Removal of Dioxin Contamination for Gas Turbine Generator Set Repair

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ABSTRACT

Decontamination projects are typically undertaken in the interest of reducing disposal costs. This goal can be achieved because decontamination concentrates the contaminant into a smaller volume or changes its form so that a lower cost disposal technology becomes available. Less frequently, decontamination adds value back to the fouled structure or contaminated piece of equipment. This removal of dioxins from a gas turbine generator set is one of the latter cases. A multi-million dollar piece of equipment could have been destined for the scrap pile. Instead, an innovative, non-destructive decontamination technology, developed under EPA and DOE demonstration programs has was employed so that the set could repaired and put back into service.

The TechXtract® chemical decontamination technology reduced surface dioxin / furan concentrations from as high as 24,000 ng / m² to less than 25 ng / m² and below detection limits.

Introduction

On October 6, 1997 a fire occurred in Independence, Missouri, at the city’s Power and Light Department Gas Turbine and Electrical Substation No. 1. One of two transformers located in the generator compartment ruptured due to an electrical fault. The transformer exploded, resulting in a fire causing nearby capacitors to rupture, and damaged the generator. Subsequent analysis of wipe samples taken from the generator’s external and internal surfaces indicated that polychlorinated biphenyls (PCB’s), polychlorinated dibenzo-p-dioxins (dioxins) and polychlorinated dibenzo furans (furans) were created and released as a result of this fire. These substances are generally recognized as having significant deleterious effects on human health. Various risk assessments show that skin contact exposure concentrations in the part per trillion have carcinogenic and teratogenic effects.

The contaminated turbine / generator set represents a significant capital investment for the city, and while idle, a significant loss of revenue. Independence contracted with Alstom Power for repair of the generator. However, before the repairs could be undertaken, the dioxin and furan concentrations on the working surfaces had to be lowered below 25 ng/m² to meet the health and safety requirement required by Alstom and its machinists. In addition, residual PCB’s concentrations had to be reduced below 10µg/100cm².

An outside contractor was hired for the initial decontamination attempt. The attempt used widely recognized non-polar solvents as cleaning agents but it failed to
reach the target clean-up levels. Despite making multiple passes, the treated
generator parts would exhibit leach-back. That is after cleaning to requisite target
concentrations, the contaminant surface concentration would rise over time back
above the target clean-up criteria.

Active Environmental Technologies, Inc., with the patented TechXtract®
chemical decontamination technology was then subcontracted by Alstom Power to
carry out the decontamination portion of the repair project. IPP&L chose the
TechXtract® technology based on its performance in an EPA Superfund Innovative
Technology Evaluation (SITE), where it overcame PCB leach-back by penetrating into a
concrete substrate to solubilize and remove contaminants.

Polychlorinated Dibenzo-p-Dioxin and Polychlorinated di Benzofurans
(PCDD’S/FS).

Polychlorinated Dibenzo-p-Dioxin and Polychlorinated di Benzofurans
(PCDD’S/FS) are produced by the incomplete combustion of Polychlorinated Bi-Phenols.
These combustion products have a visual appearance and physical properties akin to soot
produced in any heavy hydrocarbon fire. They are hydrophobic (incapable of dissolving
in water); hence, pure organic solvents come to mind when decontamination techniques
are discussed. Organic solvents are in and of themselves RCRA hazardous. Non-
chlorinated solvents, such as hexane, are very flammable, costly, and require significant
work place care in handling and disposal. Chlorinated solvents, while non-flammable,
are also RCRA hazardous and would tend to create sampling and analytical problems for
the project.

The TechXtract® (a patented sequential extraction process) chemistries are all
water based, and safer to handle, ship, and apply. As stated above, PCDD’S/FS are
hydrophobic, so some creative reagent chemistry was employed to make the PCDDs
soluble. After considerable time in research, it was decided to try to cleave the
compounds and thus make them somewhat more water-soluble. To cleave the long chain
compounds; one approach was to produce Hydroxyl Radicals (OH), by using reagent
chemistry with the base formula(s). The reagent chemistry used several oxygen
compounds with two catalysts. This will promote the Fenton reaction both full and
partial. The sequential chemistry approach allows the many pH targets to be met and side
reactions to form various etching agents.

