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SUPERFUND INNOVATIVE TECHNOLOGY EVALUATION

Emerging Technology Summary

Destruction of Organic Contaminants in Air Using Advanced Ultraviolet Flashlamps

This summary describes a new process for photo-oxidation of volatile organic compounds (VOCs) in air using an advanced ultraviolet (UV) source, and a pulsed xenon flashlamp. The flashlamps have greater output at 200 to 250 nm than medium-pressure mercury lamps at the same power and, therefore, cause much more rapid direct photolysis of VOCs, including methylene chloride (CH_2Cl_2), chloroform ($CHCl_3$), carbon tetrachloride (CCl_4), 1,2-dichloroethane (1,2-DCA), 1,1,1-trichloroethane (TCA), Freon 113, and benzene. The observation of quantum yields greater than unity indicate the involvement of chain reactions for trichloroethene (TCE), perchloroethene (PCE), 1,1-dichloroethene (DCE), $CHCl_3$, and CH_2Cl_2.

TCE was examined more closely because of its widespread occurrence and very high destruction rate. Two full-scale air emission control systems for TCE were constructed at Purus and tested at a Lawrence Livermore National Laboratory (LLNL) Superfund site. The systems were operated at flash frequencies of 1 to 30 Hz, temperatures between 33 and 60 °C, flows up to 300 standard cubic feet per minute (scfm), and 100 scfm, at concentrations up to 260 part per million per volume (ppmv) and 10,600 ppmv of TCE, respectively. Residence times ranged from 5 to 75 secs. In all cases, except at the lowest flash frequency, greater than 99% removal of TCE was observed. Careful attention was paid to product formation and mass balances. The main initial photo-oxidation product of TCE was dichloroacetyl chloride (DCAC), which upon further photolysis was converted in part to dichlorocarbonyl (phosgene or DCC) and possibly formyl chloride, and ultimately to HCl and CO_2. Further treatment of photo-oxidation products is recommended for full-scale operation.

This Project Summary was developed by EPA's Risk Reduction Engineering Laboratory, Cincinnati, OH, to announce key findings of the research project that is fully documented in a separate report of the same title (see Project Report ordering information at back).

Introduction and Background

Many environmental remediation sites are polluted with volatile organic com-

pounds (VOCs). Some of these sites are amenable to remediation by vacuum-induced soil venting and groundwater air stripping methods. VOC air emission controls for restoration activities, however, are becoming required by regulatory agencies. We report the application of a pulsed xenon lamp (flashlamp) as a UV light source for the photo-oxidation of some VOCs in air.

Previously, the only light source that was routinely used for UV photolyses on a large scale was the mercury discharge lamp and doped variations thereof. Flashlamps discharge electrical energy through a fill gas in short micro second (μs) pulses and remain off for relatively long periods of milliseconds (ms). Because flashlamps have higher temperatures ($\geq$13,000 K) and pressures than continuous lamps, the emission is shifted to shorter wavelengths, Figure 1. The xenon flashlamp has a maximum output at 230 nm and a significant output at wavelengths as low as 200 nm, whereas the mercury lamp has most of its output at wavelengths above 250 nm. A shift in peak output from 254 to 230 nm is significant because it corresponds to a 1 to 2 order of magnitude increase in absorptivity of many VOCs, thereby greatly enhancing the rates of direct photolysis.

Initially, laboratory experiments were performed on saturated and unsaturated chlorinated hydrocarbons in air to screen compounds for treatability. The kinetics of photo-oxidation were studied, and apparent quantum yields were determined for the disappearance. Efforts were made to characterize the photo-oxidation products of TCE.

A full-scale photoreactor was built for the photo-oxidation of TCE and was tested at LLNL Site 300 at Building Complex 834. This summary contains information on the laboratory screening studies and performance data collected at the LLNL site on the photochemical treatment process for TCE. The TCE destruction effectiveness and the yields of the main oxidation products were characterized under various operating conditions, including flowrates of 100 to 290 cfm and TCE concentrations of 30 to 10,000 ppmv.

These results, combined with toxicological data, were used to estimate the operating conditions suitable for reducing the total toxicity from TCE and its residual products by 99% with the use of UV photolysis alone.

Experimental Methods

Laboratory Experiments: Pilot-Scale Photolyses

Air mixtures were irradiated in a 208-L steel, cylindrical reactor containing two small fans for mixing. A high intensity, 6-in. xenon flashlamp was inserted in the middle of the reactor through its side. All photolyses were performed at atmospheric pressure, and the gas temperature ranged from 300 K to approximately 340 K.

