Cyanide Generation During Preservation of Chlorinated Wastewater Effluent Samples

1 November 2005

Los Angeles County Sanitation Districts

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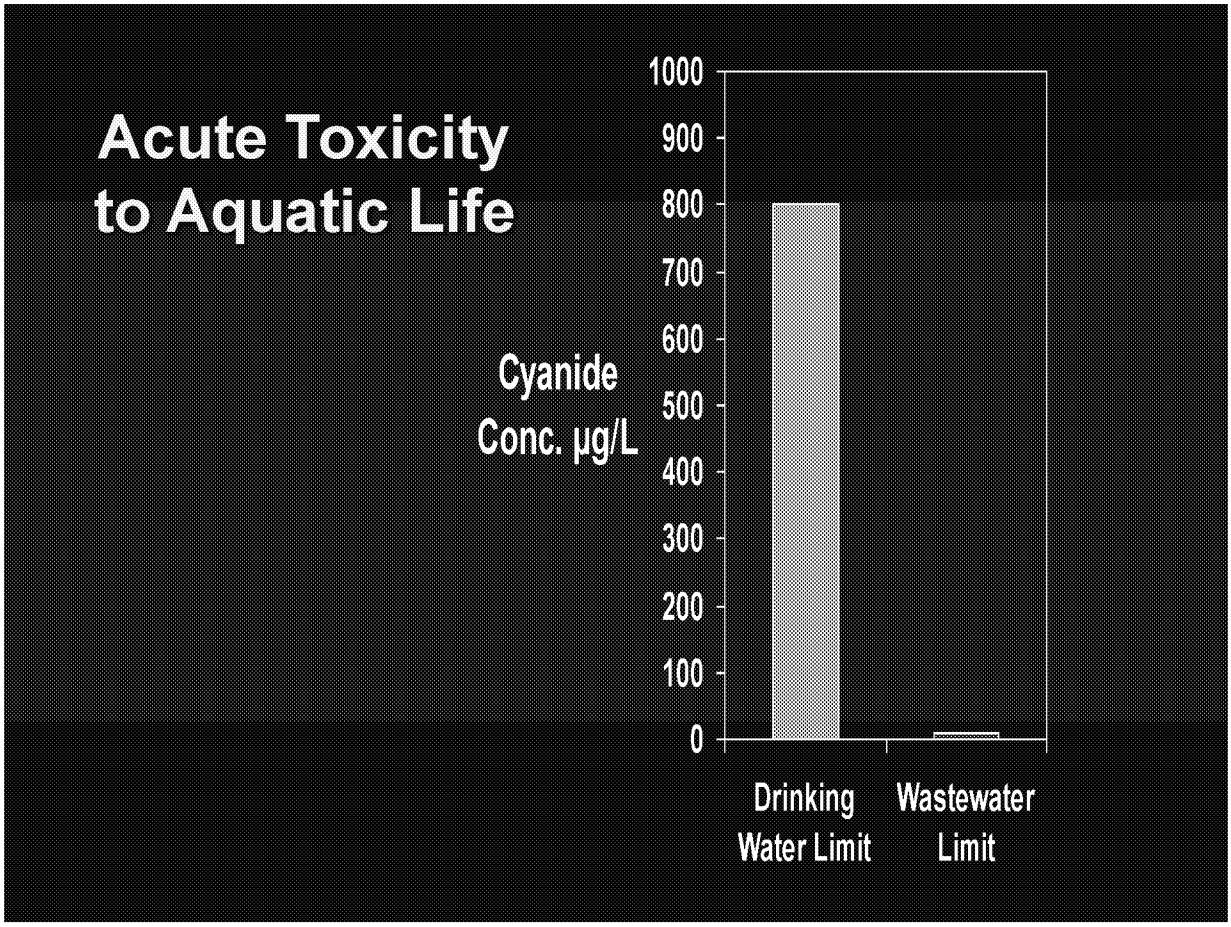
The Cyanide Problem

- Effluent levels exceed NPDES limits
- Not detected in the influent
- Disinfection by-product?
- Artifact of sample handling and analytical technique?

Cyanide Chemical Species

- Free: $HCN \rightleftharpoons H^+ + CN^-$
- Complexed: $M(CN)_6^{-n}$
- Strongly bound: Nitriles R-CN, Isonitriles R-NC
- Oxidized: Thiocyanate SCN^-,
  Cyanate CNO^-, etc..



