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Operated by Savannah River Nuclear Solutions, LLC

We Put Science To Work

Alternative Reductants for DWPF Chemical Process Cell

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Principal Engineer

November 16, 2010

EM Waste Processing Technical Exchange

EM Office of Environmental Management
safety ◆ performance ◆ cleanup ◆ closure

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Overview

- **Alternative Reductant Objectives**
- **DWPF CPC Process Summary**
- **Evaluation of Nitric-Formic-Glycolic Flowsheet**
  - Test Program
  - Results
  - Issues Identified
- **Path Foward**

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Alternative Reductant Flowsheet Selection: Objectives

- **Mitigate hydrogen generation from noble metal catalyzed formic acid decomposition**
  - Allow GC's to be eliminated or functional classification reduced
- **Eliminate/minimize handling and storage of formic acid**
- **Maintain feed processability and control melter foaming**
- **If possible, continue to remove Hg from melter feed**
  - Significant potential exists for pluggage between the melter offgas quencher and the steam atomized scrubbers
  - Potential also exists that mercury would be recycled back to the Tank Farm

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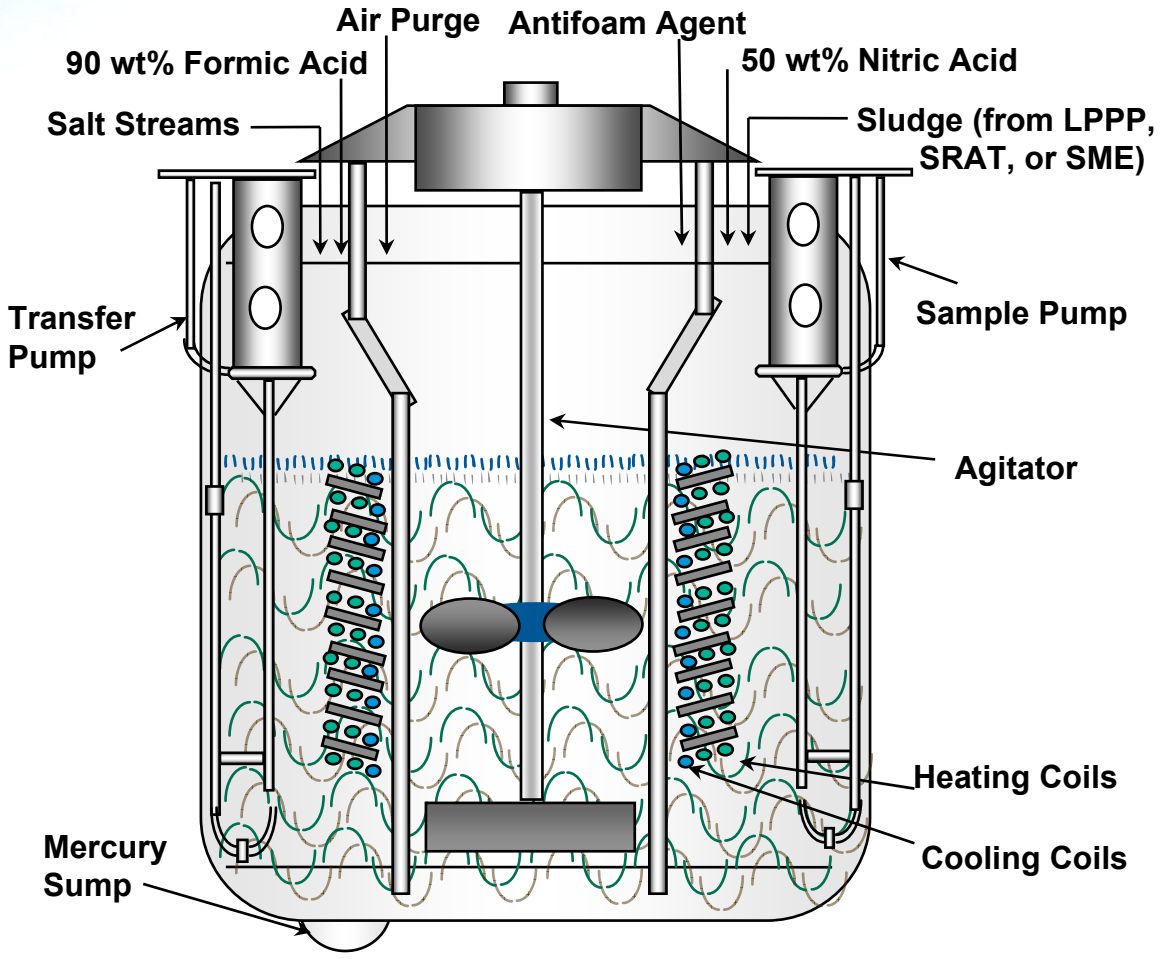
DWPF CPC Process Summary

SRAT → SME → MFT



Sludge Receipt & Adjustment Tank (SRAT)

Add formic & nitric acids at 93 ºC

Concentrate/Reflux/Chemistry

Sample product

Transfer SRAT to the SME

Slurry Mix Evaporator (SME)

Canister decontamination frit and process frit additions

Slurry concentration by boiling

Sample SME product to qualify glass waste form

Transfer from SME to MFT

Melter Feed Tank (MFT)