Known volumes of reagents were injected into the reactor by syringe, allowed to mix, photolyzed, and analyzed by gas chromatography with photoionization or electron capture detection. No reaction was observed in laboratory light or in the reactor with the lamp off. CO_2 measurements were made in one run using a Horiba PIR-2000 CO_2 monitor.

Field Measurements: Photoreactors

In the field studies at LLNL, the process stream was pumped from the extraction wells, through a heat exchanger to cool, and sent into two types of photoreactors. The Air-2 reactor (not shown) is a large steel cylinder, 4 ft in diameter by 8 ft in length, with a volume of 101 ft³. Four xenon lamps are distributed about the center of the cylinder and point radially inward. The process stream flows from one end of the cylinder to the other. Air-3 (Figure 2) is a Purus-patented reactor consisting of four disc-shaped stainless steel chambers. Each chamber is 42 in. in diameter by 6.1 in. high with a volume of 4.1 ft³ exposed to the light source. The lamps in Air-3 are positioned in the center axis of each chamber. The process flow enters the bottom of each chamber, around a deflection plate, in towards the lamp, and then out the top. The chambers in Air-3 are configured so that the flow is split through two sets of chambers in series. Some experiments were conducted with an enriched TCE air stream by gas injection from a pressurized liquid, TCE-filled, stainless-steel bubbler before the reaction chambers.

Analyses

A typical sampling session involved setting the process flowrate, adjusting the TCE concentration, and alternately taking at least three input and output TCE samples while photolyzing. The impinger samples were collected during the monitoring of the TCE concentration and were connected to the reactor port by 0.25-in. i.d. Teflon tubing.

TCE was analyzed by gas chromatography with a 30-m J&W 624 capillary column and photoionization detection. Samples were drawn by a gas-tight syringe at septum-sealed sample ports where the process flow entered or exited the reactor. TCE standards were prepared in volume-calibrated, glass sampling bulbs
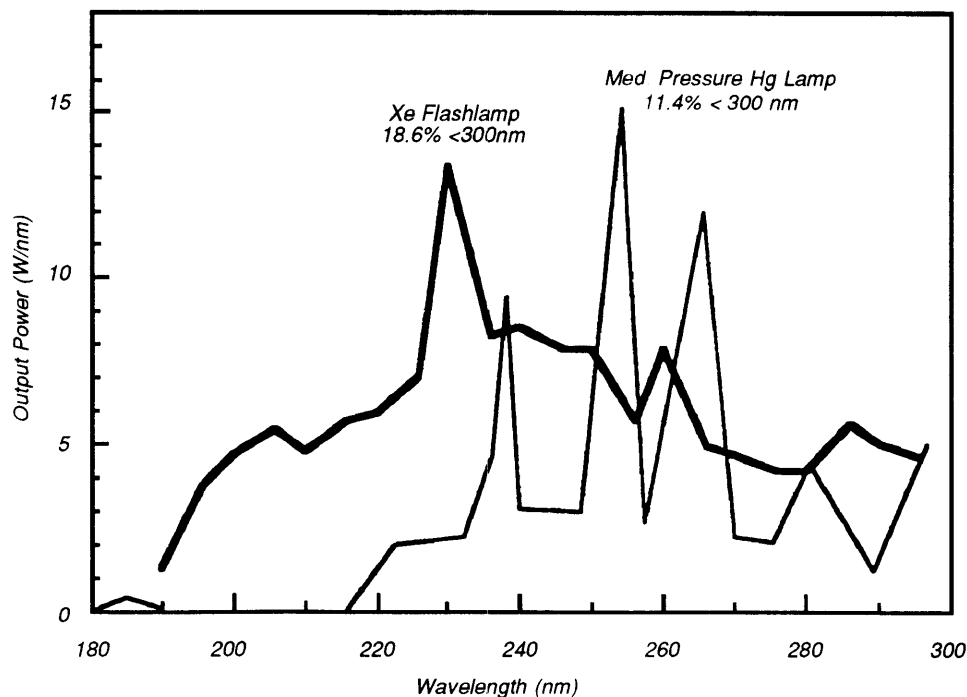

