Contract No:

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Methylmercury Retention Evaluation to Support Saltstone Waste Acceptance Criteria (WAC):

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Background: Technical Basis for Saltstone WAC

- Tank 50 Hg concentrations and species are currently monitor and controlled to ensure Saltstone passes TCLP test for Hg
- 2014 4Q and 2018 Tank 50 WAC showed high Hg and spike in Hg in Saltstone TCLP leachates
- Hg species in TCLP leachate identified as predominantly (>90%) methylmercury (MHg)
- Saltstone spiked with inorganic mercury (Hg^{2+}) at 500 mg Hg/L passed the TCLP test (Langton and Wilhite, WSRC-89-1375)
- Current Tank 50 WAC limit for total Hg is 325 mg/L
  - Hg concentrations have been much lower than WAC (< 110 mg/L)
  - Saltstone passes TCLP for Hg for the -3/8 to -5/16 inch size fraction (SCDHEC accepted)

Purpose of this work:

- Support technical basis for managing Hg, including MeHg, in the tank farm
- Identify MeHg speciation and measure leaching for Saltstone
- Identify Hg retention mechanism(s) in Saltstone (stabilization and release)

Approach: Prepare simulated saltstone with 3 concentrations of MeHg

- TCLP for 3 size fractions effects (chemical vs physical stabilization)
- Hg phase identification in saltstone
- Hg total and phase specific concentration analyses

SRS Low Level Radioactive Waste

Low activity, caustic (pH>13) salt solution is combined with cementitious materials and placed in Saltstone Disposal Units (SDUs).

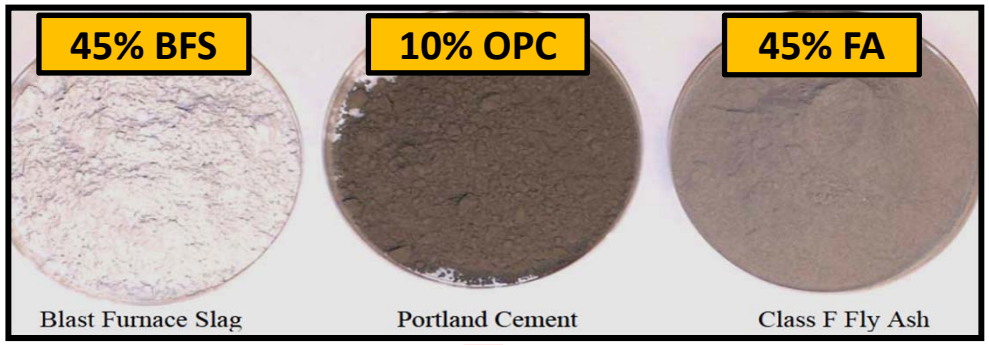
Salt Solution

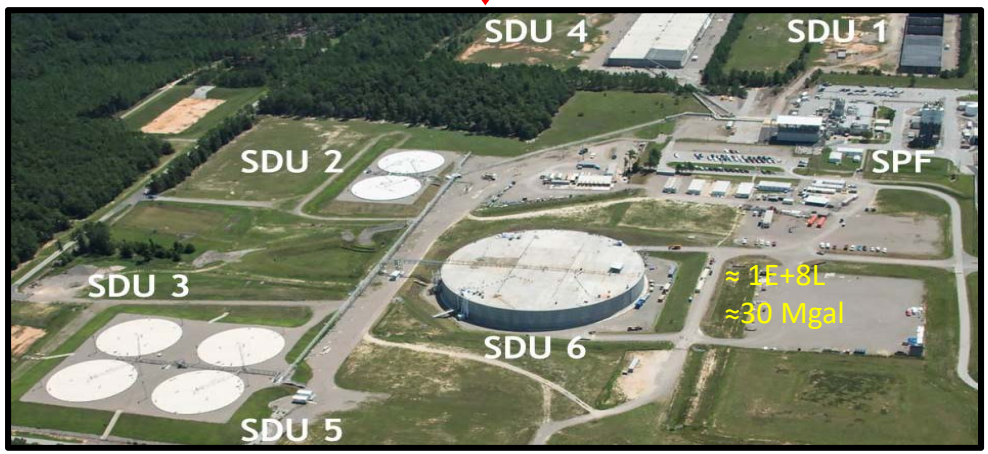
Chemical	*mol/L*
Na	6
NO_3^-	3
OH^-	2
NO_2^-	0.5
CO_3^{2-}	0.2
SO_4^{2-}	0.1

Radionuclides (nominal)

Radionuclides (nominal)		
Isotope	*Bq/mL*	*½ Life (yr)*
Sr-90	74	28.8
Tc-99	740	0.2M
I-129	37	16M
Cs-137	37,000	30.2

Cementitious Reagents (premix)





