Chemistry for Environmental Professionals – Applied

Industrial Processes
PCBs In Industry - Objectives

- Describe the chemical structure of polychlorinated biphenyls (PCBs)
- List major industries that formerly utilized PCBs
- List common trade names for PCBs
- List major modes of release to the environment
- Identify analytical methods for PCBs
- Describe remediation possibilities

PCB Overview - Volume and Scope of PCB Use

- Polychlorinated biphenyls (PCBs)
  - Class of industrially useful chemicals
  - Clear to yellow oily liquid or solid
- 1.4 billion lbs produced or imported from 1920s to 1977
  - 99% by Monsanto Corp
PCB Overview - Chemical Structure of PCBs

- 1–10 chlorine atoms attached to a biphenyl molecule
- 209 combinations (congeners)
- Molecular weight
  - 189 - 499 g/mole

PCB Overview - Industrially Useful Properties of PCBs

- Chemically and thermally stable
- Nonvolatile
- Nonflammable
- Dielectric (electrical insulator)
- Non-polar (behaves like oil)
- Dense (sinks in water)

PCB Overview - Industrial Uses of PCBs

- Capacitors and transformers (77% of all PCBs applied to this use)
- Hydraulic systems (6%)
- Heat transfer systems (2%)
- Other uses (15%)
Industrial Uses of PCBs - Transformers and Capacitors

- Transformers
  - Only 5-10% (of all) used PCBs
  - Electric power utilities (higher percentage)
  - Heavy industry (steel making, foundries, die casting, etc.)
  - Railroad engines
- Nearly all capacitors
  - Fluorescent light ballast
  - Phone connectors

Industrial Uses of PCBs

Hydraulic and heat transfer systems
- High temperature applications
- Yusho, Japan – famous poisoning incident, involved mass consumption of PCB-tainted rice (from heat exchanger leak)

Industrial Uses of PCBs

Other uses
- Natural gas pipeline compression stations
- Mining equipment (Joy Mfg.)
- Carbonless paper (NCR Corp.)
- Electromagnets (prior to 1970s)
- Chemical processes
  - Phthalocyanine pigments
- Investment casting
- Electric cable insulation
Nonflammable Lubricant desirable

Key Chemicals

<table>
<thead>
<tr>
<th>2011 ATSDR Rank</th>
<th>Polychlorinated biphenyls (PCBs)</th>
<th>Aroclor 1260</th>
<th>Aroclor 1254</th>
<th>Aroclor 1242</th>
<th>Aroclor 1248</th>
<th>Unspecified Aroclor</th>
<th>Aroclor 1221</th>
<th>Aroclor 1016</th>
<th>Aroclor 1232</th>
<th>TCDD, PCDFs</th>
<th>Trichlorobenzene</th>
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<td>14</td>
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<td>27</td>
<td>29</td>
<td>45</td>
<td>51</td>
<td>67</td>
<td>71, &gt;100</td>
<td>&gt;100</td>
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<tr>
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<td></td>
<td></td>
</tr>
<tr>
<td>Aroclor 1016</td>
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<td>51</td>
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</tr>
<tr>
<td>TCDD, PCDFs</td>
<td></td>
<td>71, &gt;100</td>
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<td></td>
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<tr>
<td>Trichlorobenzene</td>
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<td>&gt;100</td>
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</tbody>
</table>

Polychlorinated biphenyls (PCBs)
Aroclor 1254 (trade name), most toxic PCB blend
Aroclor 1260 (trade name), 60% Chlorine by weight
Aroclor 1248 (trade name), 48% Chlorine by weight
Other common Aroclors (1242, 1221, 1232)
Aroclor 1016 (attempted “safer” PCB blend)
PCDDs/PCDFs - toxic family of chlorinated byproducts
Trichlorobenzene - Askarel ingredient (40%)
Aroclors Are Mixtures - Example: Aroclor 1016

Aroclors Are Mixtures - Explained: 57% of Aroclor 1016 PCB's have 3 Chlorines attached

Other 3-chlorine PCB’s have chlorines attached in other combinations, e.g. 2', 5' and 5

