

A Full-Scale Demonstration Study Comparing UV/Cl₂ and UV/H₂O₂ for the Treatment of 1,4-Dioxane in Potable Reuse

ARIZONA WATER REUSE 2015 SYMPOSIUM



Acknowledgements

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Outline

- Background Info Leo J. Vander Lans AWTF
- Process Fundamentals: UV/H₂O₂ & UV/Cl₂
- Full-Scale AOP Results: UV/H₂O₂ vs. UV/Cl₂
- Cost considerations
- Summary



Leo J. Vander Lans Advanced Water Treatment Facility

- LJVWTF began operation in 2005
- Treating 3 million gallons/day (MGD)
- UV design basis: 1.6-log reduction of NDMA





Regulatory Framework

- Why oxidation?
- For:
 - Removal of contaminants that pass through MF and RO
 - 6-log virus disinfection
- California requires an oxidation step post-RO
- Demonstrated by removing a basket of contaminants or 0.5log 1,4-dioxane





LVLWTF Process Flow Diagram





LVLWTF Expansion

- Plant expansion to 8 MGD was completed in '14
- 2 new trains of UV added
- Hydrogen peroxide injection system was added
- Design: 2.1-log reduction of NDMA and 0.5log reduction of 1,4-dioxane
- Site acceptance testing required
- UV/Cl₂ study performed in parallel



LVLWTF UV-Oxidation System



Advanced Oxidation Processes (AOPs)

- Rely on formation of highly reactive species such as hydroxyl radicals (•OH) or chlorine radicals (•Cl) which degrade the chemical contaminants
- UV/H₂O₂ is a well-established AOP in which the OH radicals are generated through photolysis of hydrogen peroxide
- UV/Cl₂ AOP relies upon the photolysis of chlorine species to generate OH radicals <u>and</u> chlorine radicals

UV-Photolysis

Chemical Bonds are Broken by UV Light

UV-Oxidation

Hydroxyl radical

Hydrogen peroxide

> Chemical bonds are broken by hydroxyl radicals

Approach to UV/H₂O₂ System Sizing

• Develop an in-depth understanding of all significant parameters that affect the photochemical kinetics of the process and create a mathematical model of the process.



Understanding UV/Cl₂ Requires that we understand

- Free & combined chlorine speciation as a function of pH
- Photochemistry of chlorine species (HOCI, OCI⁻, NH₂CI, NHCI₂, ...)
- Reactivity of radical species (CI
 and
 •OH) toward water micropollutants and chlorine species
- Breakpoint reactions: $HOCI + NH_2CI$, etc.

Aqueous Chlorine Speciation as a Function of pH



Fig. 1 – Relative distribution of main aqueous chlorine species as a function of pH at 25 °C and for a chloride concentration of 5×10^{-3} M (177.5 mg L⁻¹).

From Deborde and von Gunten, Wat. Res. 2008.

Absorption Spectra of Chlorine Solution Varies with pH



Chloramination & Breakpoint Reactions

- Reactions between chlorine and ammonia: $HOCI + NH_3 \rightarrow NH_2CI \text{ (monochloramine)} + H_2O (1)$ $NH_2CI + HOCI \rightarrow NHCI_2 \text{ (dichloramine)} + H_2O (2)$ $NHCI_2 + HOCI \rightarrow NCI_3 \text{ (trichloramine)} + H_2O (3)$
- Distribution of these species is dependent upon pH, temperature, contact time, Cl₂:NH₃ ratio and initial chlorine and ammonia concentrations.

Effect of pH on Chloramine Species



Photochemistry of Chloramines

- Molar UV Absorbance of monochloramine $\epsilon_{254} = 371 \text{ M}^{-1} \text{ cm}^{-1}$
- Photolysis of monochloramine: $NH_2CI + hv \rightarrow \bullet NH_2 + \bullet CI$

• $k_{\rm NH2CI, \bullet OH} = 5.2 \times 10^8 \,{\rm M}^{-1} \,{\rm s}^{-1c}$

$\bullet NH_2 + O_2 \rightarrow \rightarrow NO_3^- + NO_2^- + N_2O + NH_4^+$

^a De Laat *et al.* 2010; ^b Soltermann *et al.* 2014; ^c Poskrebyshev *et al.* 2003;

Photochemistry of Chloramines

- Molar UV Absorbance of dichloramine $\epsilon_{254} = 175 \text{ M}^{-1} \text{cm}^{-1a}$
- Photolysis of dichloramine: $NHCl_2 + hv \rightarrow \bullet NHCl + \bullet Cl$
- $\Phi_{\text{NHCl2}}=1.06^{\ a}$
- $k_{\rm NHC12, \ \bullet OH} = ? < 5.2 \times 10^8 \,{\rm M}^{-1} \,{\rm s}^{-1b}$

^a Soltermann *et al.* 2014; ^b Poskrebyshev *et al.* 2003;

LVLWTF, Long Beach, CA UV/Cl₂ vs. UV/H₂O₂ Study

Full-Scale Test Conditions

- 1,4-Dioxane treatment in RO permeate water
- Moderate levels of chloramines (~2.5 mg/L);
- Electrical Energy Dose (EED) ranged from 0.09 to 0.53 kWh/kgal
- pH (not adjusted) approximately 5.5.

