An Investigation of Separable Organics for the Hanford Tank Waste Pre-Treatment

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Washington River Protection Solutions
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Wastes in Double-Shell Tank Transfer to Pre-Treatment Plant at Waste Treatment Plant (WTP)
Generic Schematic Diagram of Double-Shell Tank

- 49 ft height
- 40 ft diameter
- 37.5 ft diameter
- 1 Million Gallon Capacity
Background

• **Separable Organics:**
  • Tributyl phosphate (TBP)
  • Normal paraffin hydrocarbon (NPH): mineral oil
  • Di (2-ethylhexyl) phosphoric acid

• An organic layer in the wastes is **not acceptable** for Pre-Treatment Plant.
• Observed an organic layer in Single Shell Tanks wastes, e.g., 241-C-204.
• Wastes in C-204 have been retrieved and transferred to AN-106.
• Not well understood the fate of separable organics in the wastes
  • bound to the inorganic solids waste?
  • form a separable layer after being **mixed** and pumped into Pre-treatment Facility?
Scope of Archive Tank Sample Study

To test the formation of a separable organic layer on archive tank samples.
Can an Organic Layer Form after Mixing Tank Solids Samples with Aqueous Solution?

• **Transferred** ~4 – 15 g archive tank solids samples to cones
• **Weighed** and **mixed** with simulated supernate (AN-106)
  • Aliquots for particle size distribution
• **Centrifuged** 30 min at maximum speed, 15 min intervals
• **Observed** formation of a separable layer
  • Aliquot top layer for semi-volatile organic analysis (SVOA) and total organic carbon (TOC)
Archive Tank Samples
Centrifuged 30 min at Maximum Speed

C-204  AY-102  AY-102  AW-105
Archive Tank Samples 241-SY-102
Centrifuged 30 min at Maximum Speed
Total Organic Carbon (TOC) and Tributyl Phosphate (TBP) in Archive Tank Samples and in Organic Layer from Archive Tank Samples

C-204
- TOC: 39.5 mg/g (TWINS)
- TOC: 10.6 mg/g
- TBP: 3.48 mg/g

SY-102
- TOC: ~2 – 25 mg/g (TWINS)
- TOC: 1.67 mg/g
- TBP: < detection limit

AY-102
- TOC: ~5 mg/g (TWINS)
- TOC: < 0.17 mg/g
- TBP: < detection limit
- TBP: Not Detected

AY-102
- TOC: ~5 mg/g (TWINS)
- TOC: 0.29 mg/g
Does Centrifugation Have an Impact on Formation of a Separable Organic Layer on Archive Tank Samples?

• Attempted to measure RPM in hot cell using a tachometer
• **Selected** four archive tank samples
• **Transferred** ~6 – 11 g, **weighed** and **mixed** with simulated supernate
• **Allowed** to settle, 5 days
• **Centrifuged** at three different speeds
  • 10%, 20%, 50% of the maximum speed
• **Observed** formation of a separable layer
Comparison of Centrifuge Speeds
Tank 241-C-204

- Not Centrifuged
- 10% of Max Speed
- 20% of Max Speed
- 50% of Max Speed
- Max Speed
Scope of Simulated Solids Study

• To establish methods to retain separable organics on simulated tank solids
• To test formation of a separable organic layer from the simulated solids that retained organics
• To test factors that could have impact on formation of a separable organic layer
Simulated Solids Studies
Retain Organic Solvent in Simulated Solids

Four Simulated Solids:

• C31C-F: 61% Aluminum Hydroxide (C31C) and 39% Ferric Oxide
• C33-F: 61% Aluminum Hydroxide (C33) and 39% Ferric Oxide
• C31C-G: 61% Aluminum Hydroxide (C31C) and 39% Goethite
• C33-G: 61% Aluminum Hydroxide (C33) and 39% Goethite

Ferric Oxide: Fe$_2$O$_3$
Goethite: Fe(O)OH
Simulated Supernate and Organic Solvents
Retain Organic Solvent in Simulated Solids