Environmental Chemistry

<table>
<thead>
<tr>
<th>Aroclor</th>
<th>Wt. % chlorobiphenyl</th>
<th># Chlorine atoms attached</th>
</tr>
</thead>
<tbody>
<tr>
<td>1016</td>
<td>2 19 57 22</td>
<td></td>
</tr>
<tr>
<td>1221</td>
<td>10 50 35 4 1</td>
<td></td>
</tr>
<tr>
<td>1232</td>
<td>26 29 24 15</td>
<td></td>
</tr>
<tr>
<td>1242</td>
<td>1 13 45 31 10</td>
<td></td>
</tr>
<tr>
<td>1248</td>
<td>1 21 49 27 2</td>
<td></td>
</tr>
<tr>
<td>1254</td>
<td>1 15 53 26 4</td>
<td></td>
</tr>
<tr>
<td>1260</td>
<td>12 42 38 7 1</td>
<td></td>
</tr>
</tbody>
</table>
Trade Names for PCBs

- Monsanto
  - Aroclor
  - Pydral (hydraulic systems)
  - Askarel
    - Transformer fluid
    - 30–40% trichlorobenzene

- Imports and repackaged products
  - Nonflamol, etc.

Modes of Release

- Transformer, capacitor, and switch gear container leak or failure
  - Lightning strike, corrosion, struck by accident
  - Fire may produce PCDDs and PCDFs

- Fill and drain spills
  - Manufacturing and maintenance facilities
  - Electrical substations
  - Hydraulic systems
Modes of Release

- PCB-contaminated soil
  - Drain and fill residual
  - TSCA and RCRA limit is 50ppm
  
  Dec 2010
  Cu $3+ per lb

- Salvage operations
  - Break open and recover copper
  - Burn pits / PCDDs and PCDFs

- Manufacturing outfalls
  - Wastewater outfalls and sludge
  - Storm water

- Demolition debris
  - Inadequately cleaned spills
  - Fluorescent lighting ballast

- Disposal sites
  - Direct disposal allowed until 1979

Where Did They Go?
Fate & Transport

- Relatively water insoluble
- Soluble in fat tissue
  - Mechanism for bioaccumulation
- Strongly adsorbs to clays and natural organic matter
  - Higher concentrations in Sediments and Soil horizon
- Resists biodegradation - Half-life ~50 years
Analytical Considerations - Laboratory methods

- **SW-846 8082 (GC / ECD)**
  - Intended for intact Aroclors
  - "Fooled" by co-eluting peaks, e.g. toxaphene & phthalate esters
  - "Weathering" affects Aroclor "signature" (peak heights)

- **Method 680 (GC / MS)**
  - ID's individual PCB's, not Aroclors
  - Not fooled by co-eluting peaks

- **Other**

Field screening methods

- **Immunoassay**
  - Quantitation extrapolated from assumed distribution

- **Sodium reagent**
  - Measures chlorides

PCB Cleanups in Superfund

- Many historically
- PCB mfg halted in 1979
- 30+ years later, reduced residual PCB
  - Soil
  - Sediments
- Fox River Dredging Project
- Hudson River Dredging Project film
PCBs In Industry - Summary

- Describe the chemical structure of polychlorinated biphenyls (PCBs)
- List major industries that formerly utilized PCBs
- List common trade names for PCBs
- List major modes of release to the environment
- Identify analytical methods useful for detecting PCBs in the environment

PCBs In Industry - Video
Metal Finishing Processes

Barrel method electroplating

Metal Finishing Objectives

- List key chemicals associated with metal finishing
- Describe basic metal finishing processes
- Describe electroplating process details
- List major modes of release to the environment
- Identify analytical methods useful for detecting metal finishing contaminants in the environment

Process Overview

- SIC 347; NAICS 332813
- Billions of dollars per year, tens of thousands of businesses
- Both large and small businesses, from large scale automotive manufacturing to "mom and pop" job shops
Process Overview

- Metal surface preparation
- Surface protection and/or decoration
- Focus on electroplating