Oxidant Levels

- Hypochlorite injection: 0 5.2 mg/L
- Free chlorine: 0 3.7 mg/L
- H₂O₂: 1.0 3.5 mg/L

Byproduct Formation in the UV/Cl₂ AOP

- Bromate ion (BrO₃⁻) in bromide-containing waters.
 Bromate is regulated in drinking water at 10μg/L
- Chlorite ion (ClO₂⁻) from hypochlorite photolysis with polychromatic light. Chlorite is regulated in drinking water at 1 mg/L
- Chlorate ion (CIO₃⁻) from free chlorine photolysis at 253.7 nm. Not regulated in drinking water; on Candidate Contaminant List 3
- Chlorinated organics including DBPs, potentially responsible for water genotoxicity

Pilot-Scale UV/Cl₂ AOP at a CA Water Reclamation Plant - Byproduct Formation

 A very limited number of UV/Cl₂ effluent samples were analyzed for potential byproducts: Chlorite, perchlorate, TOX, DBPs – non-detect.

Chlorine INF (mg/L)		рΗ	Bromide Bromate/ ug/L		۲L	Chlorate/ ug/L	
total	free		ug/L	INF	EFF	INF	EFF
1.02	0.3	6.65	77	ND	ND	ND	ND
1.84	0.75	6.05	73	ND	ND	470	500
6.00	5	7.2	61	ND	15		1400

Bromate DW MCL - $10\mu g/L$ Chlorate – no DW regulation; on CCL3.

Treated Water Chlorate Levels



Chlorine Species at UV Influent/Effluent



Hypo Injected
 [Cl2]TOTAL Influent
 [Cl2]FREE Influent
 [Cl2]FREE Effluent
 [Cl2]TOTAL Effluent
 NH2Cl Effluent

Chlorine Species at UV Influent



Chlorine Species at UV Influent/Effluent



EEO as a Function of Free Chlorine



Full-Scale UV/H₂O₂ & UV/Cl₂ AOP



Full-Scale UV/H $_2O_2 \& UV/CI_2 AOP$



Cost Implications

- Assumptions
 - \$0.95/gal bulk (12.5%) hypo
 - \$750/ton gas chlorine
 - pH = 5.5
 - Chlorine and peroxide dosed at 3 ppm
- Conclusions
 - UV-Cl₂ is ~12% cheaper if quenching is required



Cost Implications

- Assumptions
 - \$0.95/gal bulk (12.5%) hypo
 - pH = 6.5
 - Chlorine and peroxide dosed at 3 ppm
 - UV-Cl₂ leads to higher electrical cost (higher EEO)
- Conclusions
 - UV-Cl₂ is actually more expensive if pH is 6.5 and quenching is not required



Full-Scale UV/Cl₂ & UV/H₂O₂ AOP Study: Conclusions

- The UV/Cl₂ AOP is a highly complex, pH dependent process
- Following hypochlorite injection in RO permeate there are several chlorine species present simultaneously with potentially changing concentrations
- These chlorine species absorb UV 3 to 6 times stronger than H_2O_2 and are significantly consumed in the UV reactor
- UV/Cl₂ AOP efficiency for 1,4-dioxane treatment in RO permeate with pH~5.5 appears to be higher than that of UV/H₂O₂ but corrected for UVT the difference is slight
- Few byproducts measured
- UV-CI has the potential to lead to lower O&M costs if removal of residual peroxide is required and if pH is low

TROJAN

Thank you

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1,4-Dioxane Treatment: Pilot Runs (1)

Experimental Conditions:

- Swift B03 reactor: 3 LPHO lamps with a total power of 0.462 kW.
- Water source: GAC & IX filtered London City water.
- The UV system run in flow-through mode, at three flowrates:
 - o 15 18 GPM;
 - 28 31 GPM;
 - 48 50 GPM
- Water pH adjusted with phosphoric acid.
- \circ 1,4-Dioxane concentration: ~300 µg/L.
- <u>UV/Cl₂:</u>
 - 2.3 3.4 mg/L free chlorine
- <u>UV/H₂O₂</u>:
 - 3.0 3.2 mg/L H₂O₂



Water Quality and Oxidant Concentrations

GAC & IX - filtered water (prior to pH adjustment)						
рН	7.53					
alkalinity (as CaCO3)	95.35)mg/L				
%T (254nm, 1cm)	99.3%					
nitrate (NO3-)	0.8	mg/L				

[Oxidant, M] $\times \epsilon$ (M ⁻¹ cm ⁻¹)					
	UV/CI ₂	UV/H_2O_2			
Set 1	1.98E-03	1.71E-03			
Set 2	2.36E-03	1.72E-03			
Set 3	2.32E-03	1.80E-03			
Set 4	2.87E-03	1.78E-03			

1,4-Dioxane Treatment: Pilot Results