The many reactions exploit the high reactivity of the hydroxyl radical (OH), this
is generated when oxygen compound(s) are oxidizes the selected catalyst (s). This was
further expanded to produce ozone (O3) (O3 is more soluble in water than O2).
Therefore, at times a photo-Fenton reaction (some times called electro-Fenton reaction or
Photo-degradation) was induced in which OH/O3 is produced. These reactions have been
proven in remedial process for organic pollutants such as Nitrobenzene and Aniline. The
research team felt confident that it could be applied to the PCDD/FS situation.
Furthermore, we believed that the hydroxyl radicals and ozone would partially
destroyed/cleave the PCDD’S/FS long chain molecule; hence, our first postulate.
In addition, the process generates Carbon Dioxide (CO2), CO2 is an excellent solvent
and lowers the interfacial tension; furthermore, forms etching agents, all with the same
reaction. Carbon Dioxide generation helps replace organic solvents. It is safe, for CO2
gas is inert, and most is converted to Carbonic Acid (H2CO3); as well as small amounts
of inorganic carbonates (CaCO$_3$, K$_2$CO$_3$, NaCO$_3$, etc.) The evolution of all the above TechXtract$^\text{®}$ chemistries lead directly to the highly successful decontamination of the turbine with sources of PCDD’S/FS.

**Remedial Approach**

The decontamination effort required implementation of a project plan that took into account

- Manipulating the large size of the equipment being cleaned. As an example, the generator’s stator alone weighed in at 20,000 lbs.
- The intricate geometry of the generator’s internals meant lots of nooks and crannies to hold dioxin’s
- Maintaining secondary containment, including containment of potential airborne contaminants
- Extremely low cleanup criteria and the potential for cross contamination between the repair and remedial work team

In addition to meeting the project cleanup criteria, IP&L had several secondary concerns.

- Community sensitivity to the presence of dioxins
- Seasonal considerations and the repair timeline
- Zero tolerance for mechanical impact on the generator
- Integration of the remedial and repair work teams

An independent third party consultant performed a risk assessment. Due primarily to the generator’s size and contaminant levels it was decided to perform the decontamination on the generator’s substation site. The decontamination plan called for disassembly of the unit on site, movement of the contaminated parts the exclusion work
zone and its secondary containment for cleaning, sampling. Depending on the analytical, the part would be re-cleaned and sampled, or put onto a truck for shipment to the repair shop.

A 40’ x 60’ x 8” concrete, epoxy coated containment structure was built next to the generator’s foundation pad. Since all the part movements would require the use of a crane, care was taken to locate the pad so that all the crane moves would be “short picks”. A central sump pit was included in the pad’s construction to collect the laden secondary liquid solutions generated as part of the TechXtract® process. The sump would be emptied at the finish of each workday.

A temporary structure was erected on the pad to provide climate control, secondary containment for any potential airborne contaminants, and to provide a screen from residences. A “Sprung™” temporary structure was chosen for the project. This structure is light enough to be lifted on and off the foundations by the same cranes used for part movement so that staging even the biggest pieces was relatively easy. The project start date was set in March so that IP&L could have the refurbished unit back in operation by the next year’s summer cooling season. This meant weather conditions were also a factor in choosing the structure. The “Sprung™” rigid structure was sufficient to withstand a hundred year windstorm, always a concern on the Kansas / Missouri plane. It also provided enough insulating value to prevent the aqueous TechXtract® chemistries from freezing.

Work tasks were assigned to two teams that would be working on the job. A repair team, which included machinists, millwrights, and riggers, was tasked with disassembly and part movement. A decontamination team of TechXtract® trained technicians performed the decontamination protocols and managed the waste streams from generation through disposal. The repair team was given 40 hour HAZWOPER training prior to beginning the generator disassembly. A local Certified Industrial Hygienist provided safety oversight to both the repair and remediation teams. An independent certified laboratory was contracted to provide confirmation sampling and analytical services. The sampling schedule was set to allow 72 hours for potential leach-back to occur with results delivered on a 72-hour turnaround time.

The TechXtract® decontamination protocol used the application and removal of three different chemical formulas. Each application and removal is considered an application “cycle”. Each cycle will typically remove 70% of the contaminant present so the number of cycles for each part was set based on the difference between the initial dioxin concentrations and the desired clean up criteria. A part was set aside for confirmation sampling only after the project number of cycles had been completed. At the project conclusion samples were also taken from the building, the pad and pad sump to confirm that the dioxins had been removed with the secondary liquids.

