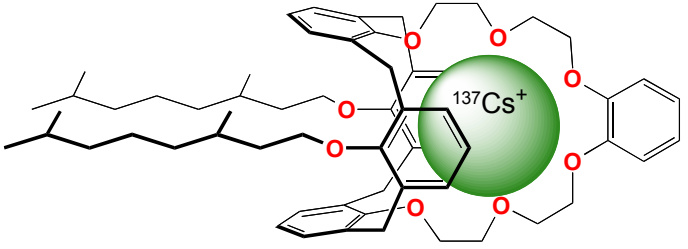
Next Generation Cesium Solvent



***Bruce A. Moyer*, Joseph F. Birdwell, Lætitia H. Delmau, Denise L. Schuh, Erica L. Stoner, Neil J. Williams**

Oak Ridge National Laboratory

***Samuel D. Fink*, Thomas B. Peters, Robert A. Pierce**

SRNL Savannah River National Laboratory

***Ralph A. Leonard*,**

Argonne National Laboratory

Mark W. Geeting

SRR Savannah River Remediation

EM Technical Exchange Meeting

Atlanta, GA, Nov. 16–18, 2010

A Next-Generation CSSX process can accelerate tank-waste cleanup

Improved Cs removal for SRS and possibly even Hanford

It is possible for SRS MCU performance to be increased to DF ≥ 40,000 and CF = 15 for SRS waste treatment, probably at increased throughput. SWPF throughput can likely be increased. A modular CSSX process for the more challenging Hanford waste is now feasible.

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EM-31 goal is to provide technology to enable these possibilities.

Outline:

- **SRS Salt Waste Disposition**
- **Background on CSSX process**
- **Results on next-generation CSSX**

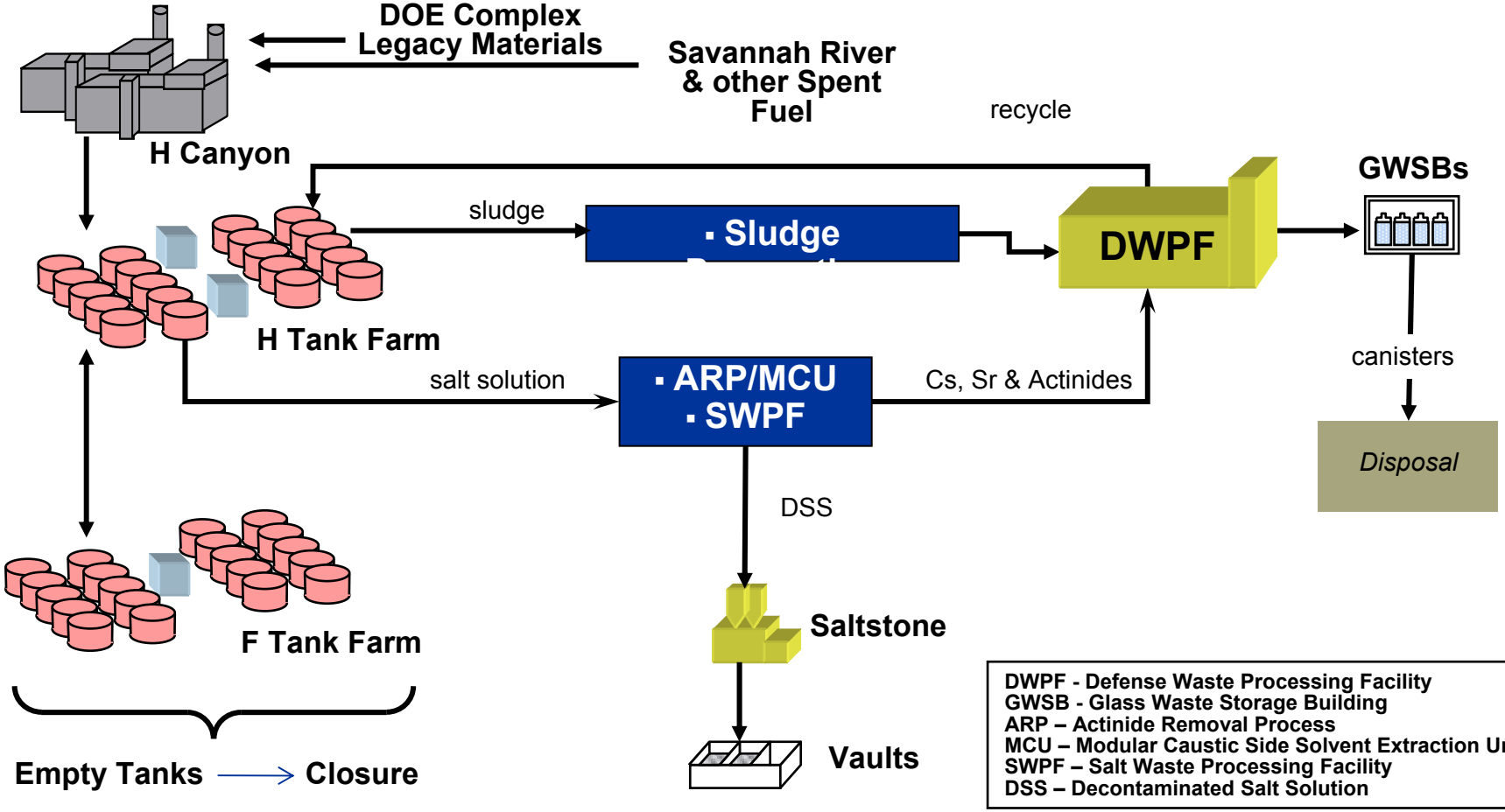
A New Day Dawns!

Cesium Processing Begins at SRS April 2008

Three-year operating life to process low-Curie feed

Current focus on SRS Liquid Waste System

Project was accelerated for early MCU deployment of NG-CSSX



DWPF - Defense Waste Processing Facility
GWSB - Glass Waste Storage Building
ARP – Actinide Removal Process
MCU – Modular Caustic Side Solvent Extraction Unit
SWPF – Salt Waste Processing Facility
DSS – Decontaminated Salt Solution

Figure courtesy of T. J. Spears, Asst. Mgr. SRS Waste Disposition

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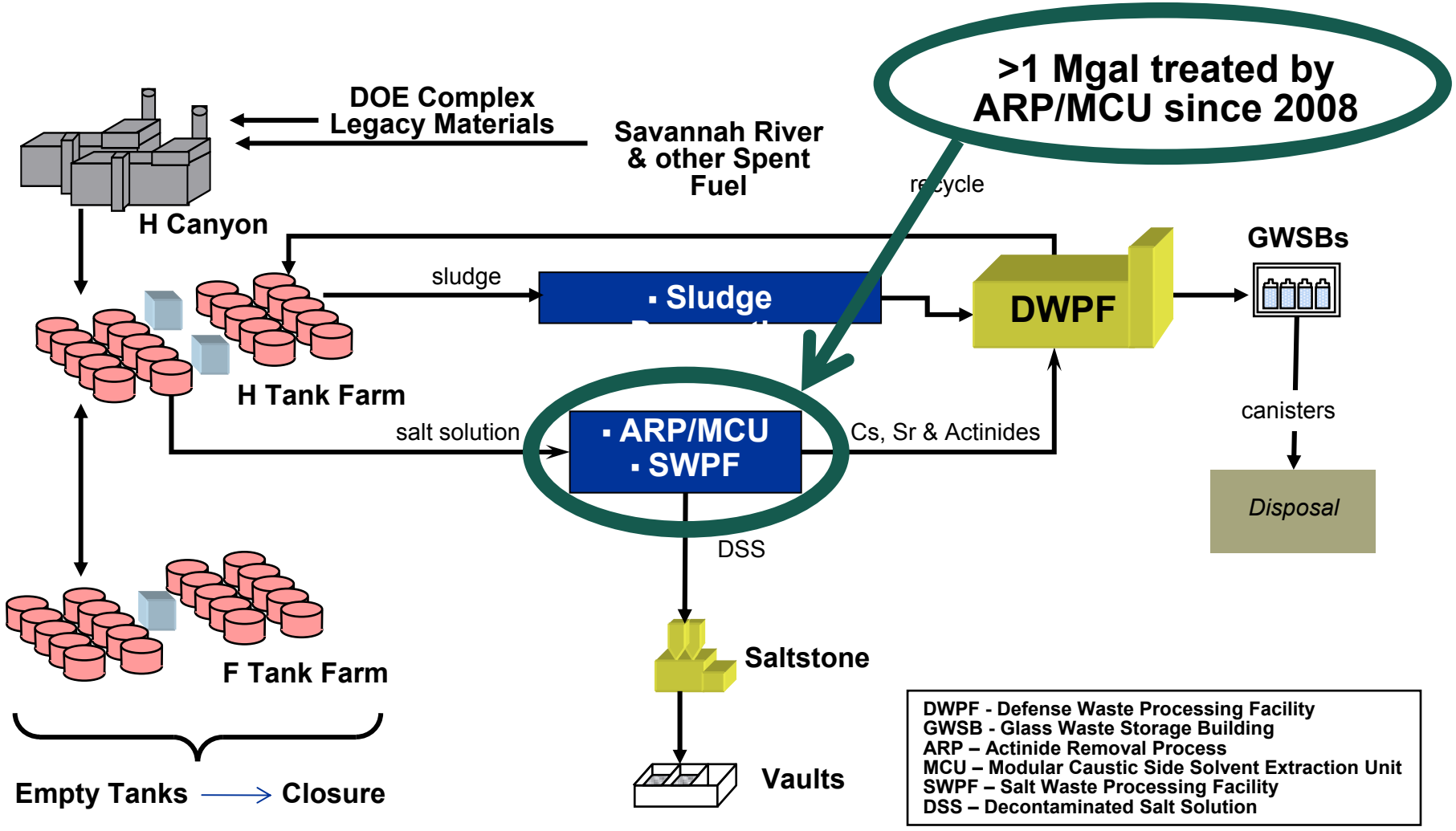

