Thermal Oxidation for Halogens and Acid Gases

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Industries with Acid Gases

- CHEMICAL
- PHARMACEUTICAL
- REMEDIATION
- GAS INDUSTRY
- AMINE TAIL GAS
- ETHANOL
- WASTEWATER TREATMENT
Many of these applications contain halogens or acidic compounds

**HALOGENS**
- Chlorine
- Bromine
- Fluorine

**ACIDIC STREAMS**
- Carbonic acid (formed from carbon dioxide and water vapor)
- Sulfuric acid (oxidation of H2S and other sulfur containing compounds)
- Acetic acid and other organic acids
Oxidation Reaction

• Oxidation reaction produces an acid

\[
\text{Halogenated Hydrocarbon} + \text{O2} \rightarrow \text{CO2} + \text{H2O} + \text{Heat} + \text{Inorganic Acid}
\]

• Scrubber neutralizes the acid

\[
\text{HCl} + \text{NaOH} \rightarrow \text{NaCl} + \text{H2O}
\]
Oxidizer Selection

- **Regenerative Thermal Oxidizer (RTO)**
- **Thermal Recuperative Oxidizer**
- **Direct-Fired Thermal Oxidizer (DFTO)**
- **Catalytic Recuperative Oxidizer**
- **Emission Concentrator**
- **Vapor Combustor**

Removal of VOC / HAP by Combustion or Oxidation
Thermal Removal of VOC / HAP at High Temperatures
Catalytic Removal of VOC / HAP at Lower Temperature
Thermal Recuperative Oxidizer Overview

**AIR FLOW RANGE**
- 100-30,000 SCFM Single Unit

**CONCENTRATION RANGE**
- 0 – 50 % LEL

**THERMAL ENERGY RECOVERY**
- 50-70%+

**DESTRUCTION RATE EFFICIENCY (DRE)**
- 99%+

**INDUSTRY FOCUS**
- PHARMACEUTICAL
- COATING
- METAL DECORATING
- CHEMICAL
- EXPANDED POLYSTYRENE
Catalytic Oxidizer Overview

**AIR FLOW RANGE**
100-40,000 SCFM Single Unit

**CONCENTRATION RANGE**
0 - 25 % LEL

**THERMAL ENERGY RECOVERY**
50-70%+

**DESTRUCTION RATE EFFICIENCY (DRE)**
99%+

**INDUSTRY FOCUS**
- **PHARMACEUTICAL**
- **COATING**
- **PRINTING**
- **CHEMICAL**
Regenerative Thermal Oxidizer (RTO) Overview

**Industry Focus**
- Oil and Gas
- Composites
- Painting
- Chemical
- Expanded Polystyrene
- Pharmaceutical
- Coating
- Metal Decorating
- Wood Finishing
- Printing

**Concentration Range**
- 0 – 25% LEL

**Thermal Energy Recovery**
- True 95%+

**Destruction Rate Efficiency (DRE)**
- 99%+

**Air Flow Range**
- 2,500-70,000 SCFM Single Unit
Temperature and Residence Time

- Catalyst operating temperature normally increases from 600°F to 890°F
- Higher residence time required = higher catalyst volume

- Chamber temperature for halogens increases to 1650°F
- Residence time for halogens increases to 1.5 seconds
Upgraded Materials of Construction

Upgrade critical items to protect against potential corrosion from acids

**Catalytic Oxidizers**
Heat exchanger and inner reactor shell fabricated out of 316L stainless steel

**Thermal Oxidizers**
Corrosion resistant outer reactor shell (coated carbon steel, alloy shell material or shroud)

**Thermal Recuperative Oxidizers**
Heat exchanger fabricated out of higher alloy
Upgraded Materials of Construction

• RTOs:
  • Media support grid material upgraded
  • Higher thermal efficiency = lower outlet temperature = condensing concerns
  • Diverter valves/connection ducts upgraded to stainless steel or AL6XN
Dew Point Considerations

• If the acid dewpoint is reached in the oxidizer, the acid could condense, increasing corrosion potential.
• Will the addition of fresh, dilution air cause condensing? Fresh air may need to be heated.
• High RTO thermal efficiency leads to low outlet temperatures. Check acid dewpoint temperatures and select appropriate materials of construction.
• Approximate dew point temperatures (needs to be calculated for exact process conditions)

HCl, HBr, HF ~ 150°F
SO3 + H2O, Sulfuric Acid ~ 300-350°F
RTO Materials of Construction - Halogens

**PREHEATING DESIGN APPROACH**
Preheat process and any dilution air to 50°F above the acid dewpoint temperature

- **Heat Recovery Chambers/Combustion Chambers:** Carbon steel coated with a vinyl ester resin or hot shell design
- **Media Support Grid:** Hastelloy
- **Diverter Valves:** 316L stainless steel
- **Lower Hoppers:** 316L stainless steel
- **Purge Valves and Ducting:** 316L stainless steel
- **Inlet Header:** 316L stainless steel
- **Outlet Header:** 316L stainless steel
RTO Materials of Construction - Halogens

