TREATMENT OF IMPACTED WATER FOLLOWING THE LAC-MÉGANTIC CATASTROPHE

Presented by
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SANEXEN
ENVIRONMENTAL SERVICES INC.

REMTECH
ENVIRONMENTAL SERVICE ASSOCIATION OF ALBERTA

Banff, October 16, 2014
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LAC-MÉGANTIC, JULY 6\textsuperscript{TH} 2013
72 tank cars, carrying 8 million liters of light crude oil were involved in the train derailment.

Pictures from La Presse
A large part of the downtown area was razed by the fire.
Area impacted by the spill and fire
Booms deployed near the shore to contain the oil
EMERGENCY RESPONSE
WATER TREATMENT

- MOBILIZATION AND SET UP
- TREATMENT OF 43 MILLION LITRES OF LIQUIDS RECOVERED FROM THE DERAILMENT SITE (WATER, CRUDE OIL AND SLUDGES) FROM JULY TO DECEMBER 2013
Locations with respect to Mégantic Lake and the Chaudière river

1. Derailment site
2. Waste water treatment plant
3. Water treatment site after October 2013
The operation of the municipal wastewater treatment plant was interrupted to prevent the release of oil to the Chaudière river.
A thick foam caused by the fire fighting agents covered the 1 million liters of water
Mobilization of equipment to treat up to one million litres per day

Mixture of water, crude oil and sludge recovered at the derailment site

Treatment at first of the municipal wastewater laden with the spilled crude oil to allow recommissioning of the facility.
Baker tank (green) used to receive the water and mobile water treatment unit (white, 200 m³/day) mobilized on July 8th
Water pumped to the mobile unit after settling
View inside the mobile unit
Larger Water Treatment System were set up in the days that followed
Activated sludge basin put back in service after one week of treatment
FILTRATION MEDIA DELIVERED IN 1 m³ BAGS
Large filters erected for the removal of colloids and soluble organics, each with a throughput capacity of 400 m$^3$/day.
A fleet of tanker trucks was used to transfer the liquids from the red zone to the water treatment area.
90,000 LITERS BAKER TANKS WERE USED TO RECEIVE THE LIQUIDS AND FOR A FIRST SEPARATION
IN THE FRONT, BAKER TANKS FOR INTERIM STORAGE AND PRE-TREATMENT (COAGULATION/FLOCULATION) OF INCOMING WATER
6 m³ sand/anthracite filter for the removal of suspended solids and oil
400 m³/day Ultrasorption™ filters
Basin with level controlled pumps to transfer water from the Ultrasorption™ units to the adsorption units.
400 m³/day adsorption units
DISCHARGE OF TREATED WATER
CHARACTERISTICS OF THE WATER

- Water was collected from sewers, basements, surface drainage, slicks confined by booms, cooling and washing operations, etc.
- The water received contained unburnt crude oil, pyrolyzed oil, soot and ashes, soil particles, fire fighting foams, burnt debris, etc.
- Initially, high concentrations of VOCs (half masks were worn initially because of benzene)
Varying water characteristics and oil/solids content for every shipment
TREATMENT PROCESS AND PERFORMANCE

- PROCESS SCHEMATIC
- TREATMENT OBJECTIVES
- INITIAL CONTAMINANT CONCENTRATIONS
TREATMENT SCHEMATIC - Processes used

INCOMING LIQUIDS → Coagulation, flocculation, settling → Periodic backwashes → H₂O₂ → Filtration (Sand/anthracite and sand filters, bag filters) → Ultrasorption™ → Adsorption → Treated water tank

Gravity separation

COMPOUNDS REMOVED:
- Oil solids
- Sulfides odours
- Suspended matter, TPH
- Colloids (TPH, PAH, etc.)
- Soluble organics (BTEX, PAHs, etc.)

Notes: Three treatment trains operating in parallel
Operation 24/7
Filter media replaced as necessary
MAIN CONTAMINANTS TARGETED

- $C_{10}-C_{50}$ PETROLEUM HYDROCARBONS
  (Objective of an average of < 1 mg/L)
- MONOAROMATIC HYDROCARBONS (MAHs)
- POLYAROMATIC HYDROCARBONS (PAHs)
- TOXICITY (Rainbow trout, Minnow, Daphnia Magna) (no acute toxicity)
## Results of July 9th