Buffer batch chemical process and continuously fed melter

Transfer from MFT to melter

Melter fills canisters

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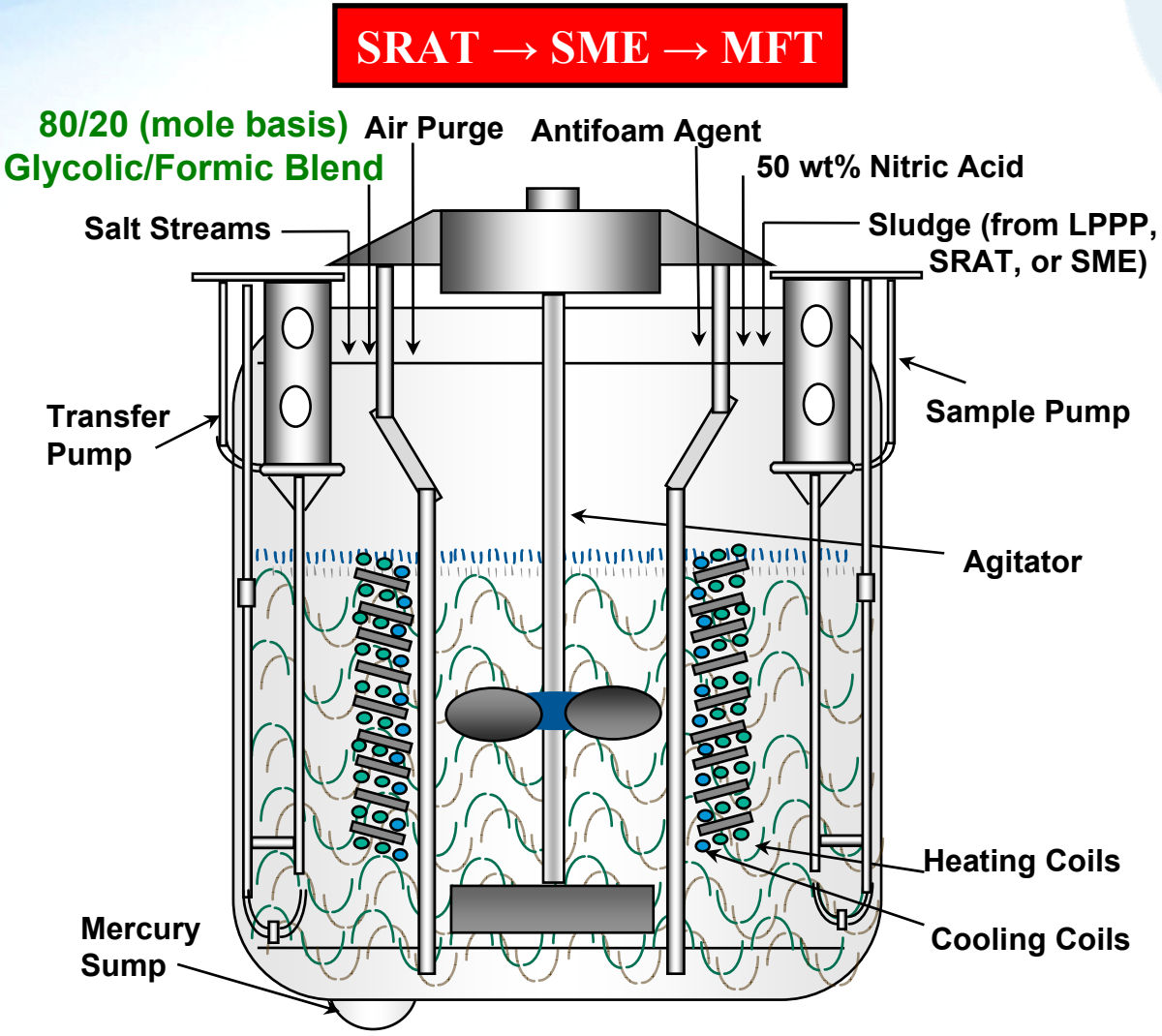
DWPF CPC Nitric-Glycolic-Formic Flowsheet



- Blend of 90% formic acid and 70% glycolic acid to generate a blend that is 80% glycolic acid on a molar basis replaces current formic acid addition
- No facility modifications required to implement revised flowsheet
- Adjustments required in acid calculations to account for differences in acid molarity and reducing strength
- Acid addition rate would need to be increased to keep same addition time

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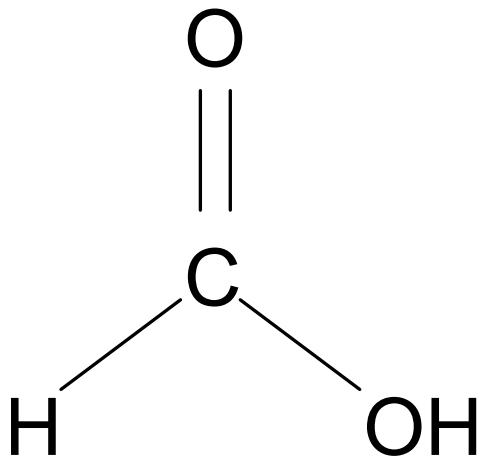
DWPF CPC Nitric-Glycolic-Formic Flowsheet

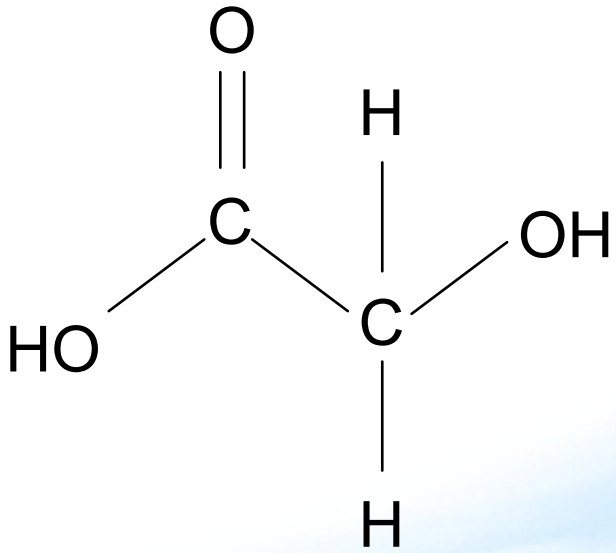
Formic Acid

- **Concentration: 90 wt%**
- **pKa: 3.75**
- **Carbon Oxidation State: +2**
- **Acid Split (125% stoichiometry)**
  - 14% Nitric
  - 86% Formic



Glycolic Acid

- **Concentration: 70 wt%**
- **pKa: 3.83**
- **Carbon Oxidation State: +1**
- **Acid Split (125% stoichiometry)**
  - 38% Nitric
  - 12% Formic
  - 49% Glycolic



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Evaluation of Nitric-Formic-Glycolic Flowsheet: Test Program

- **Glycolate anion analysis development**
- **CPC tests with non-rad simulant**
  - Hydrogen generation
  - REDOX control
  - Processing characteristics
  - Rheological properties of melter feed
- ***Melter offgas modeling***
  - *Melter testing*
- ***Radioactive waste demonstration***
  - *Qualification run*

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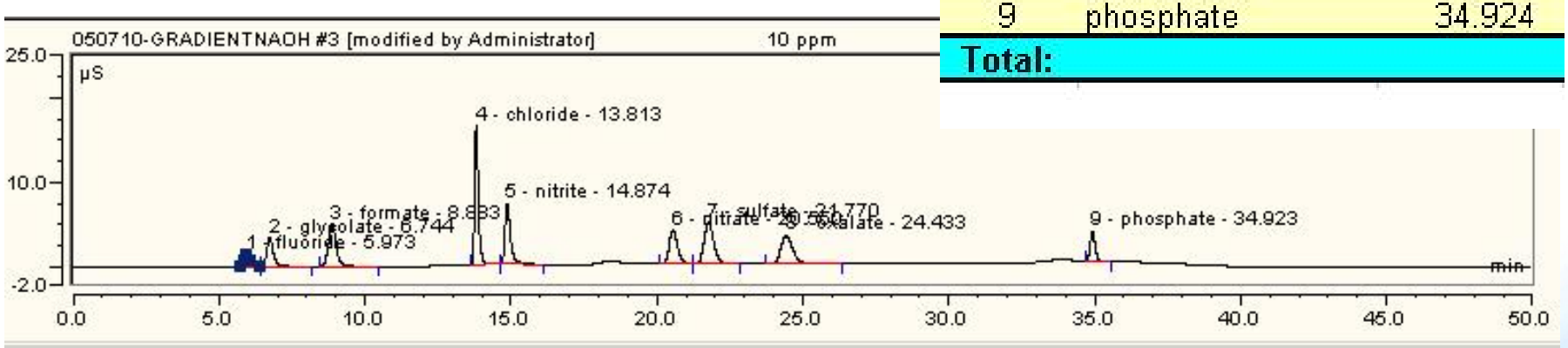
Glycolate anion analysis development

