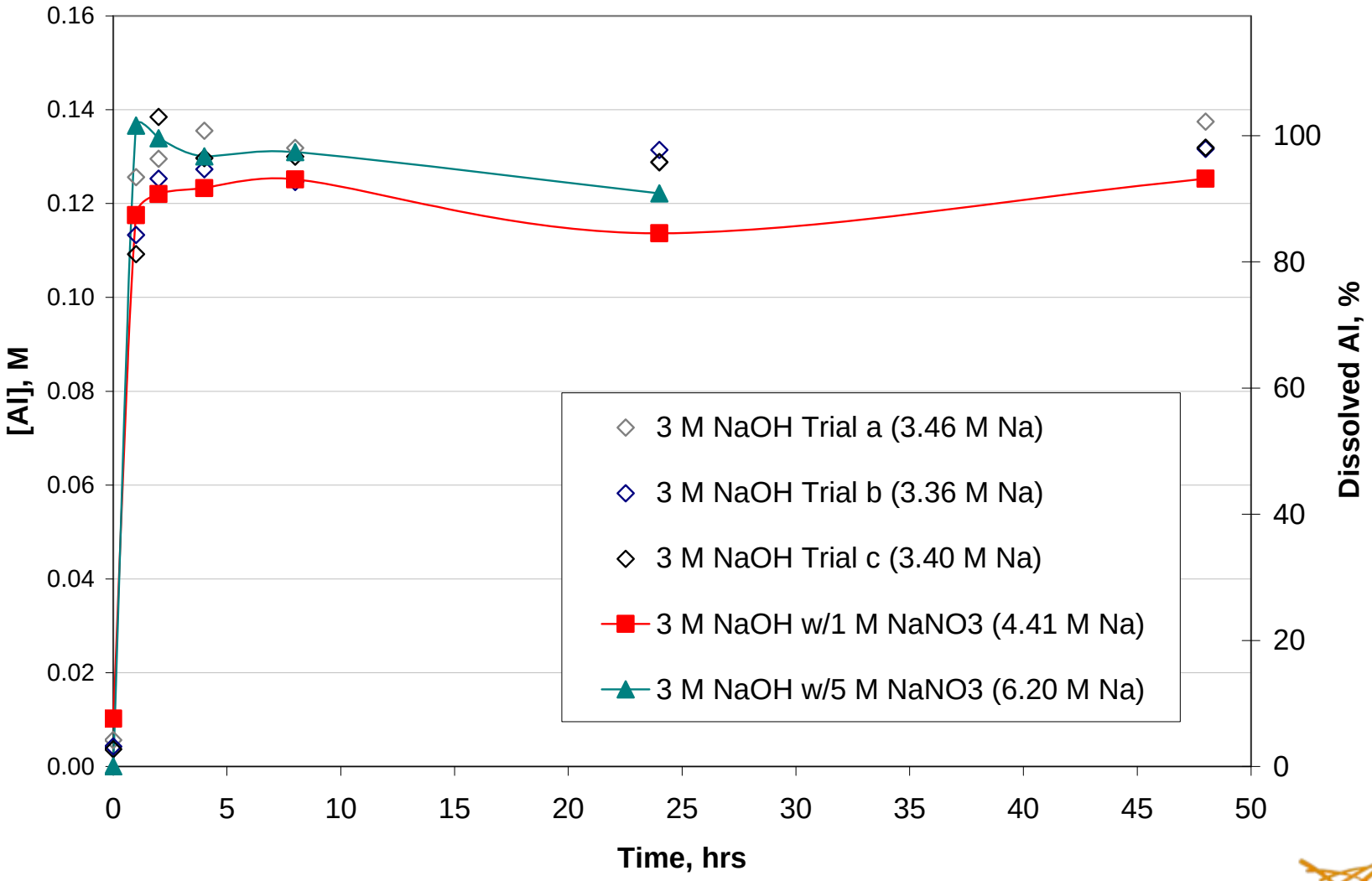
Pacific Northwest
NATIONAL LABORATORY

Group 4 Al Leaching in 1 M NaOH



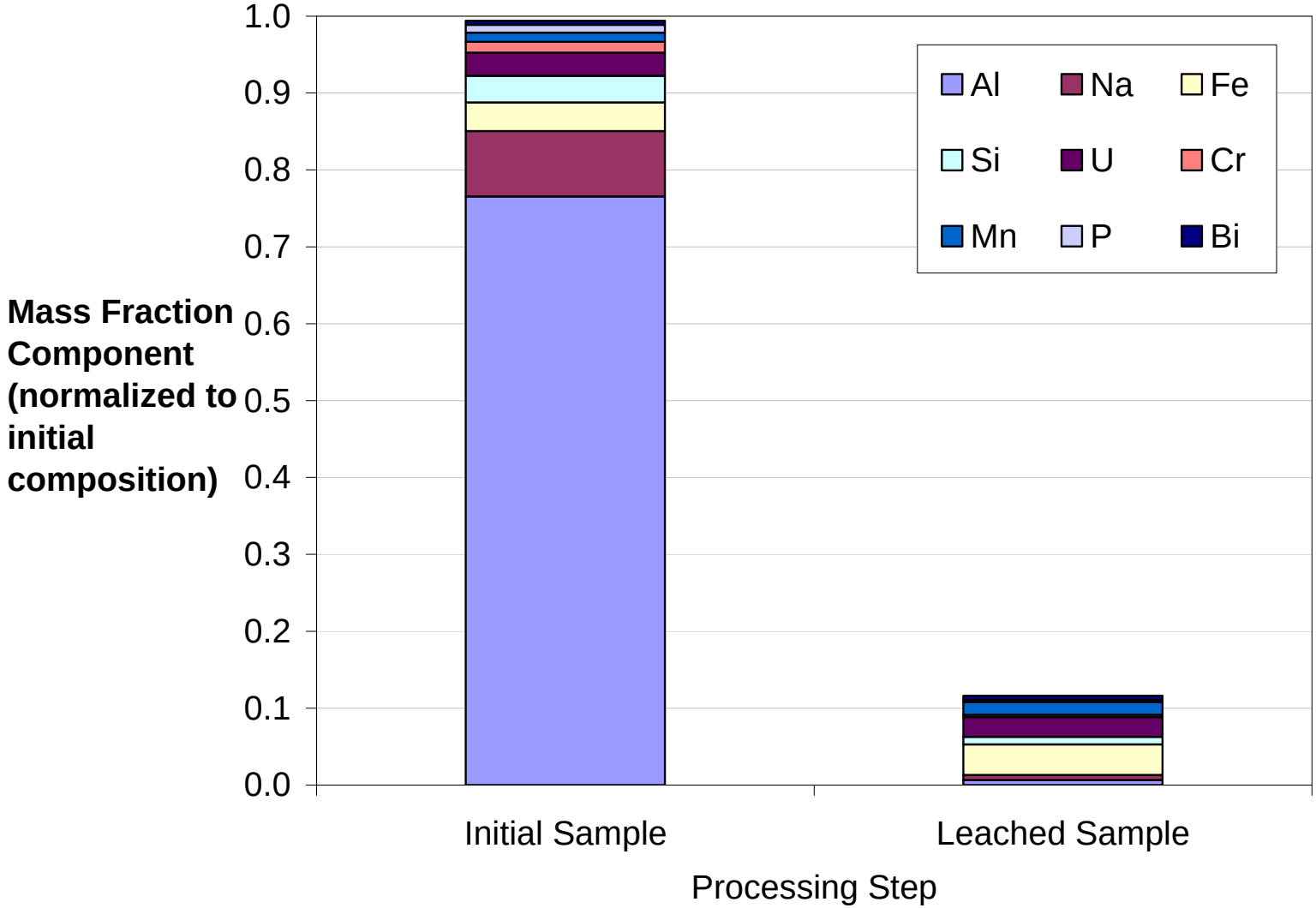
Pacific Northwest
NATIONAL LABORATORY