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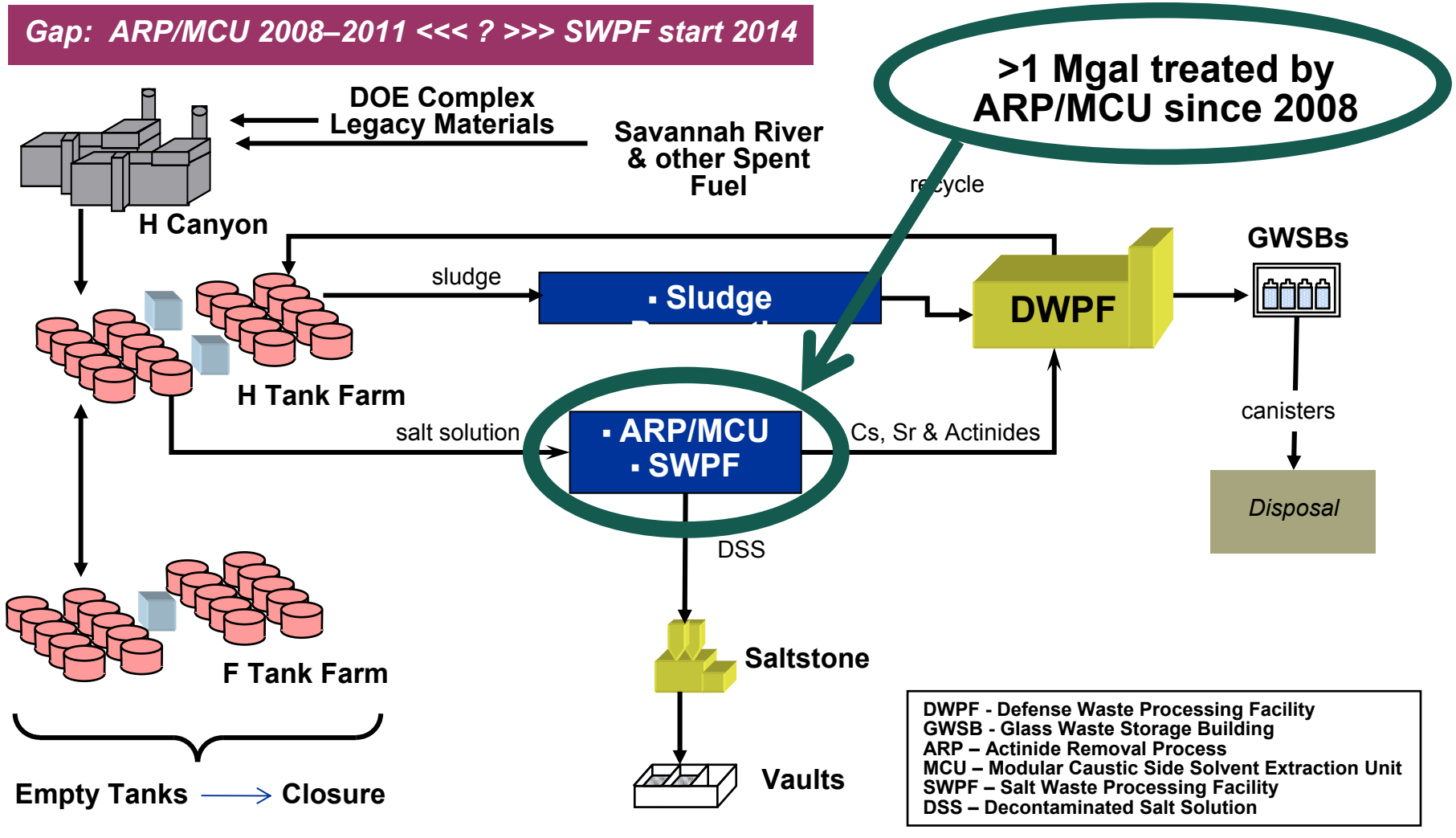


Figure courtesy of T. J. Spears, Asst. Mgr. SRS Waste Disposition

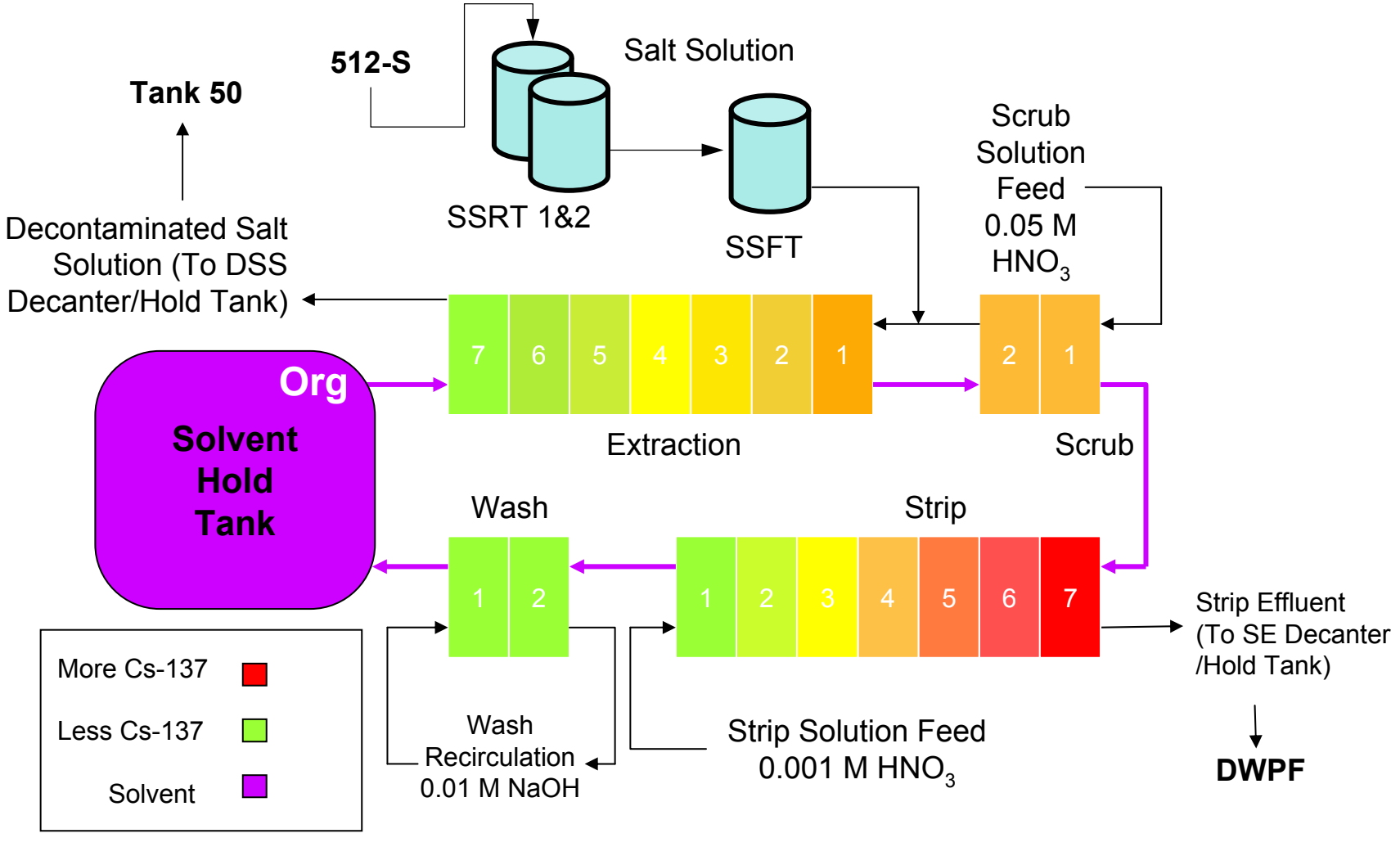
Modular Caustic-Side Solvent Extraction Unit Contactor Building

MCU Centrifugal Contactor Skid

- Centrifugal contactors have been extremely reliable
- Five inch and ten inch contactors used, based on flow
- Seven extraction, two scrub, and seven strip contactors
- MCU has provided critical operating and design data to SWPF

MCU Process Schematic

Design DF ≥ 12 (actual DF ~200)



T. B. Peters, et al., Waste Management 2009;
S. J. Brown, Waste Management 2010.

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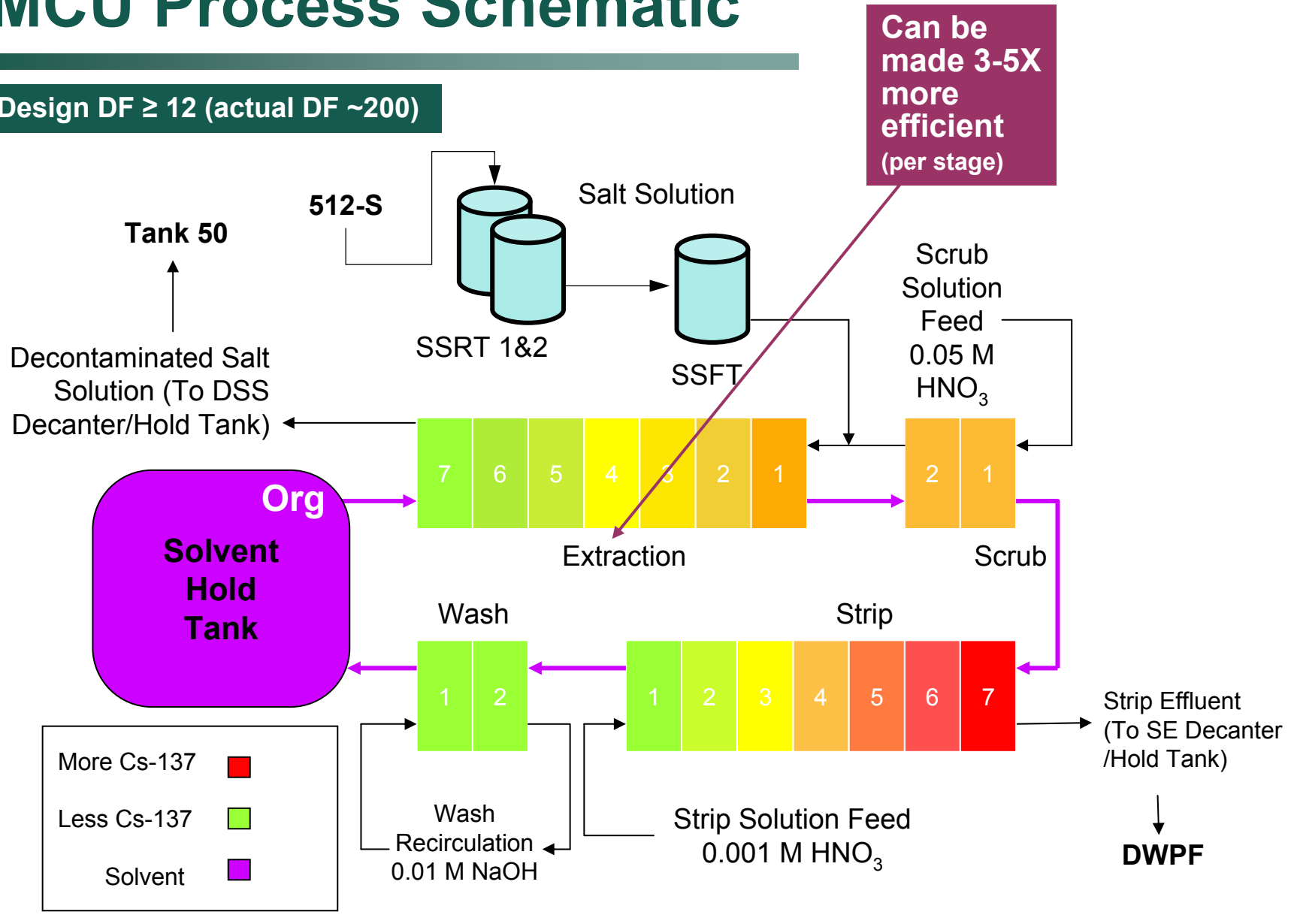