- **Ion chromatography selected as analysis method**
  - IC currently in use at DWPF
- **Gradient method developed that measures glycolate and other 8 required anions**
- **Additional method development needed to decrease sample run time**
  - 45 minutes

No.	Peakname	Ret.Time min
1	fluoride	5.974
2	glycolate	6.744
3	formate	8.884
4	chloride	13.814
5	nitrite	14.874
6	nitrate	20.550
7	sulfate	21.770
8	oxalate	24.434
9	phosphate	34.924
Total:		



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Evaluation of Nitric-Formic-Glycolic Flowsheet: CPC tests

- **Baseline Runs (125% acid stoichiometry)**
  - Nitric-formic run
  - 80-20 glycolic-formic run
  - 80-20 glycolic-formic run w/o Hg
  - 80-20 glycolic-formic run w/ salt streams from ARP/MCU
- **Acid Stoichiometry**
  - 100%, 150%, 200% runs
- **REDOX Control (100% acid stoichiometry)**
  - 0.0, 0.1, 0.2, 0.3 $Fe^{+2}/\Sigma Fe$ REDOX targets
- **Glycolic-Formic Ratio (125% acid stoichiometry)**
  - 100%, 80%, 70%, 60%, 50%, 40% glycolic acid
- ***Sludge Matrix***
  - *4 simulants designed to bound expected sludge batch compositions*

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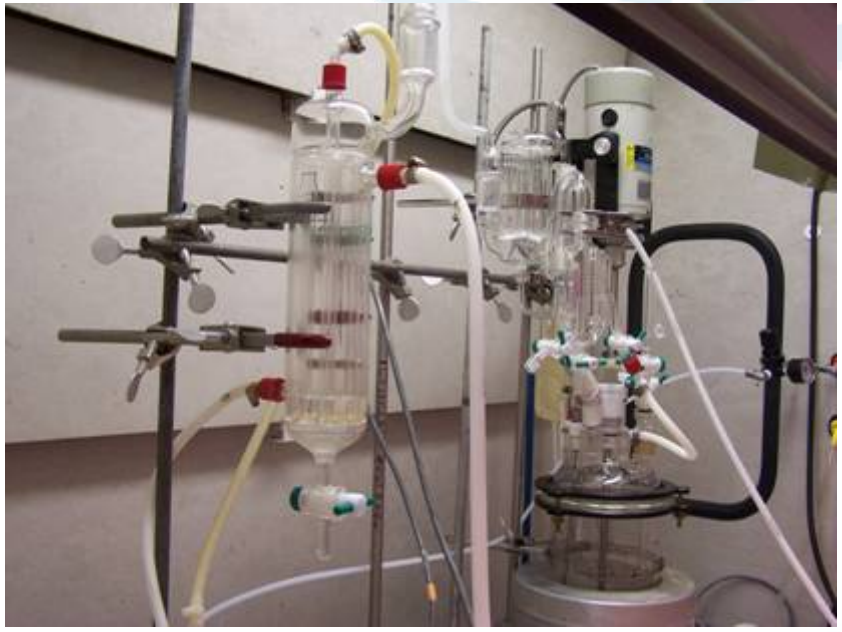
Evaluation of Nitric-Formic-Glycolic Flowsheet: CPC Tests

- **SB6H simulant utilized**
  - Highly viscous
  - Prepared by Harrell Industries
- **HM levels of noble metals**
- **SB6 levels during baseline and acid stoichiometry tests**
  - Reduced levels during REDOX and glycolic-formic ratio tests
- **4L SRAT/SME apparatus**
  - GC offgas monitoring
  - Continuous pH monitoring
  - Design basis dewater and acid addition rates



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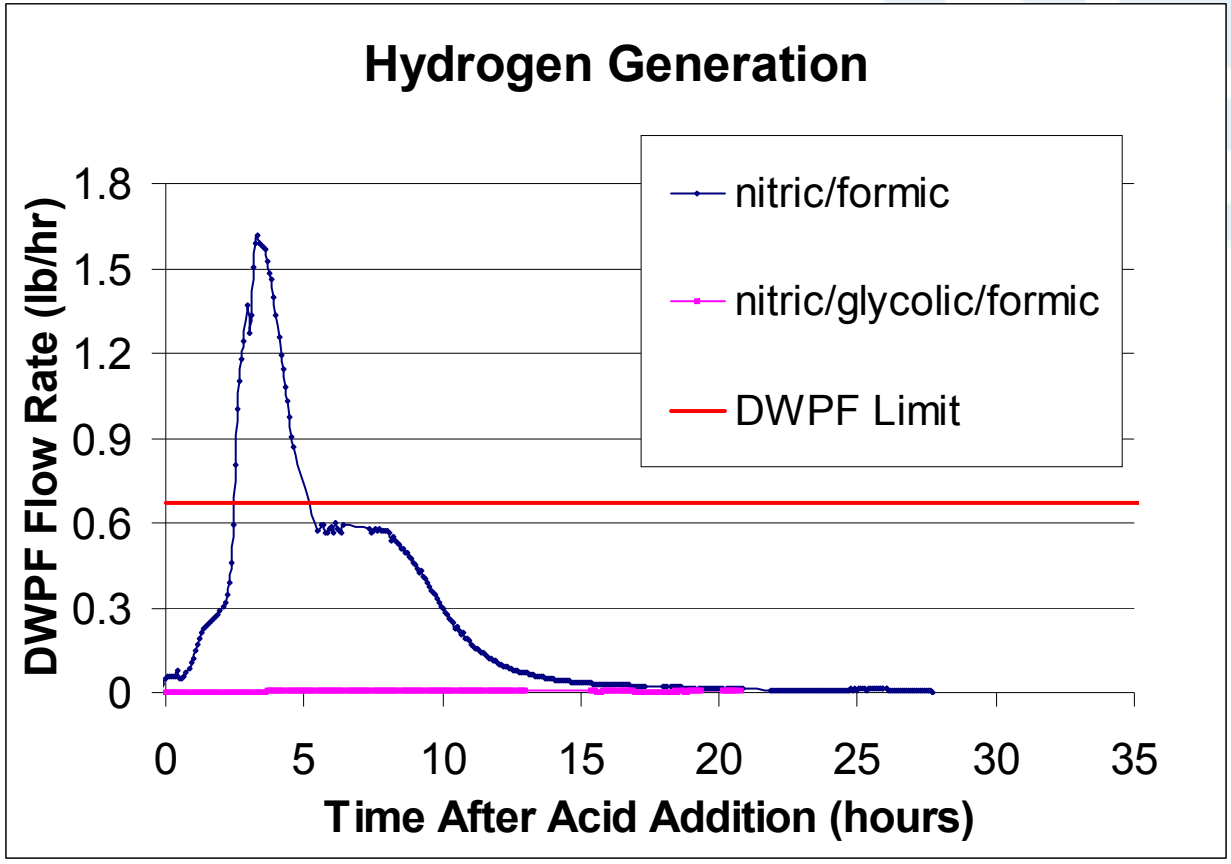
Evaluation of Nitric-Formic-Glycolic Flowsheet: Baseline Runs