Technical Basis for Saltstone WAC

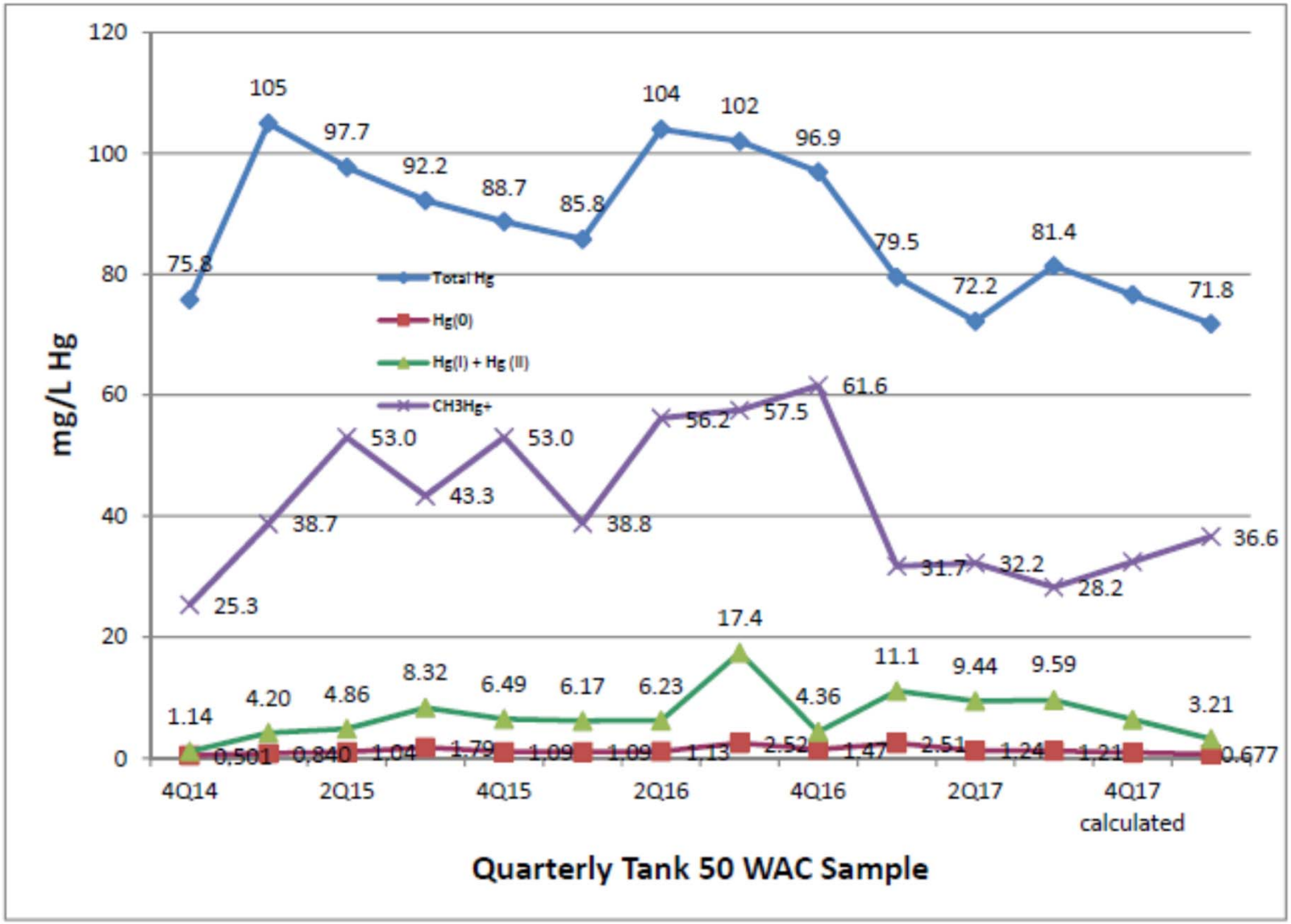
Purpose of this work:

- Establish the experimental basis (WAC limit) for managing Hg, including MeHg, in the tank farm **(Current WAC is 325 mg/L ?)**
- Identify MeHg speciation in Saltstone
- Identify MeHg/Hg retention mechanism(s) in Saltstone (stabilization and release)

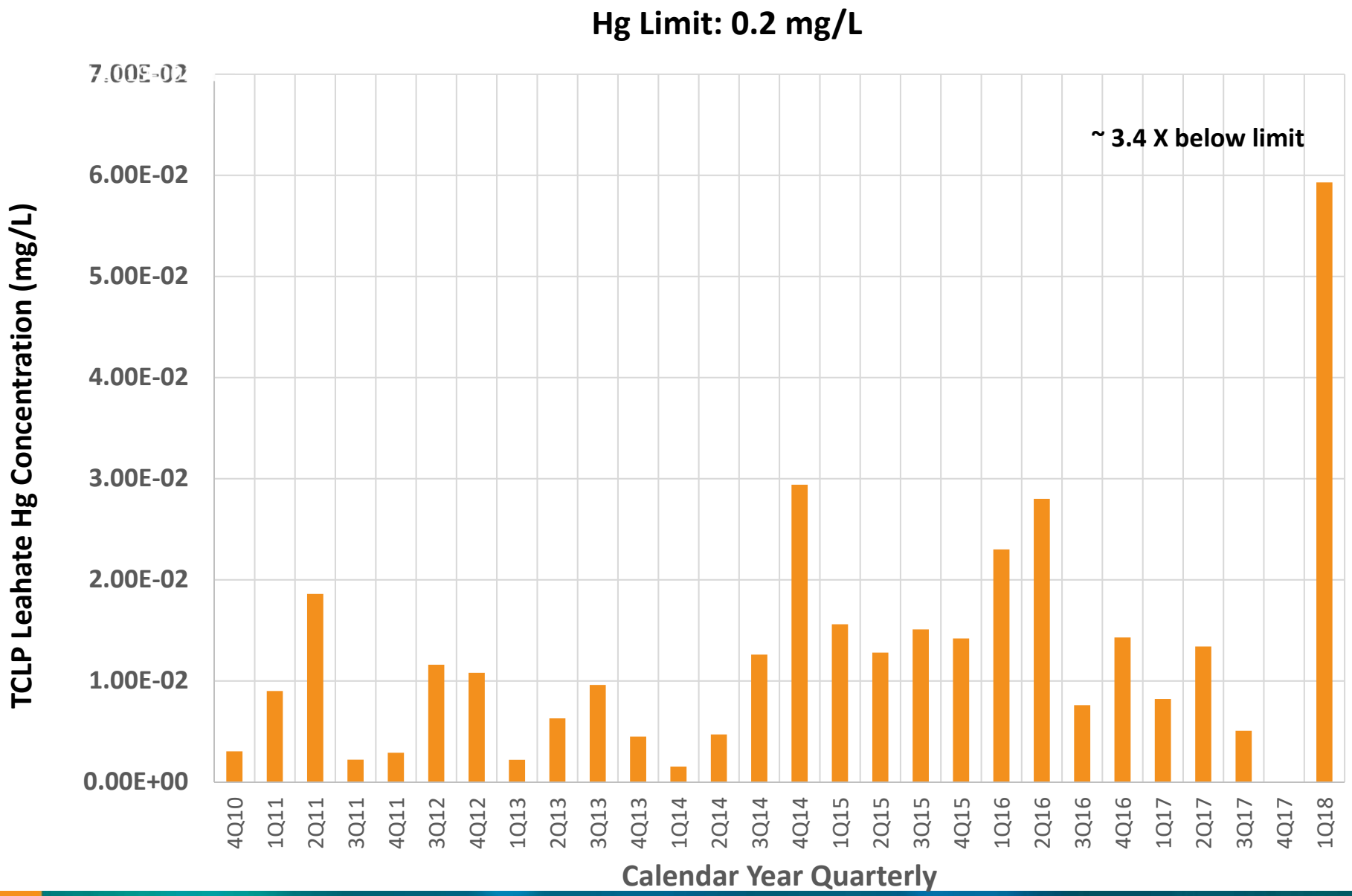
Approach to addressing these objectives:

- Measure the retention of MeHg in cured SS and identify the phases responsible for stabilizing Hg in SS.
- Prepare simulated saltstone with 3 concentrations of MHg **(150, 250 and 500 mg/L)**
  - TCLP for 3 size fractions effects **(establish which fraction @ what concentration meet the 0.2 mg/L Hg TCLP)**
  - MHg/Hg phase identification in saltstone
  - MHg/Hg total and phase specific concentration analyses

Tank 50 Methylmercury Concentrations and Speciation



Saltstone TCLP Results (Tank 50 Solution)



Simulated Saltstone Sample Preparation

Simulated Salt Solution

Component	Weight of component for 2L (g)
DI Water	1540.440
KNO_3	1.806
Na_2SO_4	14.916
50% NaOH solution	399.600
$Al(NO_3)_3.9H_2O$	111.003
$Na_3PO_4.12H_2O$	3.316
Na_2CO_3	42.011
$NaNO_3$	290.300
$NaNO_2$	62.968
72.58 wt. % water	spg = 1.233

Saltstone

Salt Solution 45 wt. %
Premix 55 wt. %

w/cm = 0.6

Saltstone Cementitious Reagents (Premix)

Component	Weight of component (g)
Lehigh Slag Cement Z-area (5-17-2016)	450
SEFA Class F Flyash (CBO) Z-Area (5-17-2016)	450
Type I/II Holcim Cement Z-Area (5-17-2016)	100
Total premix sample weight	1000

MeHg Additions

MeHg(OH) spike mg/L	**$MeHg^+$** measured mg/L
0	0
150	159
250	251
500	513

MeHgOH Spike solution Preparations, Simulated SaltsStone & TCLP Tests

Preparation and cure of "neat' Simulated Salstone:

- Premix cementitious reagents + Tank 50 simulated salt solution on a 55% to 45% weight ratio
- Water to cement ratio of 0.6
- The slurries were cast into 51 x 102 mm (2 x 4) inch molds in 100 ml containers with lids and cured for a minimum of 28 days in sealed bags.

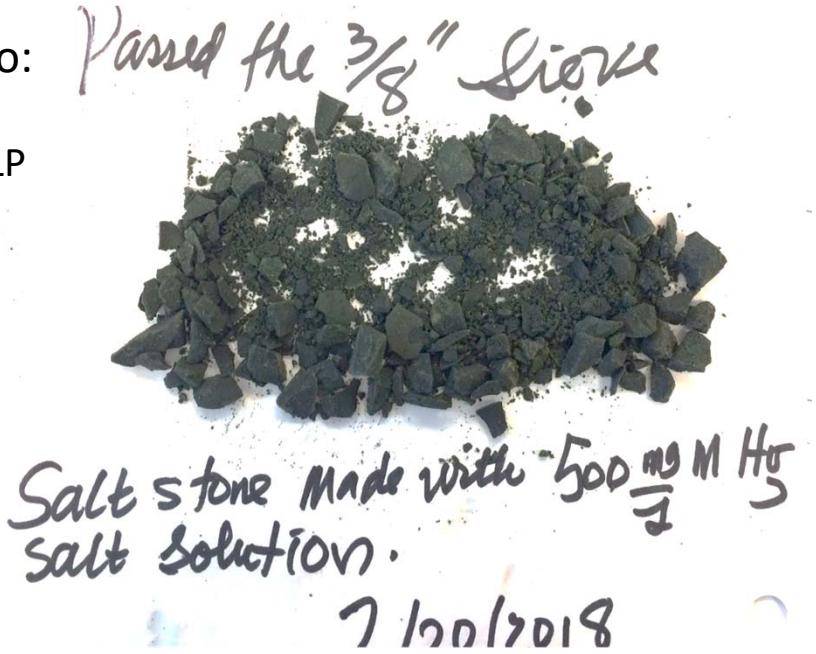
Spiked MHg(OH) Salt Solution ID (mg/L)	MHg^{+} (cation) SRNL AD analysis	Calculated concentration* MeHg(OH)
0	0	0
150	147	158.6
250	240	250.9
500	476	513.5

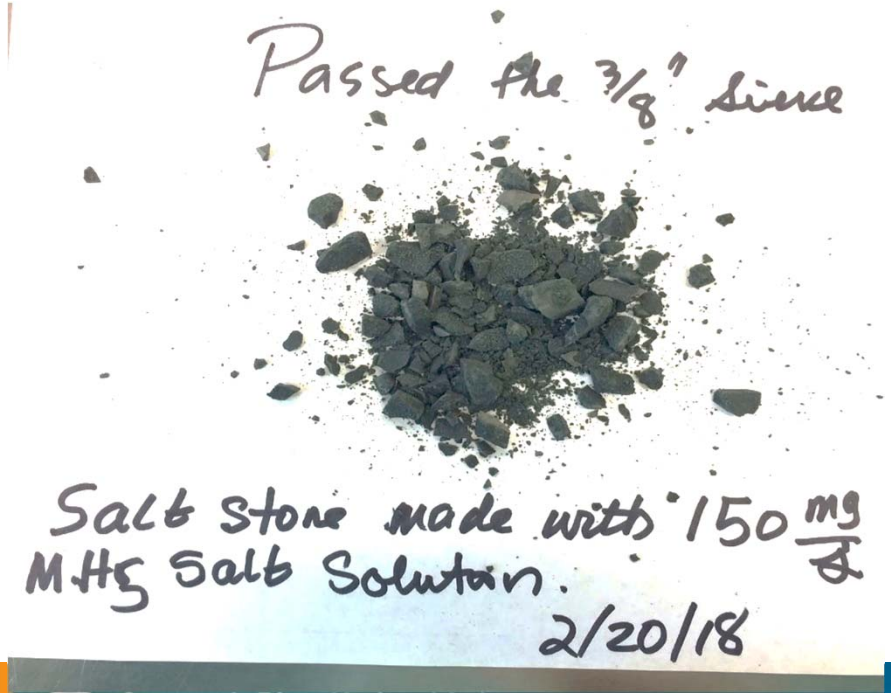
Preparation of MeHgOH Spiked Salstone and TCLP Test:

- Tank 50 Simulated salt solutions spiked with 0, 150, 250 and 500 mg/L MeHgOH were used to prepare Salstone samples which were cure for 28 days.
- These MeHgOH spiked and cured salstone samples were prepared for TCLP test by crushing them into 3 different particles size fractions (0.3 to 0.42 mm, 0.4 to 0.6 mm and <0.952 mm (<3/8")).- EPA SW-1311 procedure (modified)
- Duplicate samples were run for each size fraction and each MeHgOH waste loading.
- Analytical results were converted to total Hg values for comparison with the EPA limit. Results
- TCLP leachate results are presented graphically and in table below.