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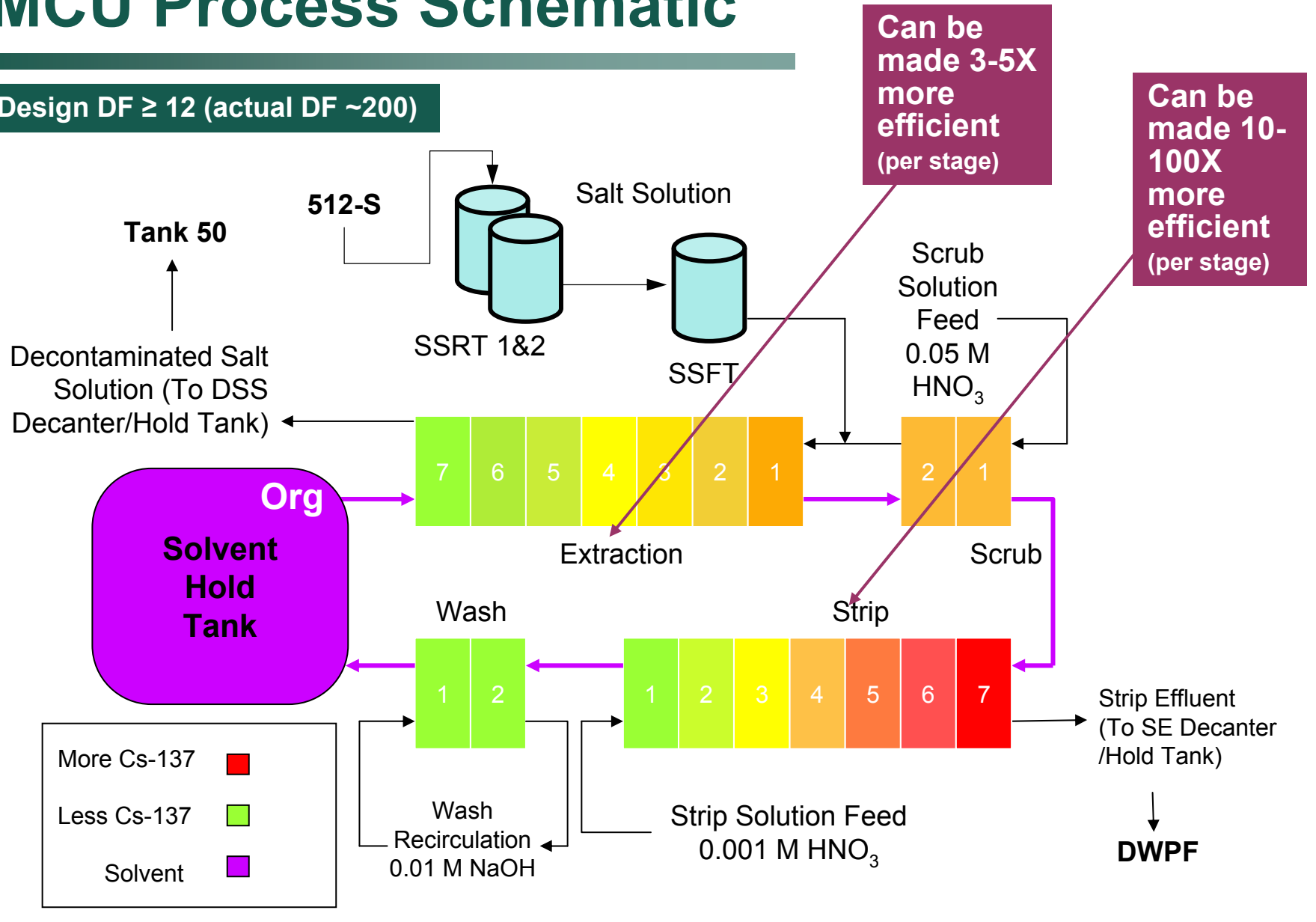
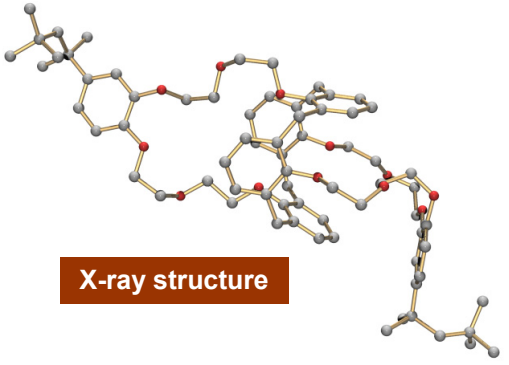


T. B. Peters, et al., Waste Management 2009;
S. J. Brown, Waste Management 2010.

Ten years ago, ORNL invented and developed the chemistry of CSSX

Cesium Extractant @ 0.007 M

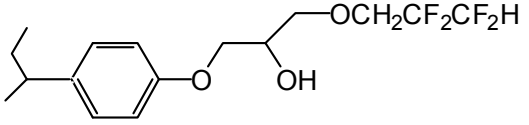
- Synthetically attractive
- Rejects sodium
- Stable to alkaline simulant



BOBCalixC6

Diluent Modifier @ 0.75 M

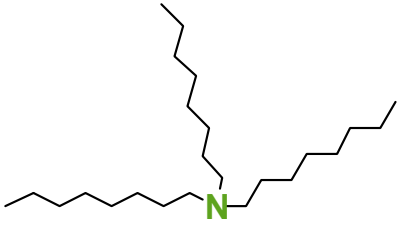
- Increases Cs extraction
- Increases extractant solubility
- Excellent stability characteristics



Cs-7SB

Suppressor @ 0.003 M

- Suppresses impurity effects
- Suppresses ion-pair dissociation
- Improves and stabilizes stripping



TOA

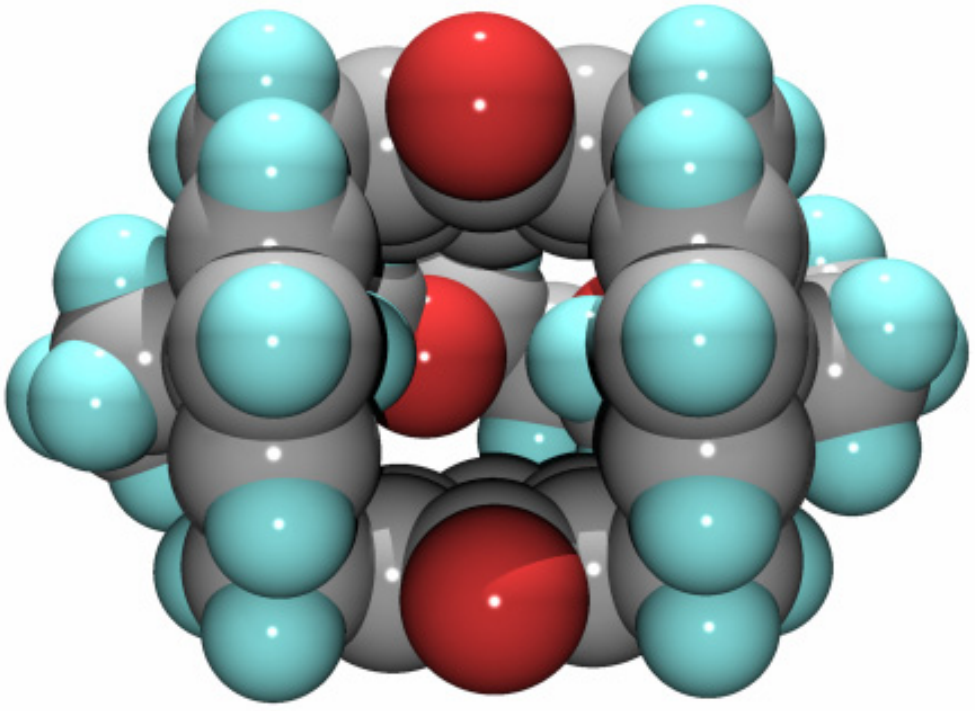
Diluent

- Isopar® L
- Branched avg. 12-carbon aliphatic
- Good stability and promotes good hydraulics

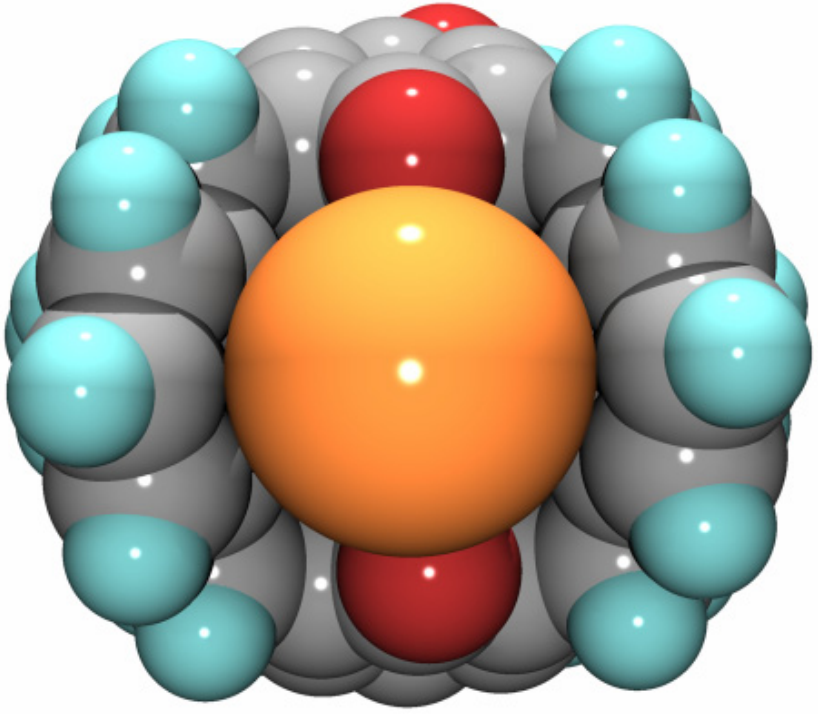
2 ORNL patents, many reports and papers
Review: Moyer, Birdwell, Bonnesen, Delmau, in *Macrocyclic Chemistry—Current Trends and Future*; Gloe, K., Ed.; Springer: Dordrecht, 2005.

The CSSX process is based on the extraordinary fit of the Cs^+ ion inside the calix-crown cavity

Note: atoms blocking view of the cavity have been removed.