Hydrogen generation nearly eliminated with new flowsheet

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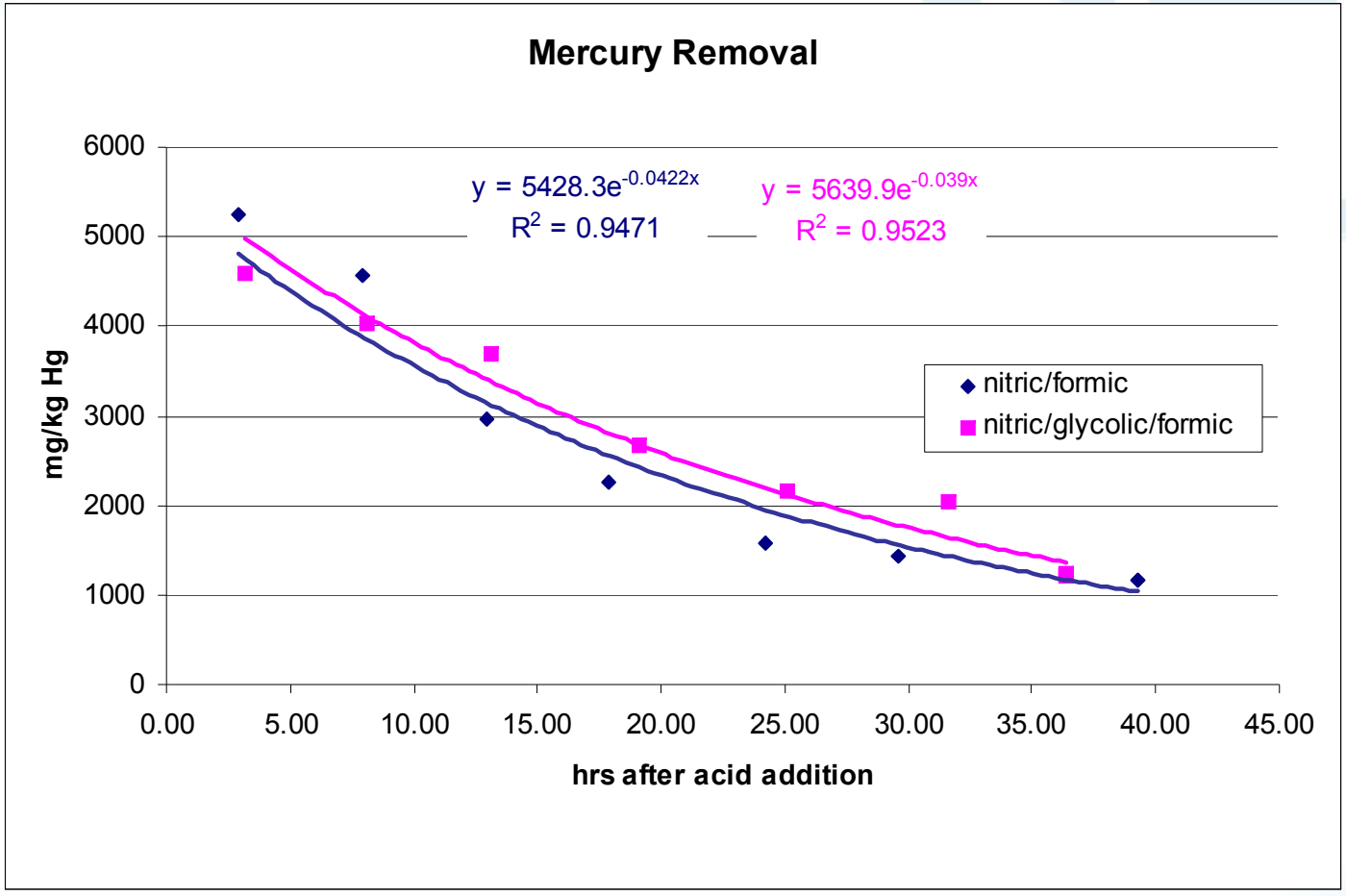
Evaluation of Nitric-Formic-Glycolic Flowsheet: Baseline Runs



Mercury stripping rate similar to current flowsheet

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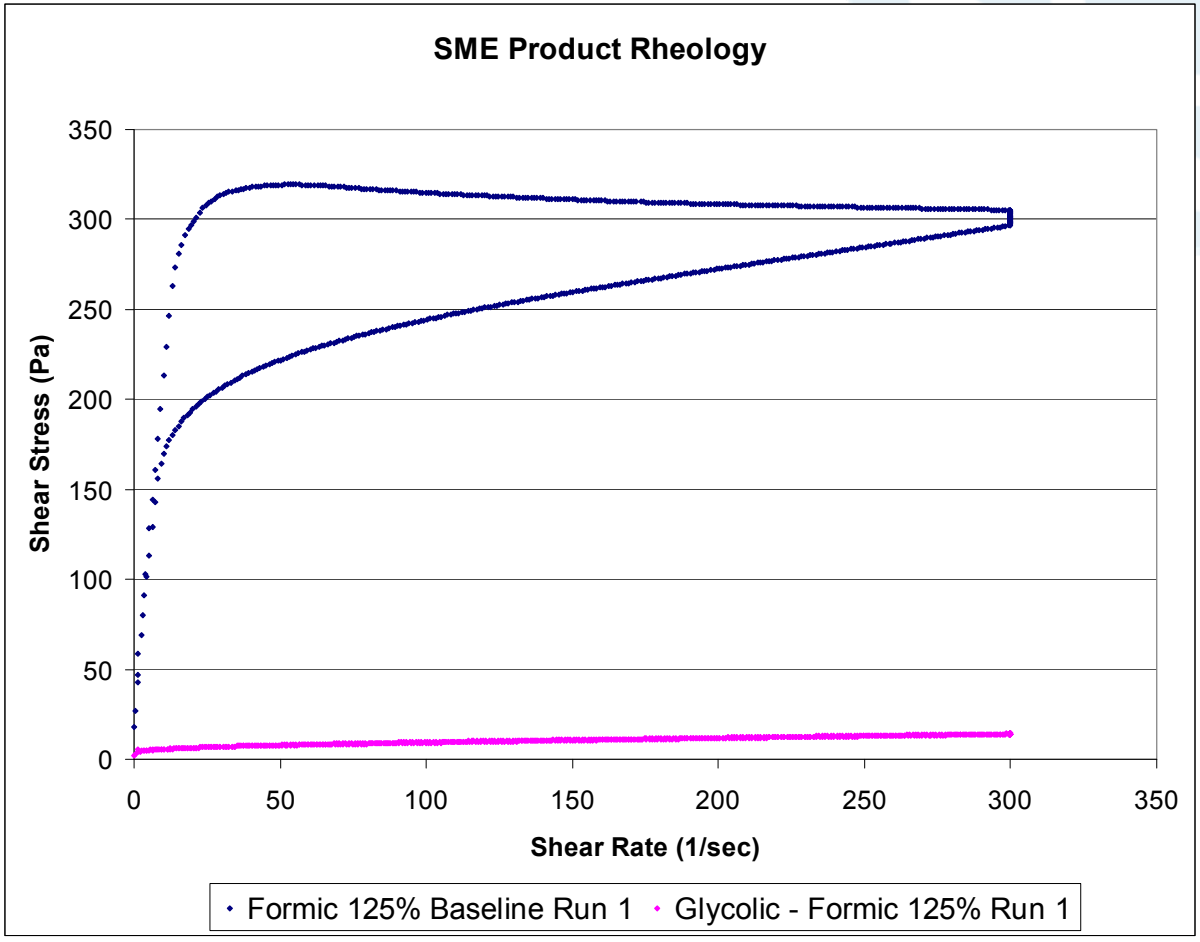
Evaluation of Nitric-Formic-Glycolic Flowsheet: Baseline Runs