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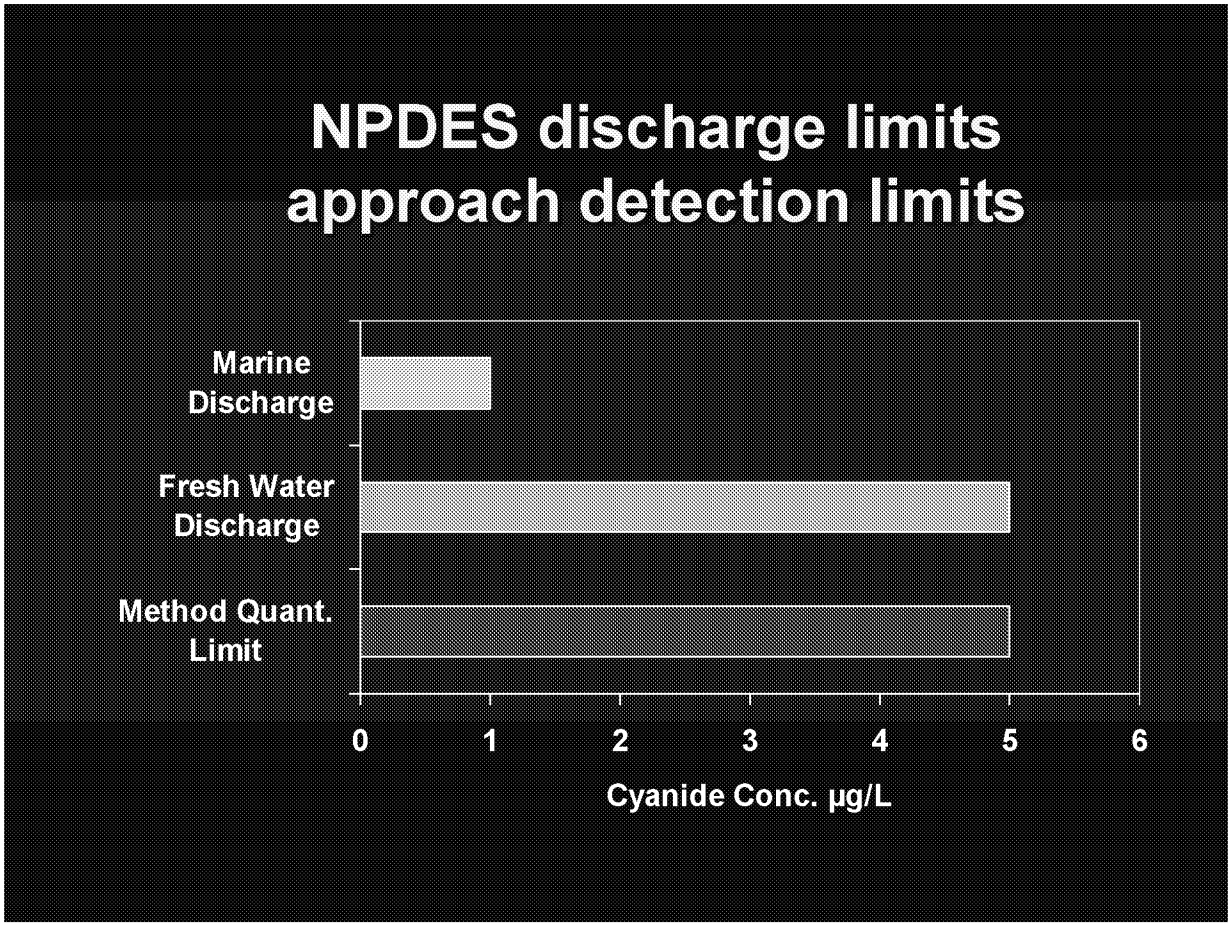

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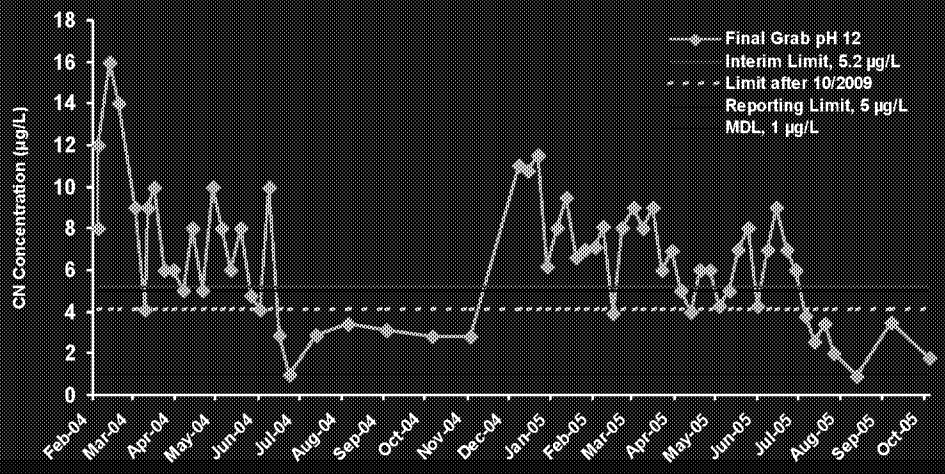
Effluent levels exceed discharge limits