Figure 1. Emission spectrum for a mercury lamp versus a 6-in. Xenon flashlamp. (Both lamp outputs normalized to 3675 W input).
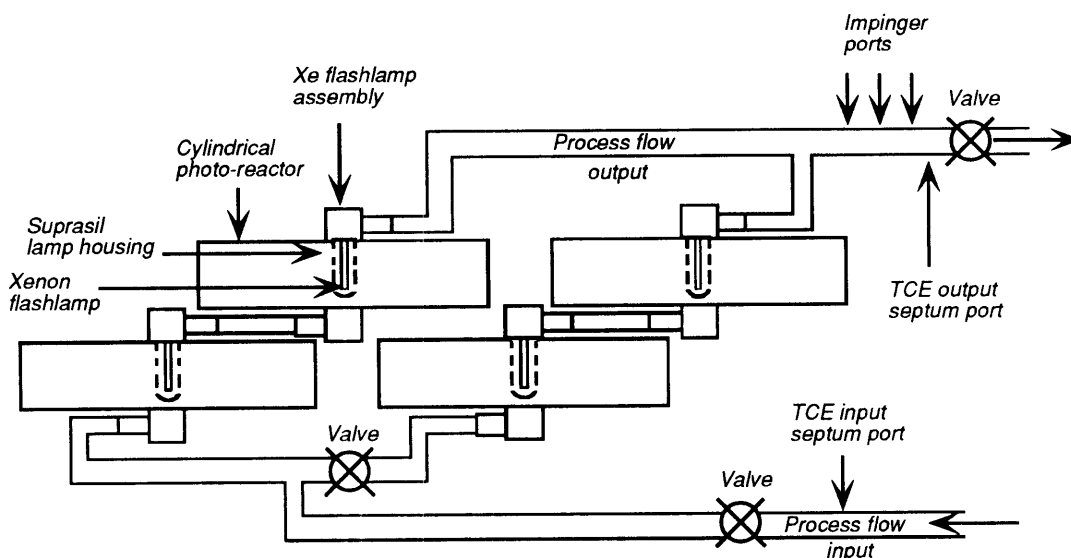
Figure 2. Schematic of Air-3 Photochemical Reactor.

by injecting liquid TCE into the bulbs; the detection limit was approximately 0.01 ppmv.

DCC was analyzed by EPA Method TO-6: 3 L of gas were collected in a series of impingers filled with 30 mL of a 2% v/v aniline/toluene solution, which reacts with DCC to give carbanilide. After solvent evaporation and take-up in acetonitrile, carbanilide was determined by high pressure liquid chromatography (HPLC) with an octadecylsilyl column and UV detection at 254 nm. The detection limit was 0.02 ppmv DCC, and the average recovery of carbanilide, based on standard samples run through the blowdown procedure, was 106 ± 19% (95% confidence interval).

DCAC was determined as methyl dichloroacetate after collection and derivatization in methanol impingers. Analysis involved gas chromatography with electrolytic conductivity detection. The detection limit was approximately 0.05 ppmv DCAC.

Total HCl and hydrolyzable organic chlorine were determined with the use of water impingers. The samples were analyzed by using EPA Method 325.3, a titrimetric method employing mercury nitrate to determine the chloride yield.

In one set of experiments, volatile organic compounds were determined by EPA Method TO-14 with the use of evacuated stainless steel (SUMMA) canisters and were analyzed by Coast to Coast Analytical Services, San Luis Obispo, CA. Agreement was reasonable; the Purus analyses

agreed with the standards within 10% and the Coast to Coast analyses within 25%.

Results and Discussion

Laboratory Experiments: Photolysis Kinetics and Quantum Yields

Table 1 summarizes the results of the laboratory experiments conducted in the pilot-scale reactor. CCl_4 was used as an actinometer assuming it has a disappearance quantum yield of 1.0, based on the literature data at 214 nm. The apparent quantum yields are averaged over the

wavelength range of overlap of the compound absorbances and the emission spectrum of the lamp. Benzene had a low quantum yield, consistent with the ability of aromatic compounds to intersystem cross, fluoresce, and thermally decay by modes that do not result in bond cleavage. The first four halogenated compounds in Table 1 have quantum yields near unity, indicating that simple C-Cl bond cleavage is highly efficient, as expected by analogy to CCl_4. Nevertheless, these compounds photolyzed relatively slowly because they absorb light weakly. Even shorter wavelengths than those available from the cur-

Table 1. First Order Decay Coefficients and Wavelength-Averaged Disappearance Quantum Yields with a 2.756 kW Xenon Lamp

