RF Resin Development Presented October 9 2007 at

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Integrated Engineering, Construction, and Management Solutions

RPP WTP

Background

- Resorcinol Formaldehyde (RF) History
  - Developed by Dr. Jane Bibler in late ’80s
  - Manufactured and tested extensively in shard form in 90’s

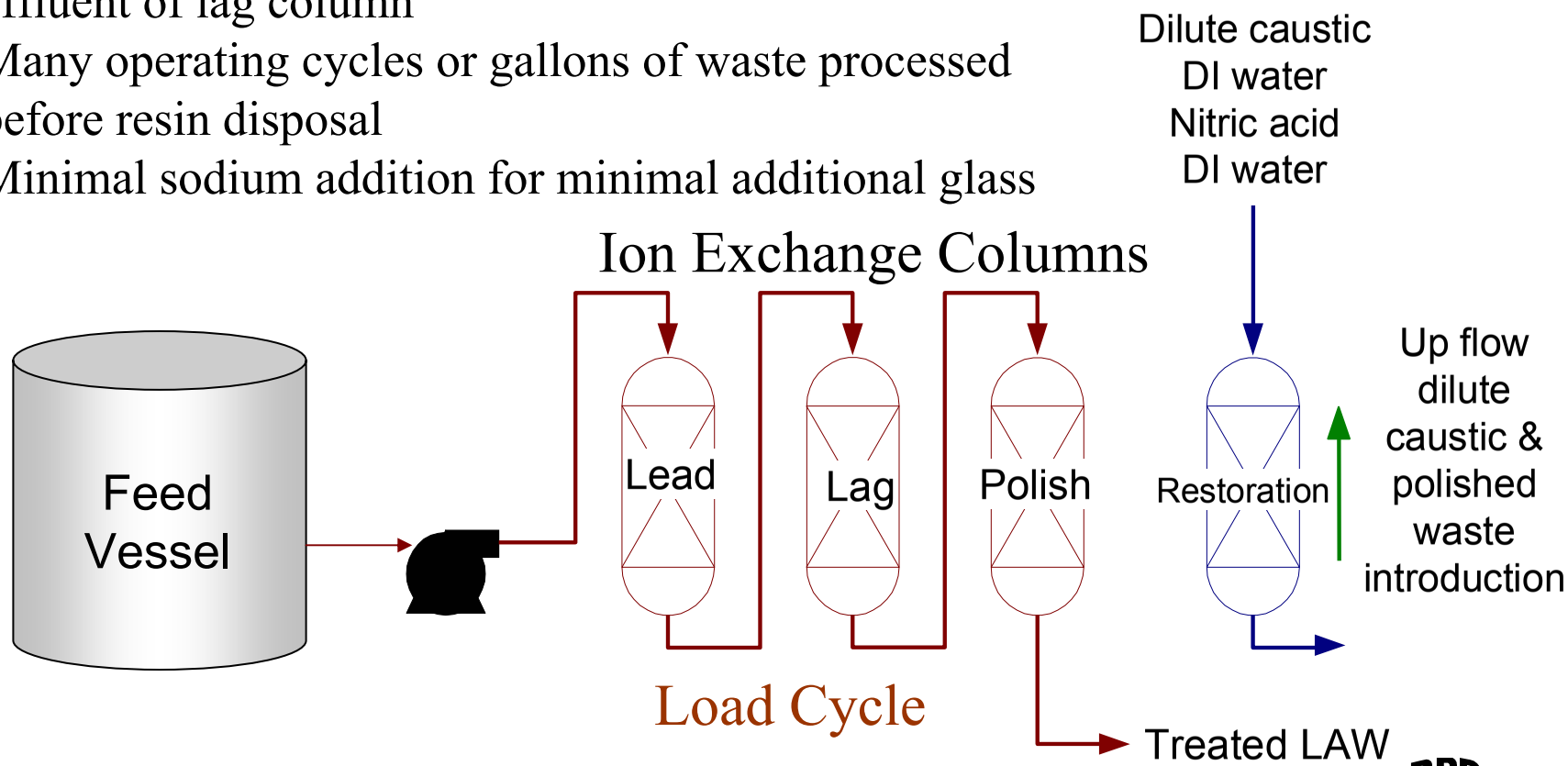
- Original WTP IX Resin - SuperLig® 644
  - Shard form
  - Life and pressure drop concerns
  - Expensive

Background (cont.)