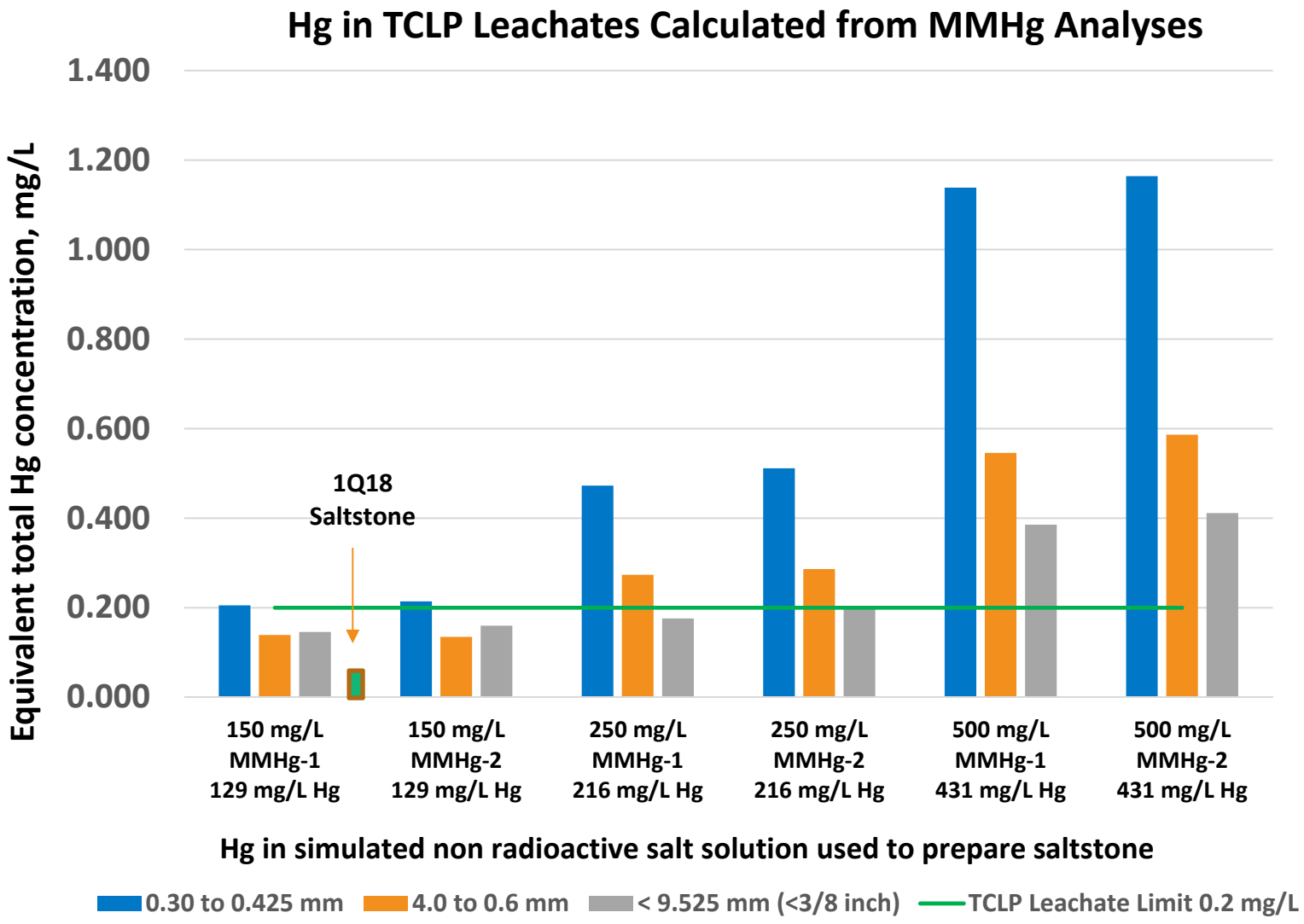
TCLP Sample Preparation

- Three saltstone particle size fractions were tested to:
  - Evaluated surface area effect on stabilization
  - Understand potential vulnerability for exceeding TCLP
  - provide indicator of stabilization mechanism
- Size fractions
  - -3/8 inch
  - 4.0 to 6.0 mm
  - 0.30 to 0.425





TCLP Leachate Results: $MeHg^{+}$ Spiked Simulated Saltstone



TCLP Leachate results cont.

	Hg (mg/L) in TCLP Leachate			
Simulated Saltstone Sample ID	0.3 to 0.425 mm size fraction	0.6 to 4.0 mm Size fraction	< 0.375 inch < 9.525 mm	TCLP Limit
150 mg/L mmHgOH-1	0.221	**0.150**	**0.157**	0.2
150 mg/L mmHgOH-2	0.231	**0.145**	**0.172**	0.2
250 mg/L mmHgOH-1	0.510	0.295	**0.190**	0.2
250 mg/L mmHgOH-2	0.552	0.309	0.219	0.2
500 mg/L mmHgOH-1	1.228	0.589	0.416	0.2
500 mg/L mmHgOH-2	1.226	0.633	0.444	0.2

Black values are above the TCLP limit and samples are characteristically hazardous for Hg. Green values are less than the TCLP limit and samples do not display the characteristic of Hg toxicity

TCLP Leachate results for saltstone made with simulated solution containing 150, 250, and 500 mg/L methyl mercury as methyl mercury hydroxide.