Rheological properties improved by new flowsheet

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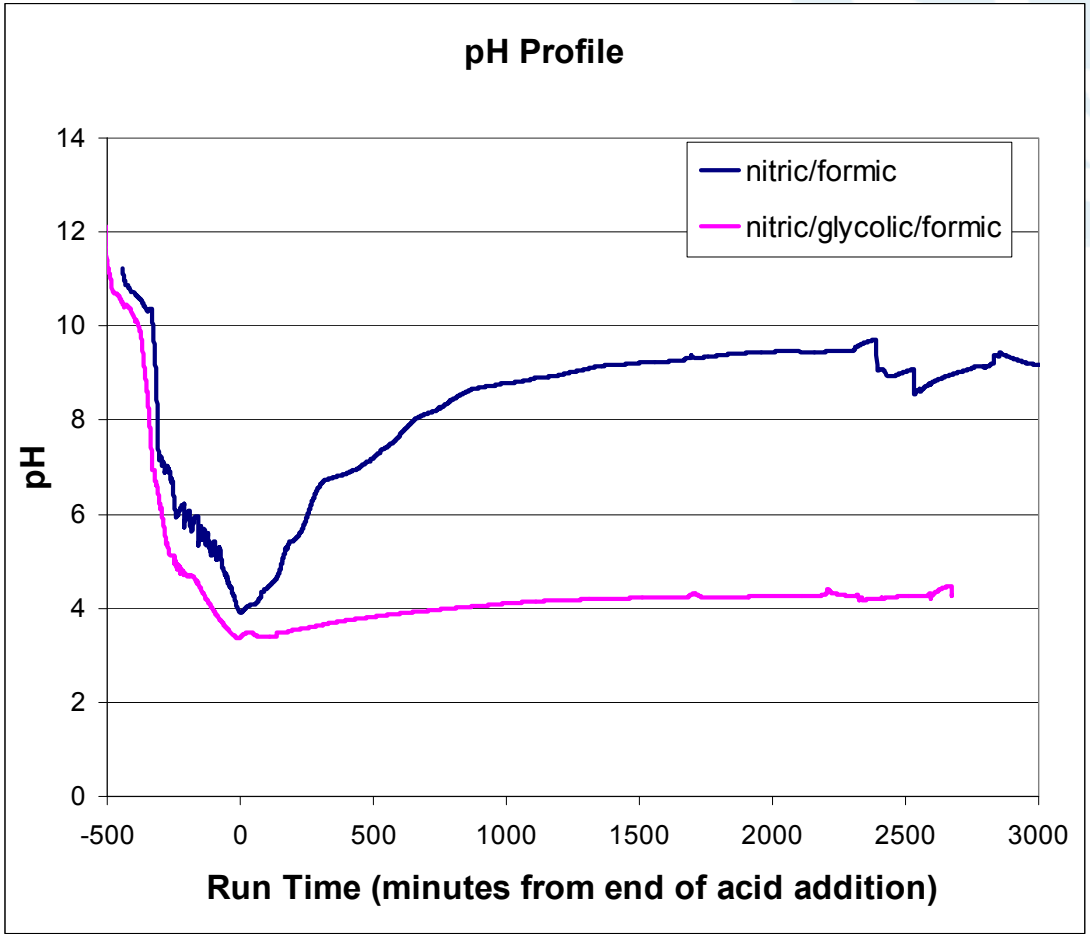
Evaluation of Nitric-Formic-Glycolic Flowsheet: Baseline Runs



pH rebound minimized by new flowsheet

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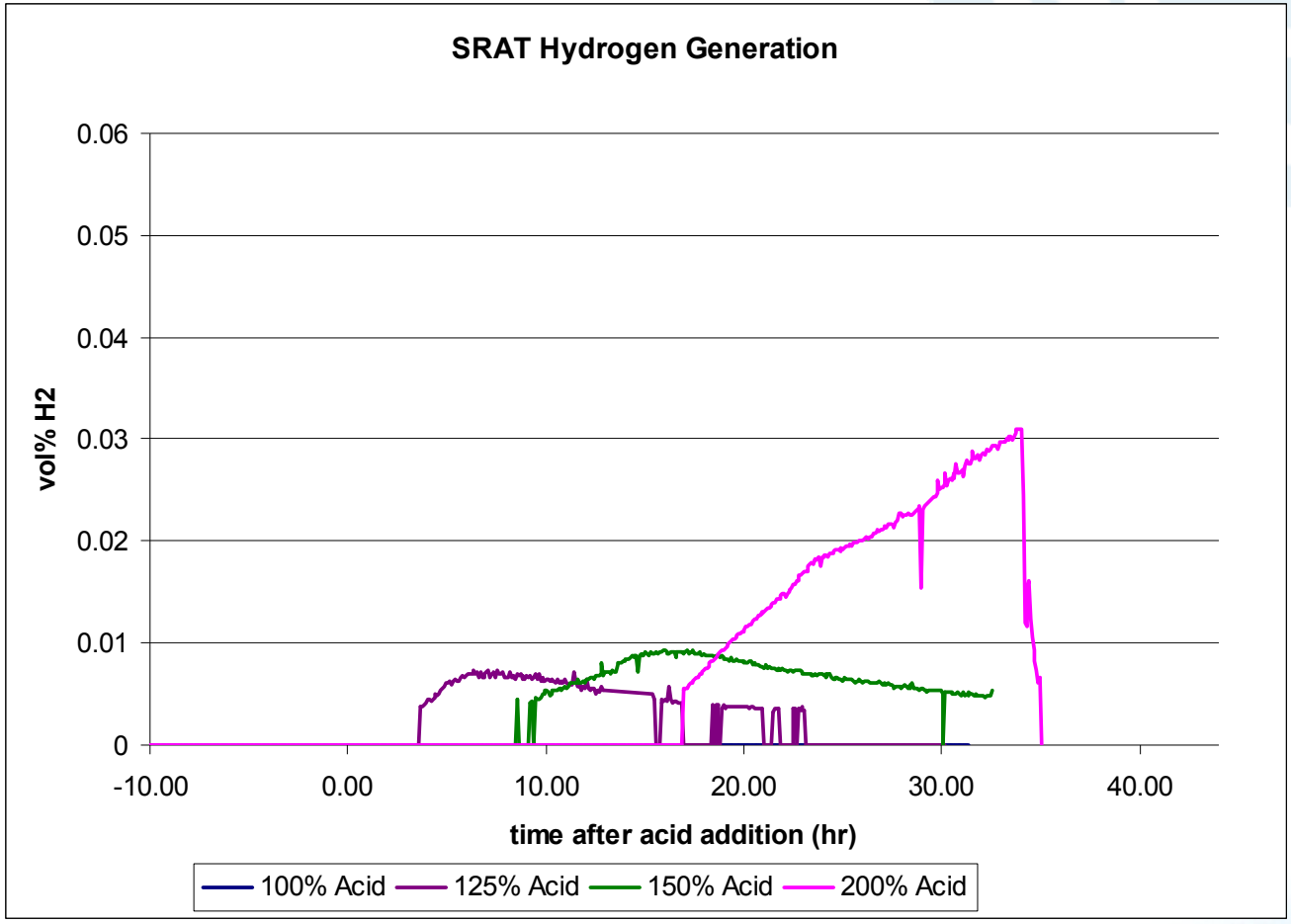
Evaluation of Nitric-Formic-Glycolic Flowsheet: Stoichiometry