Process Details - Metal Surface Preparation

- Physical modification
  - De-scale, cut, shape, smooth
- Surface oil removal
  - Wipe, dip, vapor degrease
- Final cleaning
  - Detergent, acid, base, anodic, cathodic, ultrasonic
## Process Details – Cleaning / Degreasing

Solvents that are most used:
- Trichloroethylene
- 1,1,1-Trichloroethane
- Methylene chloride
- Tetrachloroethylene (Perchloroethylene)

## Process Details - Surface Protection / Decoration

<table>
<thead>
<tr>
<th>Organic coatings</th>
<th>Inorganic / metal coatings</th>
</tr>
</thead>
<tbody>
<tr>
<td>Solvent based</td>
<td>Physical deposition</td>
</tr>
<tr>
<td>Water based</td>
<td>Chemical deposition</td>
</tr>
<tr>
<td>100% solids</td>
<td>Electrochemical methods</td>
</tr>
</tbody>
</table>

## Process Details – Chemical Conversion Coating

- Conditions surface for painting or coating
- Uses chromates, phosphates, phosphoric acid, and hexavalent chromium
Process Details - Anodizing

- Electrochemical process
- Converts surface metal to insoluble oxide
- Uses chromic, sulfuric, or boric acids

Chromic Acid Anodizing vat

Process Details - Electroplating Process

Source: Adapted from EPA 1995

Plating vat for Chrome Plating
Process Details - Electroplating Process

- Electrochemical process
- Acid, alkaline, or neutral pH
- Uses metal salts, cyanides, brighteners, solid metal anodes
  - Cyanides keep metal ions in solution
  - Brighteners make surface more reflective

Fiber drums of ZnCN concentrate in abandoned plating shop

Process Details - Common Electroplating Bath Compositions

<table>
<thead>
<tr>
<th>Bath Name</th>
<th>Composition</th>
</tr>
</thead>
<tbody>
<tr>
<td>Brass and bronze</td>
<td>Copper cyanide, zinc cyanide, sodium cyanide, sodium carbonate, ammonia, Rochelle salt</td>
</tr>
<tr>
<td>Chromium</td>
<td>Chromic acid, sulfuric acid</td>
</tr>
<tr>
<td>Cadmium cyanide</td>
<td>Cadmium cyanide, cadmium oxide, sodium cyanide, sodium hydroxide</td>
</tr>
<tr>
<td>Cadmium fluoroborate</td>
<td>Cadmium fluoroborate, fluoroboric acid, boric acid, ammonium fluoroborate, licorice</td>
</tr>
<tr>
<td>Zinc</td>
<td>Zn metal, sodium hydroxide, sodium cyanide (some non-CN baths too)</td>
</tr>
</tbody>
</table>

Source: EPA 1990
Metal Finishing Process Video

Specialty Electronic Parts - Rack Method
Cu, In, Ga, Se sequentially electroplated onto solar panels

Standard Process Schematic
Corrosion, anyone?

Modes of Release

- Air emissions
  - Solvent vapors
  - Acid mists

- Water releases
  - Rinse water
  - Spent plating bath treatment
  - Washdown liquids

Modes of Release

- Solid and hazardous wastes
  - TCLP metals (D006, D007, etc.)
  - Wastewater (F006)
  - Spent plating baths (F007, F008, F009)
  - Quenching baths, etc. (F010, F012, F019)
Modes of Release

- Soil
  - Washdown liquids
  - Solvent spills
- Groundwater
  - Hexavalent chromium (more mobile)
  - Chlorinated solvents (DNAPL)

Emergency Response Possibilities

- Fire, Explosion
- Toxic Gases
- Toxic Liquids
- Metallic Dusts

Analytical Considerations

- Laboratory methods
  - Metals: AA, ICP
  - Solvents: GC/MS
- Field analytical methods
  - Hazard Categorization
  - Metals: XRF
  - Solvents: Portable GC, Portable GC/MS
  - CN gas: Real time instruments, Draeger
### Summary

- Mostly small businesses with limited environmental control programs
- Use a wide variety of chemicals:
  - Organic solvents
  - Metals, metal salts, and cyanide
  - Corrosives
- Metal finishing wastes can affect all four media: soil, surface water and sediment, air, and groundwater
Discarded material from homes and businesses: includes product packaging, newspaper, grass clippings, clothing, furniture, bottles, food scraps, appliances, paint, batteries, etc.