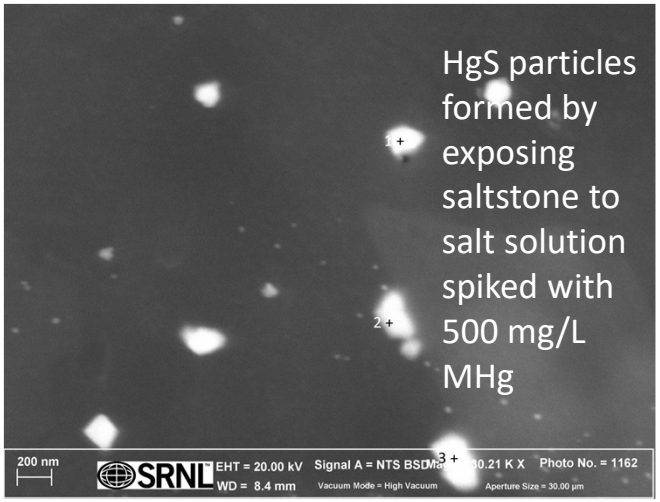
Reaction between MeHgOH and Salstone

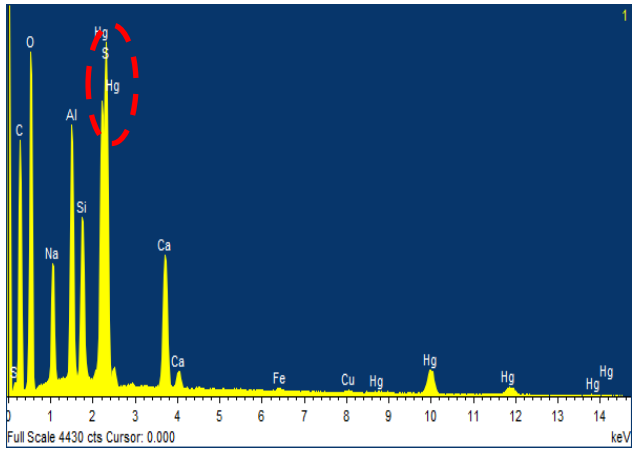
Speciation of methylmercury hydroxide in salstone was evaluated by :

- X-Ray diffraction (XRD)
- Energy dispersive spectroscopy (EDX)
- Scanning electron microscope (SEM)
- Solid state NMR, DRIFT ?

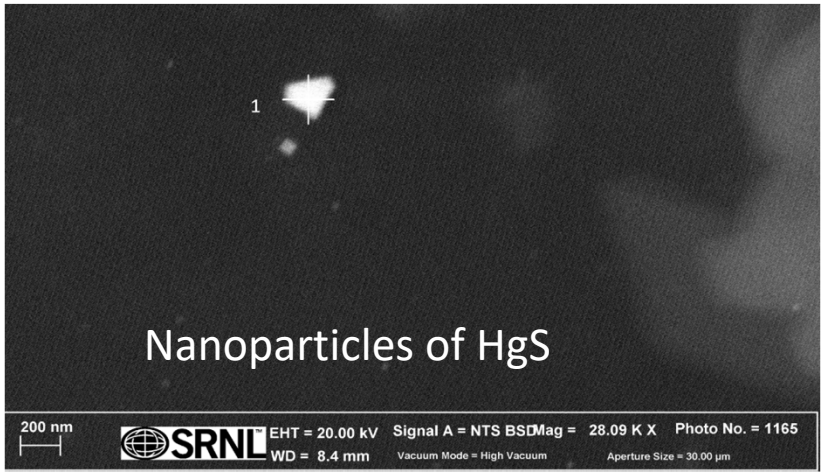
Results:

- Metacinnabar, β-HgS, was identified by EDX spectra of bright (high atomic mass elements) nano and micro particles in crushed saltstone samples
- The atomic ratios of S and Hg for in these spectra were about 1:1 which corresponds to HgS.

