Spherical Resorcinol-Formaldehyde Resin for the Removal of Cesium from Hanford Tank Waste

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We Put Science To Work

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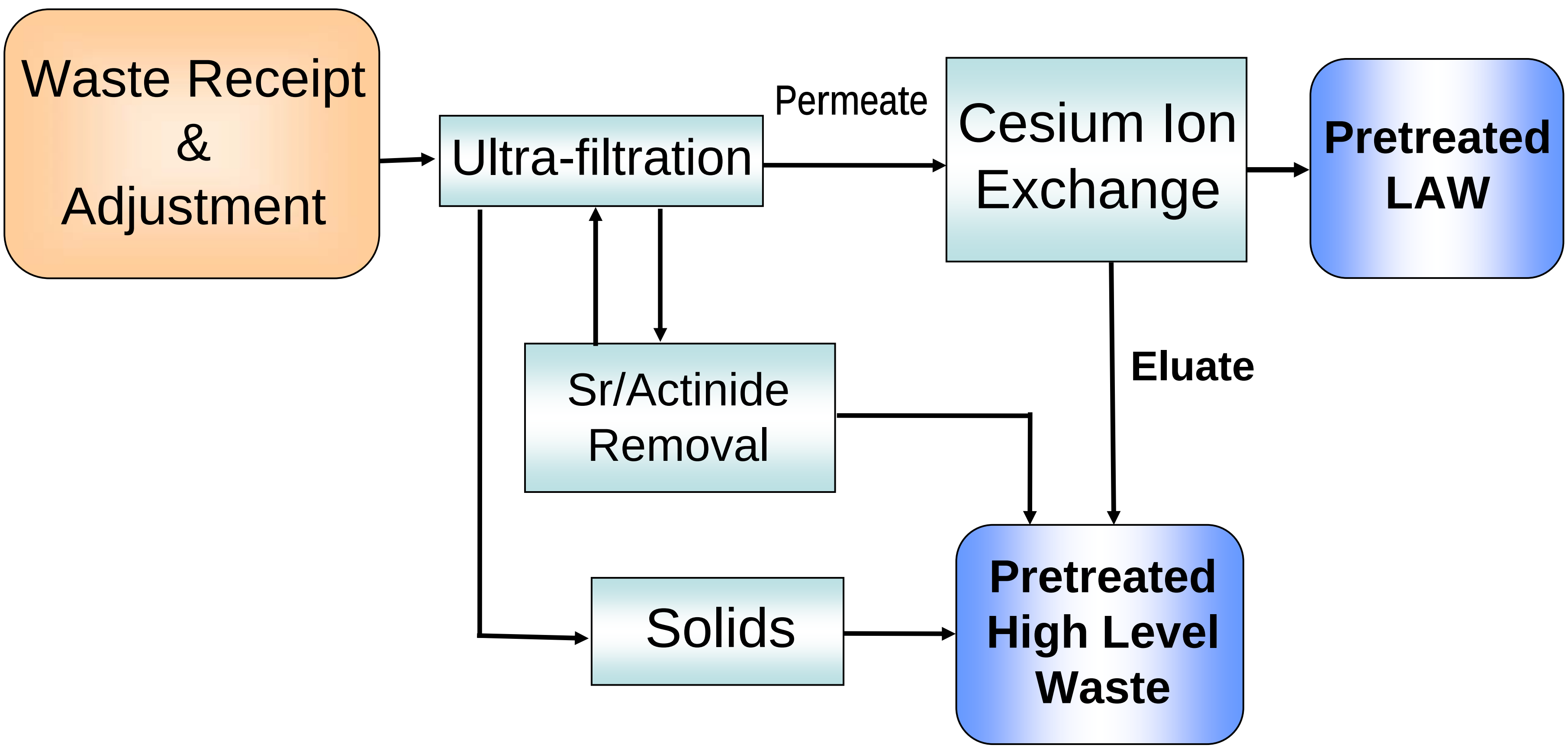
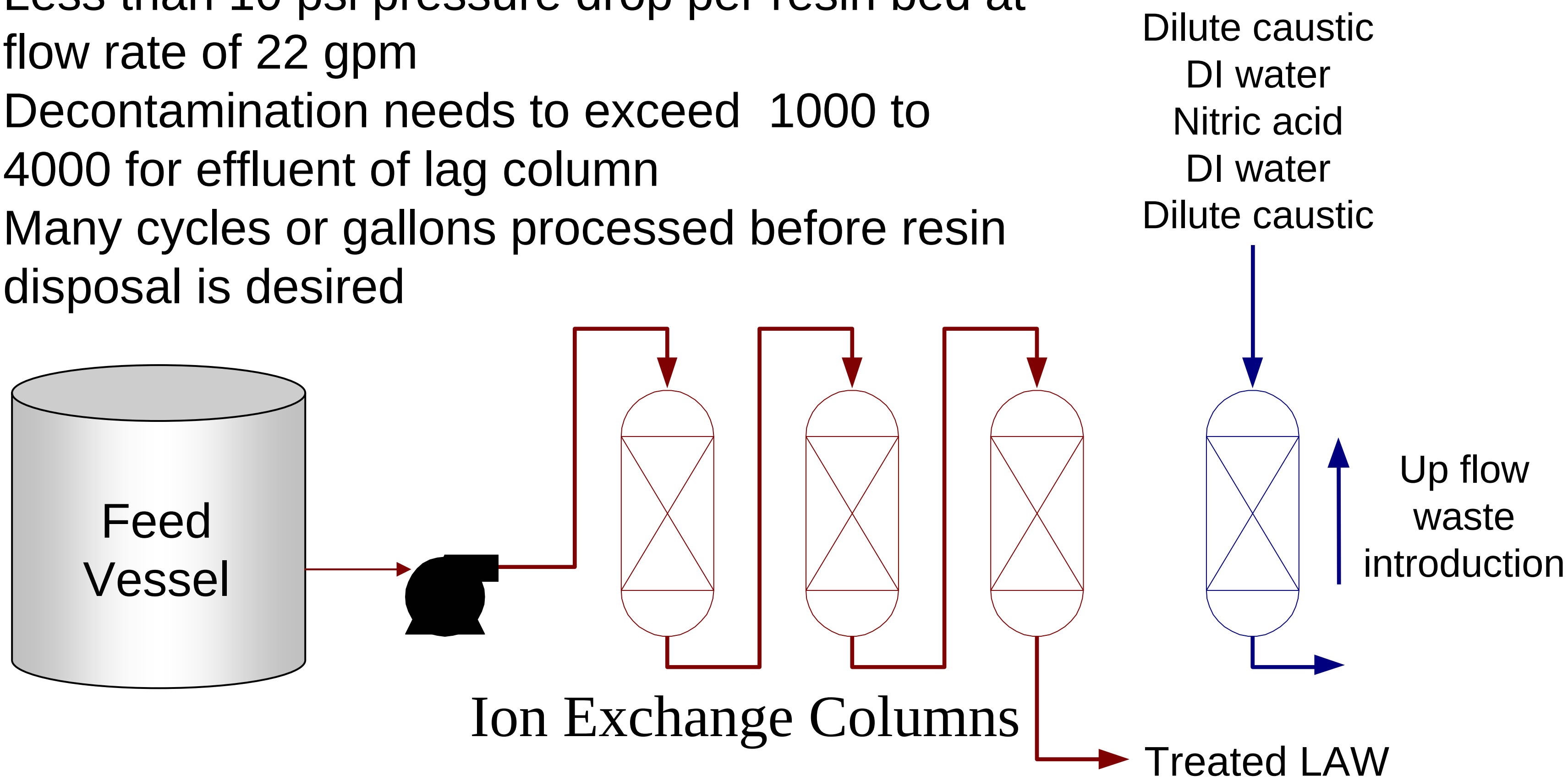
Pretreatment Process