- Municipal solid waste (MSW), to 1908 landfills (2011)
  - 250 million ton/year
  - 54% landfilled
  - 35% recycled
  - 13% combusted w. energy recovery
### Process Overview

<table>
<thead>
<tr>
<th>Past practices</th>
</tr>
</thead>
<tbody>
<tr>
<td>- Open and burning dumps</td>
</tr>
<tr>
<td>- Failed to exclude hazardous waste</td>
</tr>
<tr>
<td>- Poor siting choices</td>
</tr>
<tr>
<td>- Lack of environmental protection</td>
</tr>
<tr>
<td>- Other problems</td>
</tr>
</tbody>
</table>

### Process Overview

- Federal government-led reform
  - SWDA (1965), RCRA (1976), etc.
  - Set standards for operation (sanitary landfill)
  - Classify/segregate waste streams
  - Contain/control/monitor off-site migration
  - Noncompliant facilities (open dumps) closed

### Garland Road Landfill

**Garland Road Landfill**
Key Chemicals

<table>
<thead>
<tr>
<th>Chemical</th>
<th>2011 ATSDR Rank</th>
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</thead>
<tbody>
<tr>
<td>Lead</td>
<td>2</td>
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<tr>
<td>Mercury</td>
<td>3</td>
</tr>
<tr>
<td>Vinyl chloride</td>
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<tr>
<td>Benzene</td>
<td>6</td>
</tr>
<tr>
<td>PCB</td>
<td>5, 12, 14, etc.</td>
</tr>
<tr>
<td>Cadmium</td>
<td>7</td>
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</tbody>
</table>
CEP—A Process  Municipal Landfills

### Key Chemicals

<table>
<thead>
<tr>
<th>Chemical Type</th>
<th>2011 ATSDR Rank</th>
</tr>
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<tbody>
<tr>
<td>PAHs</td>
<td>8, 9, 10, 15, etc.</td>
</tr>
<tr>
<td>Pesticides</td>
<td>12, 14, 24, 27, 29, etc.</td>
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<tr>
<td>TCE</td>
<td>16</td>
</tr>
<tr>
<td>Methane</td>
<td>69</td>
</tr>
<tr>
<td>Corrosives</td>
<td>&gt;100</td>
</tr>
<tr>
<td>Petroleum</td>
<td>N/A</td>
</tr>
</tbody>
</table>

### Standard Process Schematic

MSW, INDUSTRIAL WASTE  
SOIL/CLAY, RAINWATER  
LEACHATE  
METHANE, CO₂, VOCs, MERCURY  
LANDFILL GAS (ENERGY GENERATION)

### Process Details

<table>
<thead>
<tr>
<th>MSW Generation by Material Type (before recycling), %</th>
<th>1960</th>
<th>1980</th>
<th>2000</th>
<th>2007</th>
<th>2010</th>
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<td>Yard Waste</td>
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<td>13</td>
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<td>4</td>
<td>11</td>
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<td>13</td>
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<tr>
<td>Metals</td>
<td>12</td>
<td>10</td>
<td>8</td>
<td>8</td>
<td>9</td>
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<td>Rubber, leather, textiles</td>
<td>4</td>
<td>5</td>
<td>7</td>
<td>8</td>
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<tr>
<td>Glass</td>
<td>8</td>
<td>10</td>
<td>5</td>
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<td>5</td>
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<tr>
<td>Wood</td>
<td>3</td>
<td>5</td>
<td>6</td>
<td>6</td>
<td>6</td>
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<tr>
<td>Other</td>
<td>3 to 4 %</td>
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</table>
Landfill Construction Methods