Compound	k (sec-1)*	$\dfrac{\Sigma\, l\lambda\varepsilon_\lambda^{CCl_4}}{\Sigma\, l\lambda\varepsilon_\lambda^{VOC}}$ +	$\dfrac{{}^kVOC}{{}^kCCl_4}$ =	Apparent Φ
CCl_4	0.00432	1.0	1.0	1.0
CCl_2FCClF_2	0.00093	5.09	0.22	1.1
Benzene	0.0019	0.067	0.44	0.029
CH_2ClCH_2Cl	0.0024	N.D.#	N.D.	N.D.
$CFCl_3$	0.0036	1.18	0.84	0.99
CCl_3CH_3	0.0041	0.79	0.94	0.74
CH_2Cl_2	0.0070*	4.60	1.62	7.5
$CHCl_3$	0.0366*	1.79	8.47	15
1,1-DCE	1.24*	0.0389	287	11
PCE	1.7*	0.0134	394	5.3
TCE	5.5*	0.0236	1300	31
TCE + ethene	0.075	0.0236	17	0.4

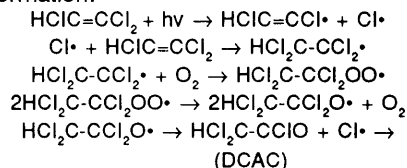* Initial rate constants are taken for non-log-linear curves.
N.D.= not determined.

rent Purus flashlamps are needed for a commercially viable, direct, photolysis process for these compounds.

The rate constants highlighted with an asterisk in Table 1 exhibited non-first order behavior, i.e., after about an order of magnitude loss, the rate constant started to decline. This same set of compounds photolyzed more rapidly (especially the chloroolefins) and had quantum yields greater than one. These results all point to the occurrence of a chlorine atom chain reaction in these cases, and this conclusion is verified by literature studies using chlorine gas to initiate chlorine atom reactions. Furthermore, when ethene was added in large excess to TCE, the TCE loss became first-order and much slower because ethene is an effective scavenger of chlorine atoms.

Chain Photo-oxidation Mechanism for TCE

Below we show that DCAC is the main initial photo-oxidation product of TCE in air. The following chain mechanism is consistent with all the product and kinetic information:

$$HClC=CCl_2 + hv \rightarrow HClC=CCl\cdot + Cl\cdot$$
$$Cl\cdot + HClC=CCl_2 \rightarrow HCl_2C-CCl_2\cdot$$
$$HCl_2C-CCl_2\cdot + O_2 \rightarrow HCl_2C-CCl_2OO\cdot$$
$$2HCl_2C-CCl_2OO\cdot \rightarrow 2HCl_2C-CCl_2O\cdot + O_2$$
$$HCl_2C-CCl_2O\cdot \rightarrow HCl_2C-CClO + Cl\cdot \rightarrow$$
$$(DCAC)$$

Similar pathways can be written for the other compounds that undergo chain decomposition. A common feature of the mechanisms for chain reacting compounds is that a Cl· atom reacts with them to generate a carbon-centered radical that has chlorine substitution, which can ultimately cleave a Cl· atom and propagate the chain. CCl_4 and the freons photolyze to the same type of radical but cannot form a chain because Cl· atoms do not react with C-Cl or C-F bonds.

Experiments with olefin mixtures demonstrated that co-contaminants can cause both sensitization and inhibition of photolysis. Thus, TCE and PCE can be expected to sensitize the photo-oxidation of the DCE isomers and vinyl chloride because the former are better light absorbers and the latter react with Cl· atom more readily. However, addition of chloroolefins will not sensitize the photoreactions of the chain promoters $CHCl_3$ and CH_2Cl_2 because the chloroolefins enhance the rate of Cl· atom scavenging as well as Cl· production.

Field Experiments

Figure 3 and Table 2 give TCE disappearance data and product data from experiments in Air-3 at LLNL Site 300. A larger data set over a broader range of conditions in Air-2 gave similar results and conclusions.

TCE Removal Efficiency

Over the range of experimental variables covered, TCE was photo-oxidized to >99% conversion except at the lowest flash frequencies and number of lamps. This conclusion held true even at TCE concentrations up to 10,000 ppmv and flowrates up to 300 scfm (data not shown). At the highest concentrations and optimal conditions, conversions of 99.9996% were achieved. Estimation of the TCE destruction efficiency was often limited by the 0.01 ppmv detection limit of the gas chromatographic method.