Group 4: Impact of added nitrate on dissolution rate at 80ºC



Pacific Northwest
NATIONAL LABORATORY

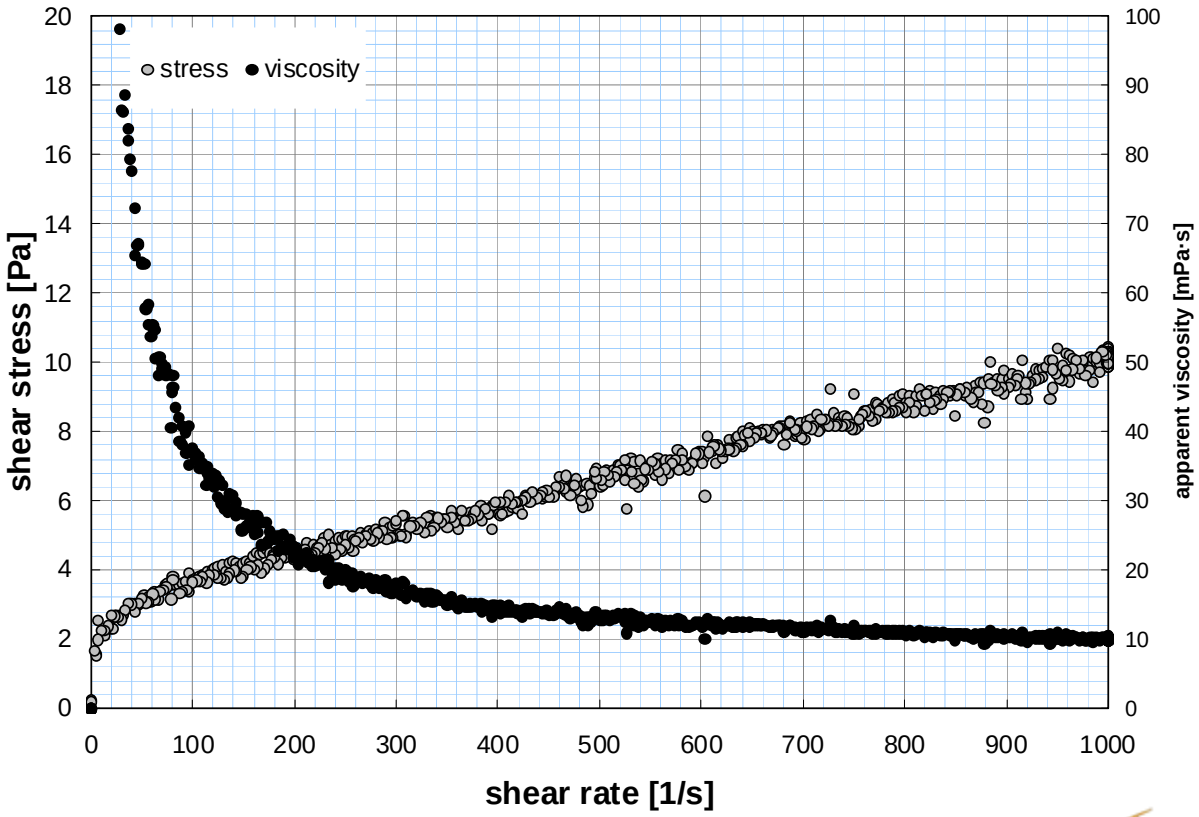
Group 4 Residual Solids



Pacific Northwest NATIONAL LABORATORY

Group 3-4 Rheology

- Initial slurry is Newtonian with 2 cp viscosity
- Dewatered initial slurry flow curve show here - ~ 2 Pa shear stress and 10 cp viscosity
- Leached slurry is Newtonian with 15 cp viscosity