Source: EPA 1972

Process Details

Landfill gas
- Produced by action of indigenous microorganisms upon degradable organic matter content of waste
- May contain CO₂, CH₄, H₂S, VOCs
- Production rates vary with waste composition, temperature, water content, air permeability, etc.
- Potential explosion hazard
Changes in Landfill Gas Composition Over Time

<table>
<thead>
<tr>
<th>Phase</th>
<th>Aerobic</th>
<th>Anaerobic</th>
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</thead>
<tbody>
<tr>
<td>I</td>
<td>100%</td>
<td>100%</td>
</tr>
<tr>
<td>II</td>
<td>90%</td>
<td>90%</td>
</tr>
<tr>
<td>III</td>
<td>80%</td>
<td>80%</td>
</tr>
<tr>
<td>IV</td>
<td>70%</td>
<td>70%</td>
</tr>
</tbody>
</table>

Gas composition (% by volume):

- CO₂: 55%
- CH₄: 40%
- N₂: 5%
- O₂: 5%
- H₂: 5%

Source: EPA 1994

Leachate Generation

Leachate: a liquid exudate, containing dissolved and finely suspended solid matter and microbial waste products.

Leachate Generation Key Factors

- Water infiltration rates
- Waste composition and leachability
- Underlying soil characteristics
- Depth / distance to receptors
Household Hazardous Wastes

- Thermometers: Mercury
- Waste oil: BTEX
- Batteries: Lead, cadmium, mercury
- Paints, Coatings, and Plastics: Driers, fillers, pigments (metals, salts, inorganics), plasticizers, etc.
- Cleaning solvents: TCE, acetone
- Others:
  - Appliances, pesticides, etc.

Source: EPA 1992

Leachate Generation with Time

Leachate Quantity vs. Time
Modes of Release

- Continuous release
  - Leachate
  - Landfill gases
- Fugitive emissions
  - Surface water runoff
  - Groundwater plume
  - Landfill gas migration
  - Construction incursion

Where Did They Go?

Organic Materials

- Relatively insoluble
- Electron donors (fuel) for biodegradation
- May create reducing environment
- Degradation byproducts may be more mobile

Where Did They Go?

Inorganic materials

- Relatively insoluble
- Sorbs to soil particles (attenuates migration)
- Transport via colloids
- Can be mobilized by pH or reducing conditions
Emergency Response Possibilities

- Explosion and/or fire
- Toxic gas emission
- Groundwater contamination

Mitigation/Remediation

- Presumptive remedy guidance
  - Gross treatment impractical
  - Containment
  - Run-on/run-off control
  - Gas collection/utilization, or flaring/venting
  - Leachate collection/control
  - Identify/remove “hot spots”
  - Monitor/remediate off-site plumes

Analytical Methods

Laboratory Methods
- TCL / TAL
- BOD, COD
- TOC, TOX
- TDS, TSS, specific conductance
- Chlorides, iron, manganese, sodium, etc.
### Analytical Methods

<table>
<thead>
<tr>
<th>Field Screening</th>
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<tbody>
<tr>
<td>- Soil gas</td>
</tr>
<tr>
<td>- Test kits</td>
</tr>
<tr>
<td>- Specific conductivity</td>
</tr>
<tr>
<td>- Eh, pH</td>
</tr>
<tr>
<td>- Direct-reading VOC meters (PID, FID)</td>
</tr>
<tr>
<td>- Explosimeter</td>
</tr>
</tbody>
</table>

### Summary

- Volume of MSW enormous
- Thousands of closed landfills
- Often contain industrial / hazardous waste
- Generate leachate / landfill gas
- Potential to degrade usable water supplies
- Cover / contain / control / monitor
Manufactured Gas Plants Objectives

- Describe the coal carbonization, producer gas and carbureted water gas processes
- List key chemicals associated with these processes
- List byproducts and wastes and their modes of release
- Identify analytical methods for detecting contaminants in environmental media

Industry Overview

- Manufactured gas produced by destructive distillation of coal and other organic feedstocks
- Later refinement reformed cracked gas with steam (a.k.a. water gas)
- Active from early 1800’s to mid - 1900’s
- Up to 50,000 former MGP sites
**Industry Overview**

