Development & Testing of the Decontamination Effluent Treatment System

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US Army Engineer Research and Development Center, Vicksburg, MS
Engineer Research and Development Center (ERDC)

2500 Employees

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Geospatial Research Laboratory
Coastal & Hydraulics Laboratory
Environmental Laboratory
Geotechnical & Structures Laboratory
Information Technology Laboratory

Field Offices
Laboratories
Problem

The Army has no capability to treat and/or recycle the effluent from its aqueous based chemical, biological, radiological and nuclear (CBRN) decontamination operations. This effluent is still very hazardous and a major handling, logistical, and potentially a political burden.
Simulant Selection

Composition of CBRN Decontamination Effluent and Development of Surrogate Mixtures for Testing Effluent Treatment Technologies

Jonathon A. Brame, Victor F. Medina, Imree Smith, and Lawrence Popoli

July 2016


VX

Malathion

Cs-133 as surrogate for Cs-137
The Decontamination Effluent Treatment System (DETS)
Treatment Strategy

- Sediment – Settling (tank or blivet) & sand filter
- Surfactant – Granular Activated Carbon (GAC)
- Bleach – GAC
- Oils/Greases/Misc. Organic Compounds – Incidental removal, GAC, Reverse Osmosis (RO)
- Chemicals – Incidental removal, GAC, RO
- Radioisotopes – Incidental removal, Sand, RO (especially Cesium [Cs])
### Costs & Flow Rate

<table>
<thead>
<tr>
<th>Unit</th>
<th>Cost</th>
<th>Comments</th>
</tr>
</thead>
<tbody>
<tr>
<td>Reverse osmosis unit with pump &amp; Prefilter Cleaning units for scale and organics</td>
<td>$13,621.44</td>
<td>Price is for all the units described</td>
</tr>
<tr>
<td>Sand Filter Media Unit</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Carbon Filter Media Unit</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Water Softener Media Unit</td>
<td></td>
<td></td>
</tr>
<tr>
<td>UV sterilization unit (not used in these studies)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Kubota Generator</td>
<td>$9922.45</td>
<td></td>
</tr>
<tr>
<td>Bredel Pumps with mounting equipment and Hoses</td>
<td>$13,283.09</td>
<td>We purchased 2, but only 1 was used. Cost is for 1 unit.</td>
</tr>
<tr>
<td>Flanges</td>
<td>$1,066.00</td>
<td></td>
</tr>
<tr>
<td>Hose Reels</td>
<td>8,939.92</td>
<td></td>
</tr>
<tr>
<td>Trailer</td>
<td>$5000.00</td>
<td>We determined upgrades were need after the initial demonstration</td>
</tr>
<tr>
<td>Trailer Upgrades</td>
<td>$1500.00</td>
<td></td>
</tr>
<tr>
<td>EZ Touch Control Unit with associated software</td>
<td>$1800.00</td>
<td></td>
</tr>
<tr>
<td>Pressure gauges</td>
<td>$1000.00</td>
<td>Estimated</td>
</tr>
<tr>
<td>Wiring</td>
<td>$500.00</td>
<td>Estimated</td>
</tr>
<tr>
<td>Total</td>
<td>$56,632.90</td>
<td></td>
</tr>
</tbody>
</table>

### Flow Rate
- Battalion Sized Event involving people and vehicles to give volume
- Assume treatment time per day of 12 hours
- Adapted from planning factors of operational DECON (Army G3/5/7 Decontamination Planning factors)
- 10 gpm

### Costs
- Table to the left summarizes costs of elements of the system.
- The equipment costs were less than $60,000.
- Keeping costs low allows for a unit to be disposed of in its entirety if it gets highly contaminated during treatment.
- Enhancement of monitoring equipment is the greatest estimated additional cost.
Vehicle Decontamination Exercise

Details
- 27 June 2017
- 6 hours of total activity
- DETS operation 2 hours
- 10 large military vehicles & 20 cars, trucks, minivans were washed w/ soapy water & rinsed.
- 1200 gallons collected and spiked with Malathion, cesium, and bleach. Target concentrations were 10 mg/L.
- Contaminated water treated with the DETS
- Observers from JPM-P, Army MSCoE, JPdM A&RS, ECBC, DTRA, & USEPA
27 June 2017 DETS demonstration
### Results