- 2002 Alternative resin selection study
  - Team of 20
  - SRNL / PNNL / WTP/ Consultants
  - Recommended RF as best alternative candidate but with re-engineered properties
- 2002 Implementation plan set development strategy
  - Qualify for commissioning and Phase 1 feeds using system description flows

WTP IX Application

- Loading time needs to exceed restoration time
- Less than 10 psi pressure drop per resin bed at flow rate of 22 gpm
- Decontamination needs to exceed 1000 to 4000 for effluent of lag column
- Many operating cycles or gallons of waste processed before resin disposal
- Minimal sodium addition for minimal additional glass



Status

- Planned manufacturing and testing is complete
  - All test reports complete (19)
  - All synthesis reports complete (9)
- Resin exceeds all WTP requirements
- Scale-up demonstrated at two facilities
- BNI recommended conversion to RF
  - ORP accepted as equivalent to SL644
- Testing for process limits, full mission, and flowsheet changes forthcoming

Development Cost and Benefits

- $14 Million development cost
- Major full mission procurement savings
- Significant commissioning savings
- 6 years development
- Superior performance
- 84% less spent resin
- 95% less curies in spent resin

RPP WTP

Development of RF as an Alternative

Identified Need

- Established need to have backup or alternative to SL-644 (Jan to Mar 2002)

Engineering Study

- Conducted engineering study
- Selected RF as best potential alternative for Cs removal (Apr to Jun 2002)

Implementation Plan

- Developed alternative IX R&T Plan as part of Implementation Plan – no equipment changes (Aug to Oct 2002)

Stage 1

- Tested 12 RF batches from four vendors
- Concluded RF will most likely meet requirements
- Recommended specific spherical macroporous RF for subsequent testing and scale-up (2003)

Stage 2

- Optimize then scale-up production
- Qualify for commissioning

(2004 to 2007)

Stage 3

- Post commissioning support testing
- Plans based on 2004 Phase I feeds

(2005 to 2007)

Stage 4 – TMP, M6 (potential new scope)

- Addresses 2007 flow sheet modifications, including solids, full WTP mission and process limits

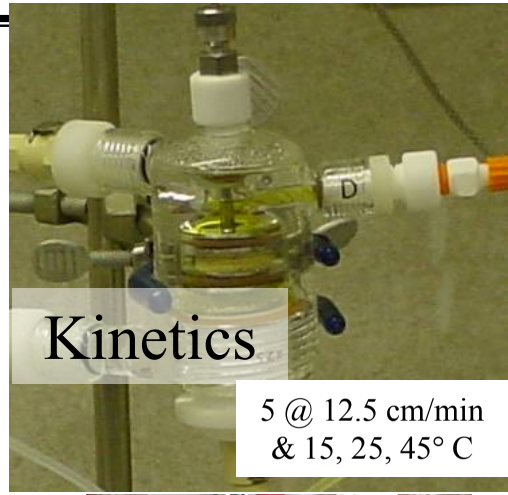
(2008 to 2010)