Large increases in acid addition did not lead to excessive hydrogen generation.



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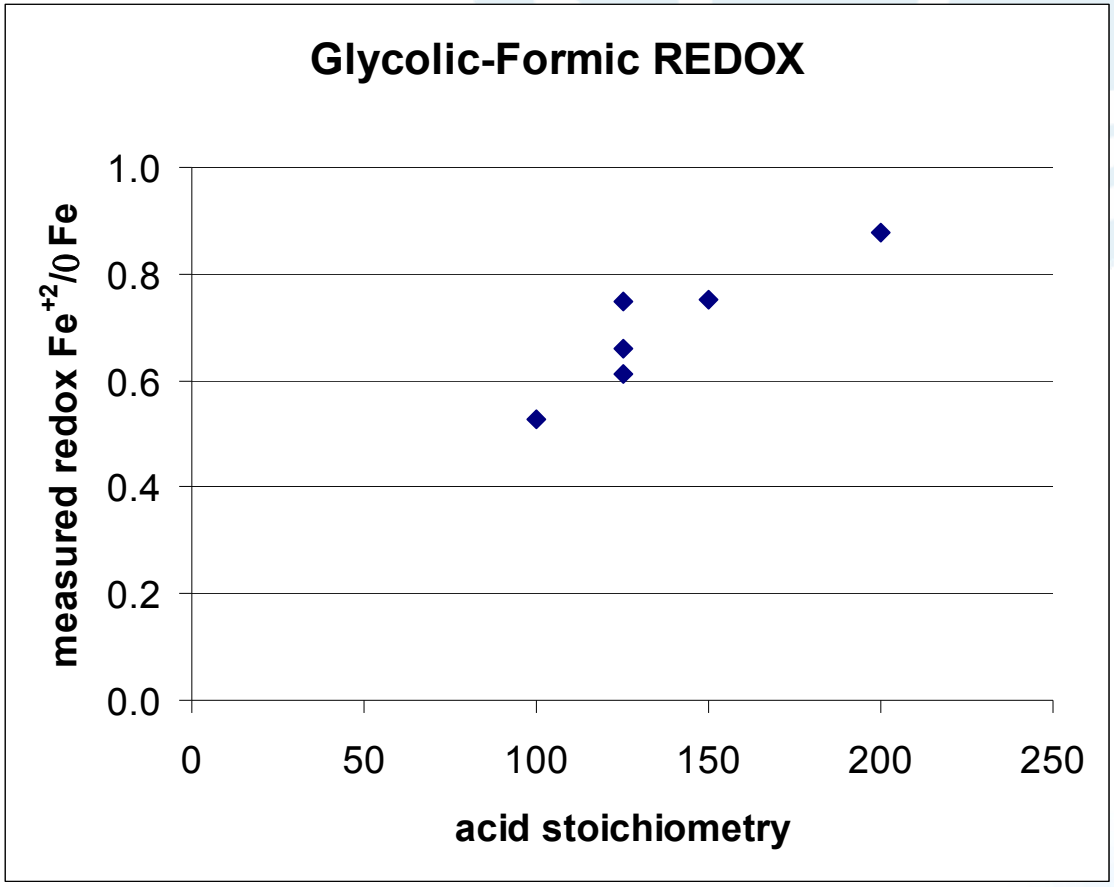
Evaluation of Nitric-Formic-Glycolic Flowsheet: Initial REDOX

- **Formic Flowsheet**
  - Fully oxidized
- **Glycolic-Formic Flowsheet**
  - Overly reducing
  - Acid calculation requires a number of processing assumptions



REDOX control not adequate using initial assumptions

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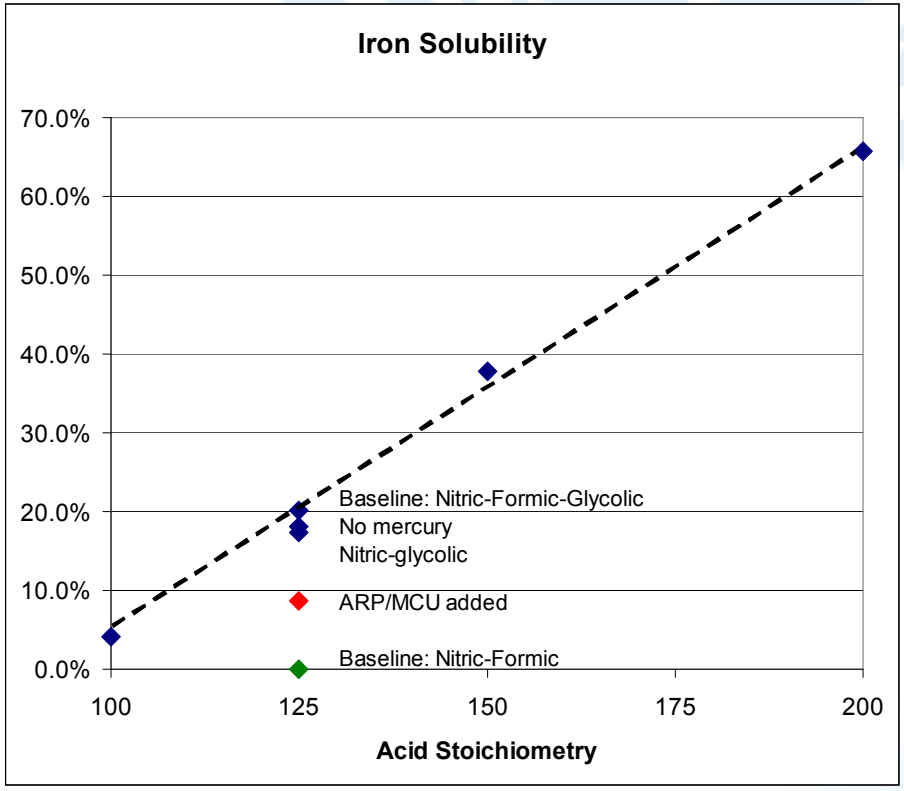
Evaluation of Nitric-Formic-Glycolic Flowsheet: Stoichiometry