• One Simulated Supernate (AN-106):
  • 0.45M NaNO₃, 0.39M NaNO₂, 0.34M Na₂CO₃, and 1 M NaOH

• Separable Organics:
  • Mineral Oil (NPH)
  • TBP
  • Di (2-ethylhexyl) Phosphoric Acid (D2EHPA)
  • TBP + Hydraulic Fluid
  • TBP + Mineral Oil
Method to Retain Organics on Solids

- **Weighed** and **mixed** equal volume of simulated solids, simulated supernate, and organic solvent. Positive control: activated charcoal
- **Tumbled** for a period of time (e.g., ~24 hr or ~48 hr) or by **filtration**
- **Separated** and **weighed** each phase, i.e., organic solvent, simulated supernate, and simulated solids
- **Added** simulated supernate to the **collected simulated solids**, then either **mixed** or **vortexed**
- **Centrifuged** (3000 RPM); then observed for a separable organic layer, or
- **Allowed** to settle, then **centrifuged** 10 min at 1000 RPM, 2000 RPM, and 3000 RPM; then observed for a separable organic layer
Mineral Oil (NPH)
Mixed with Simulated Supernate and Simulated Solids and Tumbled 24 hr
Mineral Oil (NPH)
Mixed with Simulated Supernate and Simulated Solids and Tumbled 24 hr

Charcoal  C31C-G  C33-G  Blank
Collected Mineral Oil and Simulated Supernate

Charcoal  C31C-F  C-33-F  Blank
Collected Mineral Oil and Simulated Supernate

Charcoal  C31C-G  C33-G  Blank
Collected Simulated Solids
Separated from Mineral Oil and Simulated Supernate

Charcoal  C31C-F  C33-F  Blank
Collected Simulated Solids
Separated from Mineral Oil and Simulated Supernate

Charcoal  C31C-G  C33-G  Blank
**Mineral Oil - Not Centrifuged**

Simulated Solids in Simulated Supernate, Mixed or Vortexed, and Allowed to Settle, 4 Days

Tubes #3, #5, #10, and #12 were vortexed.
Mineral Oil - Centrifuged at 1000 RPM, 10 min
Mineral Oil - Centrifuged at 2000 RPM, 10 min
Mineral Oil - Centrifuged at 3000 RPM, 10 min

C31C-F
C33-F
C31C-G
C33-G
Mineral Oil - Activated Charcoal

Simulated Solids in Simulated Supernate, Mixed or Vortexed, and Allowed to Settle, 4 Days

Tube #1 was vortexed

- Not centrifuged
- 1000 RPM
- 2000 RPM
- 3000 RPM
Tributyl Phosphate
Mixed with Simulated Solids and Simulated Supernate and Tumbled ~48 hr
TBP - Simulated Solids in Simulated Supernate

Simulated Solids in Simulated Supernate, Mixed or Vortexed, and Centrifuged at 3000 RPM

Tubes #1, #3, and #5 were vortexed

Charcoal

C31C-F

C33-F
Di (2-ethylhexyl) Phosphoric Acid
Mixed with Simulated Solids and Simulated Supernate and Tumbled ~20 hr

Charcoal  C31C-F  C33-F  Blank
Di (2-ethylhexyl) Phosphoric Acid
Mixed with Simulated Solids and Simulated Supernate and Tumbled ~20 hr
Di (2-ethylhexyl) Phosphoric Acid
Simulated Solids in Simulated Supernate
90% TBP and 10% Hydraulic Fluid (Top)
Simulated Solids in Simulated Supernate, Mixed or Vortexed, and Centrifuged at 3000 RPM (Bottom)
Tubes #1, #3, #5 were vortexed (Bottom)
## Weights of Solids, Simulated Supernate, and Mineral Oil Used and Collected (by Tumbling)