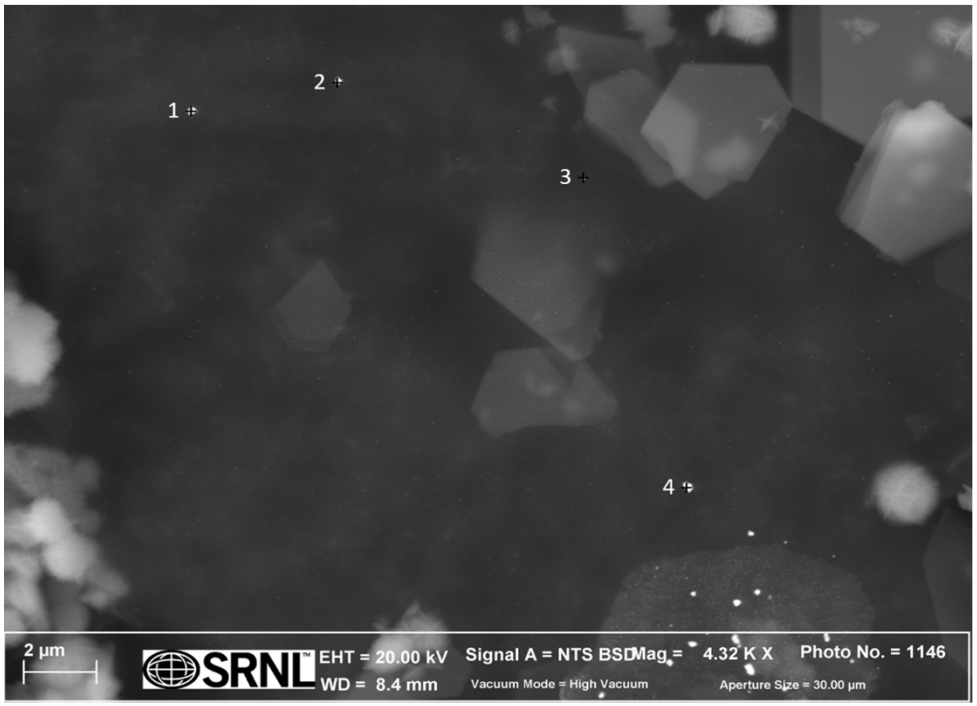




Hg Phase: Saltstone Exposed to 500 mg/L MHg Simulated Salt Solution

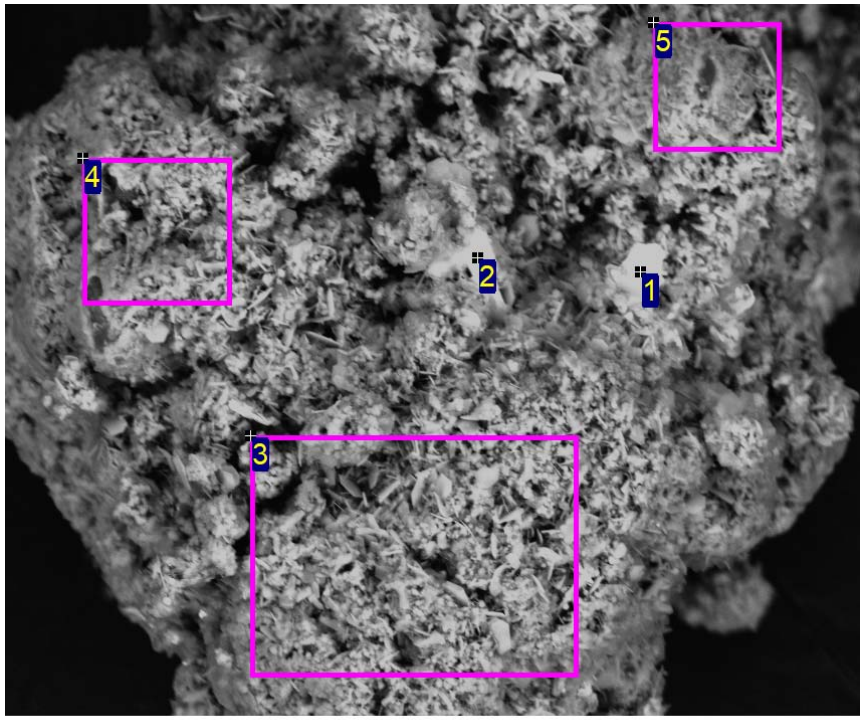


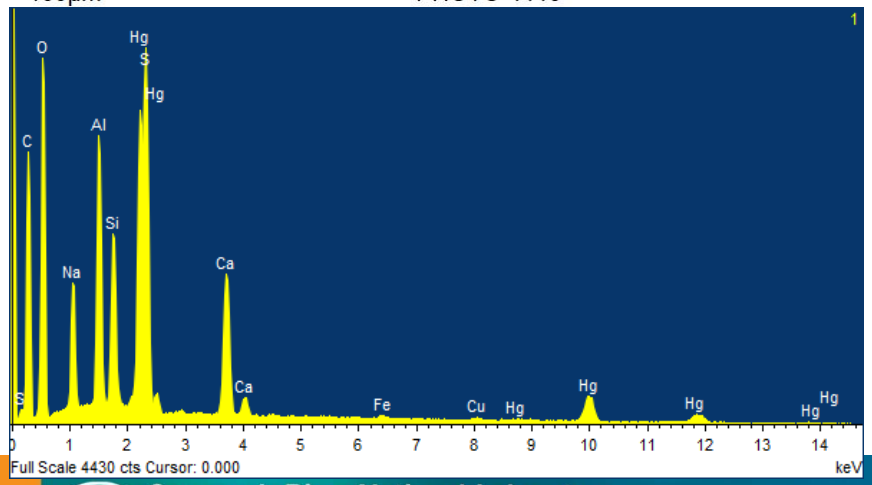
Spectrum	O	Na	Al	Si	S	Ca	Hg
Spot	Atomic %						
1	78.52		1.73	1.02	**9.53**		**9.21**



Spectrum	O	Na	Al	Si	S	Ca	Hg
1	73.74		1.46		**12.95**		**11.85**
2	74.02				**13.51**		**12.47**
3	65.44		10.7	2.1	**2.32**	17.0	**2.52**
4	72.58		0.9	0.5	**14.16**		**11.86**

Hg Phase: Saltstone Exposed to 500 mg/L MHg Simulated Salt Solution





Objective: Hg Speciation

Test: Cure saltstone (28 days), crushed, sieved (0.30 to 0.45 mm fraction), then exposed to simulated salt Solution (5M Na) for 47 days. SEM/EDX was used to characterize Hg phases.

Results:

- Large (µm) and small (nm) particles containing **Hg : S ≈ 1 : 1 atomic %**

Possible Hg Reaction Pathways (others possible)