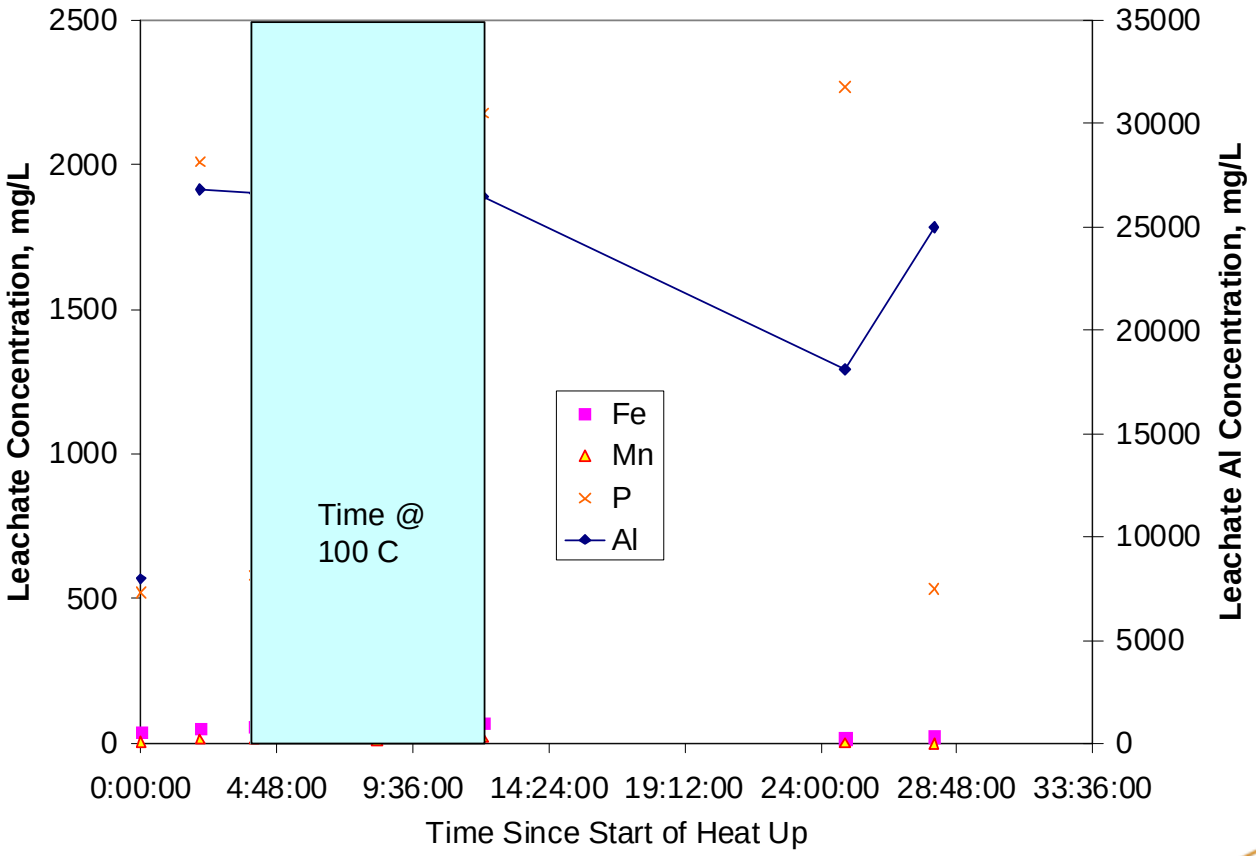


Pacific Northwest
NATIONAL LABORATORY

Group 3-4 Leaching Behavior

Gibbsite dissolution reaction was fast at 100 C.