- Producers included utilities, municipalities, railroads, industry, and (wealthy) homeowners
- Production est. (1880 -1950)
  - 15 trillion cubic feet of gas
  - 11 billion gallons of tar
- Most sites still controlled by original owners or successor entities

**Historical Highlights**

- 1796 - First U.S. experiments with gas lights (Philadelphia, PA)
- 1816 - First U.S. commercial gas light system (Baltimore, MD)
- 1850's - Gas works as far west as St. Louis
- 1870's - Carbureted Water Gas process introduced

- 1920's - Pipeline networks eliminate need for smaller plants
- 1940's - Interstate pipelines established
- 1950's - Most gas works closed
- 1990's - Last remaining industrial manufactured gas plants close
General Process Schematic

Key Chemicals

<table>
<thead>
<tr>
<th>2005 ATSDR Rank</th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Benzene</strong></td>
<td>6</td>
</tr>
<tr>
<td><strong>PAHs</strong></td>
<td>7, etc.</td>
</tr>
<tr>
<td><strong>Cyanide</strong></td>
<td>28</td>
</tr>
<tr>
<td><strong>Naphthalene</strong></td>
<td>78</td>
</tr>
<tr>
<td><strong>Phenol, coal, ammonia</strong></td>
<td>&gt;100</td>
</tr>
</tbody>
</table>

Process Details

Three Primary Processes

- Coal Carbonization
  - Developed c.a. 1800
  - Parallels coke plant technology
- Producer Gas, a.k.a. "Blue gas"
  - "Forgotten bulk" of MGP sites
  - Unsuitable for illumination
- Carbureted Water Gas Process
  - Patented by T.S.C. Lowe, c.a. 1870
  - Allowed spread to smaller towns
CEP—A Process Manufactured Gas Plants

Process Details
Coal Carbonization Process

- Developed first, c.a. 1800
- Gas suitable for fuel and illumination
- Produced salable tar and coke byproduct

Coal Carbonization Process Components

- Coal (1 ton)
- Heat
- No O₂
- Fuel &/or Illuminating Gas (11,000 ft³, 0.18 ton)
- Coke (0.6 ton)
- Tar and Other Byproducts / Waste

Chemistry for Environmental Professionals – APPLIED PROCESS

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Process Details
Producer Gas Process

- Produced medium BTU fuel gas
- Cheaper and more productive than coal gas process
- Steam injected onto "incandescent" coal or coke "reformed" to produce primarily H₂, CO, and CO₂
- Endothermic process: periodic injection or "blow" of air required to reheat coal bed
- Blue flame unsuitable for illumination.

Process Details
Producer Gas Process

Coal/Coke

Heat

No O₂

(periodic air injection to reheat fuel bed)

Produce Gas

+ Tar and Other

Byproducts / Waste

Process Details
Producer Gas Process Components
Carbureted Water Gas Process

- Patented by T.S.C. Lowe, c.a. 1870
- Cheaper process allowed spread to smaller towns
- Injected steam produces "Water gas"
- \[ C + H_2O \rightarrow H_2 + CO \]
- Injected or "carbureted" oil improved gas luminosity

Diagram:

- Coal/Coke + Steam + Oil → Heat (No O₂, periodic air injection to reheat fuel bed) → Fuel &/or Illuminating Gas + Tar and Other Byproducts / Waste
Process Details
Decline of MGP Industry

- Economics drove shift to poorer quality feedstocks, e.g. from coke to anthracite to bituminous coal, etc.
- Use of poorer feedstocks produced more watery unsalable "emulsion" tars
  - Up to 90% water
- Increasing competition from petroleum and natural gas led to MGPs' decline, deterioration, and abandonment