<table>
<thead>
<tr>
<th></th>
<th>Charcoal</th>
<th>C31C-F</th>
<th>C33-F</th>
<th>C31C-G</th>
<th>C33-G</th>
<th>Blank¹</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Mean ± SD n=</strong></td>
<td>4</td>
<td>5</td>
<td>5</td>
<td>2</td>
<td>2</td>
<td>2</td>
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<tr>
<td><strong>Sample Weight, g</strong></td>
<td>7.42 ± 0.21</td>
<td>16.84 ± 0.19</td>
<td>16.91 ± 0.99</td>
<td>8.94 ± 0.05</td>
<td>8.96 ± 0.18</td>
<td>17.08 ± 0.19</td>
</tr>
<tr>
<td><strong>Simulated Supernate Used, g</strong></td>
<td>25.83 ± 0.79</td>
<td>26.18 ± 0.51</td>
<td>26.34 ± 0.31</td>
<td>30.06 ± 0.52</td>
<td>29.98 ± 0.16</td>
<td>16.29 ± 0.52</td>
</tr>
<tr>
<td><strong>Organic Solvent Used, g</strong></td>
<td>13.69 ± 0.69</td>
<td>12.91 ± 0.28</td>
<td>13.33 ± 0.28</td>
<td>12.42 ± 0.44</td>
<td>13.17 ± 0.01</td>
<td>12.93 ± 0.22</td>
</tr>
<tr>
<td><strong>Collected S. Supernate, g</strong></td>
<td>16.41 ± 1.20</td>
<td>19.86 ± 1.26</td>
<td>19.25 ± 1.64</td>
<td>8.64 ± 0.96</td>
<td>8.33 ± 0.94</td>
<td>33.16 ± 0.50</td>
</tr>
<tr>
<td><strong>Collected Solvent, g</strong></td>
<td>10.64 ± 1.36</td>
<td>12.10 ± 0.44</td>
<td>12.06 ± 1.37</td>
<td>12.07 ± 0.96</td>
<td>11.94 ± 0.94</td>
<td>12.83 ± 0.44</td>
</tr>
<tr>
<td><strong>Collected Solids, g</strong></td>
<td>19.94 ± 1.42</td>
<td>23.87 ± 1.44</td>
<td>25.22 ± 2.33</td>
<td>30.68 ± 0.50</td>
<td>31.83 ± 0.70</td>
<td>0.28 ± 0.09</td>
</tr>
<tr>
<td><strong>Solvent Retained in solids, g</strong></td>
<td>3.21 ± 1.04</td>
<td>0.81 ± 0.23</td>
<td>1.26 ± 1.11</td>
<td>0.36 ± 0.52</td>
<td>1.23 ± 0.95</td>
<td>0.11 ± 0.22</td>
</tr>
</tbody>
</table>

1. Blank - Simulated supernate was used  
   n: Number of observation  
   SD: standard deviation  
   g: gram
### Weights of Solids, Simulated Supernate, and Tributyl Phosphate Used and Collected (by Tumbling)