Stage 2 & 3 RF Testing

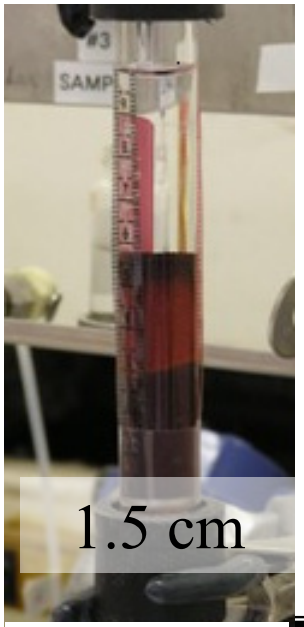
AP-101 @ 45° C,
AN-107 @ 25° C

163 Contacts;
15, 25, 45° C

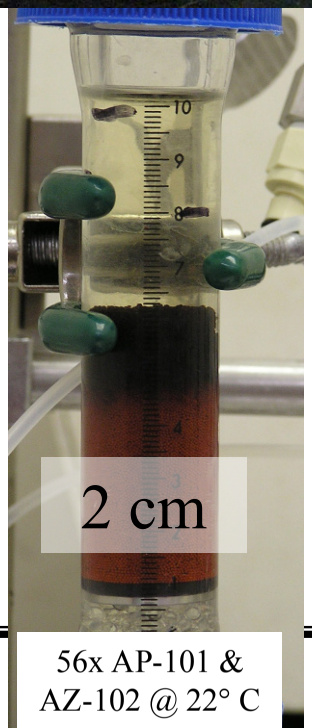
- Unique hydraulic scale-up method
- Simultaneous, multi-cycle, small column loading tests for efficient screening
- Synthesis targeted for properties