Process Details MGP Residues

<table>
<thead>
<tr>
<th>Inorganics</th>
<th>Metals</th>
<th>Volatile Aromatics</th>
<th>Phenolics</th>
<th>Aromatic Hydrocarbons</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ammonia</td>
<td>Aluminum</td>
<td>Benzene</td>
<td>Phenol</td>
<td>Acenaphthene</td>
</tr>
<tr>
<td>Cyanide</td>
<td>Antimony</td>
<td>Ethylbenzene</td>
<td>2-Methylphenol</td>
<td>Acenaphthylene</td>
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<tr>
<td>Nitrate</td>
<td>Arsenic</td>
<td>Toluene</td>
<td>2,4-Dimethylphenol</td>
<td>Anthracene</td>
</tr>
<tr>
<td>Sulfate</td>
<td>Barium</td>
<td>Total Xylenes</td>
<td>Phthoxane</td>
<td>Benzo(a)anthracene</td>
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<tr>
<td>Sulfide</td>
<td>Cadmium</td>
<td></td>
<td></td>
<td>Benzo(a)pyrene</td>
</tr>
<tr>
<td>Thiocyanate</td>
<td>Chromium</td>
<td></td>
<td></td>
<td>Benz(b)fluoranthene</td>
</tr>
<tr>
<td></td>
<td>Copper</td>
<td></td>
<td></td>
<td>Chrysene</td>
</tr>
<tr>
<td></td>
<td>Iron</td>
<td></td>
<td></td>
<td>Dibenzo[a,h]anthracene</td>
</tr>
<tr>
<td></td>
<td>Lead</td>
<td></td>
<td></td>
<td>Dibenzo(fluoranthen)</td>
</tr>
<tr>
<td></td>
<td>Mercury</td>
<td></td>
<td></td>
<td>Fluorene</td>
</tr>
<tr>
<td></td>
<td>Nickel</td>
<td></td>
<td></td>
<td>Indeno(1,2,3-cd)pyrene</td>
</tr>
<tr>
<td></td>
<td>Selenium</td>
<td></td>
<td></td>
<td>Naphthalene</td>
</tr>
<tr>
<td></td>
<td>Silver</td>
<td></td>
<td></td>
<td>Phenanthrene</td>
</tr>
<tr>
<td></td>
<td>Vanadium</td>
<td></td>
<td></td>
<td>Pyrene</td>
</tr>
<tr>
<td></td>
<td>Zinc</td>
<td></td>
<td></td>
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</tbody>
</table>
Categories of Wastes from MGP Sites

- Pumpable liquids (free tars and oils) / source material
- Organic waste or tar/oil-contaminated waters
- Organic waste or tar-contaminated soils and sediments
- Non-pumpable tars and sludges
- Purifier box (or spent oxide) wastes
- Demolition debris

Ammoniacal Liquors

- Derived from coal and added water
  - Contains ammonia, tar, light oil, and phenolics
  - Recirculated to hydraulic main
  - Excess treated, purified, discharged

- $\text{NH}_3 + \text{H}_2\text{SO}_4 \rightarrow (\text{NH}_4)_2\text{SO}_4$ (fertilizer)
- $\text{NH}_3 + \text{H}_2\text{O} \rightarrow \text{NH}_4\text{OH}$ (sold)

Condensibles

- Light oil
  - Contains BTEX (LNAPL)
- Naphthalene
  - Partially dissolves in oil
  - Partially solidifies (sublimes)
- Phenolics
  - Many constituents water soluble
### Light Oil and Naphthalene

<table>
<thead>
<tr>
<th></th>
<th>Benzene</th>
<th>Toluene</th>
<th>Xylenes (o,m,p)</th>
<th>Naphthalene</th>
</tr>
</thead>
<tbody>
<tr>
<td>m.p., °C</td>
<td>5.5</td>
<td>-95</td>
<td>-48–13.3</td>
<td>80.2</td>
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<tr>
<td>b.p., °C</td>
<td>80.1</td>
<td>111</td>
<td>138–144</td>
<td>218</td>
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<tr>
<td>sp.gr.</td>
<td>.88</td>
<td>.87</td>
<td>.86–.88</td>
<td>1.0</td>
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<tr>
<td>sol., mg/l</td>
<td>1750</td>
<td>526</td>
<td>161–185</td>
<td>31</td>
</tr>
</tbody>
</table>

