Savannah River Remediation

We do the right thing.

Enhanced Chemical Cleaning (ECC) Oxalate Destruction Testing

Presentation to:

EM Waste Processing Technical Exchange

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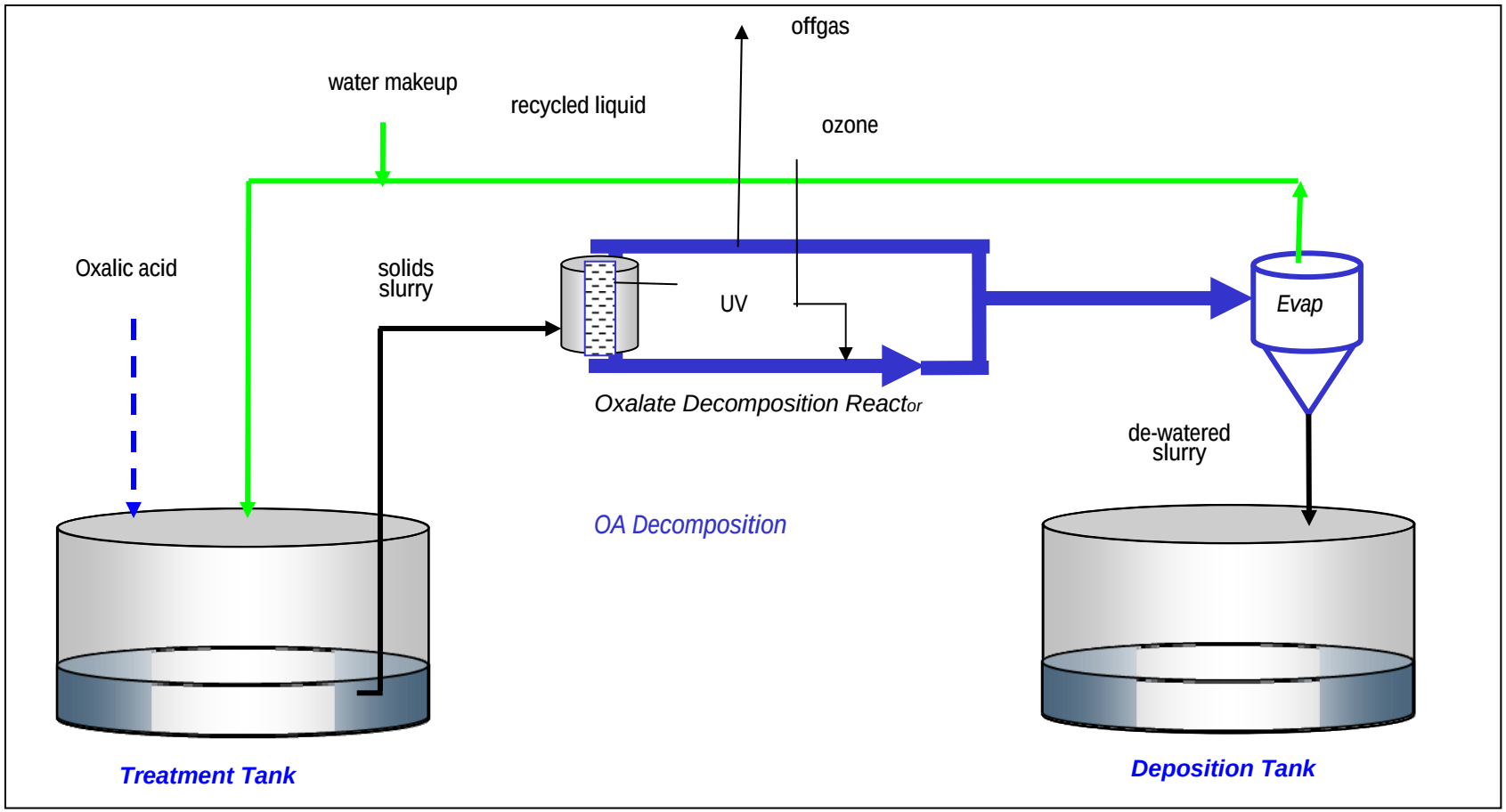
Outline/Objectives