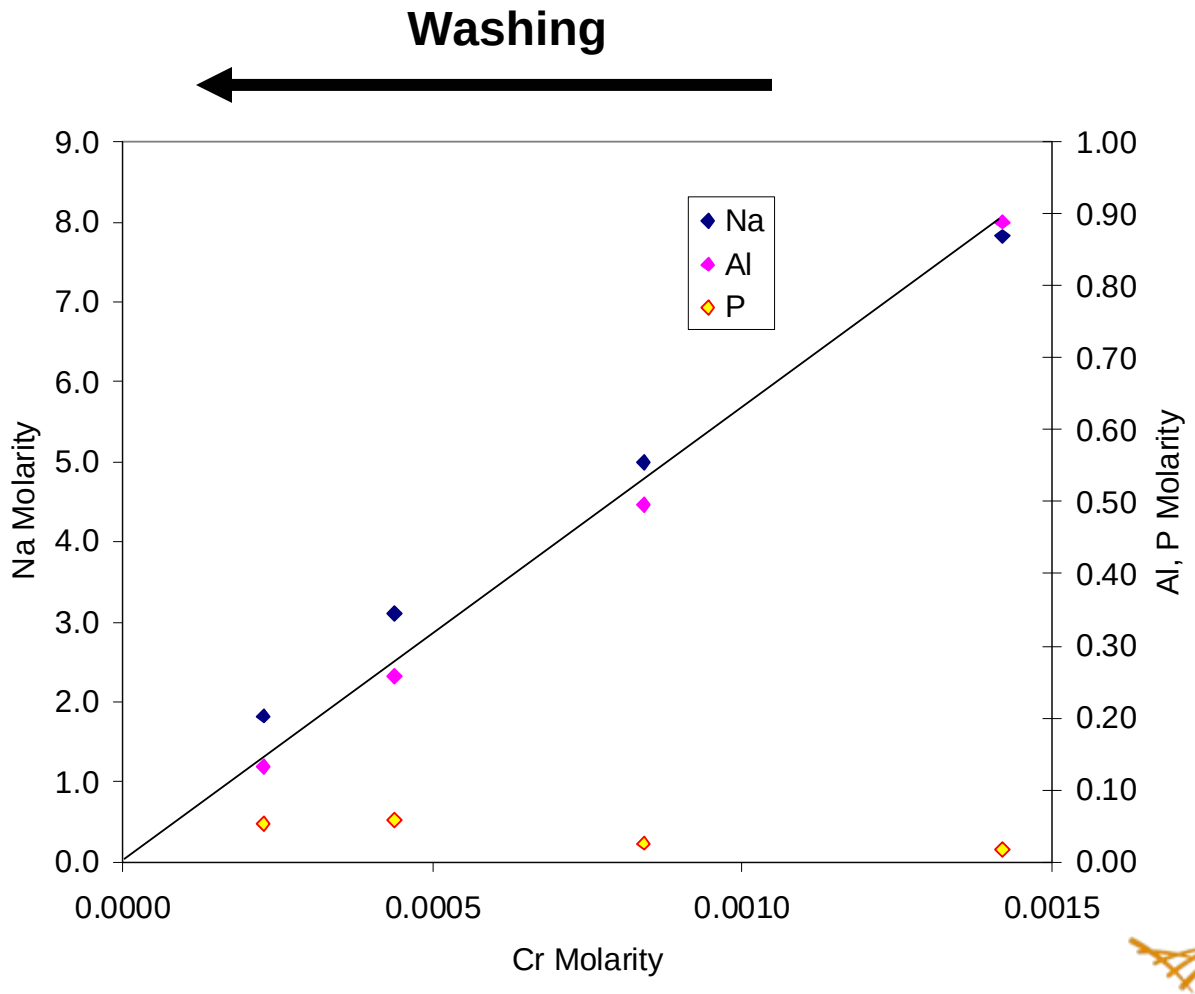
P, Fe and Mn reprecipitated on cooling



Pacific Northwest
NATIONAL LABORATORY

Group 3-4 Washing behavior

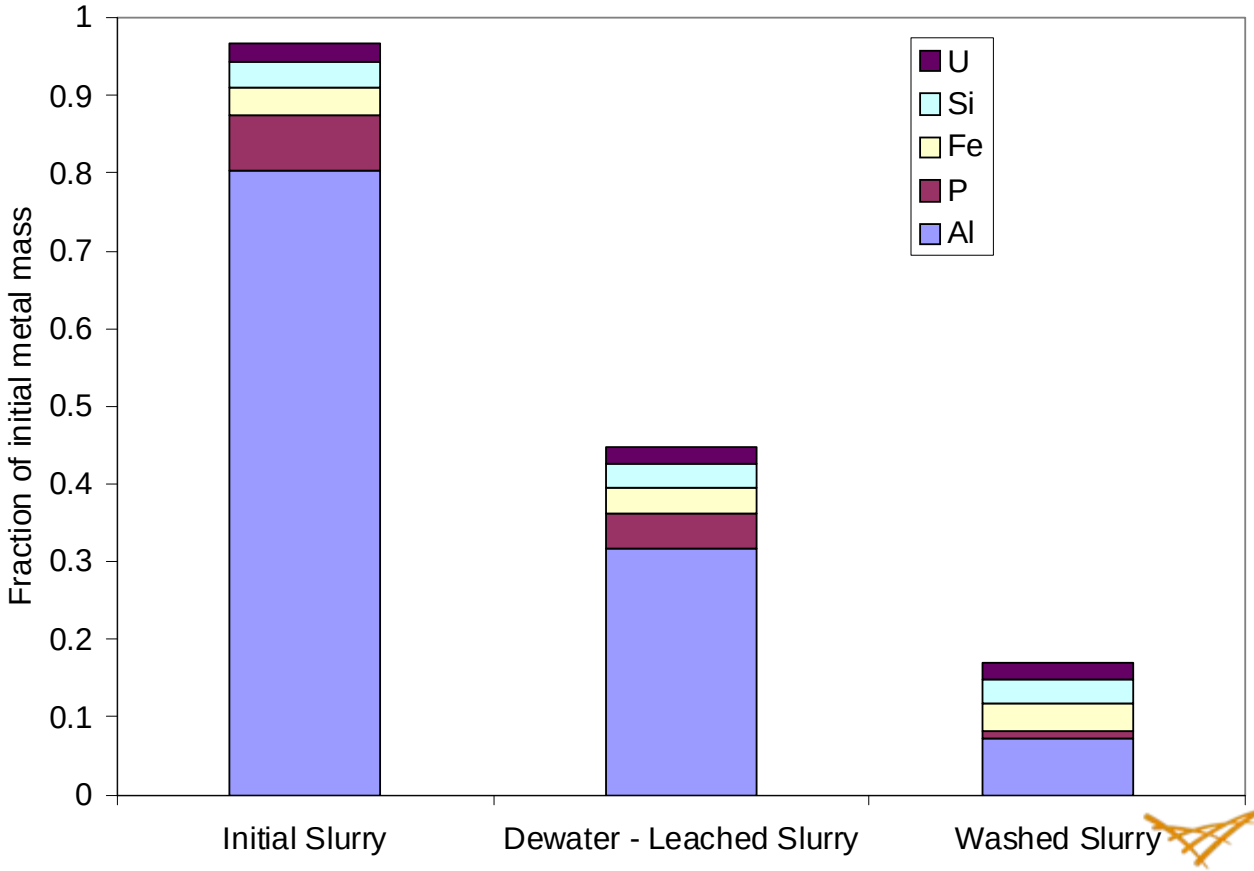
- P dissolved through 3rd wash
- Al appears to be simple dilution
- Na added to wash water to avoid Al precipitation



Pacific Northwest NATIONAL LABORATORY

Slurry Composition at various stages of Group 3-4 CUF run

- Majority of residual Al in the slurry is contained in the entrained supernate
- Leaching achieves > 90% removal of Al