Empty cavity



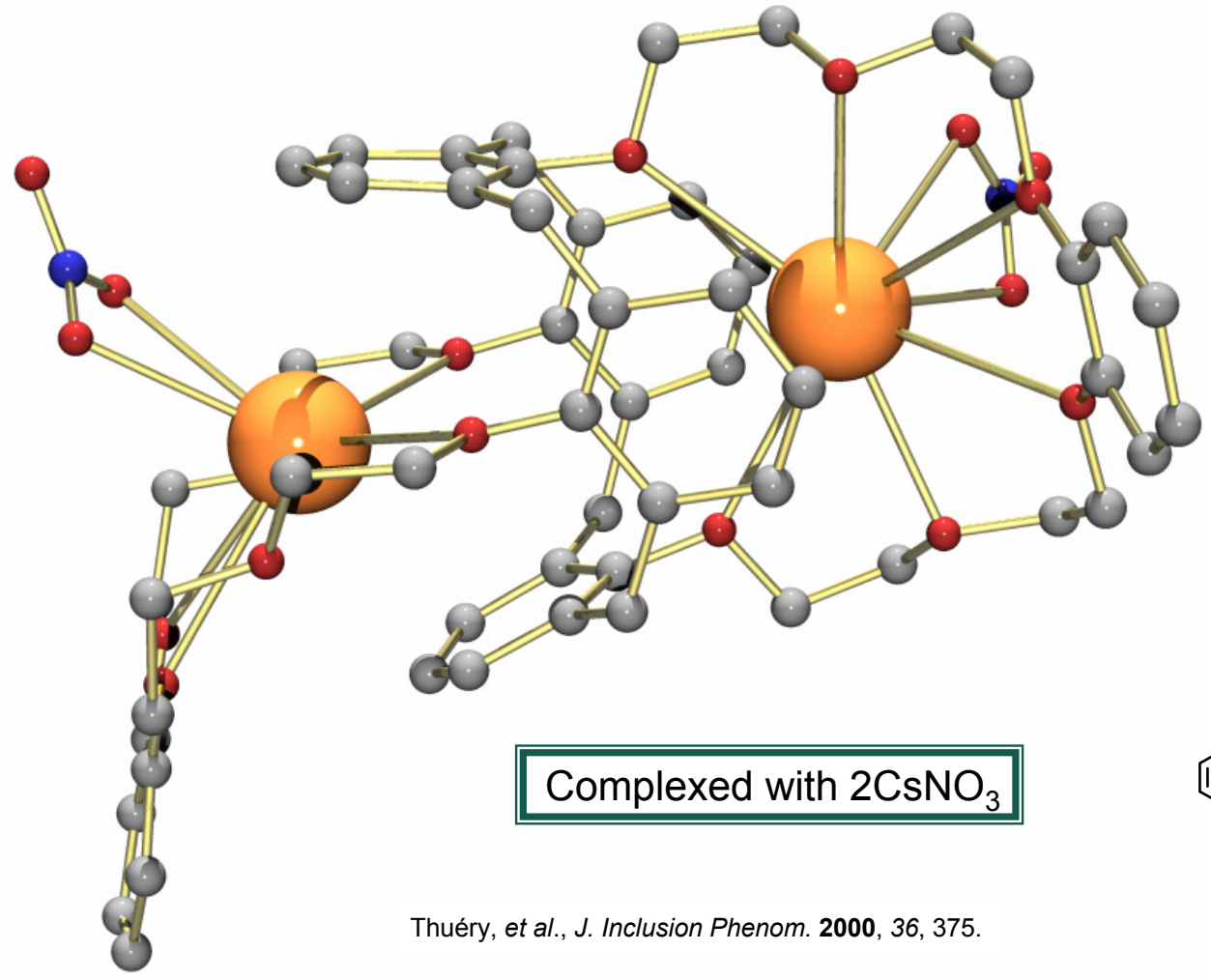
Cavity containing Cs^+ ion

Bryan, Chen, Levitskaia, Haverlock, Barnes, & Moyer, *J. Incl. Phenom.* **2002**, *42*, 241.

Thuéry, *et al.*, *J. Inclusion Phenom.* **2000**, *36*, 375.

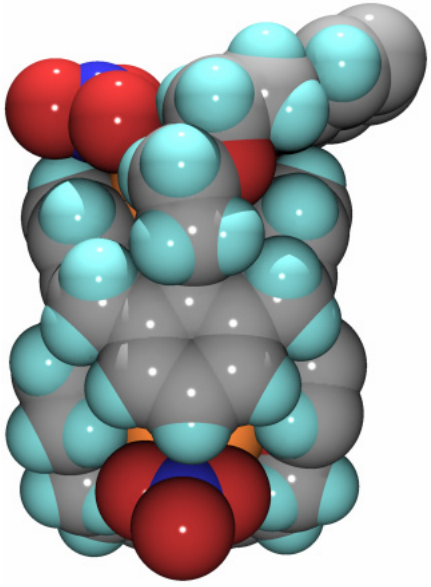
Moyer, Birdwell, Bonnesen, Delmau, in *Macrocyclic Chemistry—Current Trends and Future*; Gloe, K., Ed.; Springer: Dordrecht, 2005.

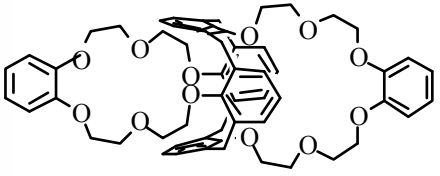
Crystal structures reveal coordination of the Cs^+ cation by ether O atoms and the aromatic pi clouds



Complexed with $2CsNO_3$

Thuéry, *et al.*, *J. Inclusion Phenom.* **2000**, *36*, 375.

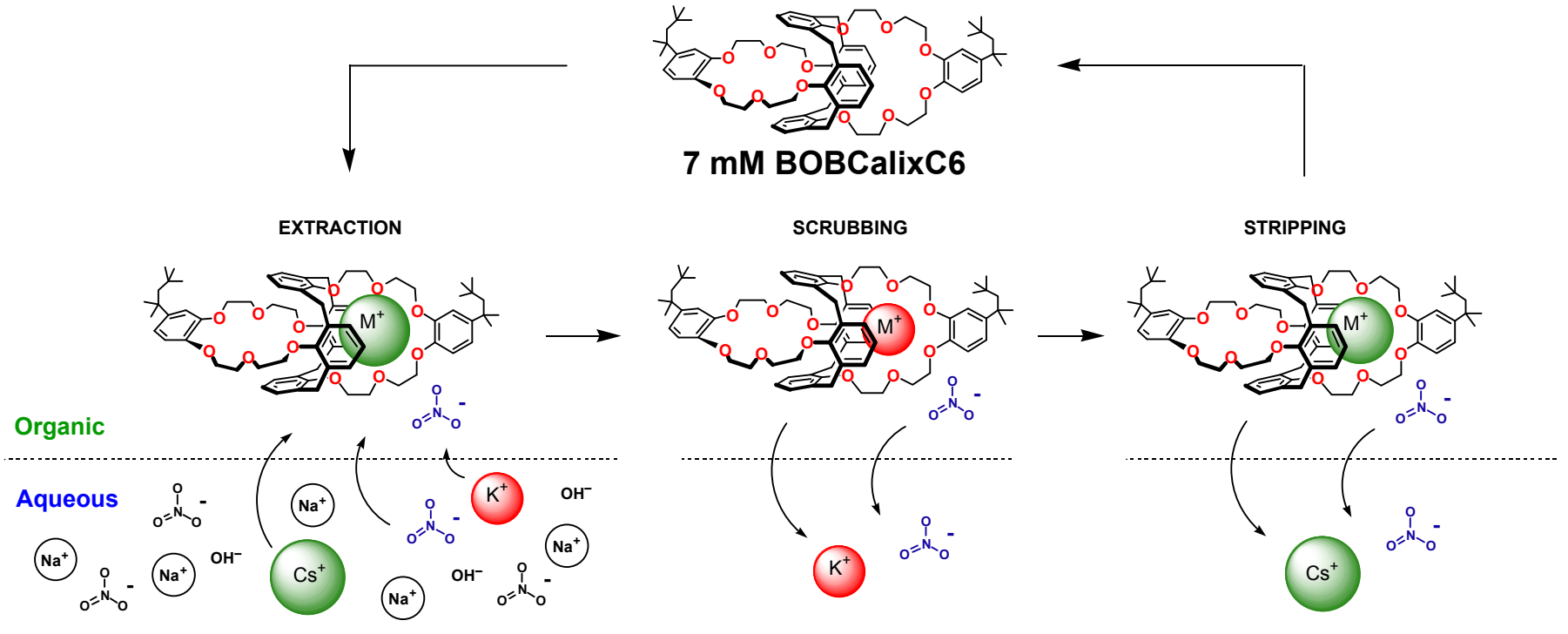




Uncomplexed

CSSX cycle efficient by nitrate swing

$$Cs^{+}_{(aq)} + NO_3^{-}{}_{(aq)} + Calix_{(org)} \rightleftharpoons CsCalixNO_{3\,(org)}$$



Alkaline nitrate tank waste | **50 mM HNO_3** | **1 mM HNO_3**

Moyer, Birdwell, Bonnesen, Delmau, in *Macrocyclic Chemistry—Current Trends and Future*; Gloe, K., Ed.; Springer: Dordrecht, 2005.

CSSX can be dramatically improved

CSSX works well, but removing its limitations will transform the technology:

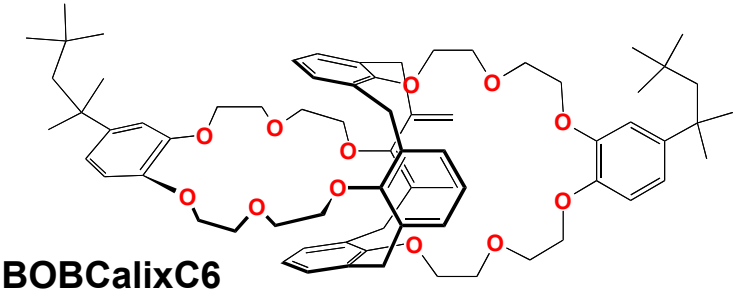
- **Use a more soluble calixarene at higher conc.**
  - BOBCalixC6 at 7 mM limits D_{Cs} and DF
  - Can increase D_{Cs} and DF and/or reduce stages
  - Can increase throughput (O/A decrease)
- **Must also improve stripping system**
  - Current nitrate swing can't be significantly improved
- **Reduce modifier concentration**
  - Solvent dense and viscous at [Cs-7SB] = 0.75 M
  - Lower [Cs-7SB] will improve contactor hydraulics, coalescer efficiency, and extraction selectivity

Starting 3/2010, EM-31 began pursuing NG-CSSX in parallel with deployment activities by SRR targeted for 1/2012.

The preferred calixarene is MaxCalix

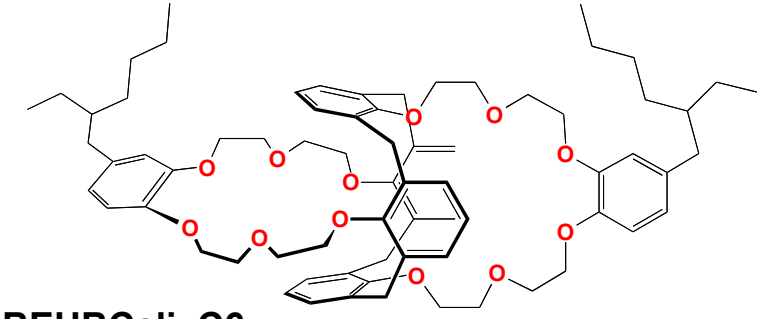
Flowsheet calculations indicated that a calixarene concentration of 50 mM should be sufficient for MCU to reach DF ≥ 40,000 worst case.