<table>
<thead>
<tr>
<th>Constituent</th>
<th>Analytical Method</th>
<th>Influent Concentration</th>
<th>Effluent Concentration</th>
<th>%Removal</th>
</tr>
</thead>
<tbody>
<tr>
<td>Turbidity</td>
<td>USEPA Method 180.1</td>
<td>&gt;4200 NTU</td>
<td>1.825 ± 1.145 mg/L</td>
<td>100.0%</td>
</tr>
<tr>
<td>Hardness</td>
<td>Summation of Ca$^{2+}$ and Mg$^{2+}$ concentrations as measured by ion chromatography</td>
<td>82.36 ± 40.79 mg/L</td>
<td>0 mg/L</td>
<td>100.0%</td>
</tr>
<tr>
<td>Total Chlorine</td>
<td>Standard Method 4500-Cl G</td>
<td>0.26 ± 0.07 mg/L</td>
<td>0 mg/L</td>
<td>100.0%</td>
</tr>
<tr>
<td>Surfactants</td>
<td>Spectrophotometric method as given in Kloos (2015)</td>
<td>1.422 ± 0.359 mg/L</td>
<td>0.019 ± 0.017 mg/L</td>
<td>98.7%</td>
</tr>
<tr>
<td>Total Organic Carbon</td>
<td>USEPA 5310B</td>
<td>58.23 ± 29.7 mg/L</td>
<td>1.18 ± 0.84 mg/L</td>
<td>98.0%</td>
</tr>
<tr>
<td>Malathion</td>
<td>Phosphorus balance</td>
<td>26.71 ± 12.16 mg/L</td>
<td>0.08 ± 0.05 mg/L</td>
<td>99.7%</td>
</tr>
<tr>
<td>Malathion</td>
<td>USEPA 8141A</td>
<td>24.7 mg/L</td>
<td>0.000097 mg/L</td>
<td>100.0%</td>
</tr>
<tr>
<td>Cesium</td>
<td>USEPA 6020A</td>
<td>2.97 ± 4.21 mg/L</td>
<td>0 mg/L</td>
<td>100.0%</td>
</tr>
</tbody>
</table>

All measurements indicate that the DETS is highly effective treating constituents found in decontamination wash water.
## Concentrate & Reuse

<table>
<thead>
<tr>
<th>Constituent</th>
<th>Average Initial Concentration</th>
<th>Concentration in Concentrate at midpoint of evaluation</th>
<th>Concentration in Concentrate at end of the evaluation</th>
</tr>
</thead>
<tbody>
<tr>
<td>Turbidity</td>
<td>&gt;4,200 NTU</td>
<td>827 NTU</td>
<td>859 NTU</td>
</tr>
<tr>
<td>Total Suspended Solids (TSS)</td>
<td>3,088 ± 1,532 mg/L</td>
<td>1,192 mg/L</td>
<td>756 mg/L</td>
</tr>
<tr>
<td>Total Organic Carbon (TOC)</td>
<td>58.2 ± 29.7 mg/L</td>
<td>35.9 mg/L</td>
<td>41.4 mg/L</td>
</tr>
<tr>
<td>Conductivity</td>
<td>218 ± 134 mS/cm</td>
<td>592 mS/cm</td>
<td>689 mS/cm</td>
</tr>
<tr>
<td>Hardness</td>
<td>82.4 ± 40.8 mg/L</td>
<td>40.7 mg/L</td>
<td>32.1 mg/L</td>
</tr>
<tr>
<td>Surfactant</td>
<td>1.42 ± 0.36 mg/L LAS</td>
<td>0.80 mg/L LAS</td>
<td>0.82 mg/L LAS</td>
</tr>
<tr>
<td>Free Chlorine</td>
<td>0.26 ± 0.07 mg/L</td>
<td>0.20 mg/L</td>
<td>0.20 mg/L</td>
</tr>
<tr>
<td>Malathion</td>
<td>26.71 ± 12.16 mg/L</td>
<td>19.08 mg/L</td>
<td>19.85 mg/L</td>
</tr>
<tr>
<td>Cesium</td>
<td>2.96 ± 4.2 mg/L</td>
<td>0.06 mg/L</td>
<td>0.08 mg/L</td>
</tr>
</tbody>
</table>