Pacific Northwest NATIONAL LABORATORY

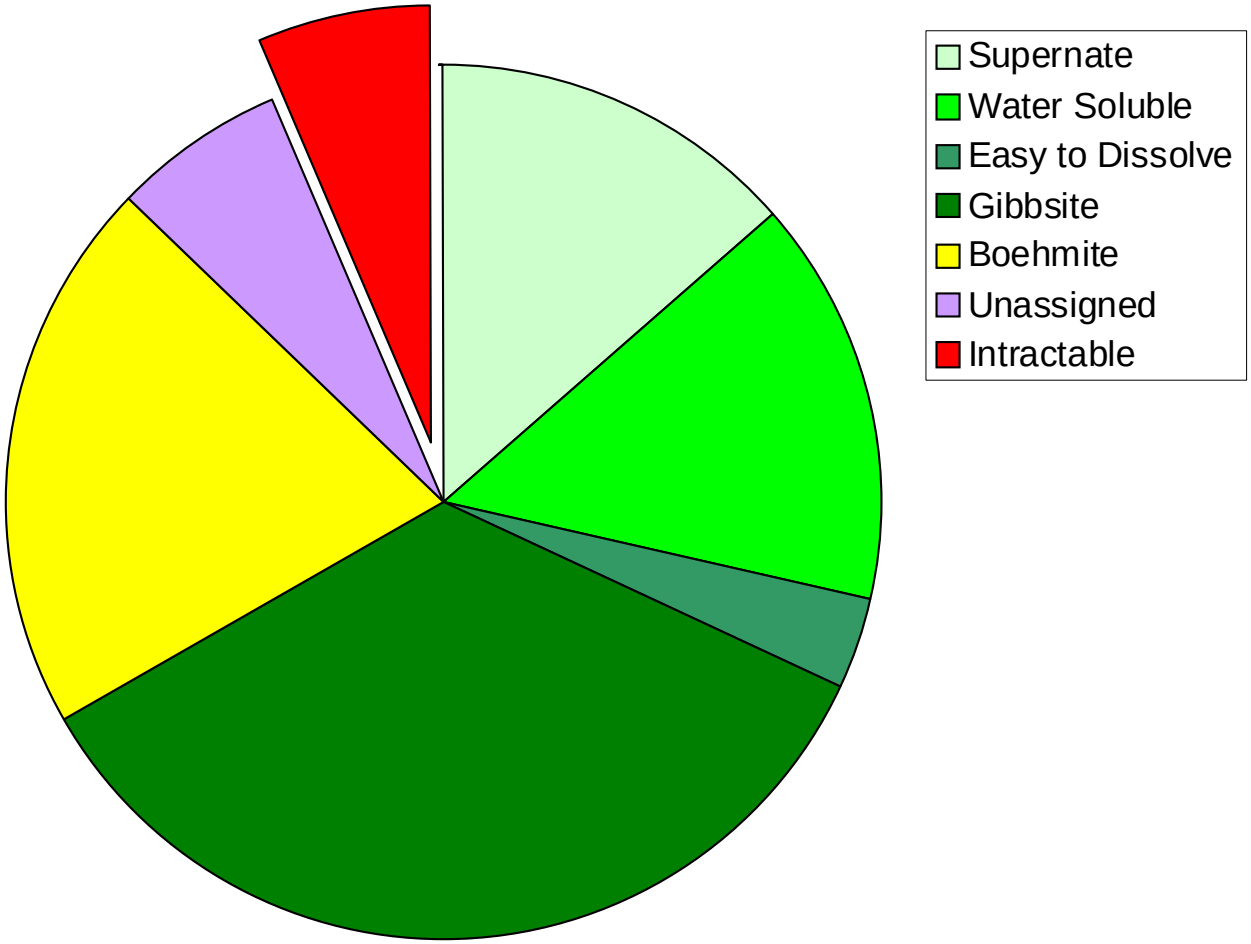
Group 3 and 4 Conclusions

- Adequate Al and P removals from the Group 3 and 4 solids were achieved at relatively low temperature(80ºC) and hydroxide concentration (1 to 3 M)
- Cladding waste waste residual solids primarily a mix of U and Fe
- Very little solids remain after leaching for Groups 3 and 4

Pacific Northwest
NATIONAL LABORATORY

Imposing this characterization data on BBI Al inventory

- 28% is water soluble
- 38% is relatively easy to dissolve
- 20% is boehmite
- Only 6% is known to be intractable



Pacific Northwest
NATIONAL LABORATORY

Conclusions

- 94% of the Al in Hanford tank waste can be removed by caustic leaching and water washing
- Gibbsite is relatively easy to dissolve
- Dissolution of boehmite requires additional reaction time to achieve complete dissolution
- Trade-offs will need to be evaluated between LAW production, HLW production and WTP pretreatment processing rate

Pacific Northwest
NATIONAL LABORATORY