TCE Oxidation Products

Figure 3 shows the evolution of products during the photolysis of TCE in Air-3 at the field site. The data are taken from Table 2 and converted to an exposure time normalized to the standard conditions of four lamps operating at 30 Hz. DCAC is the principal initial organic product, formed in > 85% yield from the lost TCE. With further exposure, DCAC was consumed and formed about 20% DCC (Figure 3) and about 2% trichloroacetic acid (TCAC; data not shown). The DCC and TCAC yields did not equal the DCAC loss, presumably because these compounds also photolyze or because other DCAC photolysis pathways exist that do not form DCC or TCAC. The unidentified
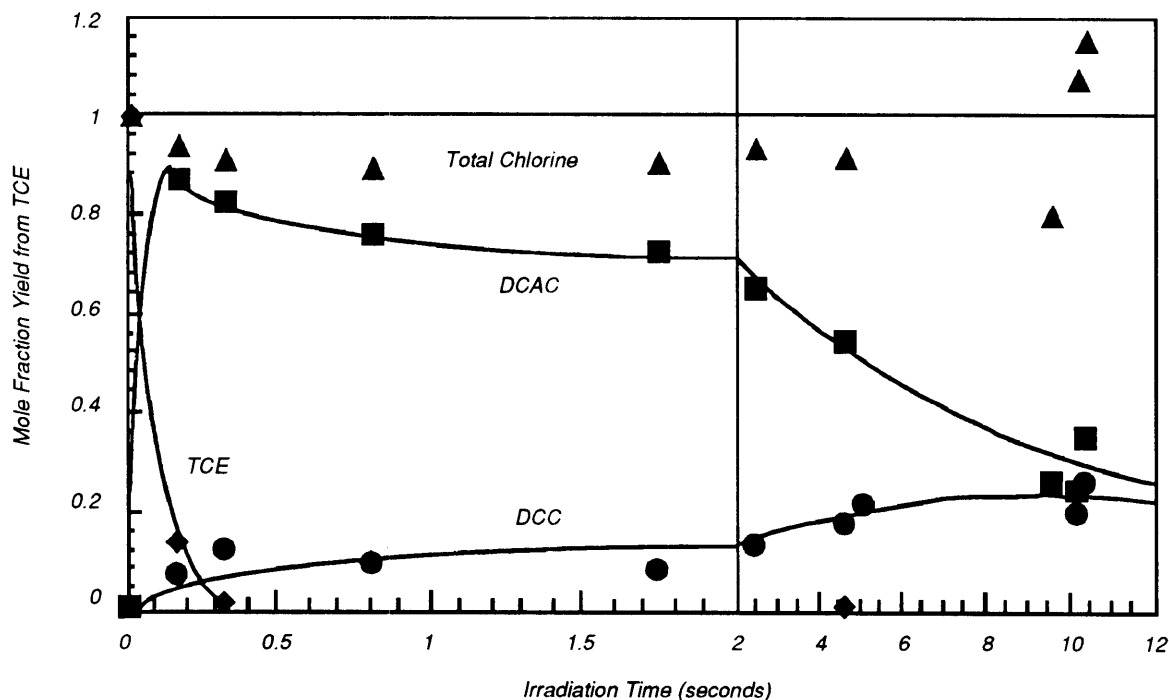

Figure 3. Product yields from the photolysis of TCE in Air-3.

Table 2. Summary of Field Results with the Air-3 Photoreactor *

Freq. (Hz)	No. of 3.7-kW Lamps	Res. Time (sec)	TCE Destruction (%)	Mole % DCC †	Mole % DCAC #	Mole % Cl-	Chlorine Balance (Mole %)
30	4	9.6	≥99.99	N.D. §	25.8	61.6	78.8
30	4	10.1	≥99.99	19.6	24.4	89.9	106.2
30	4	10.4	≥99.99	26.0	34.6	91.4	114.5
30	2	4.6	99.92	17.3	53.7	55.3	91.1
15	4	10.1	≥99.99	21.3	N.D.	68.2	N.D.
15	2	4.8	≥99.99	12.4	64.5	43.2	86.2
5	4	10.4	≥99.99	8.3	72.2	41.9	90.0
5	2	4.8	≥99.99	9.3	75.2	38.6	88.8
1	4	9.3	99.16	12.3	81.8	35.8	90.3
1	2	4.8	86.57	6.9	86.2	35.8	93.3

* Flowrate =100 cfm, initial [TCE] = 100 ppmv.
† Dichlorocarbonyl (phosgene).
# Dichloroacetyl chloride.
§ Not detectable.

carbon compounds must contain either no chlorine or only hydrolyzable forms of chlorine, because a good mass balance on chlorine is obtained (93 ± 23 %). The total chlorine recovery was defined as:

Fraction chlorine recovered = (moles chloride + 2 x moles DCAC) / (3 x moles TCE lost)

because the measured chloride was the sum of gaseous HCl and hydrolyzable organic chlorine, such as DCC, formyl chloride, and the carbonyl chloride of DCAC. Thus formyl chloride is a likely unidentified form of both chlorine and carbon. TO-14 whole air sampling tests verified that the concentrations of nonhydrolyzable chlorine compounds are low: the chloroform yield was 0.65% of the TCE input; the carbon tetrachloride yield, 0.15%; and the methylene chloride yield, 0.05%. A mass balance for carbon cannot be determined based on the measurements performed in this study; however, a preliminary CO_2 measurement indicated that most of the carbon is converted to CO_2 with enough light exposure.