BOBCalixC6 (Current CSSX)
- Solubility is only 7 mM
- Need high Cs-7SB concentration



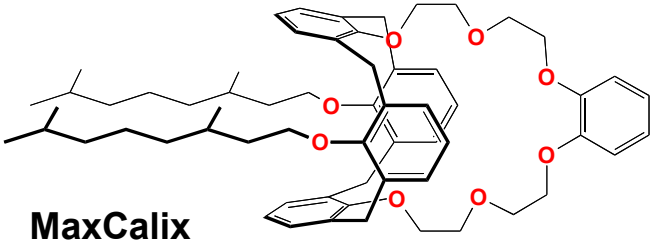
BOBCalixC6

BEHBCalixC6 (previous tests)
- High solubility (>50 mM)
- But forms third phase



BEHBCalixC6

MaxCalix (NG-CSSX choice)
- High solubility (>50 mM)
- No third-phase issue for SRS or Hanford wastes



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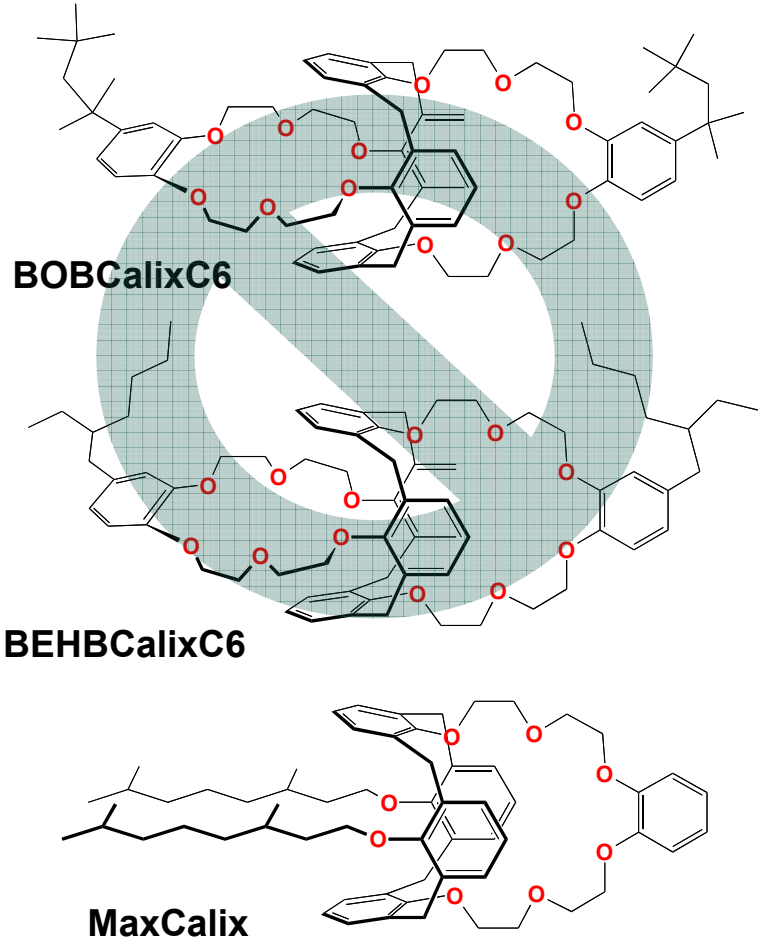
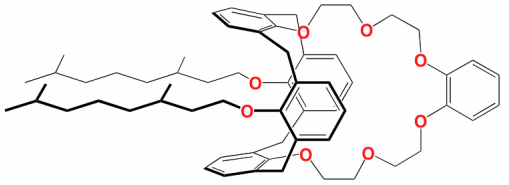


Next Generation CSSX solvent optimized for SRS MCU (DF ≥ 40,000)

Cesium Extractant @ 0.050 M

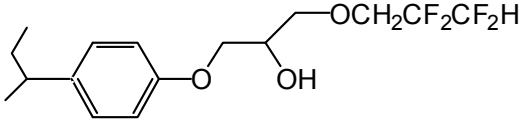
- High solubility
- Synthetically accessible
- Rejects sodium
- Stable thermally and radiolytically



MaxCalix

Diluent Modifier @ 0.50 M

- Increases Cs extraction
- Increases extractant solubility
- Excellent stability characteristics



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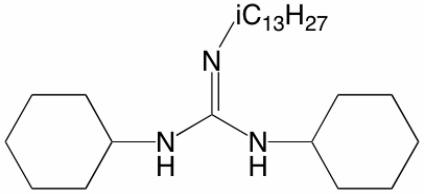


LIX® 79 Guanidine

(Alternatives being examined.)

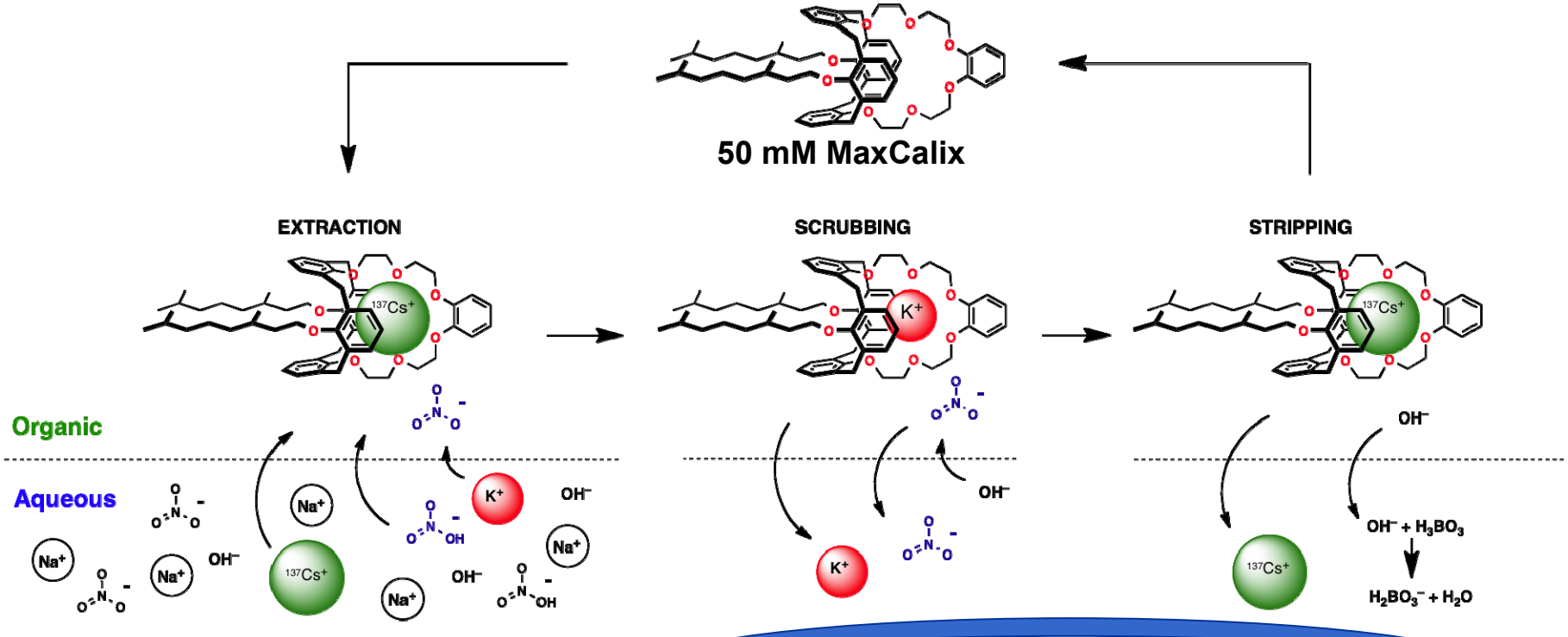
Diluent

- Isopar® L
- Branched avg. 12-carbon aliphatic
- Good stability and promotes good hydraulics

Moyer, *et al.*, *Waste Management 2011 (in preparation).*

Improved CSSX gives more efficient extraction and stripping

Good choice for DWPF feed and >10X better stripping



Alkaline nitrate tank waste

New

0.025 M NaOH

0.01 M H_3BO_3

3–5X stronger extraction

Change to OH^-, remove K^+

Consume OH^-, 10–100X stronger strip

Moyer, *et al.*, *Waste Management 2011 (in preparation).*

FY 2010 tests positive for boosted MCU performance and extended service life

- **Optimized solvent provides DF ≥ 40,000 for bounding SRS tank waste, ensuring saltstone curie limit will not be exceeded (pending flowsheet demonstration).**
- **Pending contactor testing at full scale, NG-CSSX batch data and previous full-scale CSSX contactor tests indicate that instantaneous MCU throughput increase from 8.5 to 12 gpm likely attainable.**

Waste simulants chosen for realistic tests

Three simulant compositions being used

(Major components only; many minor components not listed; mol/L)

Ion	*SRS-15 & -45* *(avg. & high K^+)*	*Hanford* *(241-AP-108, IPT worst case)*
Na^+	5.6	6.0
K^+ (competing)	0.015 (0.045) *worst case*	0.17
Cs^+	0.00014*	0.000058**
$Al(OH)_4^-$	0.28	0.61
OH^- (free)	2.06	1.45
NO_2^-	0.50	1.17
NO_3^-	2.03	1.90
CO_3^{2-}	0.15	0.37
SO_4^{2-}	0.14	0.032

*0.375 Ci/L ^{137}Cs. **0.207 Ci/L ^{137}Cs.

Print Close

FY 2010 simulant tests show excellent extract/scrub/strip (ESS) performance

Operation	Aqueous Phases	O:A Phase Ratio	Cs distribution ratio (D_{Cs})	
			SRS-15 simulant	SRS-45 simulant
Extract	SRS-15 or -45 simulants	1:4	60.7	51.1
Scrub 1	0.025 M NaOH	3.75:1	3.41	3.94
Scrub 2	"	3.75:1	1.76	2.00
Strip 1	0.010 M H_3BO_3	3.75:1	0.0022	0.0028
Strip 2	"	3.75:1	0.0006	0.0006
Strip 3	"	3.75:1	0.0004	0.0007

Note: This performance remains fairly stable over 10 batch cycles and with various stresses, including 2 MR radiation exposure, 2 mo. @ 35 °, and deliberate addition of surfactant.

Conditions:

- **0.050 M MaxCalix, 0.5 M Cs-7SB, 0.003 M LIX® 79 guanidine in Isopar L.**
- **SRS-15 is average SRS waste with full composition of minor components; SRS-45 is SRS-15 with bounding potassium concentration (0.045 M).**
- **T = 22–25 ° C; phase ratios set to give CF = 15.**
- **ESS test with fresh aqueous phases on each step.**

Moyer, *et al.*, *Waste Management 2011 (in preparation).*

Real-waste test validates ESS test performance with waste simulant

Operation	Aqueous	O:A	Cs distribution ratio (D_{Cs})		
			CSSX 6.7 M Na[1]	NG-CSSX 6.7 M Na[1]	NG-CSSX 3 M Na[2]
Extract 1	SRS Tank 49	1:3	14.1	61.8	40.8
Extract 2	SRS Tank 49	1:3	16.8	81.6	18.2
Scrub 1	0.025 M NaOH	5:1	0.88	2.32	3.36
Scrub 2	0.025 M NaOH	5:1	0.21	2.20	1.90
Strip 1	0.1 M H_3BO_3	5:1	0.018	0.00020	0.00058
Strip 2	0.1 M H_3BO_3	5:1	0.0082	<0.011	0.023[3] ?
Strip 3	0.1 M H_3BO_3	5:1	0.020	<0.44	0.116[3] ?