5 @ 12.5 cm/min
& 15, 25, 45° C

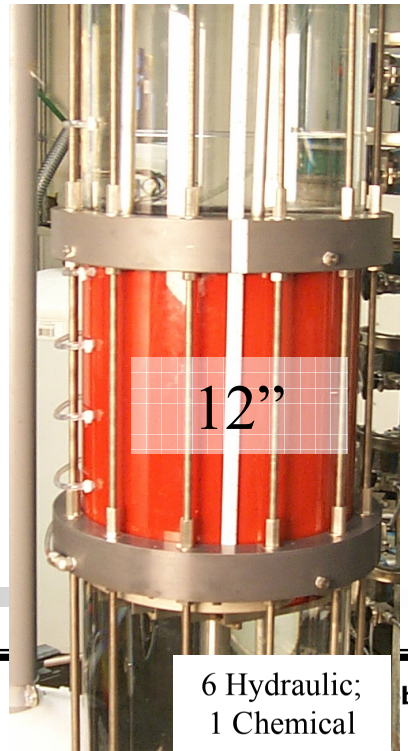


2x AP-101; 1x
AN-102 @ 25° C



56x AP-101 &
AZ-102 @ 22° C

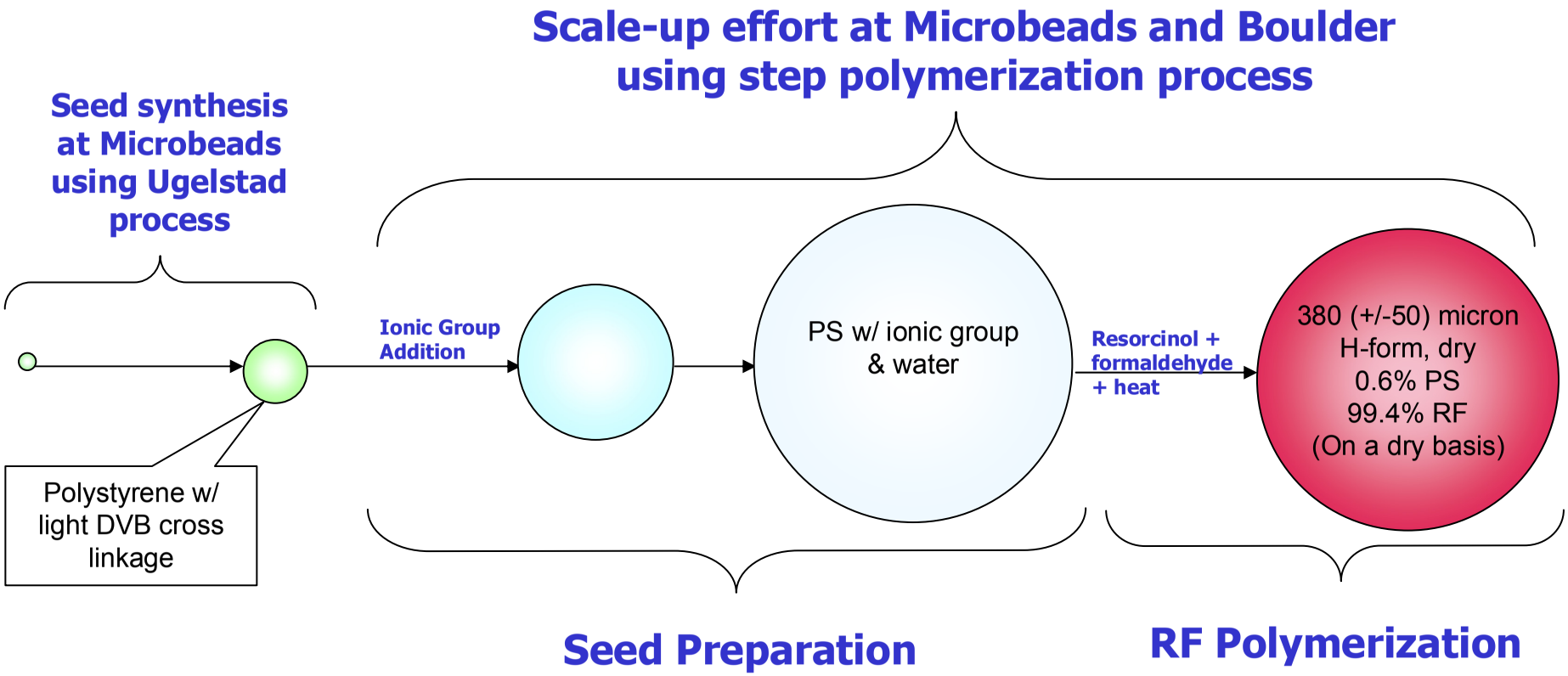
53 Hydraulic



6 Hydraulic;
1 Chemical

14 Hydraulic;
2 Chemical

RF Synthesis Schematic



RF Production Development / Scale-up

Scale-up

2006

Two 100-gallon lots produced in March & May 2006

2005

- **Four 100-gallon lots produced in May, Sept & October 2005**

Optimization

- **Two 3-gallon lots**
- **Four 1-gallon lots**
- **Numerous smaller lots**
- **Optimized synthesis method for best cesium kinetics and production economics**