DESIGN APPROACH WITHOUT PREHEATING

- Heat Recovery Chambers/Combustion Chambers: Carbon steel coated with a vinyl ester resin or hot shell design
- Media Support Grid: Hastelloy
- Diverter Valves: AL6XN
- Lower Hoppers: AL6XN
- Purge Valves and Ducting: AL6XN
- Inlet Header: 316L stainless steel or AL6XN
- Outlet Header: AL6XN
Thermal Oxidizers: Hot Shell Design vs. Coatings

• An alloy reactor shell can be costly
• As an alternative the reactor shell can be designed to be kept warm with a shroud or coated with a corrosion resistant compound
• Either one or the other can be used. They cannot be used together.
• Coating is temperature sensitive
Hot Shell Design - Shroud

• A shroud is placed around the thermal oxidizer outer shell. The reactor shell is kept warm, above the dewpoint temperature of the acid present.

• The inner insulation thickness is reduced to keep the shell warm.

• A 3”- 4” air gap is placed between the shell and the shroud. Allows for air flow in the gap. The shroud protects the shell from rain and weather that may cool the shell below the dewpoint.
Hot Shell Design - Shroud

304L stainless steel shroud over a carbon steel reactor

304L stainless steel shroud over an AL6XN reactor
Coatings

• Vinyl ester resin – used on applications with HCl, HBr and sulfuric acid
Coating Applications

Sandblasting & Inspection
Surface and insulation pins are sandblasted to near white finish.

First Coat
First coat is applied to surface and insulation pins.

First Inspection
First coating application is inspected by a third-party inspector.

Infrared Imaging
Infrared images are taken during start-up to make sure that there are no hot spots present on the shell.

Final Coat
Final coat is applied.

Final Inspection
Final coating application is inspected by a third-party inspector.
Coating Application
Forced Draft vs. Induced Draft

- For acid gas systems induced draft is preferred
- With induced, system is under negative pressure, at any leak point fresh air would be drawn into system; acid would not leak out
- Any odor or safety concerns, induced draft is preferred
Acid Gas Scrubber

- Acids may require further treatment after the oxidizer
- Typically hastelloy quench and FRP scrubber sump, tower and stack
- All controls, instrumentation and piping by Anguil
- Over 80 oxidation systems operating with scrubbers
Case Study – RTO with Scrubber

- Chemical application, HCl formed
- Carbon steel reactor with vinyl ester coating
- Hastelloy media support grid
- AL6XN poppet valves, crossover duct
- FRP induced draft fan after scrubber
Case Study – DFTO

- Chemical application, HBr
- Carbon steel reactor with 304L SS shroud
- FRP induced draft fan after scrubber
- Inert process stream sent to burner
- Dilution air introduced into chamber; eliminates condensing issues
Case Study – Amine Tail Gas Plant RTO

• Sulfuric Acid concerns, H2S present
• Fresh air / process gas is heated to 350F with slip stream from hot side bypass
• 316L SS media support and poppet valves
• Internal coating
Acid Gas Scrubber

- $\text{HCl} + \text{NaOH} \rightarrow \text{NaCl} + \text{H}_2\text{O}$
- Countercurrent packed bed scrubber
We typically recommend a 25% solution of NaOH.
Complete RTO / Scrubber System
15,800 Nm$^3$/h (10,000 SCFM) RTO with Scrubber

- Pharmaceutical, HCl formed
- AL6XN crossover duct
- Hastelloy quench
- FRP scrubber tower
- FRP induced draft fan after scrubber
7,900 Nm$^3$/h (5,000 SCFM) RTO with Scrubber

• Soil remediation, HCl formed
• AL6XN crossover duct
• Hastelloy quench
• FRP scrubber tower
• Rubber lined induced draft fan after scrubber
55,200 Nm³/h (35,000 SCFM) Three Chamber RTO with Scrubber

• Pharmaceutical, HCl formed
• Hastelloy crossover duct
• Hastelloy quench
• FRP induced draft fan after scrubber
55,200 Nm$^3$/h (35,000 SCFM) Three Chamber RTO with Scrubber
47,300 Nm³/h (30,000 SCFM) Chamber RTO and Scrubber

- Pharmaceutical, HCl formed
- Shroud over RTO
- Hastelloy quench
- FRP induced draft fan after scrubber
141,300 Nm³/h
(90,000 SCFM)
Catalytic and Scrubber

- PTA process, HBr formed
- Steam preheaters to preheat process
- 316L stainless steel heat exchanger and crossover duct
- Hastelloy quench
205,000 Nm3/hr
(Dual 65,000 SCFM RTO)

- PTA process, HBr formed
- Steam pre-heater to preheat process
- 316 SS valves, RTO coldface
- Internal coating for corrosion protection
2,350 Nm³/h (1,500 SCFM) Thermal Oxidizer and Scrubber

- Pharmaceutical, HCl formed
- Alloy 800 (nickel-chromium) heat exchanger
- Hastelloy quench
- Rubber lined induced draft fan after scrubber