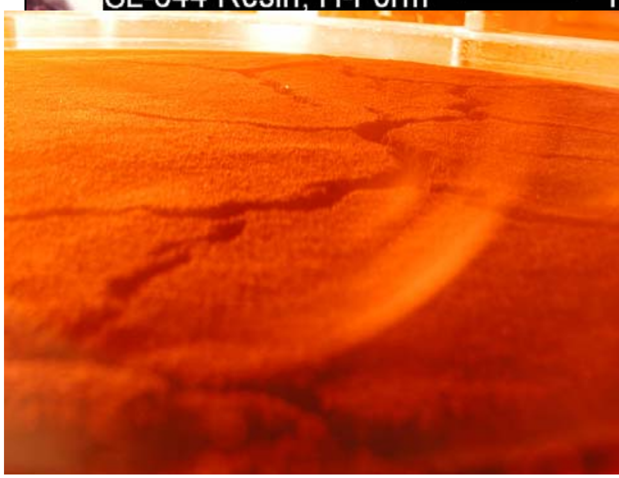


Cesium Ion Exchange System

- 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 cycles or gallons processed before resin disposal is desired



Baseline IX Resin - SuperLig® 644



- WTP contract specified resin
- Meets contract cesium removal and throughput needs
- Qualified for use in WTP
- Processes 900 to 1500 gallon waste per gallon resin (Envelope A, up to 10 cycles)
- Sole source, proprietary product
- Ground gel non-spherical form: Fractures, softens and adheres in multiple cycles limiting number of cycles of use due to pressure drop or channeling

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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)

Testing – Stage 1

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

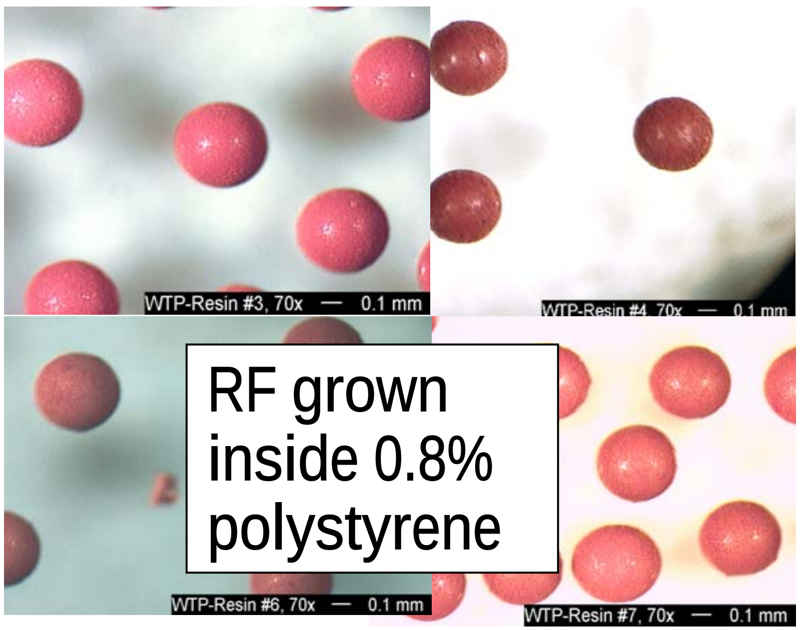
Testing – Stage 2

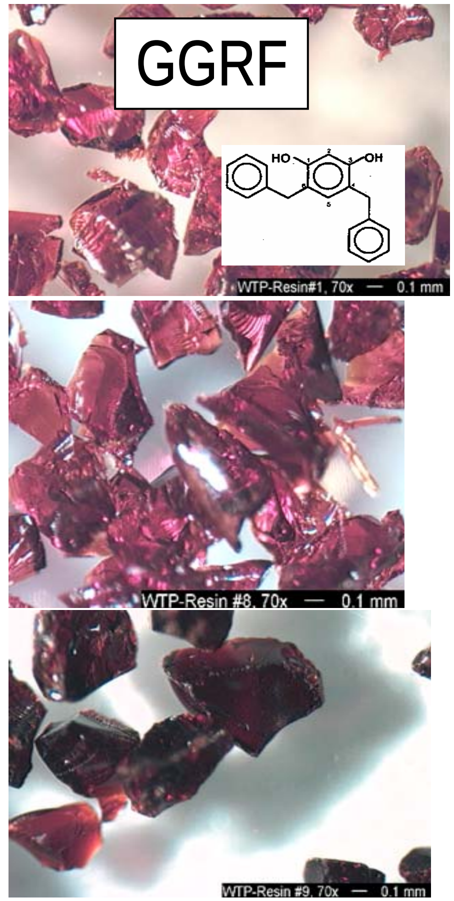
- Scale-up production
- Qualify for commissioning In-Progress (2004 to 2006)

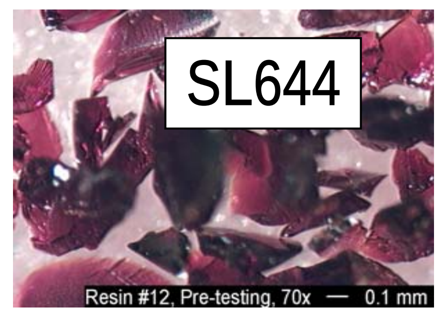
Testing – Stage 3

- Support resin production for commissioning
- Resolve any post-commissioning operating information needs (TBD)