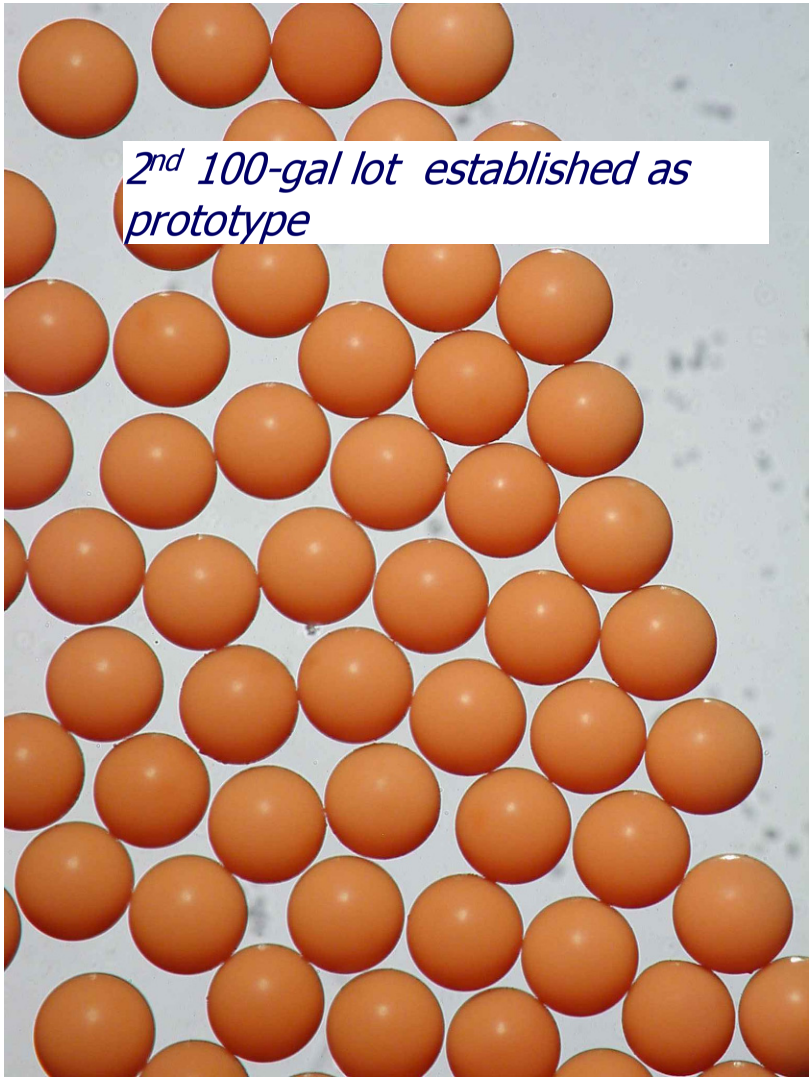
2004

- **Four 0.3-gallon lots**
- **Numerous smaller lots**
- **Optimized cesium capacity, kinetics, resin size, bead clean-up**

Initial

2003

- **Four 0.3-gallon lots**



Bead Properties → Bed Properties

As-received in DI water under N_2 gas

380 (+/-50) micron
H-form, dry
0.6% PS
99.4% RF
(On a dry basis)

+1.6 mole NaOH/liter in CRP-VSL-00001

Reacts quickly with dissolved O_2 destroying cesium capacity

445 (+/-50) micron
Na-form, in 0.5 M NaOH

+1.6 mole HNO3/liter in IX column

Reacts slowly with dissolved O_2 destroying cesium capacity

415 (+/-50) micron
H-form, in water

$\rho_{Polymer\ (Skeletal)}$ = 1.5 g/ml

$\varepsilon_{bead\ (void\ space)}$ = 0.48

$\rho_{bead\ in\ water}$ = 1.26 g/ml

Terminal vel. in water = 84 cm/min

$\rho_{Polymer\ (Skeletal)}$ = 1.61 g/ml

$\varepsilon_{bead\ (void\ space)}$ = 0.61

$\varepsilon_{bed\ (after\ upflow\ waste\ intro)}$ = 0.42

$\rho_{bead\ in\ water}$ = 1.24 g/ml

I-factor (dry mass Na-form/ dry mass H-form) = 1.25

Terminal vel. in 0.5 M NaOH = 99 cm/min

Angle internal friction = 25°

$\rho_{Polymer\ (Skeletal)}$ = 1.5 g/ml

$\varepsilon_{bead\ (void\ space)}$ = 0.58

$\rho_{bead\ in\ water}$ = 1.21 g/ml

Terminal vel. in water = 80 cm/min

Technical Comparison of RF vs. SL644

RF

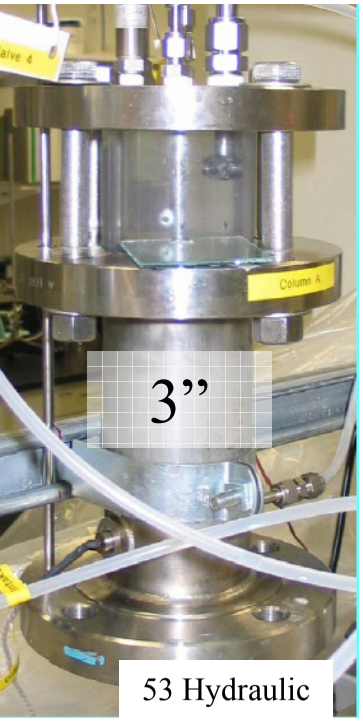
- Much better hydraulics
  - Higher flow rate options
  - Higher temperature options
  - Larger bed size options
  - Less risk of plugging or channeling
- 1/5th as much less spent resin volume, 5x cleaner spent resin (1/25th as much total curies)
- 1/8th as much Pu & Cr diverted to eluate
- Less to-go testing to qualify
- Less cesium bleed
- Less Ba^{137m} shedding with better cesium detection
- >50x better shelf-life
- More durable [oxygen (3x), radiation (5x), osmotic shock (>20x)]
- Less chemical bleed into process