[1]Undiluted SRS Tank 49 feed. [2]Diluted Tank 49 feed. [3]Near background.

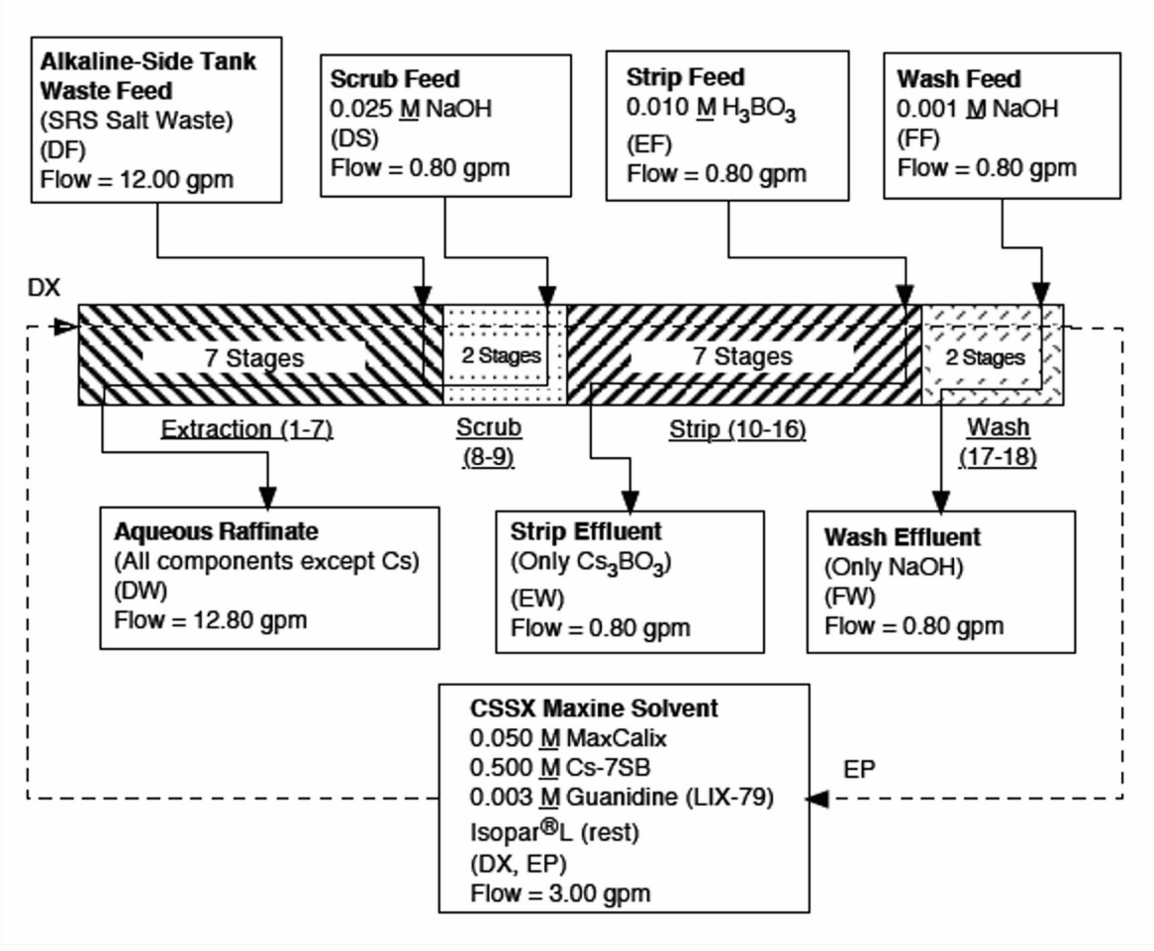
Conditions:

- **NG-CSSX: 0.050 M MaxCalix, 0.5 M Cs-7SB, 0.003 M LIX® 79 guanidine in Isopar L.**
- **CSSX: 0.007 M BOBCalixC6, 0.75 M Cs-7SB, 0.003 M TOA in Isopar L.**
- **Tank 49H blend, ~6.8 M Na, ^{137}Cs activity of 1.50 x 10^8 dpm/mL (0.26 Ci/gal).**
- **T = ambient but close to 25 ° C; D_{Cs} corrected to 25 ° C as shown.**
- **ESS test with fresh aqueous phases on each step.**

T. B. Peters and S.D. Fink, SRNL-STI-2010-00586, September 2010; 3 M Na data unpublished.

Preliminary flowsheet with NG-CSSX solvent based on batch results and contactor correlations indicate feasibility of DF > 40,000 in MCU

- **Calculated from D_{Cs} values obtained with SRS-45 simulant (bounding K^+)**
- **Predicts DF > 40,000, CF = 15, and 12 gpm feed.**
- **Assumes >90% stage efficiency; 0.5% other-phase carryover; T = 25 ° C; $N_{Di} \geq 0.0008$.**



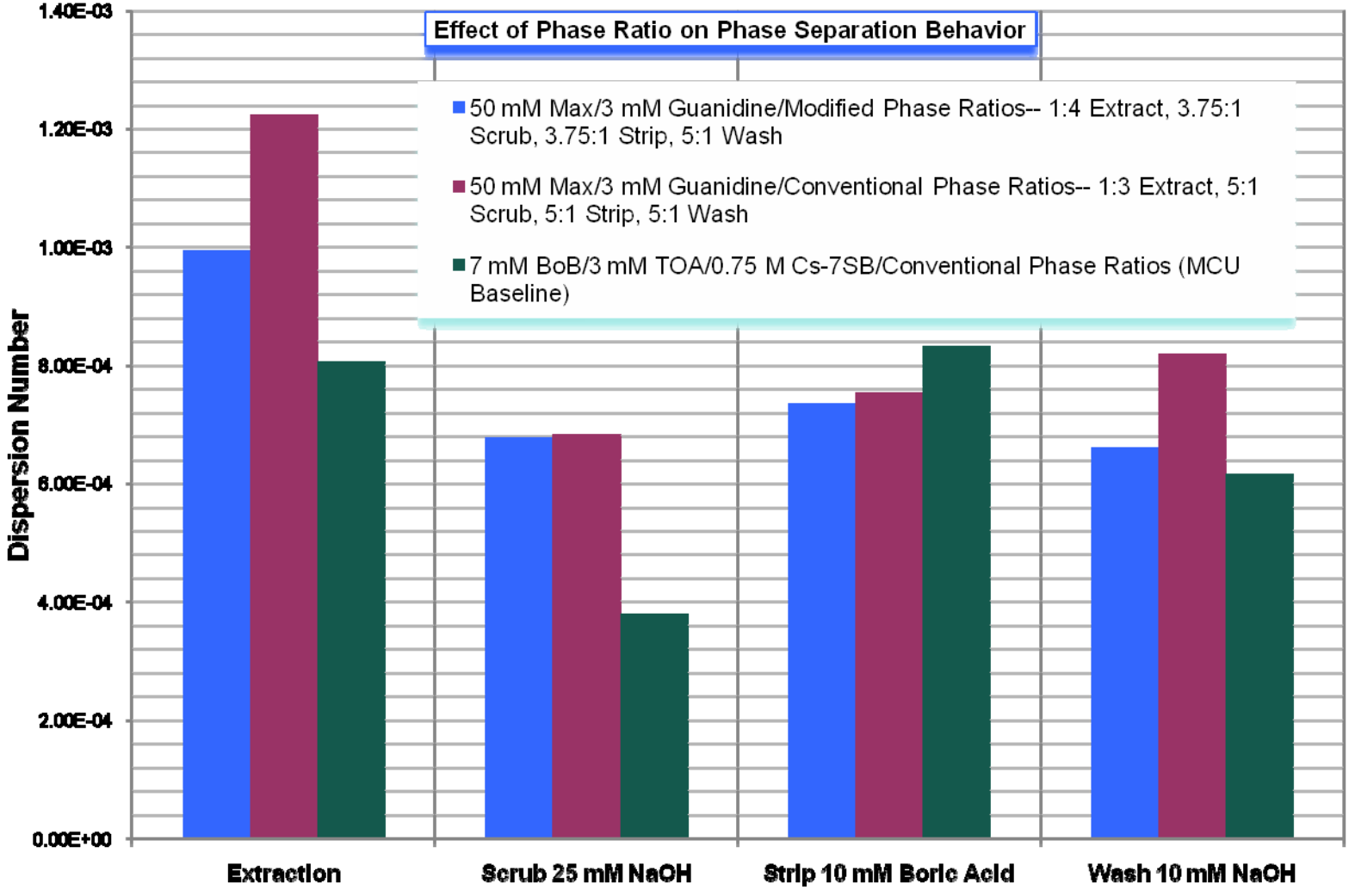
R. A. Leonard, NG-CSSX report, ANL, September 30, 2010.

Throughput increase likely, pending contactor tests—applies to MCU (target 12 gpm) and SWPF

- **Dispersion numbers all good**
  - Batch break-time measurements good
  - Lower [Cs-7SB] gives lower density and viscosity
  - Increasing coalescence rate with decreasing [Cs-7SB]
- **Can decrease O/A ratio on extraction**
  - High D_{Cs} allows lower relative volume solvent flow
  - This means increased waste flow rate
- **Salt concentration can be increased**
  - D_{Cs} = 62 at 25 °C with 6.7 M Na real waste
  - D_{Cs} = 61 at 25 °C with 5.6 M Na simulant
- **Previous CSSX full-scale contactor results**
  - Stage efficiency increases with throughput and rotor speed