<table>
<thead>
<tr>
<th></th>
<th>Charcoal</th>
<th>C31C-F</th>
<th>C33-F</th>
<th>C31C-G</th>
<th>C33-G</th>
<th>Blank&lt;sup&gt;1&lt;/sup&gt;</th>
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</thead>
<tbody>
<tr>
<td><strong>Mean ± SD</strong></td>
<td>n=4</td>
<td>n=5</td>
<td>n=5</td>
<td>n=5</td>
<td>n=5</td>
<td>n=2</td>
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<td><strong>Sample Weight, g</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Sample Weight, g</td>
<td>7.16 ± 0.11</td>
<td>15.84 ± 0.51</td>
<td>15.91 ± 0.80</td>
<td>na</td>
<td>na</td>
<td>16.68 ± 0.05</td>
</tr>
<tr>
<td><strong>Simulated Supernate Used, g</strong></td>
<td>25.46 ± 0.64</td>
<td>26.46 ± 0.45</td>
<td>26.26 ± 0.77</td>
<td>na</td>
<td>na</td>
<td>16.65 ± 0.05</td>
</tr>
<tr>
<td><strong>Organic Solvent Used, g</strong></td>
<td>15.62 ± 0.41</td>
<td>14.79 ± 0.43</td>
<td>14.78 ± 0.49</td>
<td>na</td>
<td>na</td>
<td>14.68 ± 0.06</td>
</tr>
<tr>
<td><strong>Collected S. Supernate, g</strong></td>
<td>17.23 ± 1.19</td>
<td>18.45 ± 2.26</td>
<td>18.76 ± 1.31</td>
<td>na</td>
<td>na</td>
<td>15.29</td>
</tr>
<tr>
<td><strong>Collected Solvent, g</strong></td>
<td>10.14 ± 0.54</td>
<td>14.69 ± 0.26</td>
<td>14.55 ± 0.83</td>
<td>na</td>
<td>na</td>
<td>15.17</td>
</tr>
<tr>
<td><strong>Collected Solids, g</strong></td>
<td>20.60 ± 0.33</td>
<td>23.49 ± 2.41</td>
<td>23.12 ± 2.09</td>
<td>na</td>
<td>na</td>
<td>17.33</td>
</tr>
<tr>
<td><strong>Solvent Retained in solids, g</strong></td>
<td>5.48 ± 0.72</td>
<td>0.10 ± 0.39</td>
<td>0.23 ± 0.63</td>
<td>na</td>
<td>na</td>
<td>-0.45</td>
</tr>
</tbody>
</table>

1. Blank - Simulated supernate was used  
   n: Number of observation  
   g: gram  
   SD: standard deviation
Weights of Solids, Simulated Supernate, TBP, and Mineral Oil Used and Collected (15 mL Sample Size & By Filtration)

<table>
<thead>
<tr>
<th></th>
<th>Mean ± SD</th>
<th>Charcoal (2 mL TBP + 3 mL Mineral Oil)</th>
<th>C33-G (5mL TBP)</th>
<th>C33-G (2mL TBP + 3 mL Mineral Oil)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Sample Weight, g</td>
<td>7.29 ± 0.21</td>
<td>10.36 ± 0.52</td>
<td>10.21 ± 0.09</td>
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</tr>
<tr>
<td>Simulated Supernate Used, g</td>
<td>27.86 ± 0.41</td>
<td>28.11 ± 0.19</td>
<td>27.72 ± 0.14</td>
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</tr>
<tr>
<td>Organic Solvent Used, g</td>
<td>4.87 ± 0.19</td>
<td>5.02 ± 0.52</td>
<td>4.77 ± 0.61</td>
<td></td>
</tr>
<tr>
<td>Collected S. Supernate, g</td>
<td>23.85 ± 1.52</td>
<td>20.30 ± 1.51</td>
<td>22.22 ± 0.99</td>
<td></td>
</tr>
<tr>
<td>Collected Solvent, g</td>
<td>0</td>
<td>4.02 ± 0.68</td>
<td>3.67 ± 0.38</td>
<td></td>
</tr>
<tr>
<td>Collected Solids, g</td>
<td>14.99 ± 1.03</td>
<td>15.41 ± 0.56</td>
<td>15.04 ± 0.22</td>
<td></td>
</tr>
<tr>
<td>Solvent Retained in solids, g</td>
<td>4.87 ± 0.19</td>
<td>1.01 ± 0.25</td>
<td>1.10 ± 0.26</td>
<td></td>
</tr>
</tbody>
</table>

TBP: Tributyl phosphate  g: gram  SD: Standard deviation
Percent of Retained Solvent in Solids Relative to Spiked

![Graph showing percent of retained solvent in solids relative to spiked.](image-url)

- **Charcoal**: Mineral Oil (MO)
- **C31C-F**: TBP
- **C33-F**: TBP-Hydraulic
- **C31C-G**: TBP - Filtration
- **C33-G**: TBP-MO Filtration
Summary

• Successfully retained solvent in the simulated solids.
  • By mixing (tumble with supernate and solvent) and by filtration.
  • Percent of organics retained in simulated solids.