Tested Resins







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SRNL Phase II Objectives

- **Determine physiochemical stability of Spherical RF as a function of chemical thermal and radiolytic exposure**
- **Determine gas generation rates under**
  - **Normal operation to assist purge ventilation design**
  - **Abnormal operation to size column relief devices**
- **Measure extent of nitration of resin during exposures to nitric acid**
- **Perform pilot-scale testing to assess resin viability**
- **Measure resin performance as a function of waste composition, regulatory compliance and develop modeling capability**

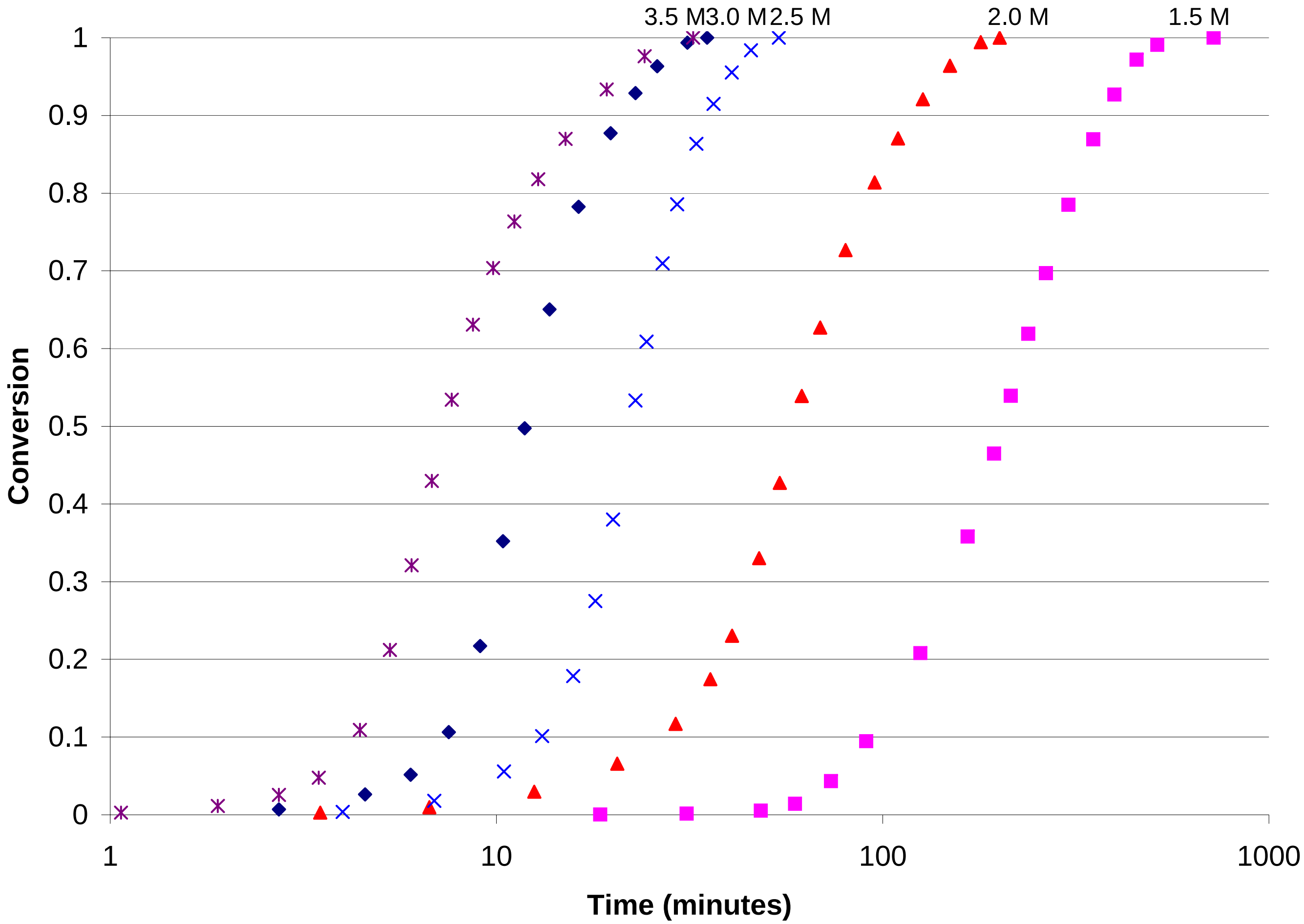
Status of Resin Stability

- **Spherical RF and SuperLig ® 644 exhibit reaction with nitric acid with 2 reactions**
  - **Nitration and Oxidation**
  - **Energy of nitrated resin product is very low**
- **Thermal and radiolytic stability of Spherical RF exceeds baseline resin dramatically**
- **Not without any drawbacks**
  - **Higher gas generation during extreme acid contact**
  - **Same H_2 generation under normal radiation dose rates but less total gas**

Modeling Nitration Reaction

- **Heat and gas generation rate in the column is determined by the rate of reaction between the resin and nitric acid. To determine the intrinsic rate of reaction between nitric and RF resin a series of tests were conducted looking at**
  - **different nitric acid molarity (to determine reaction rate dependence on nitric acid)**
  - **different temperatures at a given molarity (in this case 3M) to determine the activation energy of the reaction.**
- **Testing was conducted using a Differential Scanning Calorimeter and an Accelerated Rate Calorimeter. The DSC data was used to generate the model. The ARC data was used against the model predictions for scale up process**

Effect of Nitric Acid Molarity: Functional Form of the Reaction



- **The resin reaction with Nitric acid at different nitric acid molarity clearly shows a "S" shaped curve indicative of autocatalytic behavior.**
- **In addition the onset of the reaction occurred faster the higher the nitric acid concentration (again indicative of a slow initiating reaction that depends on [HNO_3]**

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Modeling: Results

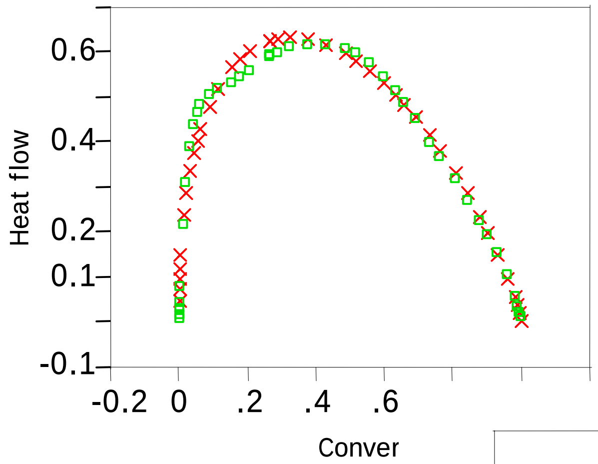
- **Based on the molarity tests, the deduced reaction is as follows:**
  - **Resin + HNO_3 → Resin-NO_2 + Intermediates**
  - **Resin + Intermediates → 2 Intermediates**
  - **Resin-NO_2 + HNO_3 → gas**