Coalescence of NG-CSSX Solvent is very good

Expect successful contactor performance

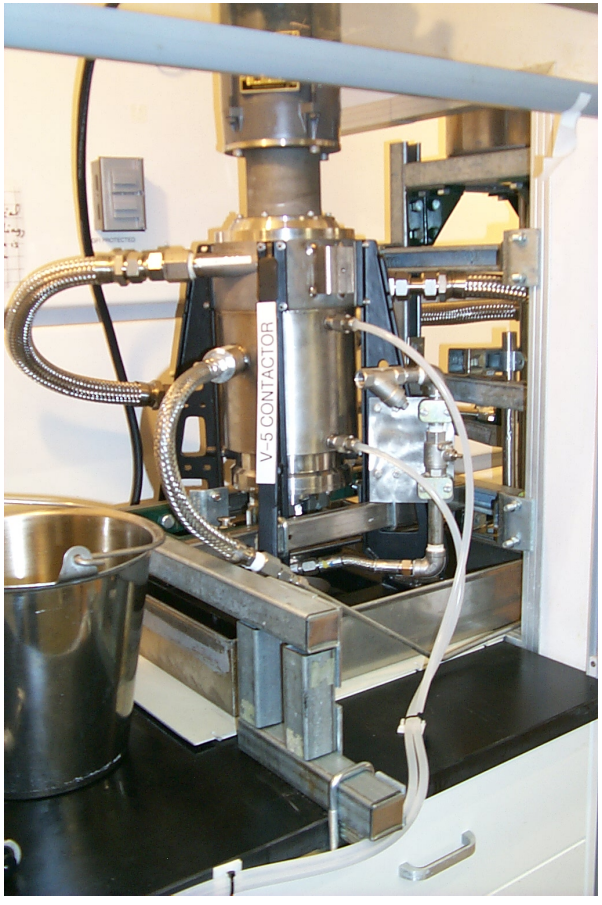


Print

Close

Engineering scale-up is focus of FY11

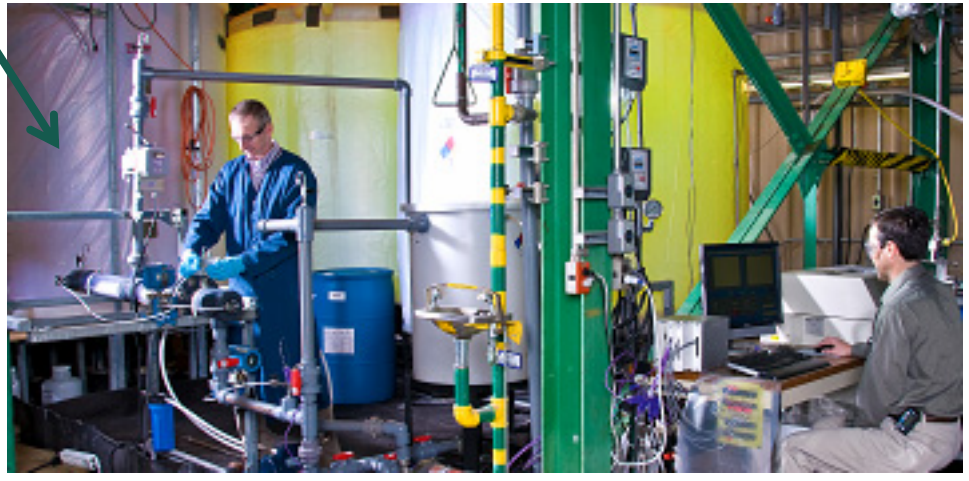
Full-scale contactor hydraulics testing at SRNL



We will zero-in on the question of throughput.

Real-waste 2-cm contactor demo at SRNL (10 gal RW)

Coalescer performance test at SRNL



Benefit for SWPF is increased throughput

Could potentially trim several years off of operating life

- **ORNL will optimize solvent for SWPF**
  - **Somewhat higher D_{Cs} for lower O/A**
  - **Can also increase salt concentration**
  - **Even lower [Cs-7SB] for better hydraulics**
- **Possible 2-cm contactor flow testing at SRNL**

Benefit for Hanford is backup alternative

A modular CSSX unit for Hanford is feasible

- D_{Cs} = 10.5 for 20 mM MaxCalix, 0.5 mM Cs-7SB
  - Value pertains to worst-case IPT Hanford simulant
  - Obtained D_{Cs} = 19 at 50 mM MaxCalix
- Expect modular unit about same size as MCU
  - Can get DF = 40,000, CF = 15
  - SEPHIS calculations
- In FY11 solvent will be optimized for Hanford
- Possible 2-cm contactor flow testing at SRNL

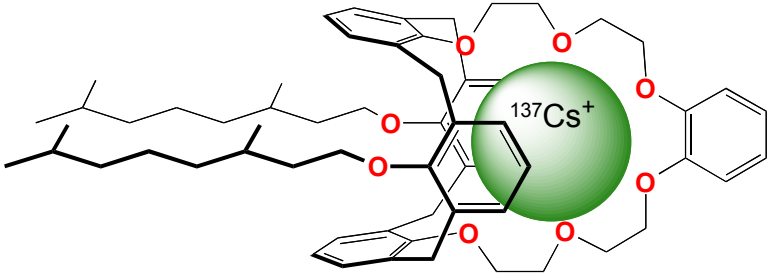
A Next-Generation CSSX process can accelerate tank-waste cleanup

Improved Cs removal for SRS and possibly even Hanford

It is possible for SRS MCU performance to be increased to DF ≥ 40,000 and CF = 15 for SRS waste treatment, probably at increased throughput. SWPF throughput can likely be increased. A modular CSSX process for the more challenging Hanford waste is now feasible.

Questions?

R&D funded by the Office of Technology Innovation and Development (EM-31)



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Major milestones met in FY 2010

- **NG-CSSX solvent optimized**
- **Successful RW batch tests at SRS**

Other accomplishments:

Hydraulic tests with V02 contactors initiated.

Mass-transfer efficiency tests started with V02 contactors.

Modification of centrifugal contactors started.

Preliminary DWPF impacts identified.

Coalescer designs reviewed, possible improvements seen.

Contactors and parts ordered for RW countercurrent flow test.

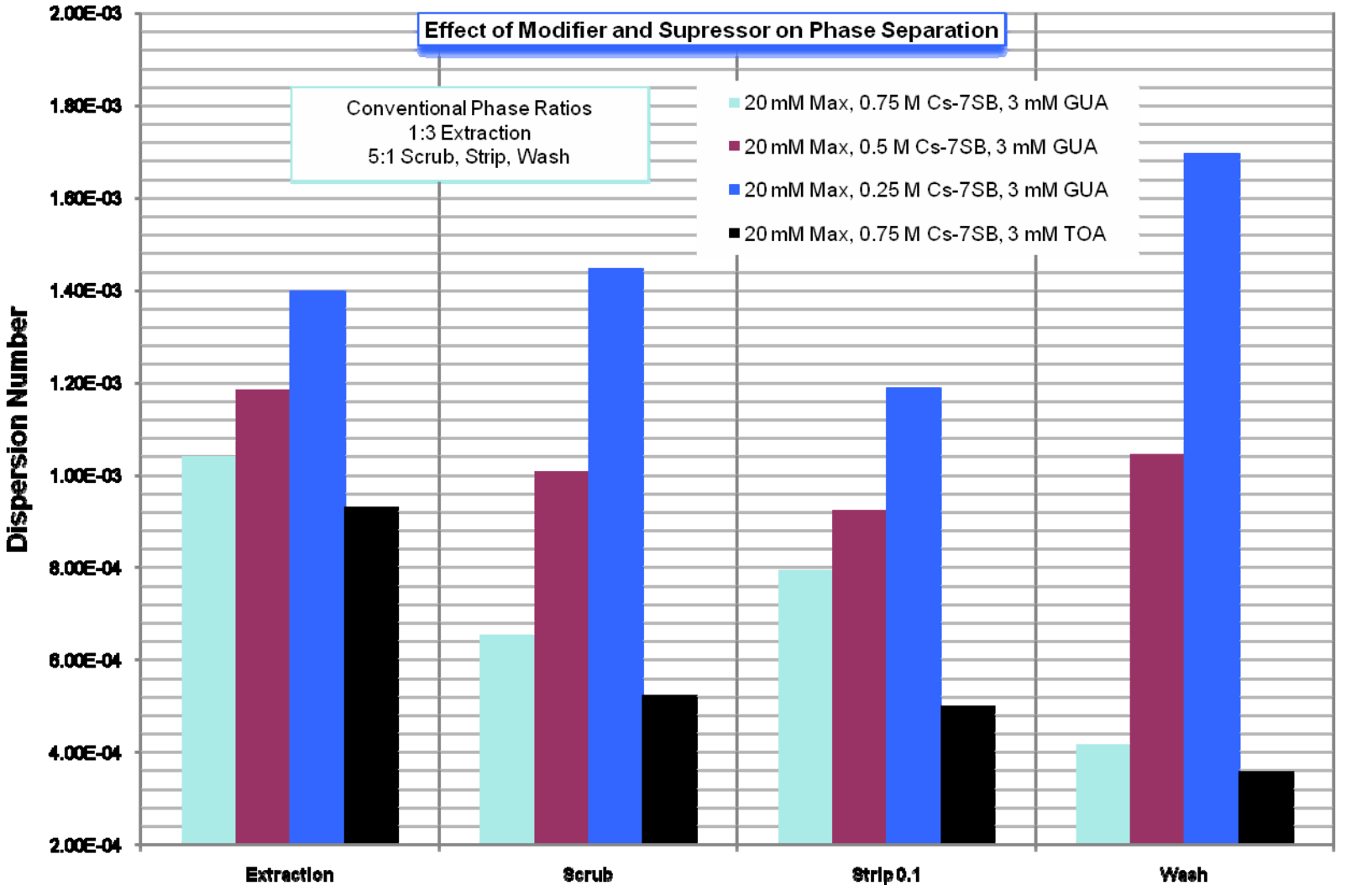
Manufacture of calix at 0.1–0.2 kg/wk being scaled to 1.5 kg/wk.

Thermal and radiation stability tests of NG-CSSX initiated.

FY 2011 ORNL Plan

- **ORNL chemical development**
  - Temperature effects
  - Minor component effects
  - Solvent washing stage defined
  - Complete blending strategy
  - Solvent stability and losses
  - Distribution model (Tenn. Tech. Univ.)
  - SWPF and Hanford NG-CSSX solvents
- **ORNL V02 contactor testing**
  - Single-stage hydraulics
  - Mass-transfer efficiency
  - Contactor modifications
  - SWPF and Hanford solvent testing

Reducing the modifier (Cs-7SB) concentration improves phase disengagement, as does conversion of the suppressor from trioctyl amine to guanidine



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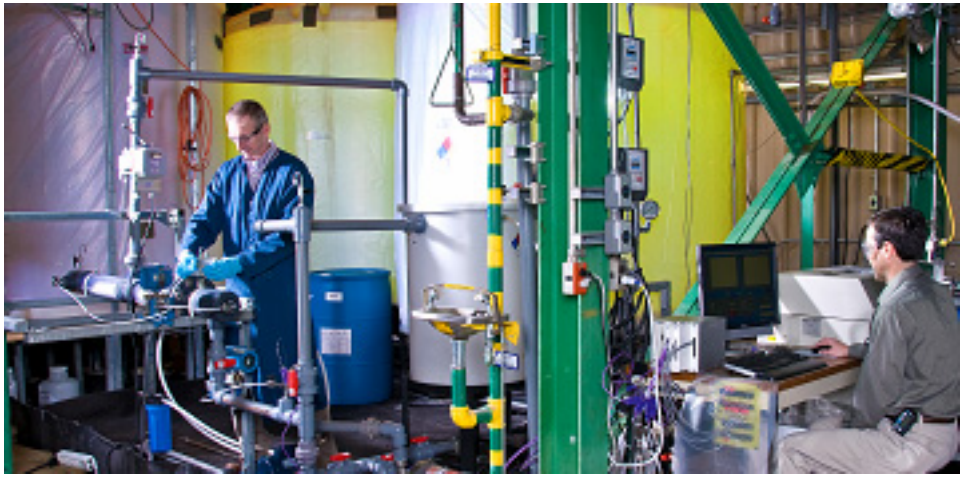
FY11 SRNL Task: Real-waste 2-cm Contactor Flowsheet Demonstration

- Demonstration will use 12 2-cm contactors of similar design to those used for MCU original development.
- ANL will supply new rotors (12/2010) and critical spare contactors (4/2011).
- SRR will supply 10 gallon sample of salt solution from current MCU macrobatch (expected 12/2010).
- Test team will include visiting scientists from ORNL, ANL, and SRR.