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Cyanide Compliance Program

- Plant Operations: UV disinfection
- Analytical Methods
- Sample Collection Protocols

Analytical Methods

- Total Cyanide by acid distillation
- Weak acid dissociable cyanide
  - Acid distillation, colorimetric detection
- Available cyanide by flow injection
  - Ligand exchange, amperometric detection
- HPLC methods
  - Chemical derivatization
- Metal cyanides by ion chromatography
- Total cyanide by flow injection analysis

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Sample handling for CN analysis

Sample Chlorinated Wastewater → Dechlorinate, add NaOH to pH=12 → Hold for less than 2 weeks → Analyze

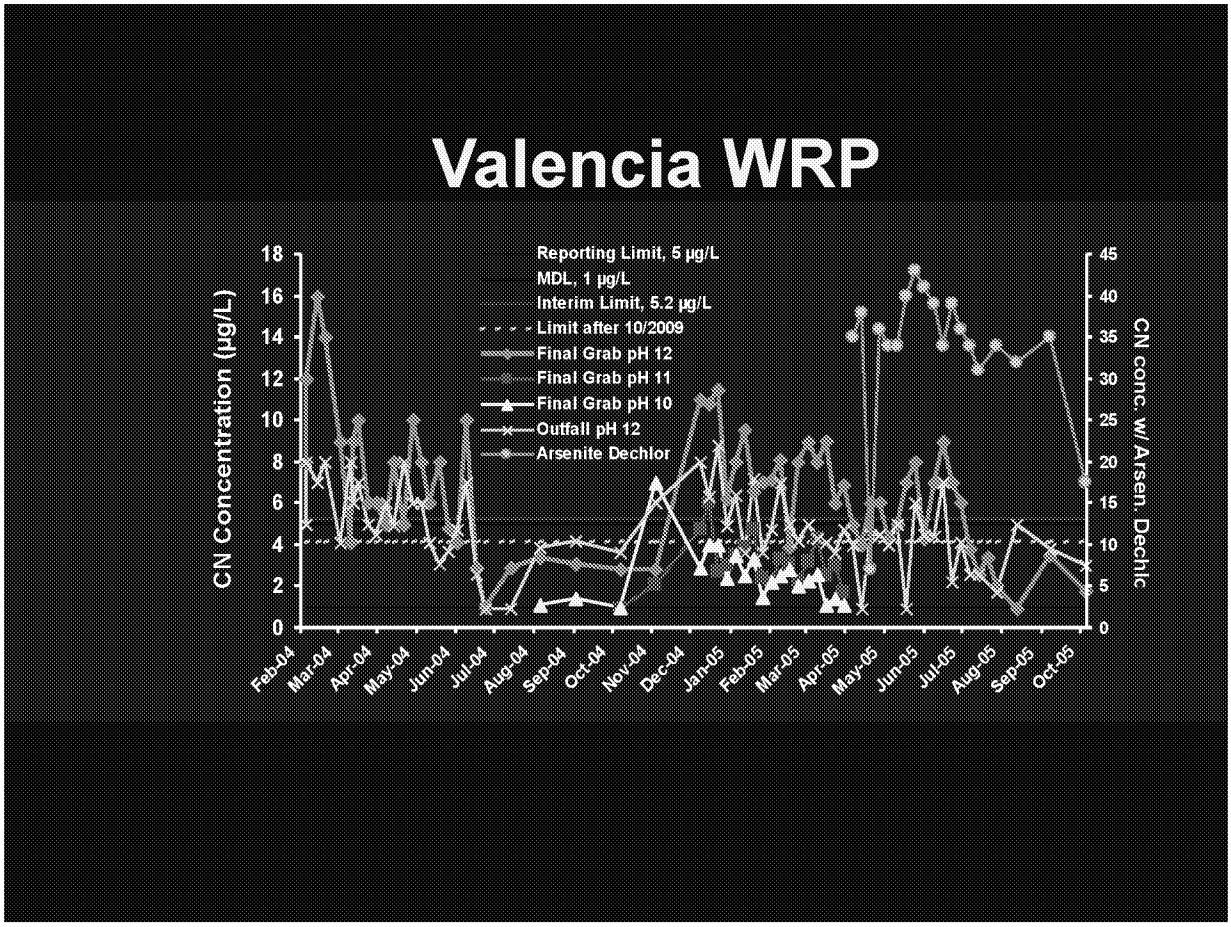
Necessary conditions for CN formation

- Wastewater effluent matrix
- Chlorine
- Reducing agent (dechlorination)
- High pH

Cyanide Results from 8 Water Reclamation Plants

- Chlorinated Final Effluent, Thiosulfate,
  pH=12
  pH=11
  pH=10
- Outfall, pH=12.
- Chlorinated Final Effluent, Arsenite, pH=12

Stored at 4°C, and analyzed within 14 days



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