- **The rate of the reaction is then given as follows:**
  - **$-\text{Rate} = k_1 (\text{resin})^n (HNO_3)^m + k_2(HNO_3)$**

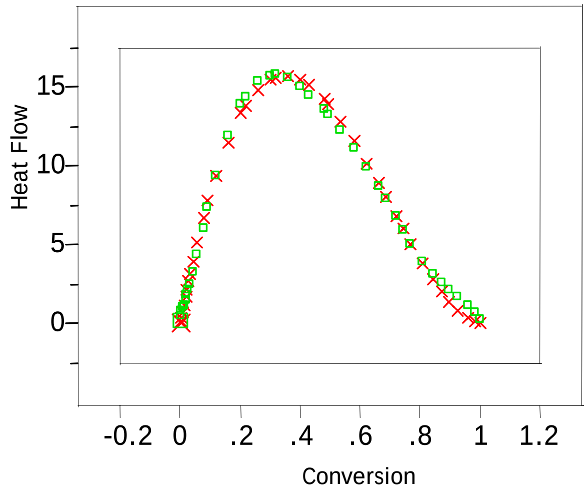
- **Determined the concentration of resin from the partial areas of the DSC curve.**

Dependency of the Nitric Acid and Resin on the Reaction Rate

1.5 Molar HNO_3



3 Molar HNO_3



- **Output from the DSC data fitted to the autocatalytic model to determine the exponent of the resin and nitric acid dependency.**
- **Best values for the nitric acid and resin exponent is 1.5 and 1 respectively as can be seen in the table.**

Molarity	Resin (n)	Nitric Acid (m)
1.5	0.4	1.3
2	0.91	1.2
2.5	1.22	1.6
3	1.4	1.4
3.5	1	1.46

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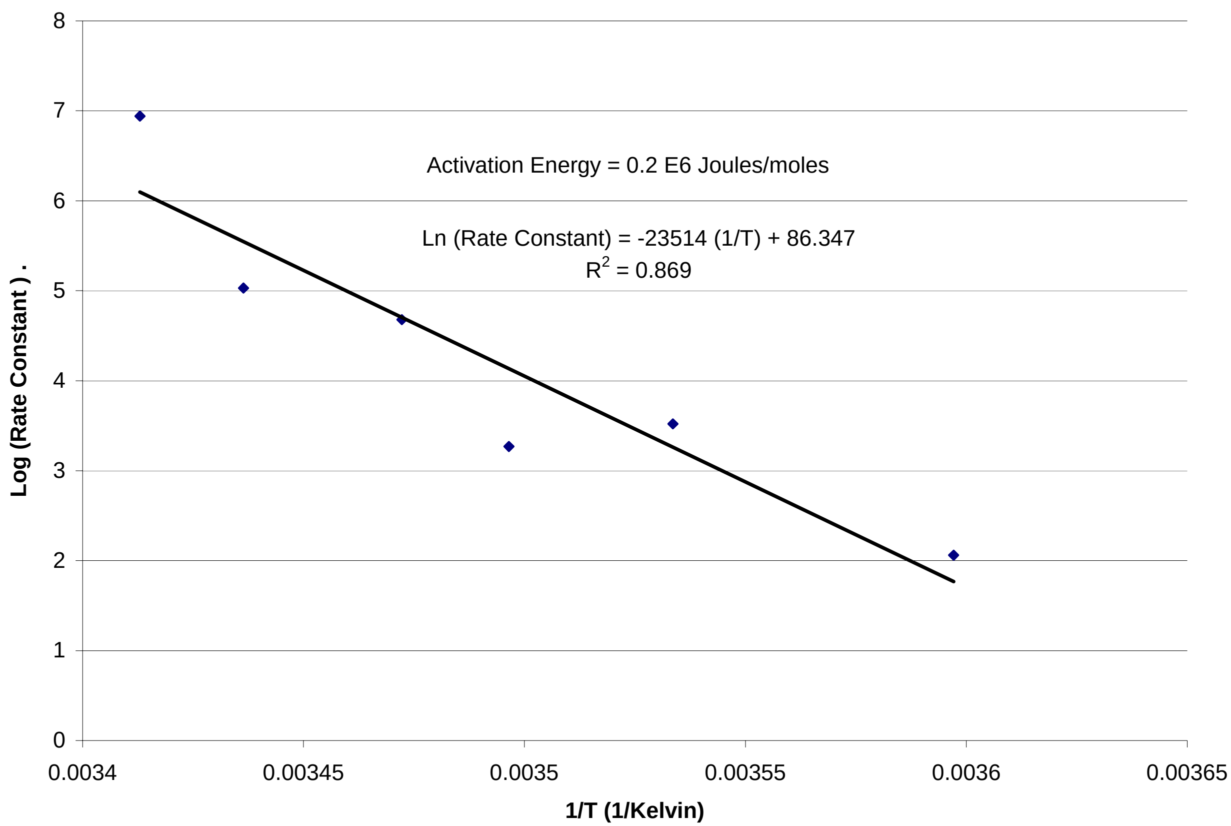
Model: Rate Constant Determination



- Determine the overall rate constant for the nitration reaction from the experiments where the reaction was conducted at different temperatures.