- What is Enhanced Chemical Cleaning?
  - The Mission/Vision/Goal
  - Process overview
- Types of Testing required
  - Focus on Corrosion & Process Testing
- Need for UV-light testing
- Primary reactions that create hydroxyl radicals
  - Ozone UV reaction
  - Pseudo-Fenton's type reactions
  - Intermediate ferrio-hydroxyl
- Goals for the UV/No-UV test
- Discuss results from preliminary data
  - Decomposition rates
  - Resultant pH values

Simplified Process

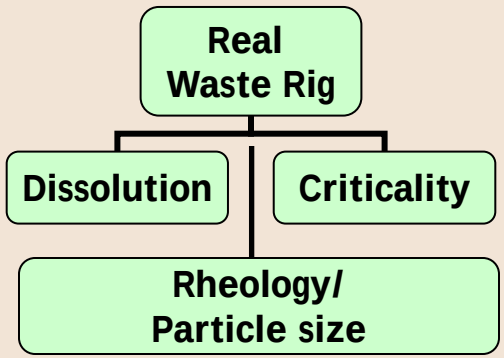


Breadth of ECC Testing

1) **Efficacy**

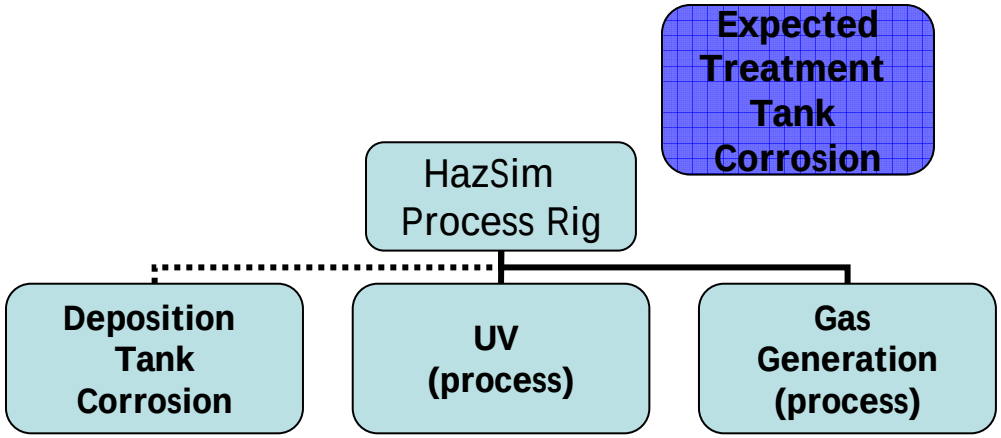
Initial Efficacy/Bench Top

2) Real Waste Testing



- Physical limitations of hot cells limit scope of Real Waste testing.

3) Hazardous Simulant (HazSim) Testing



- Dashed line shows test not actually performed with rig, but uses feed
- Expected Treatment Tank corrosion does not use the HazSim Rig. Performed by SRNL at SRNL.

Importance of OH Radical

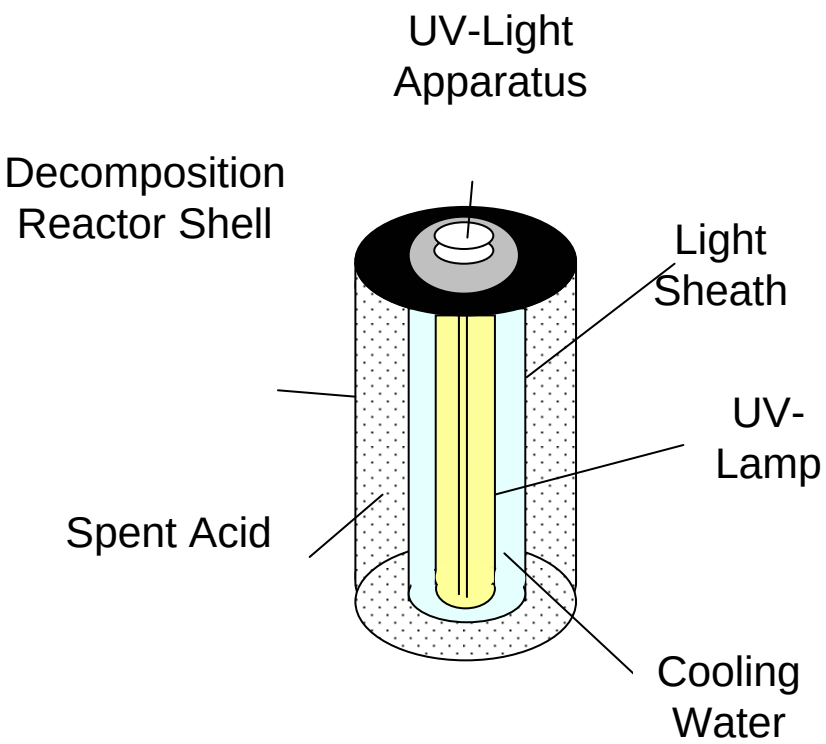
Oxidizer	Potential (V)	K_{C2O4} ($M^{-1}s^{-1}$)
F	2.87	NA
•OH	2.86	5.3E+6
O_3	2.07	0.04
H_2O_2	1.78	2
Cl	1.36	NA