Estimation of Parameters to Achieve Recommended Treatment Levels at LLNL Site 300

Because of the formation of toxic products, the efficacy of treatment at LLNL Site 300 cannot be measured simply in terms of TCE removal. The major product DCAC has approximately 40 times greater long-term toxicity than TCE, and DCC (phosgene) exhibits acute toxicity. Thus, these products would need to be removed by further photolysis or other post-treatment before emission to the atmosphere. A risk assessment indicated that the most

one can emit is 0.025% DCAC or 0.45% DCC of the initial TCE concentration to reach the goal of 99% reduction in initial toxicity. Our data indicate that a flowrate of 13 to 20 cfm in Air-2 or Air-3 with four 3.7-kW lamps can achieve the desired DCAC reduction. It is uncertain if the DCC concentration would be low enough when this DCAC treatment goal is reached. DCC could easily be removed with a water scrubber, where it would would rapidly hydrolyze to CO_2 and HCl. Traces of DCAC, however, would also hydrolyze to dichloroacetic acid (DCAA) and HCl, and with reasonably low water flows, the residual DCAA would still be at least an order of magnitude above the proposed drinking water limit of 0.2 ppb. Use of a relatively dry scrubber, such as slaked lime is a possibility because it would trap both DCC and DCAC. However, DCAA is likely to leach out when the lime is landfilled. Promising approaches include using very small flows of water and treating them by incineration or other thermal processes.

Conclusions

Kinetics of VOC Photo-oxidations

The low-wavelength emission of the pulsed xenon lamps allows direct photolysis of many VOCs, particularly chlorinated compounds and freons, that is not possible with commercial mercury lamps. Nevertheless, light absorption by some VOCs is still weak enough at 230 nm that either photosensitization or an even lower-wavelength source is needed for the photolyses to be rapid enough for commercialization at present. On the other hand, very rapid and efficient destruction is observed

for compounds that undergo chain reactions initiated by light, notably TCE, PCE, and DCE, in order.

TCE Photo-oxidation Products

The main product (> 85%) from the chain photo-oxidation of TCE is DCAC. Further oxidation of DCAC is approximately 100 times slower than the photolysis of TCE and forms DCC in about 20% yield, TCAC (≤ 2%), $CHCl_3$ (~0.65%), CCl_4 (~0.15%), CH_2Cl_2 (~0.05%), and possibly formyl chloride and DCAA. Evidence was found that the carbon-containing products are eventually converted to CO_2 with enough exposure.

Estimation Of Process Parameters for Remediation

Although both full-scale reactors demonstrated very efficient removal of TCE, the formation of undesirable intermediates required that their toxicity be taken into consideration. A reduction in toxicity for TCE of 99% requires that the residual DCAC concentration be 0.025% of the TCE input concentration, and the DCC concentration must be 0.45% of the TCE input concentration. The maximum flowrate that meets the DCAC reduction goal at LLNL using four 3.7-kW lamps was estimated to be between 13 and 20 cfm. At this level of treatment, the DCC concentration may still be excessive and additional treatment may be needed. Scrubbing with water under these conditions would rapidly hydrolyze the DCC to CO_2 and HCl and the DCAC to DCAA and HCl. The accumulation of even a trace of DCAA may, however, result in a disposal problem for the water because the expected EPA drinking water limit for DCAA is so low (~0.2 ppb).

Recommendations

Further studies on the use of low-wavelength lamps for the destruction of VOCs should be directed at (1) verifying the effectiveness of dry or wet scrubbers to remove acidic photo-oxidation products, (2) developing thermal or other methods for post-treatment of products such as DCAA present in the water after scrubbing, and (3) examining the use of shorter-wavelength UV lamps or catalysts for photolysis of a broader range of VOCs. Purus will examine some of these issues together with Argonne National Laboratory in continued demonstrations at the Department of Energy Savannah River site.

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