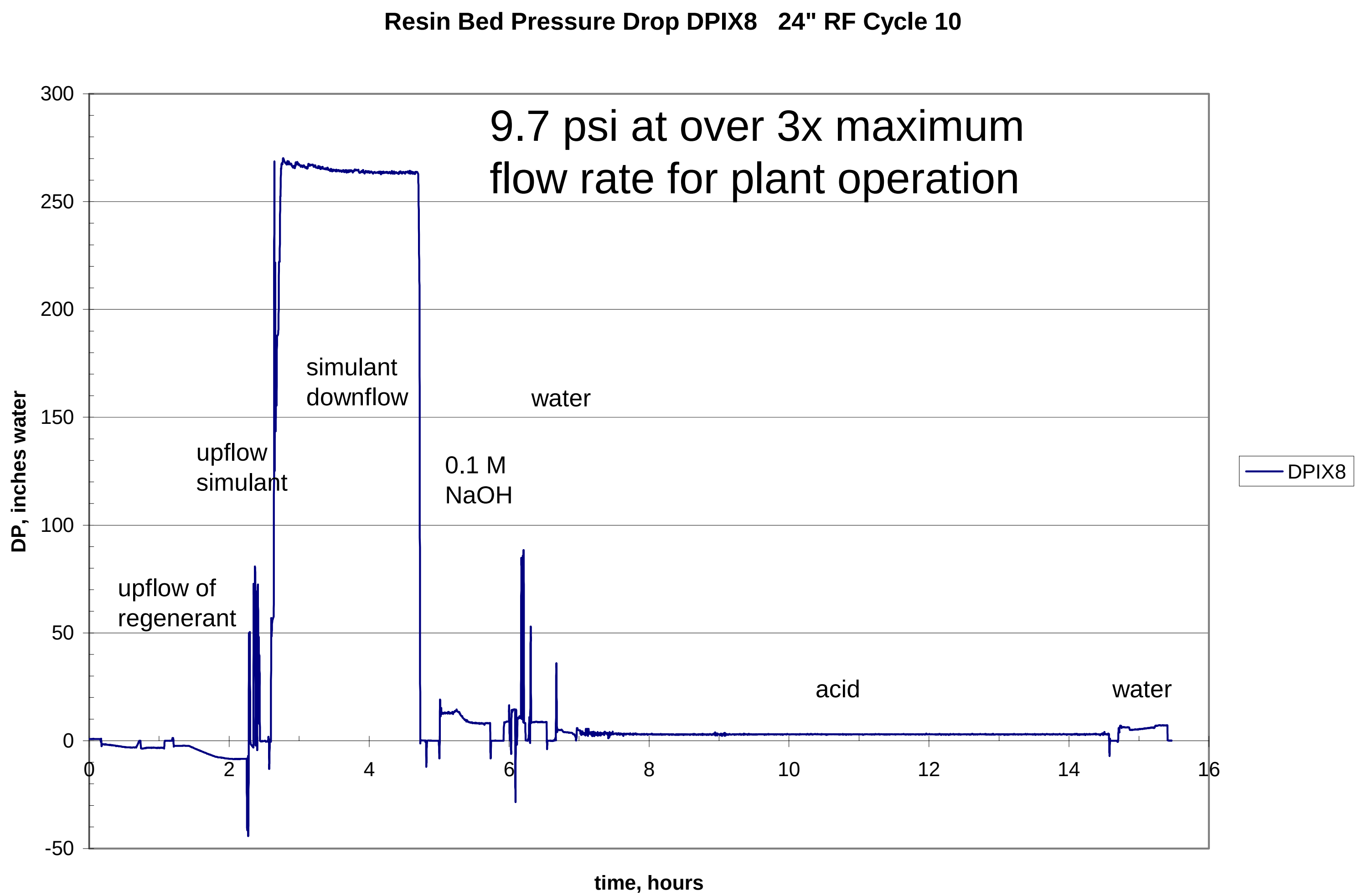
- **Rate (mol/m3sec) = 2.25 E 16 Exp (-198,133/RT) (HNO3){1+(HNO3)0.5}**

24” IX Column Hydraulic Summary

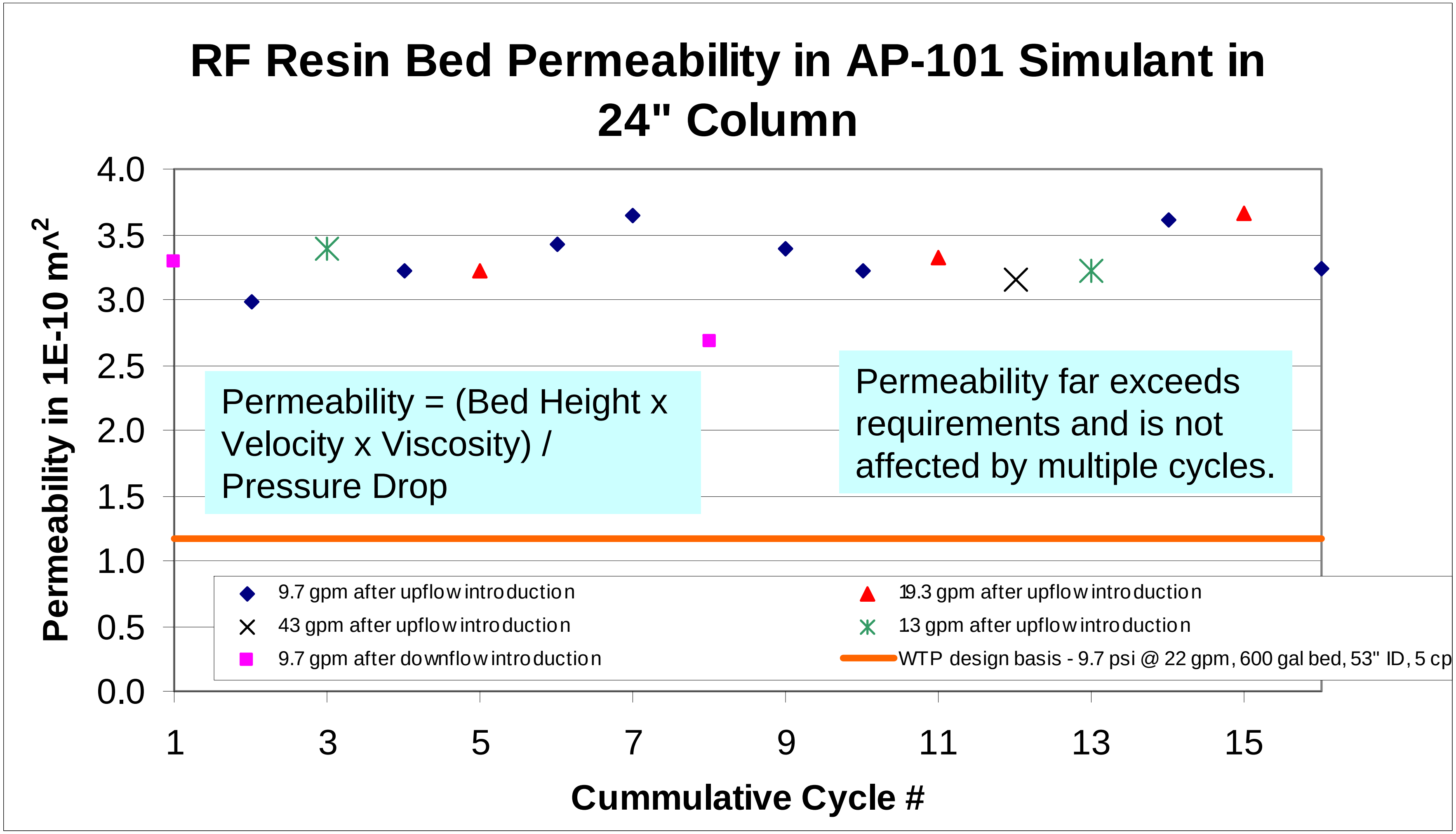
Cycle	Simulant Velocity cm/min	Simulant DP, Inches H2O	resin ht. in simulant cm	Simulant Viscosity cp	Simulant density g/mL	Permeability 10^6 * cm^2	Simulant flow, gpm
* **Cycle 01**	13.39	61.8	73.0 (unlevel)	3.10	1.26	3.29	9.69
Cycle 02	13.41	64.4	71.2	3.00	1.26	2.98	9.7
Cycle 1	1.81	7.9	72.5	3.05	1.26	3.39	1.31
Cycle 2	13.41	61.0	73.0	3.00	1.26	3.22	9.70
Cycle 3	26.95	123.0	72.3	3.04	1.26	3.23	19.50
Cycle 4	13.42	58.0	73.5	3.01	1.25	3.43	9.71
Cycle 5	13.39	55.0	73.2	3.05	1.26	3.64	9.69
* **Cycle 6**	13.39	74.0	73.5 (unlevel)	3.00	1.25	2.67	9.69
Cycle 7	13.41	58.0	73.7	2.98	1.25	3.40	9.70
Cycle 8	13.42	58.0	73.9	2.81	1.25	3.22	9.71
Cycle 9	26.95	118.0	73.4	2.96	1.25	3.32	19.50
Cycle 10	59.05	263.5	73.5	2.86	1.24	3.16	42.73
Cycle 11	1.80	7.9	73.9	2.85	1.24	3.22	1.30
Cycle 12	13.42	52.5	74.1	2.85	1.24	3.62	9.71
Cycle 13	26.95	104.2	74.3	2.85	1.24	3.67	19.50
Cycle 14	13.41	58.5	74.4	2.84	1.25	3.24	9.70