At the project’s conclusion, 10 fifty-five gallon drums of waste liquids and 7 drums of solids were accumulated for disposal.

**Sampling and Analytical Methods**

Hexane wipe samples were taken from surface of the generator internals pre and post decontamination. Sample locations were selected to be along the generator’s air flow line. When it is operating, the generator stator spins, drawing air through the windings in order to cool the unit. Unfortunately, the PCB fire location was at the
generator’s air intake, so smoke from the fire was drawn directly into the unit. Sample locations were further biased toward the air inlet on the assumption that more fire soot would be caught toward the source fire. The area sampled varied with the size of the generator part to avoid magnifying potential sampling errors. Care was also taken to avoid sampling the exact same areas pre and post decontamination.

Once collected, the wipe samples were extracted and analyzed by EPA method 8290. Each wipe sample was spiked with $^{13}$C$_{12}$-labeled PCDD/PCDF internal standards and extracted with toluene in a Soxhlet extractor. The extract was quantitatively transferred to a Kuderna-Danish concentrator, concentrated, and solvent exchanged to hexane. The hexane extract was then spiked with 2,3,7,8-TCDD-37Cl$_4$ enrichment efficiency standard and processed through an analyte enrichment standard.

Each sample extract was analyzed for the presence of PCDDs and PCDFs using combined capillary column gas chromatography/high resolution mass spectrometry. The instrumentation consisted of a Hewlett Packard Model 5890 gas chromatograph interfaced to a VG Model 70SE high-resolution mass spectrometer, providing high sensitivity with minimum degradation of the chromatographic resolution. The mass spectrometer was operated in the electron impact ionization mode at a mass resolution of 10,000 – 11,000 (M/∆M, 10 percent valley definition). This resolution is sufficient to resolve most interference, such as PCBs, providing the highest level of confidence that the detected levels of PCDD/PCDF were not false positives.

The data were acquired by selected – ion – recording (SIR) using groups of ion masses similar to those described in USEPA Method 8290. The five groups correspond to the tetra chlorinated through octachlorinated congener classes. Each group contained two masses for the PCDDs, two for the PCDFs, the corresponding ion masses from the two isotopically labeled internal standards, and the ion mass characteristic of the polychlorinated diphenylether (PCDE) which, if present, could cause false responses in the dibenzofuran channels.

Each group of ion masses also contained a lock mass, which was used by the data system to automatically correct the mass focus of the analyte, and internal standard ion masses to assure that the centers of the mass peaks were being monitored.

The criteria used to judge positive responses for a PCDD/PCDF isomer included:

- Simultaneous response at both ion masses of the PCDD or PCDF
- Signal to noise ration equal to or greater than 2.5:1.0 for both ion masses
- Chlorine isotope ratio within 15% of the theoretical value
- Chromatographic retention time within +/- 2 seconds of the expected retention time
- Chromatographic retention times within elution windows determined from analyses of standard mixtures
- Absence of simultaneous response in the PCDF and PCDPE ion traces
Table 1
Summary of Laboratory Results
Dioxin / Furan Wipe Samples