- Iron concentration is basis for criticality control
- Must stay in same phase as the plutonium
- Appreciable iron solubility could invalidate criticality control method



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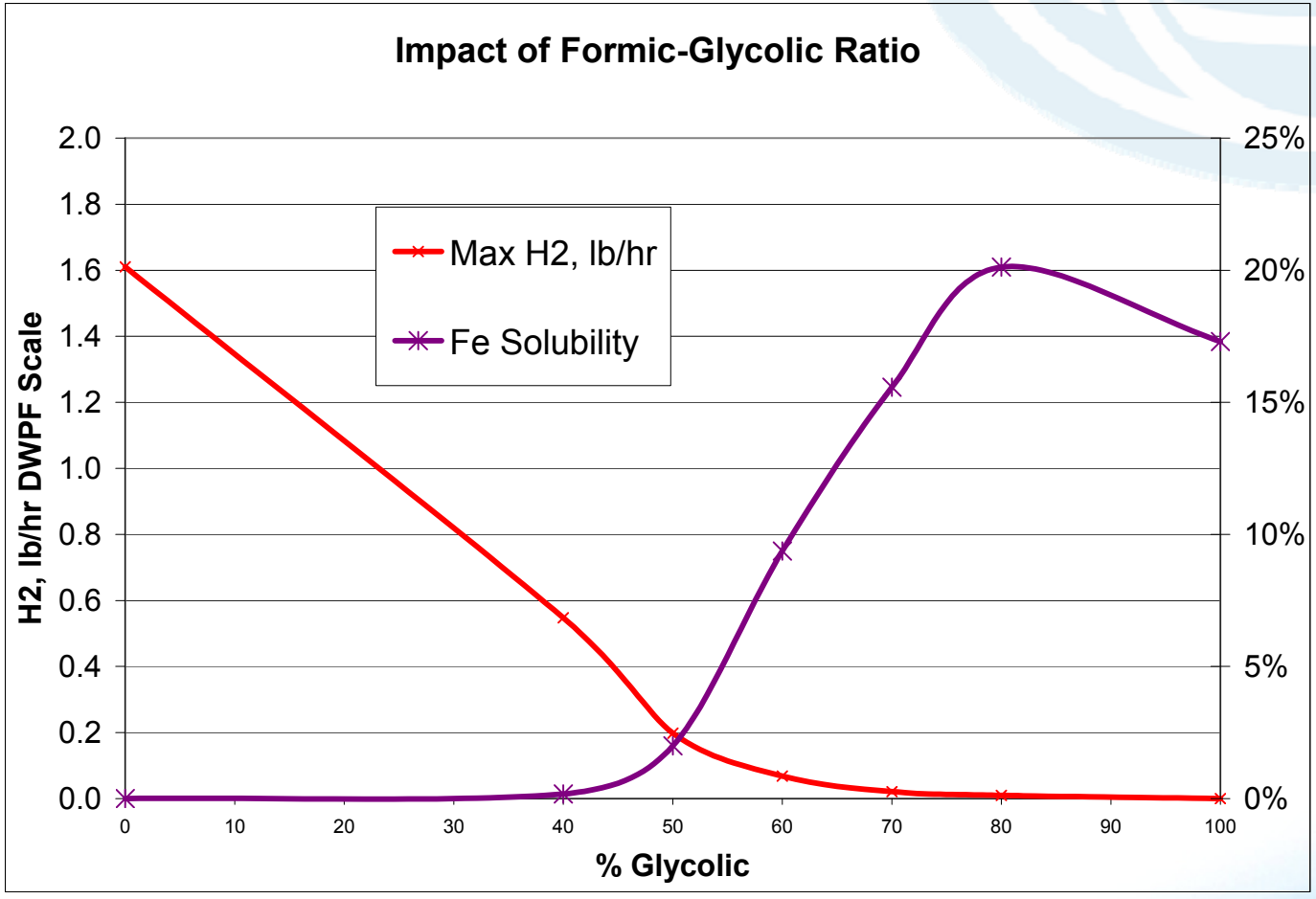
Evaluation of Nitric-Formic-Glycolic Flowsheet: Acid Ratio



All runs performed at 125% acid stoichiometry

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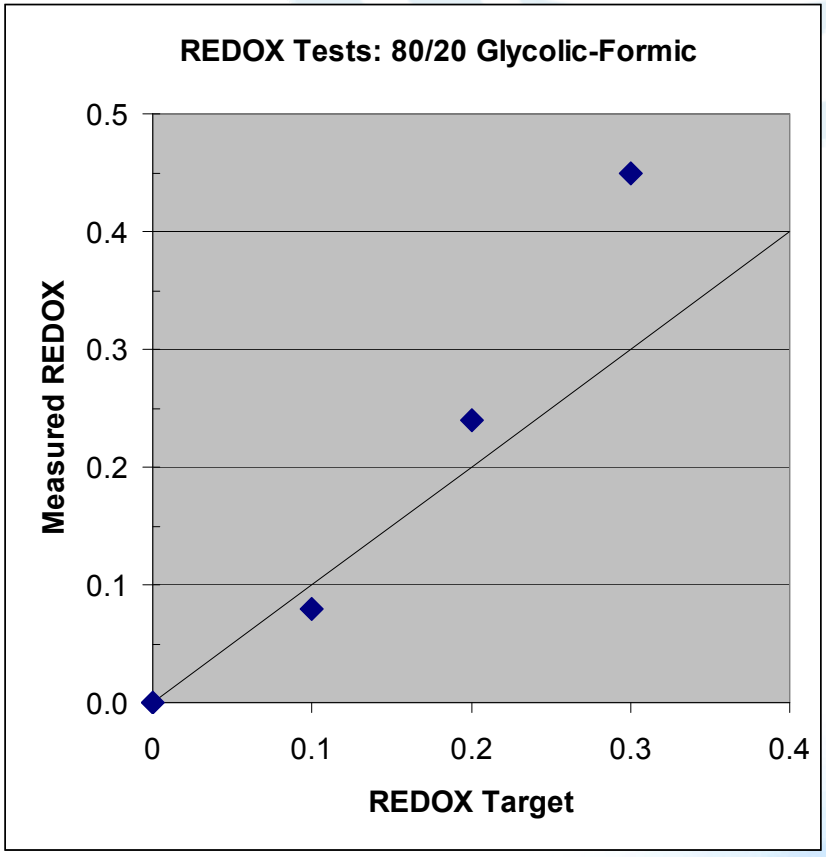
Evaluation of Nitric-Formic-Glycolic Flowsheet: REDOX