1) Potential of •OH > O_3

2) Rate, K_{C2O4}, Constant •OH>>O_3

For commercial processes with similar chemistry, UV shown to increase decomposition rate by ~10x

Disadvantages of UV Light



Oxalate Decomposition Reactor With UV-light

Complexities

- Scale formation
- Cleaning
- Replacement difficult
- Creates mixed waste
- Safety related component

- Preliminary tests showing UV effectiveness degraded

Is UV Really Needed ?

- Basic photocatalytic reactions creating OH radical

$$O_3 + H_2O \xrightarrow{hv} 2\circ OH \qquad O_3 + H_2O \xrightarrow{hv} H_2O_2 + O_2 \longrightarrow 2\circ OH + O_2$$

- UV is commonly preferred because its “green,”
- Some process based reactions are “equally green”
  - intrinsic pseudo-Fenton’s type

$$Fe(II) + H_2O_2 \longrightarrow Fe(III) + \circ OH + OH^-$$

$$Fe(III) + H_2O_2 \longrightarrow Fe(II) + HO_2 / O_2^- + H^+$$

- intermediate ferrio-hydroxyl

$$Fe^{2+} + O_3 \longrightarrow FeO^{2+} + O_2 + H_2O \longrightarrow Fe^{3+} + \circ OH + OH^- + O_2$$