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Units</th>
<th>Raw Water</th>
<th>Treated Water</th>
<th>Removal efficiency</th>
</tr>
</thead>
<tbody>
<tr>
<td>PH (C\textsubscript{10-50}) *</td>
<td>mg/L</td>
<td>980</td>
<td>&lt; 0,1</td>
<td>&gt; 99,99%</td>
</tr>
<tr>
<td>Benzene</td>
<td>μg/L</td>
<td>620</td>
<td>&lt; 0,1</td>
<td>&gt; 99,98%</td>
</tr>
<tr>
<td>Toluene</td>
<td>μg/L</td>
<td>880</td>
<td>&lt; 0,1</td>
<td>&gt; 99,99%</td>
</tr>
<tr>
<td>Ethylbenzene</td>
<td>μg/L</td>
<td>155</td>
<td>&lt; 0,1</td>
<td>&gt; 99,9%</td>
</tr>
<tr>
<td>Xylenes</td>
<td>μg/L</td>
<td>1600</td>
<td>&lt; 0,1</td>
<td>&gt; 99,99%</td>
</tr>
<tr>
<td>Styrene</td>
<td>μg/L</td>
<td>3,8</td>
<td>&lt; 0,1</td>
<td>&gt; 99,7%</td>
</tr>
<tr>
<td>Other VOCs</td>
<td>μg/L</td>
<td>ND</td>
<td>ND</td>
<td>-</td>
</tr>
<tr>
<td>Naphtalene</td>
<td>μg/L</td>
<td>ND</td>
<td>ND</td>
<td>-</td>
</tr>
<tr>
<td>Σ PAH</td>
<td>μg/L</td>
<td>ND</td>
<td>ND</td>
<td>-</td>
</tr>
</tbody>
</table>

* : 15 mg/L oil and grease x 0.7 for conversion in PH (C\textsubscript{10-50})

n. d. : Not detected

- : No value
Concentrations 5 days later

### Results of July 14th

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Units</th>
<th>Raw Water</th>
<th>Treated Water</th>
<th>Removal efficiency</th>
</tr>
</thead>
<tbody>
<tr>
<td>PH (C_{10-50})</td>
<td>mg/L</td>
<td>42,7</td>
<td>&lt; 0,1</td>
<td>&gt; 99,8%</td>
</tr>
<tr>
<td>Benzene</td>
<td>μg/L</td>
<td>568</td>
<td>&lt; 0,3</td>
<td>&gt; 99,9%</td>
</tr>
<tr>
<td>Toluene</td>
<td>μg/L</td>
<td>741</td>
<td>&lt; 1</td>
<td>&gt; 99,9%</td>
</tr>
<tr>
<td>Ethylbenzene</td>
<td>μg/L</td>
<td>103</td>
<td>&lt; 0,3</td>
<td>&gt; 99,7%</td>
</tr>
<tr>
<td>Xylenes</td>
<td>μg/L</td>
<td>827</td>
<td>&lt; 1</td>
<td>&gt; 99,9%</td>
</tr>
<tr>
<td>Styrene</td>
<td>μg/L</td>
<td>&lt; 20</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>Other VOCs</td>
<td>μg/L</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>Naphtalene</td>
<td>μg/L</td>
<td>32,9</td>
<td>1,2</td>
<td>96,4%</td>
</tr>
<tr>
<td>Σ PAH</td>
<td>μg/L</td>
<td>62</td>
<td>1,2</td>
<td>98%</td>
</tr>
</tbody>
</table>

*: 15 mg/L oil and grease x 0,7 for conversion in PH (C_{10-50})

n. d.: Not detected
- : No value
## Average concentrations
### First 10 days of operations

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Units</th>
<th>Average concentrations</th>
<th>Removal efficiency</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>Pre-treated water</td>
<td>Treated water</td>
</tr>
<tr>
<td>C10-C50 PHs</td>
<td>mg/L</td>
<td>28*</td>
<td>0.7</td>
</tr>
<tr>
<td>MAHs</td>
<td>µg/L</td>
<td>1472</td>
<td>1.5</td>
</tr>
<tr>
<td>PAHs</td>
<td>µg/L</td>
<td>44</td>
<td>0.5</td>
</tr>
</tbody>
</table>

* Excluding the water of the first day that contained 980 mg/L
FLUOROSURFACTANTS

- **PFOA**: Perfluoro-octanoic carboxylic acid \((C_{7}F_{15}CO_{2}H)\)
- **PFOS**: Perfluoro-octane sulfonic acid \((C_{8}F_{17}SO_{3}H)\)
- and other fluorinated organic compounds (PFAS, Polyfluoroalkyl substances)

- Persistent compounds, with a potential for bioaccumulation and with effects on human health
- Oleophilic and hydrophilic compounds used in some fire fighting foams
REMOVAL OF AFFFs

AFFF: Aqueous Film Forming Foam (for fire fighting)

PFOA and PFOS now targeted as contaminants to be controlled in Canada

Removal rate in water of 80-99 % of AFFFs compounds possible with the technologies used

Concentrations and removal rates verified by the team of Dr Jinxia Liu at McGill University; the slides that follow were prepared by them in the context of a joint R&D project
PFAS in Telomerization-Based AFFFs