### Phenolics

<table>
<thead>
<tr>
<th></th>
<th>Phenol</th>
<th>Cresols (o,m,p)</th>
<th>Catechol, et al.</th>
<th>Xylenols</th>
</tr>
</thead>
<tbody>
<tr>
<td>m.p., °C</td>
<td>43</td>
<td>12–35</td>
<td>105–173</td>
<td>27–75</td>
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<tr>
<td>sp.gr.</td>
<td>1.06</td>
<td>~1.03</td>
<td>1.15–1.35</td>
<td>&lt;1.0</td>
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<tr>
<td>sol., mg/l</td>
<td>8.3%</td>
<td>~2%</td>
<td>7%–infinite</td>
<td>&quot;slight&quot;</td>
</tr>
</tbody>
</table>

### Coal Tar Liquids

- Polynuclear aromatics
  - Creosote oil
  - Refined tar
  - Pitch, bitumen
- Significant volumes produced
- Sell it or dump it today
- Tars are DNAPL - most environmentally damaging
**Polycyclic Aromatic Hydrocarbons (PAHs)**

<table>
<thead>
<tr>
<th></th>
<th>Anthracene</th>
<th>Phenanthrene</th>
<th>Pyrene</th>
<th>Chrysene</th>
</tr>
</thead>
<tbody>
<tr>
<td>m.p., °C</td>
<td>216</td>
<td>100</td>
<td>151</td>
<td>254</td>
</tr>
<tr>
<td>b.p., °C</td>
<td>340</td>
<td>340</td>
<td>404</td>
<td>488</td>
</tr>
<tr>
<td>sp.gr.</td>
<td>1.25</td>
<td>1.03</td>
<td>1.27</td>
<td>1.27</td>
</tr>
<tr>
<td>sol., mg/l</td>
<td>1.3</td>
<td>0.9</td>
<td>0.16</td>
<td>0.006</td>
</tr>
</tbody>
</table>

**Other MGP Byproducts/Wastes**

- **Coke**
  - Usually reused in retort ovens, boiler, CWG process, or sold
- **Solid Waste**
  - Demolition debris, e.g. bricks, piping, etc.
  - Spent refractory bricks
  - Coal ash and "clinker" wastes
  - Purifier box waste

**Other MGP Byproducts/Wastes**

- **Captured sulfur and particulate**
- **Consists primarily of wood chips, iron or limestone**
- **May contain:**
  - cyanide
  - heavy metals
  - sulfates
  - some PAHs
What About Cyanide?

- Both mobile and immobile forms may be found
- Ferric Ferrocyanides (FFC) are brightly colored after exposure to air, e.g., Prussian Blue
- EPA has determined that FFC's are "cyanides" subject to CWA and CERCLA, 10/03 (Commonwealth of Mass. v. Blackstone Valley Electric)
- FFC can release free cyanide under certain conditions, including pH >7 and exposure to sunlight

Where Did That Chemical Go?

- Tars and tar emulsions
  - Low solubility, specific gravity >1 (DNAPL)
  - Resists biodegradation (esp. >4 rings)
  - Low volatility
  - Variable viscosity

- Tars and tar emulsions – cont.
  - High vertical migration potential
  - Preferential migration pathways
  - Particle and colloidal transport (vadose)
Where Did That Chemical Go?

- Light oils
  - Constituent of produced tars and/or brought on-site (CWG and oil gas process)
  - Low solubility, specific gravity <1 (LNAPL)
  - High volatility
  - Biodegradable
  - Localized plumes (mainly from leaks)
  - Minor constituent of other wastes

Analytical Considerations

- Metals
  - AA, ICP, XRF

- Light oils
  - GC, GC/MS

- Tars/solids
  - Wet chem extraction, separation
  - HPLC, IR, MS

- Cyanides
  - Total (colorimetric), Amenable (Cl₂+ colorimetric)

Summary

- Three main processes
- Tars are primary legacy waste
- Tars are DNAPL and sometimes more mobile than expected
- Some metals, including free and complexed cyanides