Understanding the Suspended Solids in the Inland Empire Brine Line

SAWPA Workshop
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Presentation Overview

• Review Previous Workshop Findings
• Current Solids Characterization
• Historical Data Analysis
• Next Steps
PREVIOUS WORKSHOP REVIEW
Back in September

- Directly measured POC (two samples)
  - Suggested more organics than previously observed by indirect measurements (TOC – DOC)
- Characterized crystalline structures of inorganics (XRD + ICP)
  - Amorphous Calcium Phosphate (ACP) & Calcite
  - Bulk of inorganics
- Large fraction of VSS remained unknown
  - Water?
  - Ratio of TOC to organic solids?
  - Other inorganic volatilization?
Estimate of Solids Breakdown

- nVSS (50%)
- VSS (50%)

Applies only to September TT Samples
Estimate of Solids Breakdown

Applies only to September TT Samples

- Calcite and ACP (44%)
- Biological Organic Matter* (20%)
- Unknown VSS (30%)
- Other inorganics (6%)

* Assumes BOM = 2 x POC
Next Steps from September

• Continue to quantify the solids make-up
  – Two months of sampling to improve understanding of variability in solids over time
  – XRD, ICP, TSS/VSS, optimize POC measurements

• Explain more of unknown fractions
  – Unknown nVSS ➔ SEM-EDX
  – Unknown VSS ➔ TGA and organics characterization

• Characterization of the organics
  – FTIR, EEM, HPC, fluorescence microscopy
CHARACTERIZATION OF SOLIDS TODAY
Overview of analyses

Brine Line Solids at County Line

Inorganic analyses
1. Mineral composition (XRD)
2. Elemental composition (ICP, EDX)
3. Waters of hydration (TGA)

Organic analysis
1. Estimate organic contribution from indirect and direct POC measurements
2. Organic matter characterization (TGA, FTIR, EEM)
3. Biological characterization (HPC, fluorescence microscopy)

Other analyses

Solids Analysis
1. TSS/VSS

Solids Analysis

Other analyses
DETERMINING THE MAKEUP OF THE INORGANICS
Elemental analyses verifies predominance of Ca.

- **Elemental Analysis:**
  - Babcock & MWH: ICP of redissolved solids
  - Camet Labs: EDX of solids

- **Conclusions:**
  - Ca is predominant mineral
  - P is high
  - Si is also significant

<table>
<thead>
<tr>
<th></th>
<th>EDX % of mass</th>
<th>ICP g/Kg</th>
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<tbody>
<tr>
<td>Ca</td>
<td>62.2%</td>
<td>125</td>
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<tr>
<td>P</td>
<td>15.1%</td>
<td>50</td>
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<tr>
<td>Si</td>
<td>9.4%</td>
<td>25</td>
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<td>Fe</td>
<td>3.8%</td>
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<tr>
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<tr>
<td>Mg</td>
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<tr>
<td>S</td>
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</tr>
<tr>
<td>K</td>
<td>1.1%</td>
<td>3</td>
</tr>
<tr>
<td>Na</td>
<td>0.7%</td>
<td>8</td>
</tr>
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</table>
Mineral Identification: X-Ray Diffraction (XRD)

- Identifies samples based on their crystalline structure

Previous results:
- \( \text{CaCO}_3 + \) amorphous calcium phosphate (ACP) = ~80-90% of minerals
- \( \text{SiO}_2 \) (1-2%)
Example of recent XRD result

(Camet Labs)

1. Trussell Technologies: "brine sludge" received 11-18-11
2. X-ray powder diffraction
3. CAMET XRD 11-28-11
4. Cu Kα radiation
5. Fixed slits
6. Calcined at 550°C in air
7. D-SiO₂: alpha-quartz
8. Ca₅(PO₄)₃(OH): hydroxylapatite
9. CaCO₃: calcite
10. α-SiO₂: alpha-quartz
Findings:
• 5 additional rounds of XRD show consistent results
• Only 3 mineral species found:
  • Calcite (CaCO$_3$)
  • ACP/hydroxyapatite [Ca$_5$(PO$_4$)$_3$OH]
  • Quartz