* Simulant Introduction Downflow

Cycle 10, dP Across RF Bed



Pilot Column Performed



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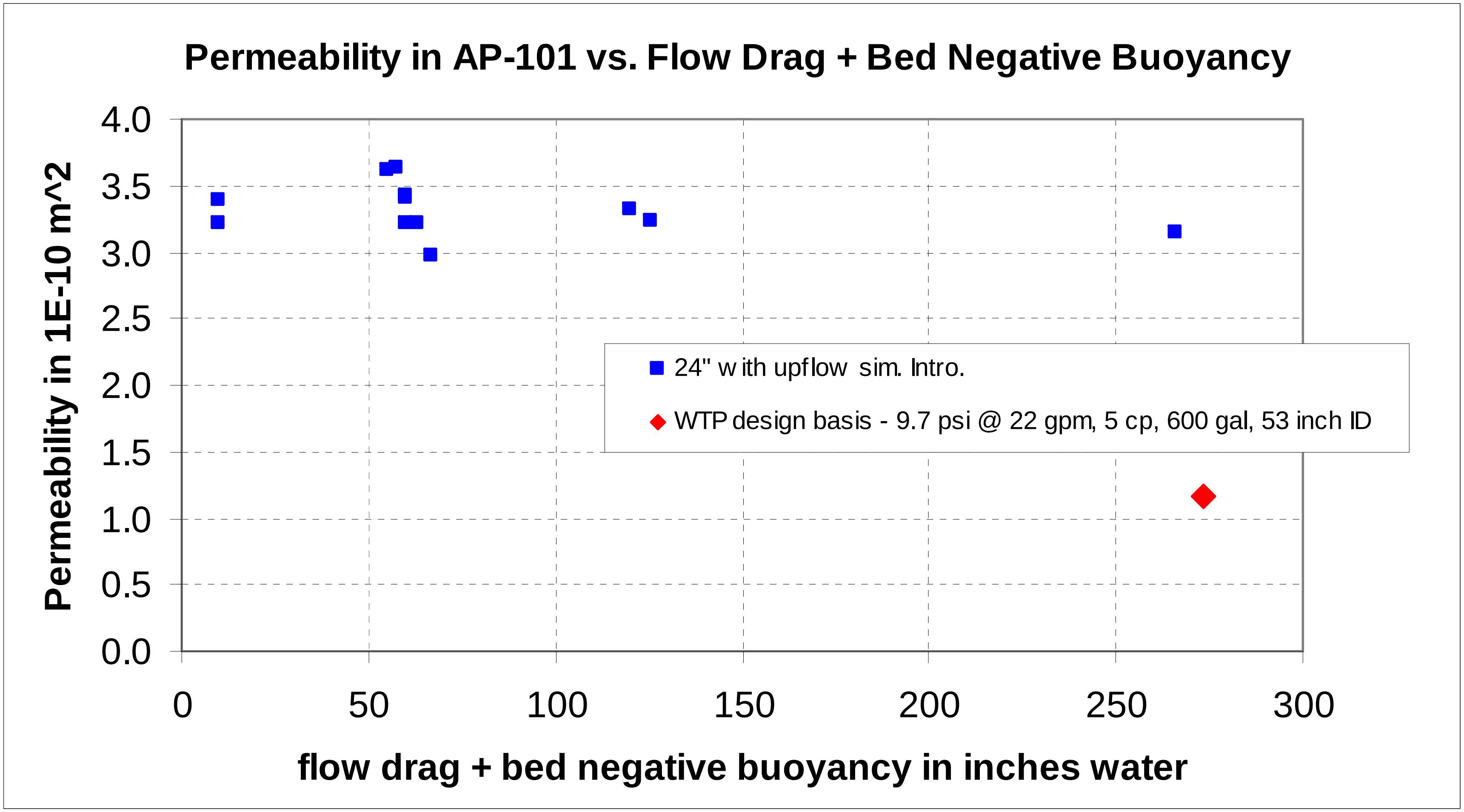
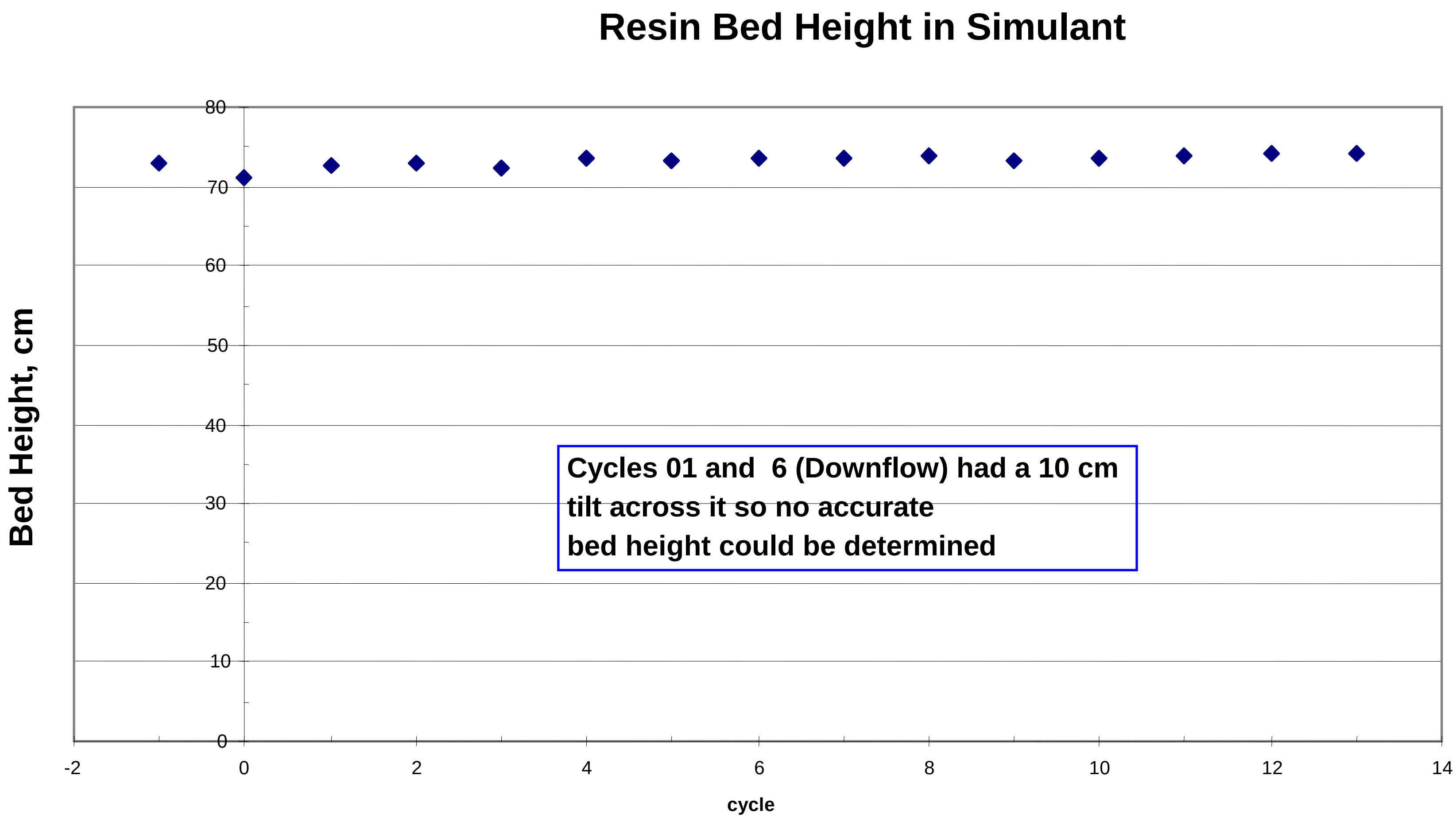
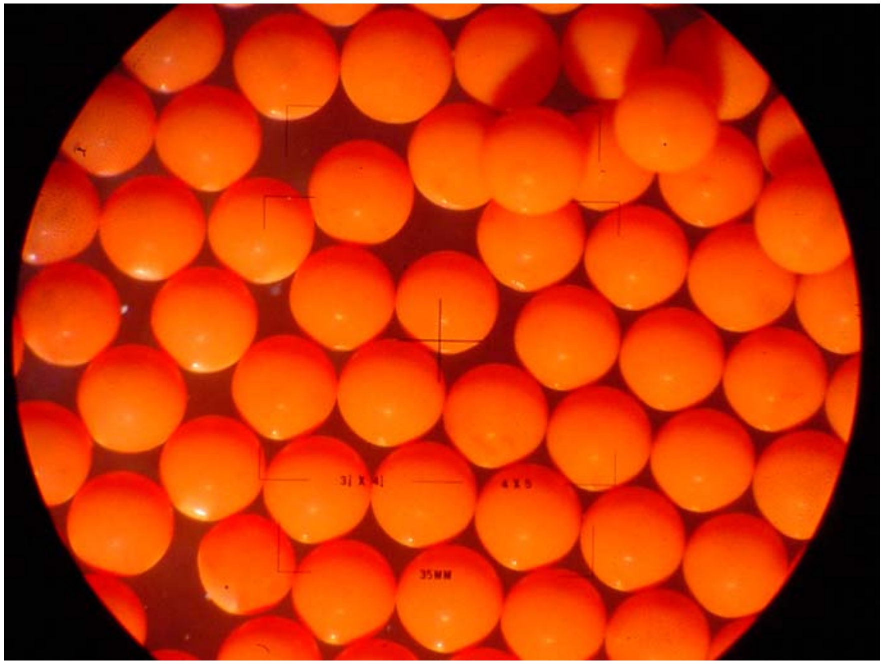
Permeability vs. Frictional Forces