• Separable organics retained in the simulated solids can form an organic layer.
  • Simulated solids: aluminum hydroxide & ferric oxide and/or goethite.
  • Mineral oil, TBP, and mixtures of 90% TBP & 10% hydraulic fluid or 40% TBP & 60% mineral oil.
  • Di (2-ethylhexl) phosphoric acid also appears to form an organic layer.
  • Density and concentration.

• A separable layer was observed in archive tank waste sample after mixing with simulated supernate (without and with centrifugation).
  • Archive tank sample came from tanks that had received separable organics (e.g., TBP, NPH).

• This raises a challenge as one of the pre-treatment facility acceptance criteria requires that no organic layer exist.
Acknowledgements

Archive Tank Samples: Liem Dinh and Tony Valero
Hot Cell Support: Mike Purcell from Advanced Technologies and Laboratories International, Inc., and staff in hot cell

Dr. Jason Page, SEM-EDS

Technical Review: Gary Cooke and Dr. Dan Herting
Project Support: Bryce Eaton, Karen Sanders, John Trechter, Jr., & Doug Kraft
Dr. Ridha Mabrouki

Particle Size Analyzer
Alex Pappas
Thanks
Questions?
Weights of Solids, Simulated Supernate, TBP, and Hydraulic Fluid Used and Collected (10 mL & by Tumbling)

<table>
<thead>
<tr>
<th></th>
<th>Charcoal</th>
<th>C31C-F</th>
<th>C33-F</th>
<th>C31C-G</th>
<th>C33-G</th>
<th>Blank$^1$</th>
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<td>n=1</td>
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<tr>
<td><strong>Sample Weight, g</strong></td>
<td>4.83</td>
<td>11.89</td>
<td>10.58</td>
<td>6.27</td>
<td>6.03</td>
<td>11.27</td>
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<tr>
<td></td>
<td>0.06</td>
<td>0.11</td>
<td>0.20</td>
<td>0.11</td>
<td>0.01</td>
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<tr>
<td><strong>Simulated Supernate Used, g</strong></td>
<td>16.21</td>
<td>17.33</td>
<td>18.30</td>
<td>19.67</td>
<td>20.09</td>
<td>11.27</td>
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<td></td>
<td>0.3</td>
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<td>0.14</td>
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<tr>
<td></td>
<td>0.69</td>
<td>0.15</td>
<td>0.44</td>
<td>0.15</td>
<td>0.19</td>
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<tr>
<td><strong>Collected S. Supernate, g</strong></td>
<td>9.39</td>
<td>6.49</td>
<td>14.76</td>
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<tr>
<td><strong>Collected Solvent, g</strong></td>
<td>6.40</td>
<td>6.13</td>
<td>1.96</td>
<td>7.49</td>
<td>5.88</td>
<td>12.73</td>
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<td>1.15</td>
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<td><strong>Collected Solids, g</strong></td>
<td>15.04</td>
<td>25.88</td>
<td>21.69</td>
<td>21.02</td>
<td>22.08</td>
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<td></td>
<td>0.38</td>
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<td>0.18</td>
<td>0.82</td>
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</tr>
<tr>
<td><strong>Solvent Retained in solids, g</strong></td>
<td>3.58</td>
<td>3.29</td>
<td>7.61</td>
<td>1.96</td>
<td>3.64</td>
<td>-3.28</td>
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<tr>
<td></td>
<td>0.54</td>
<td>0.59</td>
<td>1.72</td>
<td>0.29</td>
<td>1.34</td>
<td></td>
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</tbody>
</table>

1. Blank - Simulated supernate was used  
   n: Number of observation  
   g: gram  
   SD: standard deviation
TBP & Mineral Oil - Not Centrifuged
Simulated Solids in Simulated Supernate and Allowed to Settle
TBP & Mineral Oil - Centrifuged at 3000 RPM, 10 min
Simulated Solids in Simulated Supernate and Allowed to Settle