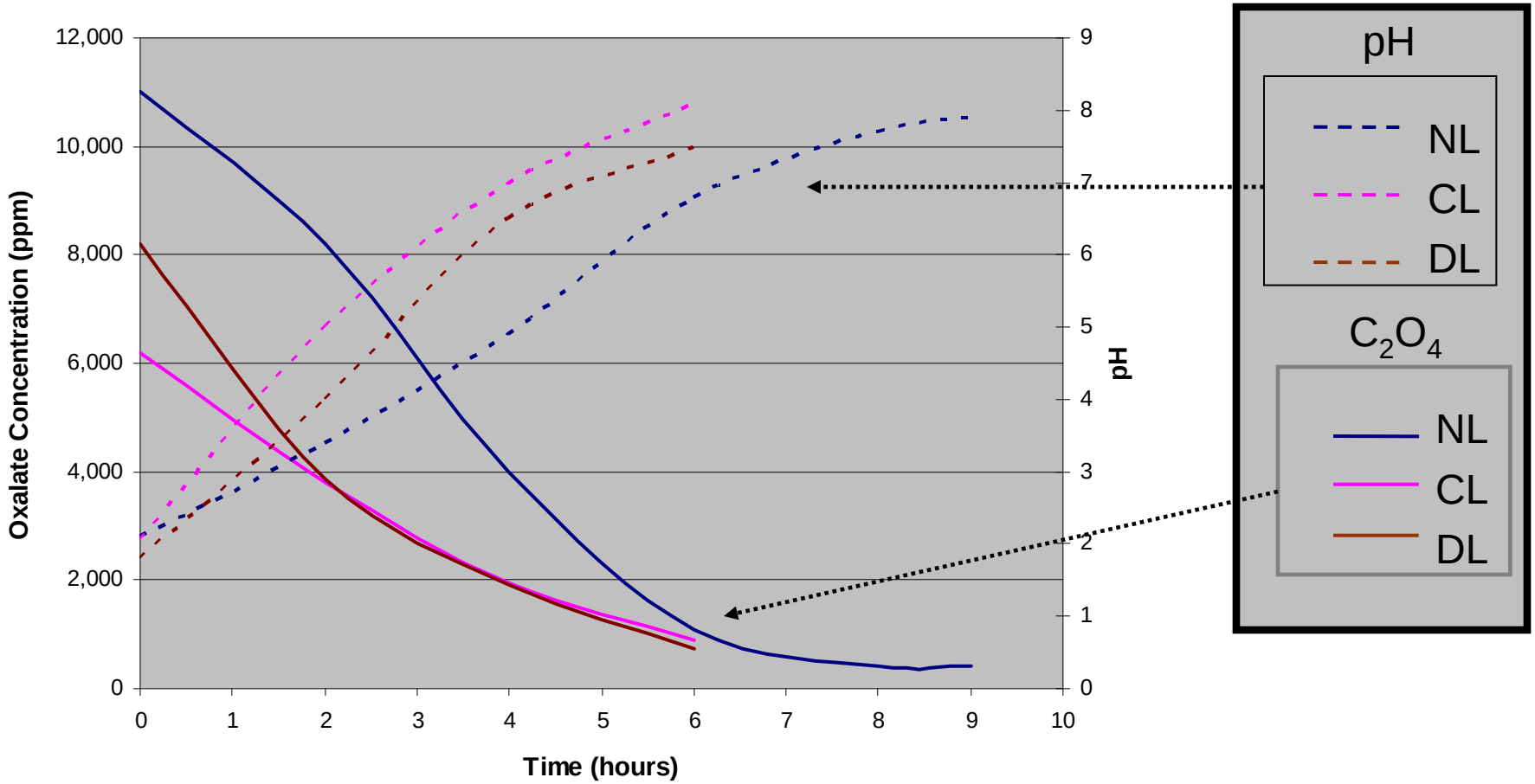
Initial Test Questions

- Is the UV light needed for an acceptable decomposition rate (i.e., ≤16 hrs per batch)?
- Does the destruction rate decrease for low Fe/high Al sludge concentrations?
- Are there any differences without the UV light that would significantly impact ECC
- Can pH be used for a process indication of oxalate destruction?

UV Light Test

- Tested under ECC process conditions using 60 liter HazSim Test Rig
- Test Matrix
  - Both F& H simulants used (i.e., different Fe/Al ratios)
  - 3 possible UV-light conditions
    - NL = No light
    - ML = Maintained (Clean) light
    - DL = Non-maintained (Dirty) light
  - 3 consecutive strikes of treatment tank
    - Strikes 1, 2 and 3
- All 18 combinations tested

Oxalate Decomposition



Note: Preliminary Data

Preliminary Test Results

- Saturated spent C_2O_4 started at about 10,000 ppm decomposed down to <100 ppm
- H-Area decompositions were generally faster than F-Area
  - On average 5.5 hrs vs. 6.3 hrs
  - Longest in F-area decomposition, NL-1, required 8 hrs
  - Longest in H-area decomposition , NL-1, required 6.2 hrs
- All pH values after decomposition were $\geq$7, except one with a pH=6.8
- All required significantly less time than the maximum allowed time of 16 hrs

Conclusion

- Decomposition required << time than the maximum allowed
  - All require ≤ ½ the allowed time
  - 8 hrs or less vs. 16 hrs
- The ability to remove the UV light seems likely
  - Based on preliminary data, needs to be confirmed
  - Confirmation with Real Waste Testing
- Questions
- Thanks for listening

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Acronym List

Cl = chlorine
C_2O_4=oxalate
DL = dirty (unmaintained) UV light
ECC = Enhanced Chemical Cleaning
F = fluorine
Fe = iron
HazSim = simulant containing RCRA metals
H_2O_2 = peroxide
K = rate constant $M^{-1}s^{-1}$
ML= maintained (clean) UV light
NL = no UV light
•OH = hydroxyl radical
O_3 = ozone
UV = ultraviolet light