(1) $CH_3Hg(OH) + S^{2-} \rightarrow HgS + CH_4 + ½O_2$

(2) $CH_3Hg(OH) + S^{2-} \rightarrow HgS + CH_4O$

(3) $2CH_3Hg(OH) \rightarrow 2CH_3Hg^+ + 2OH^-$

$2CH_3^{\cdot} + 2Hg^+$

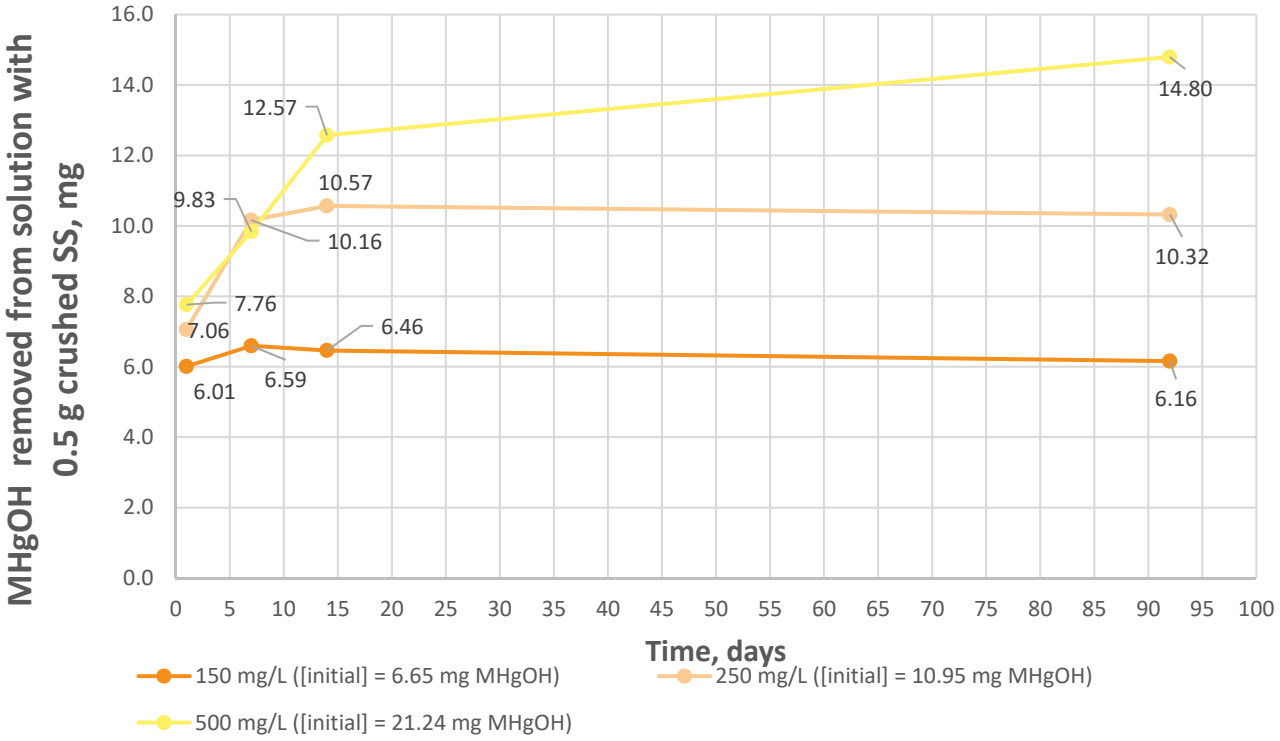
S^- from slag rxn: $+ S^-$, $+ 2S^-$

$(CH_3)_2S$ dimethylsulfide

$2HgS$ Hg sulfide

MeHgOH liquid-Solids partitioning

(Mass of MHgOH removed from solution per 0.5 g crushed SS premix)



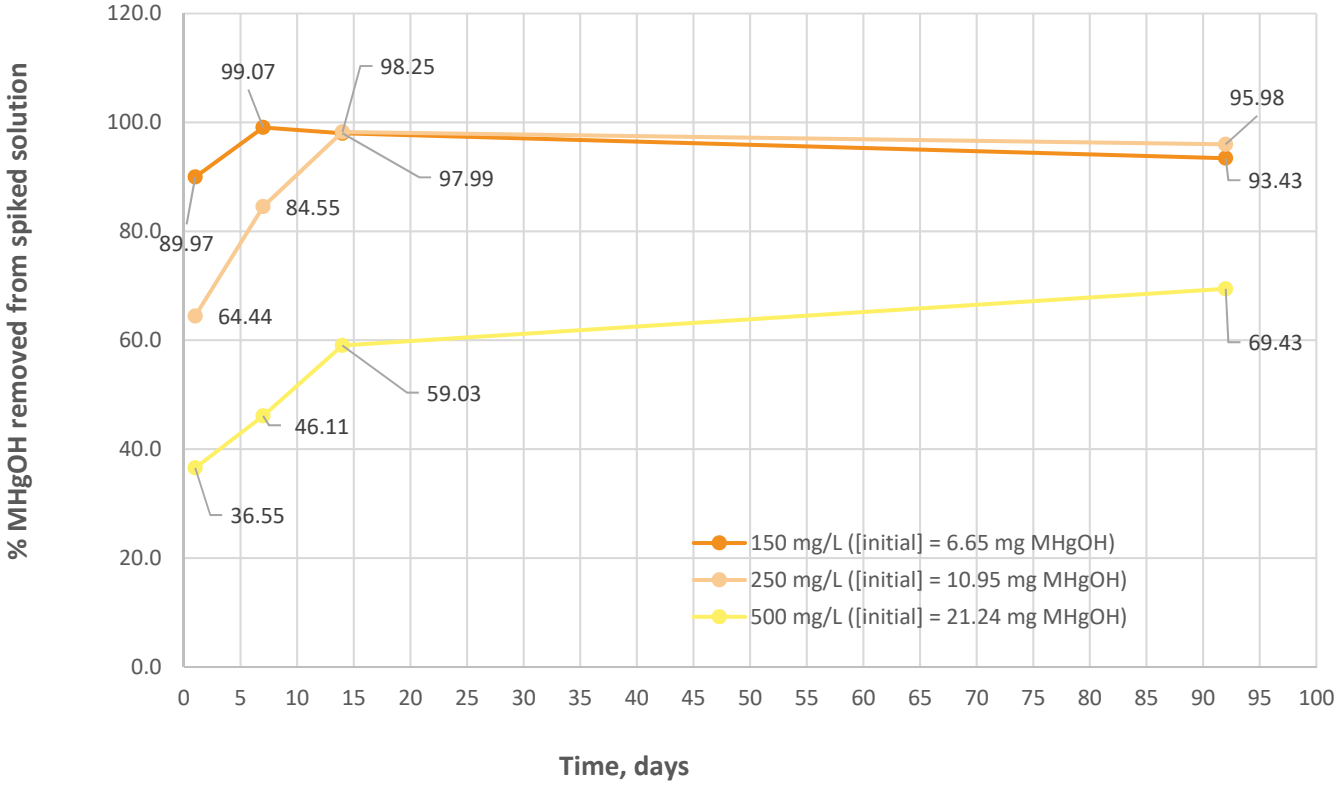
Objective: Estimate how fast MeHgOH is removed from salt solution by SS premix

Result: The removal of MeHgOH from salt solution by SS premix is rapid

- > 90% of the MeHgOH is removed from the 150 and 250 mg/L spiked solutions within 24 hours.
- Slower for the 500 mg/L solutions
- More than 99% removed after 7-14 days of contact.

Time, Days	150 mg/L ([initial] = 6.65 mg MHgOH)	250 mg/L ([initial] = 10.95 mg MHgOH)	500 mg/L ([initial] = 21.24 mg MHgOH)
1	6.01	7.06	7.76
7	6.59	10.16	9.83
14	6.46	10.57	12.57
92	6.16	10.32	14.80

MeHgOH liquid-Solids portioning. Cont.



Summary

- **Tank 50 WAC = 325 mg/L Hg**
- **1Q18 Tank 50 Sample**
  - Tank 50 salt solution Hg (total) = 72 mg/L, MHg = 37 mg/L
- **1Q18 TCLP**
  - Hg only 3.4X below limit for - 3/8 to + 5/16 particle size fraction
- **Slag source used to make TCLP sample at SRNL was updated. New slag supplier**
- **Experimental Findings**
  - Total Hg concentration 216 mg/L total Hg as MHg (250 mg/L MHg) in simulated Saltstone borderline fails TCLP for -3/8 inch size fraction including fines
  - MHg reacts with S in Saltstone
    - SEM images EDX atomic % (Hg : S ≈ 1:1)
    - XRD βHgS, metacinnabar

HgS particles formed by exposing saltstone to salt solution spiked with 500 mg/L MHg

Follow on Work

- Additional testing to understand and enhance Hg stabilization. Goal 100 % insoluble HgS
- Determine fate of CH_3
- Provide input to Tank 50 WAC for organic Hg

Acknowledgement

This work was funded **by DOE-EM Technology Development TCR 2.3.6: Develop organomercury based WAC for grout materials** to understand the chemical reactions between organic mercury and saltstone reagents and to identify the mechanisms for stabilization in the resulting waste form.