SL644

- 1/10th as much gas generation rate with acid exposure
- Slightly more initial cesium capacity per volume resin
- 1/3rd as much sodium eluted into acid

RF Hydraulic Testing

- Flow permeability is 2.8 times requirements
- No permeability degradation in 16 cycles with oxygen saturate feeds
- Upflow regeneration and waste introduction specified
- No channeling
- 24” Cs removal exceeds bench scale
- Tests from 3” to 24” diameter gave same results
- High flow rate used to simulate full scale pressure drop
- Excellent fluidization



"To Go" Testing & Study Requirements

- Full WTP mission
- Process limits
- Flowsheet changes
- Column design issues
- Hydrogen venting
- Shelf-life of seed material
- Extensive resin reuse

Development of CXP "to-go" Testing & Study Plans

EFRT Issues:

M6, Process Limits

1. Effects of high cation concentrations on Cs removal
2. Effects of high oxygen exposure on resin mechanical strength
3. Effects of solids in feed on column pressure drop & Cs removal
4. Plutonium buildup in resin with oxidative leaching
5. Effects of high temperature on column load performance

M14, Conversion to RF resin

1. Effects of high cation concentrations on Cs removal
2. Modeling of full column operation (Addressed: WTP-RPT-RT-07-0004)
3. Full height column testing (not required per CCN 160266)

Trend TN 2704

1. M6 - Items 1-5
2. M12+ - Items 1-4
3. TMP - Items 5-7 & 9
4. Column Design - Items 1-3
5. M14 - Item 1

Long-Term Supply Agreement:

1. Determine seed shelf-life
2. Manufacture 5-10 years of seed

Column Design: (CD)

1. Bubble removal
2. Resin removal
3. Solids toleration

Issue Resolution: Recommended Studies	TMP	M6	M14	Stg. 2&3	CD	Supply	M12+	TN 2704
1. H_2 removal								
2. IX feed solids mitigation								
3. Resin removal effectiveness								
New Tests								
1. Small column multi-cycle cesium removal								
2. 3 inch column hydraulic test with rad & O_2 exposure								
3. Full height narrow diameter columns with solids in feed								
4. Pilot-scale (44%) testing with WTP column design								
5. Seed aging tests								
6. Batch contacts with modeling								
7. Determine Pu buildup after multi-cycle post oxidative leaching conditions								
Testing Dependant on VE Study								
1. H_2 removal testing								

TRA Issues:

TMP

1. RF documentation
2. H_2 removal - VE study & testing
3. Gas retention in IX column
4. Assess & mitigate solids precipitation in IX feed
5. Column performance with solids in feed
6. Resin removal effectiveness (>99%)
7. Column performance with organics in feed
8. Resin mechanical strength after high radiation exposure
9. Required nitric Acid purity & strength

Leaching Modification Impacts (M12+):

1. Effects of solids on:
   - Column pressure drop
   - Cesium removal
   - CXP eluant to CNP evaporator
2. Effects of high cation concentrations on Cs removal
3. Effect of high temperature feed on column performance
4. Effect of oxidative leaching on Pu buildup with multiple cycles
5. Assess & mitigate solids precipitation in IX feed

R&T/ORP Correspondence:

Stage 2 & 3 RF Testing

1. Effect of antifoam on column load operation

Summary

- Major WTP savings
- Significant performance improvement
- Resin developed and accepted as equivalent
- Qualification scope complete - 2007
- To-go scope, excluding seed aging, complete - 2010

Discussions

Potential Other Uses

- Early WTP LAW
- SRS
- International

Lessons Learned

- Synthesis for target improved resin, not testing
  - Partnering with best technology
- Hydraulic scale-up
- Multi-cycle, multi-column testing vs. batch contacts

Follow-up

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