<table>
<thead>
<tr>
<th>Sample Designation</th>
<th>Sample Name</th>
<th>2,3,7,8 TCDD Equivalent per Wipe (ng)</th>
<th>Wipe Area (m²)</th>
<th>Initial Conc. 2,3,7,8 TCDD Equivalents (ng/m²)¹</th>
<th>Final Conc. 2,3,7,8 TCDD Equivalents (ng/m²)</th>
</tr>
</thead>
<tbody>
<tr>
<td>001TEWS</td>
<td>Turbine end plate, winding side</td>
<td>0.014</td>
<td>1 m²</td>
<td>44.48</td>
<td>0.014</td>
</tr>
<tr>
<td>002GEWS</td>
<td>Generator end plate, winding side</td>
<td>0.0053</td>
<td>1 m²</td>
<td>63.4</td>
<td>0.0053</td>
</tr>
<tr>
<td>003ED</td>
<td>Interior of door</td>
<td>0.050</td>
<td>1 m²</td>
<td>--</td>
<td>0.050</td>
</tr>
<tr>
<td>004MR</td>
<td>Interior of roof</td>
<td>0.70</td>
<td>1 m²</td>
<td>--</td>
<td>0.70</td>
</tr>
<tr>
<td>005SPI</td>
<td>S. end pedestal inside wall (pre)</td>
<td>8.8</td>
<td>1 m²</td>
<td>8.8</td>
<td>--</td>
</tr>
<tr>
<td>006LLT</td>
<td>Lead Line tunnel</td>
<td>0.0039</td>
<td>100 cm²</td>
<td>544.4</td>
<td>0.39</td>
</tr>
<tr>
<td>007PAF</td>
<td>Plenum air flow</td>
<td>0.00067</td>
<td>100 cm²</td>
<td>24,788</td>
<td>0.067</td>
</tr>
<tr>
<td>008GFBE</td>
<td>Generator fan bearing end</td>
<td>0.000036</td>
<td>100 cm²</td>
<td>--</td>
<td>0.0036</td>
</tr>
<tr>
<td>009RRW</td>
<td>W side retaining ring</td>
<td>0.00</td>
<td>100 cm²</td>
<td>4769</td>
<td>0.00</td>
</tr>
<tr>
<td>010RE</td>
<td>East side RR</td>
<td>0.00</td>
<td>100 cm²</td>
<td>3548</td>
<td>0.00</td>
</tr>
<tr>
<td>016LGE</td>
<td>Load gear, East</td>
<td>0.00</td>
<td>100 cm²</td>
<td>45.21</td>
<td>0.00</td>
</tr>
<tr>
<td>017LGT</td>
<td>Load gear, Top</td>
<td>0.00</td>
<td>100 cm²</td>
<td>21.35</td>
<td>0.00</td>
</tr>
<tr>
<td>018LGCE</td>
<td>Load gear coupling, East</td>
<td>0.00</td>
<td>100 cm²</td>
<td>35.02</td>
<td>0.00</td>
</tr>
<tr>
<td>023SPI</td>
<td>South end of pedestal inside wall</td>
<td>0.031</td>
<td>100 cm²</td>
<td>8.8</td>
<td>3.1</td>
</tr>
<tr>
<td>023SPI-2⁴</td>
<td>South end of pedestal inside wall</td>
<td>0.12</td>
<td>100 cm²</td>
<td>3.1</td>
<td>0.12</td>
</tr>
<tr>
<td>024SC</td>
<td>Sump center</td>
<td>0.030</td>
<td>100 cm²</td>
<td>--</td>
<td>30</td>
</tr>
<tr>
<td>024SC-2⁴</td>
<td>Sump center</td>
<td>0.00</td>
<td>100 cm²</td>
<td>30</td>
<td>0.00</td>
</tr>
<tr>
<td>025CS</td>
<td>Concrete sump</td>
<td>0.011</td>
<td>100 cm²</td>
<td>--</td>
<td>1.1</td>
</tr>
<tr>
<td>027LV</td>
<td>Lamination vent</td>
<td>0.00015</td>
<td>100 cm²</td>
<td>--</td>
<td>.015</td>
</tr>
<tr>
<td>028SPS</td>
<td>Stator pressure plate</td>
<td>0.00085</td>
<td>100 cm²</td>
<td>--</td>
<td>0.085</td>
</tr>
<tr>
<td>029L</td>
<td>Stator lamination</td>
<td>0.014</td>
<td>100 cm²</td>
<td>--</td>
<td>1.4</td>
</tr>
<tr>
<td>030SBFS</td>
<td>Stator box face</td>
<td>0.035</td>
<td>100 cm²</td>
<td>--</td>
<td>3.5</td>
</tr>
<tr>
<td>031SH</td>
<td>Stator housing</td>
<td>0.014</td>
<td>100 cm²</td>
<td>--</td>
<td>1.4</td>
</tr>
</tbody>
</table>

Results and Conclusions

¹ Burns and McDonnell Waste Consultants, Inc., August 1999
² -- = No Data Available
³ First Round Sampling Event
⁴ Second Round Sampling Event
The project took 6 weeks to complete from pad pouring to final clean part shipment. Dioxin / furan concentrations were lowered below clean up criteria with most parts coming clean on the first pass. No leach back was observed and the generator was successfully repaired and put back into service.