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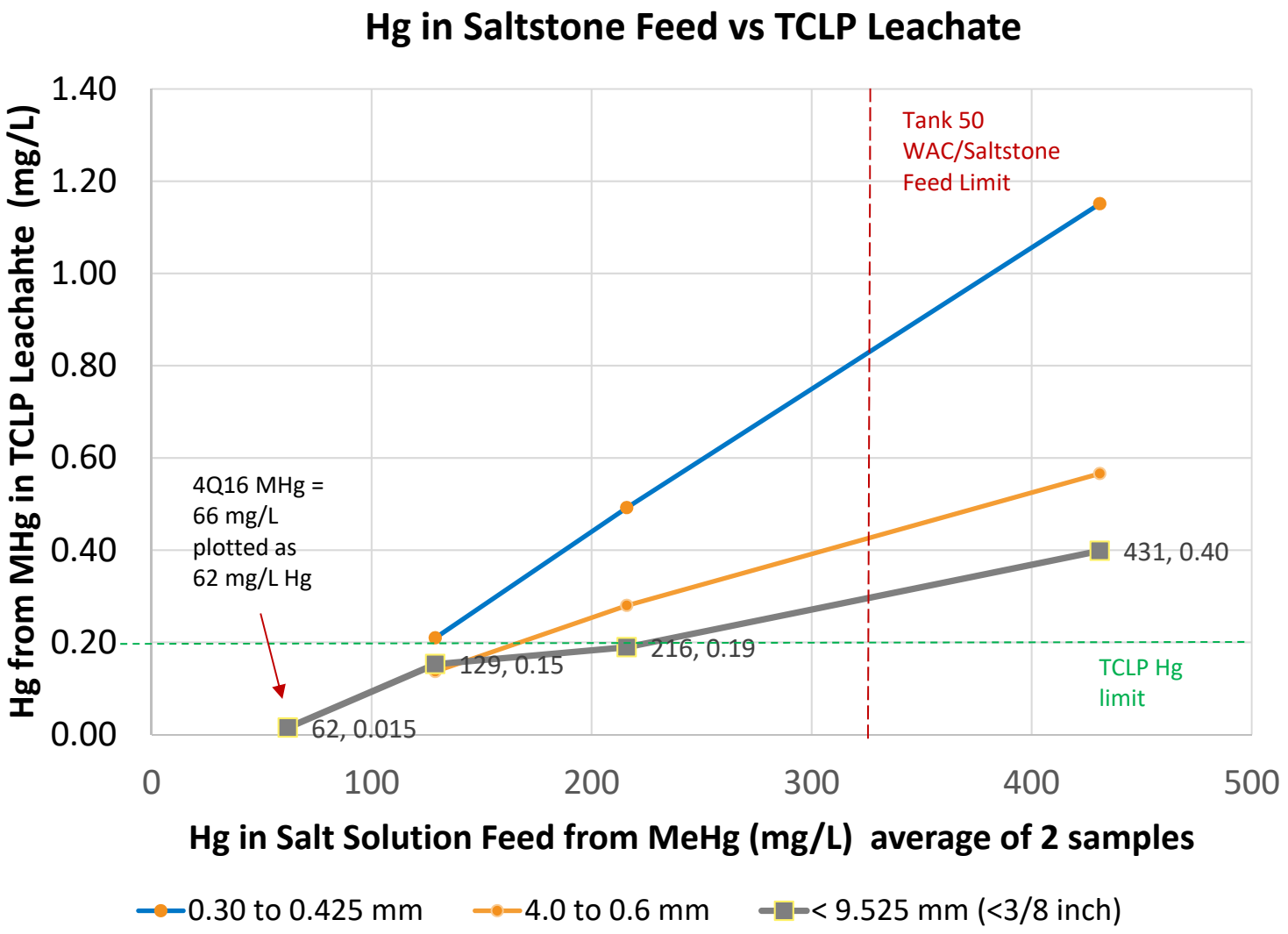
TCLP Results Versus MHg in Saltstone Feed (reported as Hg)

Graph Assumption: Organic Hg is much more extractable than other forms of Hg



Summary (continued)

- **Current Tank 50 WAC = 325 mg/L Hg**
- **Recommended WAC 150 mg/L Hg to satisfy TCLP of 0.2 mg/L Total Hg; irrespective of size fraction and mercury species**
- **MeHg reacts with S in Saltstone to produce nanoparticles of metacinnabar (HgS)**
- **Fate of methyl group needs to be confirmed**
- **Incomplete reaction of MeHg+ to form HgS + organic is not understood and has consequences for organic Hg stabilization and Saltstone WAC**
- **Enhanced stabilization of Hg in addition to HgS precipitation should be evaluated**

Path Forward

- We are in the discovery phase of this study
- Additional testing required to understand and enhance Hg speciation and stabilization and TCLP results using direct Tank 50 low level radioactive supernatant liquids.
- Phase 2 Testing
  - Lower [MHg] and refined size fraction (TCLP)
  - Mixed inorganic and MHg (TCLP)
  - Tank 50 solution
  - Reaction products resulting in HgS formation
  - Binding and release mechanisms
    - Solubility of HgS formed in Saltstone
  - Slag properties that affect stabilization of MHg
  - Apply results to Tank 50 WAC
  - MeHg binding and performance (TCLP) in Saltstone grout

    Mixed inorganic/MlHg

    Actual tank waste

TCLP Sample Preparation

- Three saltstone particle size fractions (0.3 to 0.42 mm, 0.4 to 0.6 mm and <0.952 mm (<3/8”)) were tested to (1) evaluated surface area effect on Hg stabilization, (2) understand potential vulnerability for exceeding the 0.2 mg/L TCLP limit for Hg (3) provide indicator of stabilization mechanism