Conclusions:
• Calcium minerals are the dominant inorganic fraction
XRD shows calcium minerals dominate

- Next question: *how much* is present?
  - XRD: only semi-quantitative info on mineral fraction

- 2-step process

  1. Elemental Analysis (ICP, SEM-EDX)
  2. Mineral Analysis (XRD)

Maximum Mineral Fraction (Calculated)

- Calcite: 45%
- ACP: 37%
- SiO2: 12%
Inorganics - Summary

- Conclusions: same answer as last time
- Ca + Si minerals: >90% of nVSS (41 of 45%)
DETERMINING THE AMOUNT AND COMPOSITION OF ORGANICS
What is the organic material?

- Biological organic matter?
  - Initial hypothesis for solids formed in line

- Testing for presence of biological material
  - Bacterial cell culture: heterotrophic plate counts (HPC)
  - Fluorescence microscopy
  - Chemical analyses: Fourier-transform infrared analysis (FTIR), excitation-emission matrix (EEM)
  - Physical assays: thermogravimetric analysis (TGA)
HPC suggests low biological content

• Culturable heterotrophs account for ~0.3% of the TSS mass

• Limitations of HPC:
  – Only measures culturable heterotrophs
  – Selects for certain bacterial types over others (aerobic vs. anaerobic)
Microscopy supports low biological estimates

• Method: microscopic analysis of live/dead bacteria
  – Green dye: living bacteria
  – Red dye: dead bacteria
Microscopy supports low biological estimates

- Method: microscopic analysis of live/dead bacteria
  - Green dye: living bacteria
  - Red dye: dead bacteria

Mass concentration of bacteria still small (~1%)  
(note: based on one sampling date)
Chemical analyses support biological estimates

- **FTIR (Fourier-Transfer Infrared) Results**
  - Low bio content based on comparison with biological control
  - Side note: potential match with fossil material (CaCO$_3$ and HA)?

- **Excitation-emission matrix (EEM) results**
  - SAWPA solids show *different profile* than biological control
If it’s not biological organic matter, then what is it?
Thermogravimetric Analysis (TGA)

Continuous measurement of mass change with temp

LOI 100°C: 3.7%
LOI 200°C: 6.5%
LOI 300°C: 30.9%
LOI 450°C: 9.2%
LOI 550°C: 5.6%
LOI 650°C: 1.1%
LOI 700°C to 950°C: 3.9%

CaCO₃ \rightarrow CaO + CO₂
TGA suggests new organic candidate

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CaCO₃ → CaO + CO₂

232°C (451°F)
TGA suggests new organic candidate

The one major TGA spike suggests: cellulose or cellulosic material
Is cellulose a reasonable candidate?

- Visual inspection: Wet solids
Is cellulose a reasonable candidate?

- Dried solids
Is cellulose a reasonable candidate?

- Dried solids: A closer look
Is cellulose a reasonable candidate?

- Dried and ground solids
Is cellulose a reasonable candidate?

- Dried and ground solids: A closer look
Is cellulose a reasonable candidate?

- Dried and ground solids: A closer look

Cellulose hypothesis passes the visual inspection
Is cellulose a reasonable candidate?

• From the FTIR report:
  – Peak in all 3 SAWPA samples may indicate presence of “cellulose or other polymeric carbohydrate material…wood, paper, cellophane, and cellulose derivatives”
Is cellulose a reasonable candidate?

- Fluorescence Microscopy
  - Cellulose = blue
  - Live cells = green
  - Dead cells = red
Is cellulose a reasonable candidate?

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Is cellulose a reasonable candidate?

- Fluorescence Microscopy
  - Cellulose = blue
  - Live cells = green
  - Dead cells = red

*Cellulose or cellulosic material is present*
How much cellulose is there?