Change in Bed Height with Cycles



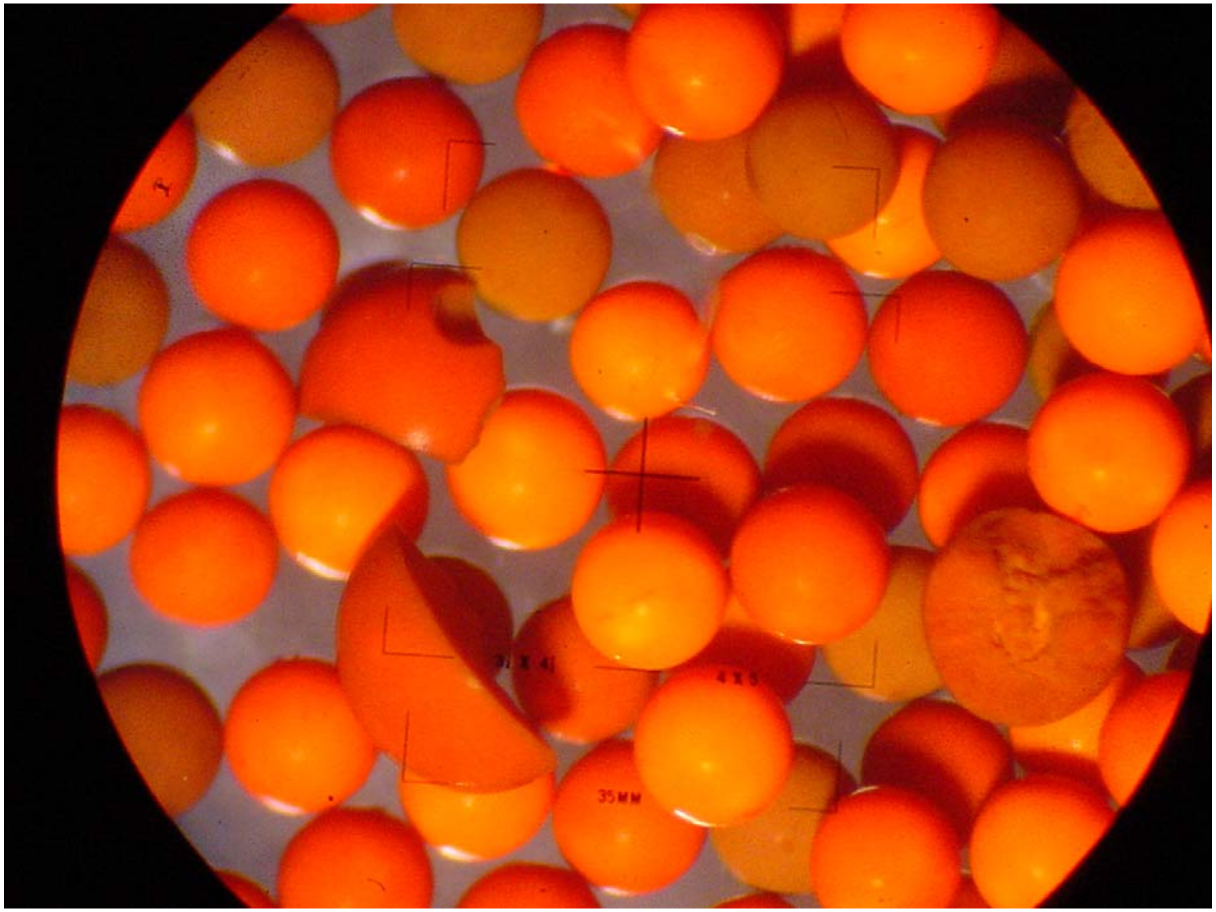
RF Resin Micrographs Before and After Cycling



New Virgin RF-641, H form

RF-641 after 16 Cycles, H form

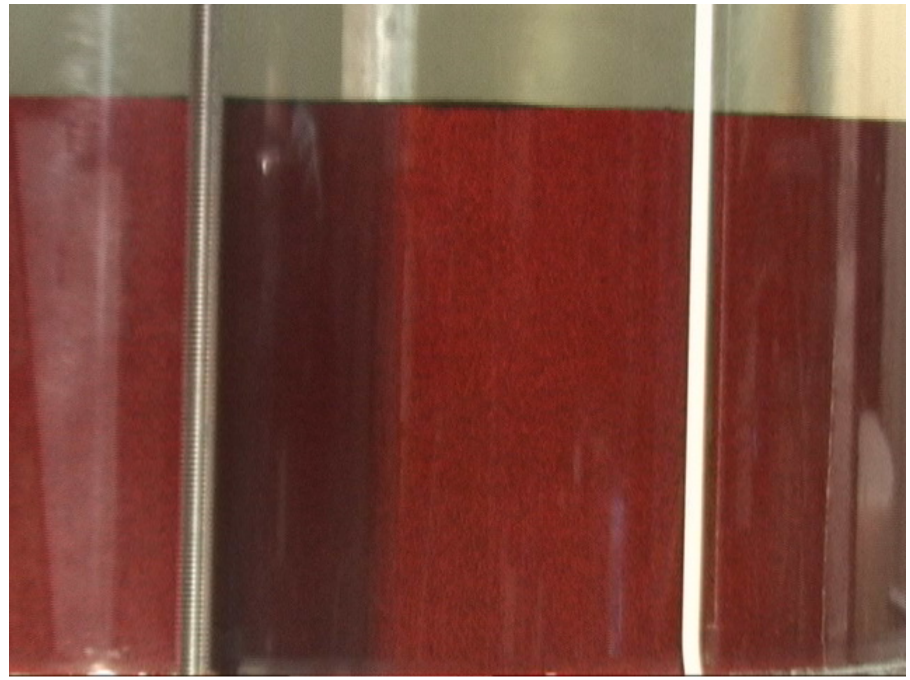
Micrograph of Fines



RF-641 brownish colored fines after 16 cycles

Color Change over Test Campaign

Cycle 01 Upflow Regeneration



Cycle 14 Upflow Regeneration

Note the dark colored particles throughout the resin bed after 16 total cycles

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Resin in Spent/Recycle Streams 24” IX Column

Only the Collection Tank 1 Rinse Water Sock had resin fines of interest

Pilot-scale RF Testing Overview

- **A total of 16 cycles were completed in the 24” IX System**
- **The RF resin performed very well throughout the campaign**
- **No pressure drop increase across the bed with cycles**
  - **9.7 gpm simulant flow, approximately dP 60" w.c.**
  - **19.5 gpm simulant flow, approximately dP 120" w.c.**
  - **43 gpm simulant flow, dP 264" w.c.**
- **Radial dP indicates no channeling occurring in RF bed**
- **Bed permeability essential remained constant**
  - **3.3×10^{-6} cm^2 average and well above design limits**
- **No fissures or channeling observed**
- **RF resin "bleeds" none to very little**
- **Before and after testing PSD of RF indicate excellent results**
- **Micrographs indicate some resin particle breakage/damage**

Pilot-scale RF Testing Overview Cont.

- **Upflow Regeneration performed best**
  - **9.0 gpm for 30 minutes then reduce flow to**
  - **1.42 gpm for 20 minutes**
- **Upflow Simulant Introduction performed best**
  - **1.81 gpm for 52 minutes and increase flow to**
  - **2.89 gpm to finish CV**
- **Downflow Introduction of simulant created undesirable bed**
  - **Cycle 01 and Cycle 6**
- **Bed floated higher than expect during Upflow Simulant Introduction on Cycle 12 and Cycle 14**
- **Cs removal of RF resin excellent after 13 cycles, 24" IX**
  - **Cs in the effluent never exceeded the detection limit, 1µg/L**

Summary

- **Spherical RF continues to out perform baseline technology (SuperLig® 644)**
  - **Increased radiation stability from Cs Capacity perspective**
  - **Hydraulic performance is outstanding**
  - **Flammable gas generation same as baseline technology**
- **Actual waste testing at PNNL going well**
- **Isotherm modeling continuing at SRNL**
- **Regulatory analysis of spent resin planned for early summer 2006**