Take home message: The concentrate is not much different than the initial concentration. So, it can also be returned to the reactor & treated

### Approach Zero Discharge

Recycling analysis assuming 600 gal reused after treatment:
- Without concentrate treatment: 4000 gal
- With single concentrate treatment: 7000 gal
Documentation

Videos
Vehicle exercise
https://youtu.be/d9TZvYzUMn0

Marketing video
https://youtu.be/9aNgCDKj_fU

Control system
https://youtu.be/S2JQ6ZWqKCw

Publications
Military Engineer Article
https://www.researchgate.net/publication/322552627_Treating_Contaminated_Effluent

Army Chemical Review – In Press
Technical Report – In editing
Mass Personnel Decontamination (MPD) study

- 24 May study on at Vicksburg station
- prepare a simulant of MPD in a 3000 gal blivet based on grey water simulant formulations (1800 gal of solution)
- spike with CBRN simulants (malathion & cesium)
- Contact me if interested in observing

3000 gal blivet

<table>
<thead>
<tr>
<th></th>
<th>Malathion</th>
<th>Cs</th>
<th>Surfactants</th>
<th>Sediment</th>
</tr>
</thead>
<tbody>
<tr>
<td>Concentration</td>
<td>0.064 3.5mL/55gall for 10 ppm</td>
<td>6.33 mg/L CsCl for 5 ppm of Cs</td>
<td>0.3785455 g/gall for 10 ppm of Dawn</td>
<td>34065 mg of soil for 5ppm</td>
</tr>
<tr>
<td>For 1800 gallons</td>
<td>114.54545 mL for 10 ppm</td>
<td>43126.29 mg of CsCl</td>
<td>681.4 g of Dawn</td>
<td>34.065 g of soil</td>
</tr>
<tr>
<td></td>
<td>57.3 mL for 5 ppm</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

MPD Simulant Formulation (1800 gal)
Allied Studies at Edgewood Chemical & Biological Center

• Purposes:
  • To test DETS treatment processes on actual agent (VX)
  • Provide comparison with Malathion simulant
• Studies Tested interactions with:
  • Sand
  • Granular activated carbon
  • *Membrane Removal.
• Funding by ERDC and DTRA
• Presented with approval by Larry Procell
Results suggest that although not identical, Malathion and VX perform similarly in our most important unit process.
Novel Membrane Technologies

Successful Implementation of Cross-Current Testing of GO Membranes – the most advanced system we have identified to date

1. A chitosan/graphene oxide (CSGO) membrane was prepared. We found that these membranes can swell, but by sandwiching them between paper filters, the swelling could be controlled.
2. Our cross flow reactor. The flow was set at 10 mL/min. Pressure was 50 psi. Flux was ~1.4 gfd (2.3 LMH). We treated 1 liter of solution.
3. The beaker is the permeate.
4. The results – a 10 mg/L dye solution was treated. The permeate had a concentration of 0.4 mg/L, a 96% reduction. The concentrate was 37.1 mg/L.
Treatment of Malathion, comparison to NF

Chitosan-graphene oxide composite membrane (CSGO) vs. Nanofiltration (NF) Dow Filmtec Flat Sheet Membrane, NF, PA-TFC

1000 mg/L Malathion before & after treatment. Treated samples visually less turbid

- Removal of Malathion by CSGO comparable to that of NF, even better at low concentration.
- Differenced due to different removal mechanisms
- CSGO flux rates about 3.5 to six times lower than NF, but more consistent.
Scalable and Freestanding Membranes

Can this process be modified for surface remediation?