- **From TGA analysis**, we can quantify the amount of cellulosic material from the spike

**Cellulosic Material:**
Avg: 34% of TSS
4 samples: 31-37%

**Other VSS:**
Avg: 22% of TSS
4 samples: 19-23%
Organic Carbon Analysis

- What fraction of the solids is organic?
- Particulate organic carbon (POC) → organic matter
- Indirect POC
  - Measure raw sample (TOC)
  - Measure filtered liquid (DOC)
  - POC = TOC - DOC
- Direct POC
  - Measure the TOC of the suspended solids (POC = TOC_{ss})
- Previous results: Direct POC (TT) > Indirect POC
Limitation of OC Liquid Suspensions

Well-mixed suspension of brine line sample

TOC Sample Vial

Large particulates may settle or become clogged in instrument tubing: Need another method
Organic Carbon Analysis

Direct POC (Babcock soil instrument)
• Detects significantly more OC than direct POC (TT), indirect POC (TT, BL)
• Best method for POC measurement

Findings
• Significantly more OC in SAWPA solids than previously thought
• POC accounts for 23% of TSS (2 samples tested)
  – 2/3 is Cellulose; 1/3 is bio-organic matter
• Converting this to total mass
  – Cellulose = 34% of TSS (TGA) (assumes OC/SS = 44%)
  – Bio-organic matter = 13% of TSS (assumes OC/SS = 60%)
• Organic mass now explains most of VSS
Organics Summary

• Organic content higher than previously thought
• Most of organic mass is cellulose-like material
• Biological contribution is low: HPC, FTIR, microscopy, EEM
• Previous hypotheses:
  – Biological material
  – Organic precipitates
  – Organic particulates discharged into Brine Line
SUMMING IT ALL TOGETHER
INORGANICS + ORGANICS
Estimate of TSS Breakdown*

nVSS (45%)  VSS (55%)

nVSS = non-VSS = inorganic fraction
*Based on 6-sample avg. of TSS, VSS data
Add in what we learned about VSS
Putting It All Together

1. Calcium Minerals: 37%
2. Cellulose: 34%
3. Bio-Organsics: 13%
4. Silicates: 5%
5. Other nVSS: 3%
6. Water: 8%
UNDERSTANDING THE PROBLEM:
A LOOK AT HISTORICAL DATA
What goes into the Brine Line*

Breakdown by Flow

- Domestic WW (23%)
- Commercial WW (7%)
- Waste Haulers (<1%)

* Represents data from Aug 2010 to Aug 2011
What goes *into* the Brine Line*

Breakdown by Hardness

* Represents data from Aug 2010 to Aug 2011
What goes into the Brine Line*

Breakdown by TSS Load

- Commercial WW (12%)
- Brine Discharge (16%)
- Domestic WW (72%)

* Represents data from Aug 2010 to Aug 2011
What goes *into* the Brine Line*

Breakdown By Suspended Solids Source

- nVSS (27%)
- VSS (73%)

* Represents data from Aug 2010 to Aug 2011
What goes *into* the Brine Line*

* Represents data from Aug 2010 to Aug 2011

Breakdown By Suspended Solids Source

- Domestic VSS (63%)
- Commerical VSS (8%)
- Domestic nVSS (14%)
- Commerical nVSS (5%)
- Brine VSS (3%)

* Represents data from Aug 2010 to Aug 2011
What comes out of the Brine Line*

Discharged nVSS (8%)

Discharged VSS (23%)

Extra* nVSS (27%)

Extra* VSS (42%)

Note: Change in VSS/TSS from 73% to 65%

*Extra is the difference between County Line and sum of all dischargers

* Represents data from Aug 2010 to Aug 2011
Current Estimate of Solids Breakdown

- Calcium Minerals: 37%
- Cellulose: 34%
- Bio-Organoics: 13%
- Silicates: 5%
- Other nVSS: 3%
- Water: 8%
What can be done to control solids formation?

- **Cellulose**: mostly inert and not likely to form in the line
- **Biological organic matter**: control options not feasible
- **Calcite & ACP**: changes in pH may help control formation
- **Data**: Possibility for increasing data accuracy by increasing collection frequency
NEXT STEPS
Next Steps: Solids Formation Control

1. Assess pH Reduction Strategy
   a. Conduct Survey of discharger practice
      1) pH before/after adjustment
      2) Caustic use
   b. Conduct Bench-scale study
      1) Solids @ Co. line,
      2) Upstream blends
   c. Assess potential

2. Continue *special* direct POC measurements, include discharger survey

3. Continue *routine* TOC and Ca measurements for dischargers