- Hydraulics tests (simulants) 12/2010
- Equipment complete 3/2011
- Simulant tests (SRS and Hanford) 6/2011
- Real-waste test 10/2011

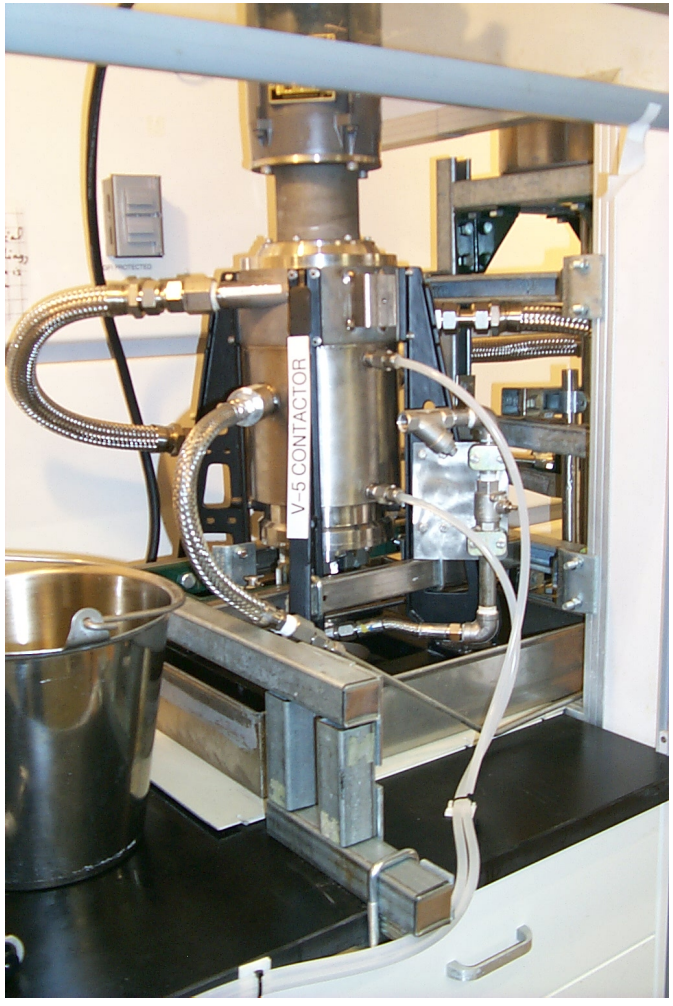
Coalescer Performance Test (SRR Project Funded Task)

- SRNL will install a coalescer flow loop using a full-scale coalescer housing for the Pall® polyphenylene sulfide elements.
- Testing will inject a suspension of solvent droplets in the aqueous stream and organic concentration and droplet size for exiting stream using techniques developed in earlier program testing.



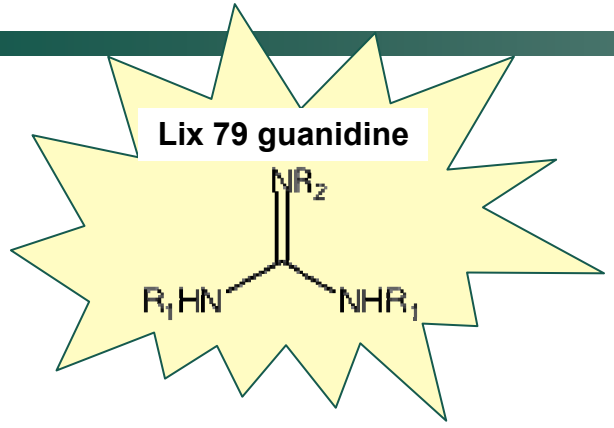
- Equipment installed 4/2011
- Testing complete 7/2011

Full-scale Contactor Hydraulic Testing



- SRNL will install separate flow loops each with a full-scale V-5 and V-10 contactor for assessing hydraulic performance and organic carryover.
- Tests will monitor droplet size distribution and organic content for Strip Effluent and Decontaminated Salt Simulant at range of flow rates.
- SRR will supply contactors and an SRR Project will fund equipment installation.
- EM-31 will fund the test campaign.
    - Equipment installed 4/2011
    - Testing complete 7/2011

Possible enhancement with alternative suppressor



- A base is needed in the organic phase
- TOA effective, but Lix 79 guanidine stronger

Solvent (CSSX):

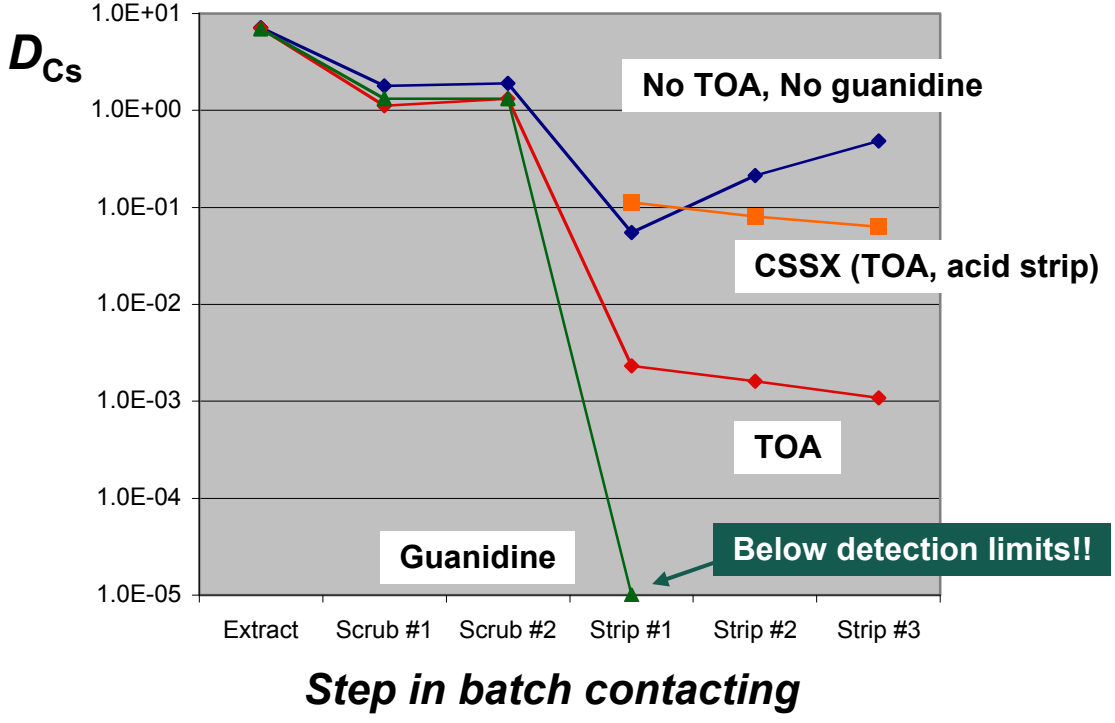
7 mM BOBCalixC6
0.75 M Cs-7SB modifier
3 mM TOA or guanidine
Isopar L diluent

Aqueous phases:

Extract: 3 M $NaNO_3$, 2 M NaOH, 50 mM KOH, 0.5 mM $CsNO_3$
Scrubs: 0.1 M NaOH
Strips: 10 mM H_3BO_3

Conditions:

25 ° C, O:A = 1:1 all contacts



Delmau; Haverlock; Bazelaire; Bonnesen; Ditto; Moyer *Solvent Extr. Ion Exch.*, 2009.

But Lix 79 unstable—further research needed
TOA performs well and is baseline suppressor

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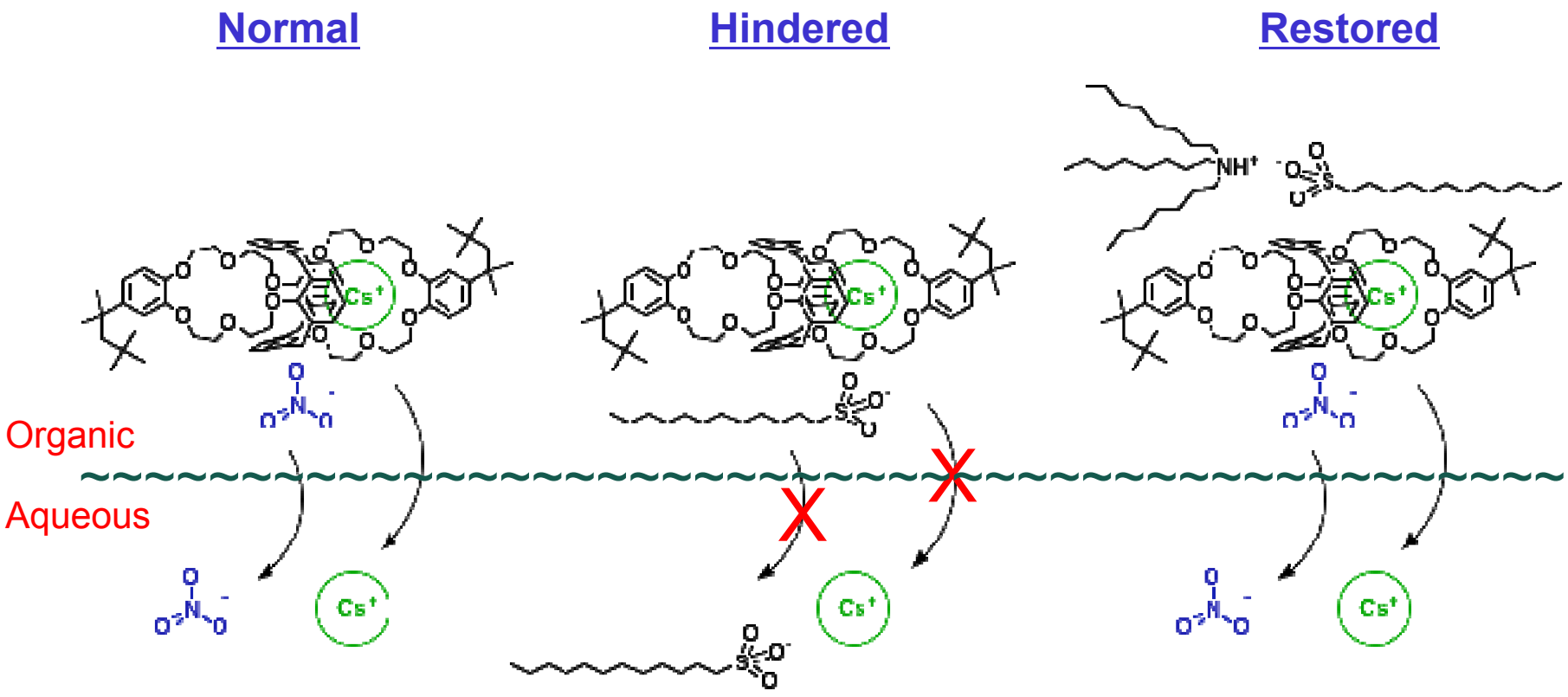
Lipophilic surfactant impurities hinder stripping but are neutralized by alkylammonium cation



Moyer, Birdwell, Bonnesen, Delmau, in *Macrocyclic Chemistry—Current Trends and Future*; Gloe, K., Ed.; Springer: Dordrecht, 2005.