Fluorinated surfactants deemed “safe”

Phased-out surfactants

PFAS: Poly/perfluoroalkyl substances

(Place and Field 2012, ES&T)
1 ng/ml standard solution was used to demonstrate the excellent resolution of the 21 target compounds. Note that this result was achieved within the same run.
Sample Collection

- **Sand Filter**
- **Ultrasorption® Filter**
- **Activated carbon Filter**

Small filtration system

Large filtration system

- **Sand/Anthracite Filter**
- **Ultrasorption® Filter**
- **Activated carbon Filter**
Total PFAS in the Raw Water before/after Persulfate Oxidation

- Most of the PFAS in the AFFF-impacted water are not directly measurable
- Persulfate oxidation is required for AFFF sample quantitation

![Graph showing total PFAS concentration before and after persulfate oxidation](image)

Raw water sample and the same sample treated by TOP. (n=3)
Removal Efficiency

Removal rate of each filtration stage:

<table>
<thead>
<tr>
<th>Filtration Stage</th>
<th>Small System</th>
<th>Large System</th>
</tr>
</thead>
<tbody>
<tr>
<td>Sand Filter</td>
<td>0 %</td>
<td>31 – 32 %</td>
</tr>
<tr>
<td>Ultrasorption® Filter</td>
<td>36 – 52 %</td>
<td>16 – 46 %</td>
</tr>
<tr>
<td>Activated carbon Filter</td>
<td>86 – 97 %</td>
<td>77 – 99.8 %</td>
</tr>
<tr>
<td>Overall Removal Rate</td>
<td>90 – 98 %</td>
<td>87 – 100 %</td>
</tr>
</tbody>
</table>

* Rates are respectively for the removal of directly quantified PFAS and of total PFAS.
PFOS ≤ 0.3 µg/L (Health Canada); ≤ 0.2 µg/L (US EPA)
PFOA ≤ 0.7 µg/L (Health Canada); ≤ 0.4 µg/L (US EPA)

The raw water contained only a low concentration of these two compounds (0.5 µg/L of PFOA, no PFOS) and about 17 µg/L of compounds in the PFAS family;

The treated water contained 0.1 µg/L of PFOA and 1.2 µg/L of PFAS compounds.

With a river to effluent flowrate ratio of 3200 to 1 and with the removal efficiency obtained, AFFFs were therefore not a concern in this project.
CHALLENGES

- The changing quality of the incoming water
- Getting rapid results for continuous discharge
- Surfactants playing with the chemistry of the contaminants
- Logistics of 24 hour/day, 7 days/week work three hours away from our base
- Not knowing what comes next
Coagulation/floculation tests conducted to identify how best to clarify the water in the pre-treatment step

The characteristics of the liquids received were highly variable.

Different selection of products and injection rates would ideally have been required from one day to the next.

The pre-treatment step could not be optimal and the subsequent filters had to perform better than usual to meet a good quality of effluent.
Occasional batches with high concentrations of surfactants
Work 24/7 during the first two 2 months
... in all sorts of weather
SOLUTIONS

- Use of an unconventional process (Ultrasorption™) to help deal with surfactants and colloids
- Overdesign; not trying to optimize things on a batch per batch basis; use a compromise as a coagulation recipe; operate with long residence times
- Use of a UV photo-ionizer to check the quality of the water
- Using turbidity and surface tension as indicators that treatment is either adequate or incomplete
- Use of local people to work with experienced Sanexen technicians
- Work very closely with suppliers
Field assessment of water quality

- Certified laboratories located 3 hours away from the site
- Turbidity used as a prime indicator of water quality
- PID used to quickly assess residual hydrocarbon concentration in water and to assess when filtration media had to be replaced
- Water odour used to adjust the injection rate of hydrogen peroxide
- A zeta meter would have been useful to adjust coagulant dosage

Test kits to verify water quality
Surfactants make treatment more difficult, but turbidity is a good indicator of water quality.
Prior experience helps ...

TREATMENT OF 140 MILLION LITERS OF CRUDE OIL LADEN WATER UPON THE REVERSAL OF THE SARNIA-MONTREAL CRUDE OIL PIPELINE
Thanks to the other organizations involved

Government of Quebec
Municipality of Lac-Mégantic
MDUN, Solvarec and RSR Environnement
McGill University

Thanks to our suppliers and sub-contractors

Canada Colors & Chemicals
Quatrex, Chemco, Durpro and A.C. Carbone
AGAT, Exova and Maxxam
Rollex, Pompes Ultra, Équipement Terra
Transport Robert
and others
Thanks to our employees
(who worked long hours away from their families)
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Questions? Discussion?

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