- **Four SRAT runs**
  - 125% Acid Stoichiometry
  - REDOX targets
    - 0.0
    - 0.1
    - 0.2
    - 0.3
  - SRAT acid calculation assumptions adjusted based on initial tests
  - Predicted values from SRAT product data do not follow expected trends



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Evaluation of Nitric-Formic-Glycolic Flowsheet: Baseline Run Comparison

- **Nitric-Formic Flowsheet**
  - DWPF hydrogen limits exceeded
  - Yield stress well above DWPF limit
  - Large pH rebound
  - Mercury successfully stripped
  - Very little dissolution of metal species in product
    - No soluble iron
  - Highly oxidized feed
    - Formic acid destruction too high to accommodate at 125% acid
    - Acid addition amounts low enough to accommodate hydrogen generation would likely lead to feed too viscous to process

- **Nitric-Glycolic-Formic Flowsheet**
  - Minimal hydrogen generation
  - Acceptable rheological properties
  - Minimal pH rebound
  - Mercury successfully stripped
  - Significant dissolution of metal species
    - Soluble iron noted
  - Overly reducing feed
    - Processing assumptions need to be refined
  - Salt streams addition led to small decrease in hydrogen generation and metal solubility
  - Mercury free run exhibited some hydrogen generation
    - No Hg free sludge at SRS

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Evaluation of Nitric-Formic-Glycolic Flowsheet: CPC Summary

- **Proof of concept demonstrated for nitric-formic-glycolic flowsheet**
  - Exceeded performance of baseline flowsheet
- **Issues Identified**
  - Acid equation assumptions need further refinement to incorporate glycolate
    - REDOX model may need refinement
  - Iron solubility could require a change in criticality control methods
  - Analytical method for glycolate needs refinement

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Path Foward

- **Complete data regression on acid ratio and REDOX testing**
- **Perform CPC testing with sludge matrix simulants**
  - Testing planned in Feb 2011
- **Perform melter tests (DM-10 testing at VSL)**
  - Feed preparation will begin this month at SRNL
  - Evaluate melter processing
  - Obtain data for melter offgas flammability model
- **Perform melter offgas flammability modeling**
- **Downselect alternative flowsheet**
  - Nitric-formic-glycolic
  - Nitric-formic-sugar (currently being evaluated by VSL)
- **Radioactive waste demonstration**
  - Will be performed as part of qualification of sludge batch when alternative reductant flowsheet is implemented

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Questions / Contact Information

Contact Information

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Alternative Reductant Flowsheet Selection: Scoping Tests

- **Mercury reduction**
  - Supernate tests for mercury reduction potential
    - Baseline case (formic acid)
    - Acidic Reductants: Glycolic, oxalic, proprionic, citric, acrylic, ascorbic, malic, maleic, malonic, succinic, pyruvic acids
    - Non-acidic reductants: Tin chloride
    - Mercury reduction only noted with formic and acrylic acids
- **REDOX Control**
  - SRAT product prepared with nitric acid only
  - Each reductant above plus Antifoam 747, Dolapix CE64, and Disperse-Ayd W28 tested to determine REDOX control
    - Most reductants shown to be effective
    - Development of correlations not possible from data due to scatter
- **Minimum formic acid SRAT tests**
  - Tests at 7, 20, 40, 60 and 80% formic acid (molar basis)
    - All but 7% run reduced mercury
  - One test with nitric-formic-glycolic flowsheet (80-20 blend of glycolic-formic)
    - Mercury reduction noted
    - 13% formic acid during test (molar basis)

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Alternative Reductant Flowsheet Selection: Candidates

Acidic Reductants

Reductant	Formula	Solubility 25 C g/100 ml	Molarity at Saturation	Carbon Oxidation State	Reductant	Formula	Solubility 25 C g/100 ml	Molarity at Saturation	Carbon Oxidation State
Formic Acid	CH2O2	Miscible	23.6*	2	**Glycolic Acid**	C2H4O3	80	10.5	1
Oxalic Acid	C2H2O4	14.3	1.6	3	**Acrylic acid**	C3H4O2	miscible	13.9	0
Propionic Acid	C3H6O2	miscible	13.5	-0.667	**Ascorbic Acid**	C6H8O6	33	1.9	0.67
Malic Acid	C4H6O5	55.8	4.2	1	**Citric Acid**	C6H8O7	133	6.9	1
Maleic Acid	C4H4O4	78	6.7	1	**Succinic Acid**	C4H6O4	7.69	0.7	0.5
Malonic Acid	C3H4O4	miscible	8.7	1.33	**Pyruvic acid**	C3H4O3	Miscible	14.2	0.67

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Evaluation of Nitric-Formic-Glycolic Flowsheet: Baseline Runs

Baseline Run		80/20 Formic-Glycolic Run	
Solids:	46 wt%	Solids:	45 wt%
Calcine Solids:	40 wt%	Calcine Solids:	34 wt%
Target REDOX:	0.20	Target REDOX:	0.20
Predicted REDOX:	<0	Predicted REDOX:	0.10
Measured REDOX:	<0	Measured REDOX:	0.75

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Evaluation of Nitric-Formic-Glycolic Flowsheet: Baseline Runs

	SRAT Products		SME Products	
anions (mg/kg)	**Nitric-Formic**	**Nitric-Formic-Glycolic**	**Nitric-Formic**	**Nitric-Formic-Glycolic**
F	<100	<100	<100	<100
Cl	1085	976	1390	<100
NO2	<100	<100	<100	<100
NO3	25000	55950	25350	53100
SO4	1920	1765	2475	1855
C2H3O3	<100	55400	<100	52550
C2O4	296	2405	519.5	2690
HCO2	12900	<100	22200	<100
PO4	<100	<100	<100	<100
wt% total solids	17.5%	21.8%	46.3%	44.7%
wt% calc. solids	12.2%	11.4%	39.8%	33.7%
wt% insol. solids	11.0%	9.0%	38.3%	31.3%
wt% sol. solids	6.5%	12.8%	8.0%	13.3%
Predicted Redox			<0	0.1
Measured Redox			<0	0.75

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Evaluation of Nitric-Formic-Glycolic Flowsheet: Baseline Runs

- **Elimination of mercury**
  - Hydrogen generation rates increased significantly
    - Similar trends noted in past runs with baseline flowsheet
    - Generation rates far below baseline run
  - All sludge batches contain significant amounts of mercury
- **Processing with salt streams added**
  - Hydrogen generation slightly decreased
  - Solubilities of metal species decreased
  - Slight increase in foaming
    - Similar trends noted in past runs with baseline flowsheet

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