Setting video: [https://youtu.be/BplAGoNMz54](https://youtu.be/BplAGoNMz54)

Crosslinking Graphene Oxide and Chitosan to Form Scalable Water Treatment Membranes- Mattei Masters Thesis MSU 2017
Advanced Upscaling
Antimicrobial properties

Flocculation of cyanobacteria onto a GO composite (a), control cyanobacteria (b), CSGO composite showing loss of green pigmentation (c), and AgNO3-CSGO composite showing significant loss of green pigmentation (d).

FTIR surface mapping shows wrinkled surface of CSGO associated with physical microbial deactivation. *Can we enhance this property?*

Microbial density (as optical density) Solutions with same size swatches of CSGO vs. Whatman Filter Paper
Graphene oxides have been found to create reactive oxygen species (ROS), including superoxide and hydroxyl radical.

We used two assays, Superoxide dismutase (SOD) and Ellman’s Assay (oxidation of glutathione) to confirm ROS activity in the CSGO composite.

ROS are highly effective oxidants.

They may contribute to antimicrobial properties.

They directly react with chemical contaminants.

Is this property “tunable”?


Download at: https://www.researchgate.net/profile/Victor_Medina9
Conclusions

- The DETS addresses a key gap in aqueous CBRN decontamination
- 10 gpm is a suitable target for a battalion sized event
- The capital costs for such a system are reasonable
- Laboratory testing showed effective treatment.
- A field evaluation focusing on vehicular decontamination showed that the wash water could be easily captured.
- The field evaluation showed effective treatment for environmental contaminants, decontamination agents, and simulants.
- Testing with live VX agent by ECBC shows that our assumptions of similarity with malathion are reasonable.
- Allied experimental work with Graphene Oxide composite membranes show promising results.
Questions?!

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Treatment Goals

- **OCONUS**
  - Discharge – Meet OEBGD requirements for discharge
  - Reuse – No requirements, but APHC indicated reuse is acceptable.

- **CONUS**
  - There are no documents for discharge
  - Sanitary Sewer – Agreement with POTW
  - Stormwater – Meet NPDES
  - Reuse – No requirements to date.
  - Potable
Process control and instrumentation

Control architecture: EZAutomation EZ-Touch HMI/PLC
Customizable and programmable interface with ladder logic control
Data recording
Modular I/O
Pressure sensitive touch screen – compatible with heavy gloves
Power Supply

- Kubota Diesel 9875 Watt Generator
- 240 V, 40 amp
- 60 gallon subbase fuel tank and a two-wire auto start control.
- Sound enclosure keeps noise at 68 dB(A) at 7 m (23 ft), which is helpful for communications.
- The system is also designed to be suitable for operation of sensitive electronic equipment.
- Fuel consumption varies from 0.41 to 0.84 gal/hr
- The system can also simply be plugged into a 240 V, 40 amp source.
Alpha Version of Mobile Treatment System

Our pilot reactor capable of treating aqueous effluent from decontamination of 200 people and 10 large vehicles per day for 3 to 5 days.

Our system treated a simulated effluent with soap, bleach, clay and cesium. The removal was >99 percent of each constituent.
VX in Sand & Anthracite

- Immediate breakthrough on both materials
- Small generation of breakdown products (assume to be hydrolysis)
- Breakdown product generation also found in untreated feed solution samples.

### Feed Solution before and after Experiment (24 hours)

<table>
<thead>
<tr>
<th></th>
<th>Concentration, ng/mL</th>
<th>Percent Composition</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>VX</td>
<td>EMPA</td>
</tr>
<tr>
<td>initial</td>
<td>11,950 ± 226</td>
<td>171 ± 73</td>
</tr>
<tr>
<td>final</td>
<td>12,026 ± 113</td>
<td>462 ± 6</td>
</tr>
</tbody>
</table>

### Sand Material

![Graph showing VX concentration over time for Sand Material](image)

### Anthracite Material

![Graph showing VX concentration over time for Anthracite Material](image)
VX in Granular Activated Carbon Column

- Adsorption effect evident.
- Complete removal for 18 hours.
- Line steepens at 72 hours.
- Percent breakthrough was less than 5% at end of experiment (37.5 gal or 142L treated).
- Transformation products not detected.