

Gaseous Controls

Chapter 6: Adsorption

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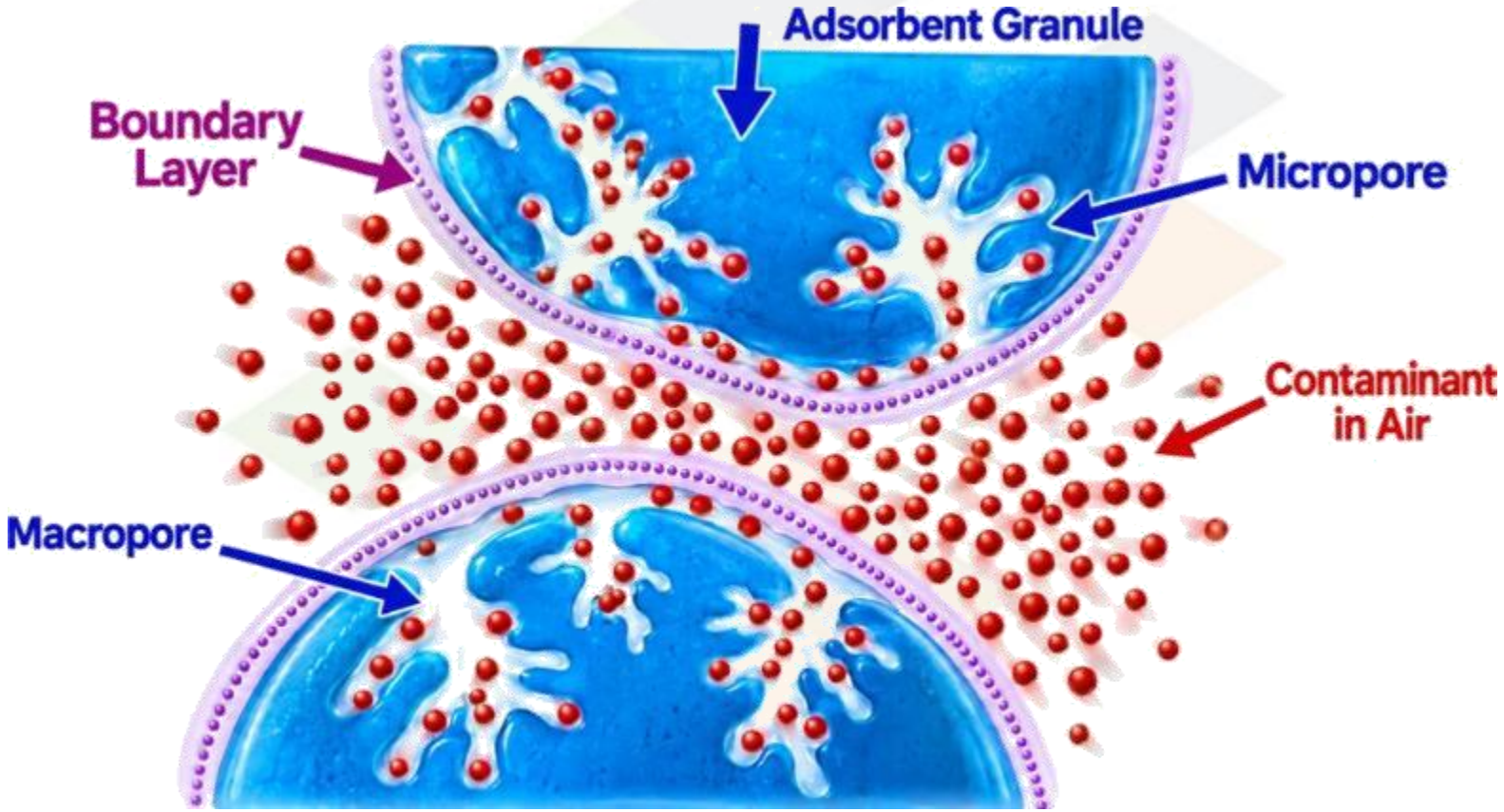
Chapter 6: Adsorption
Objective

In this chapter, we will discuss:

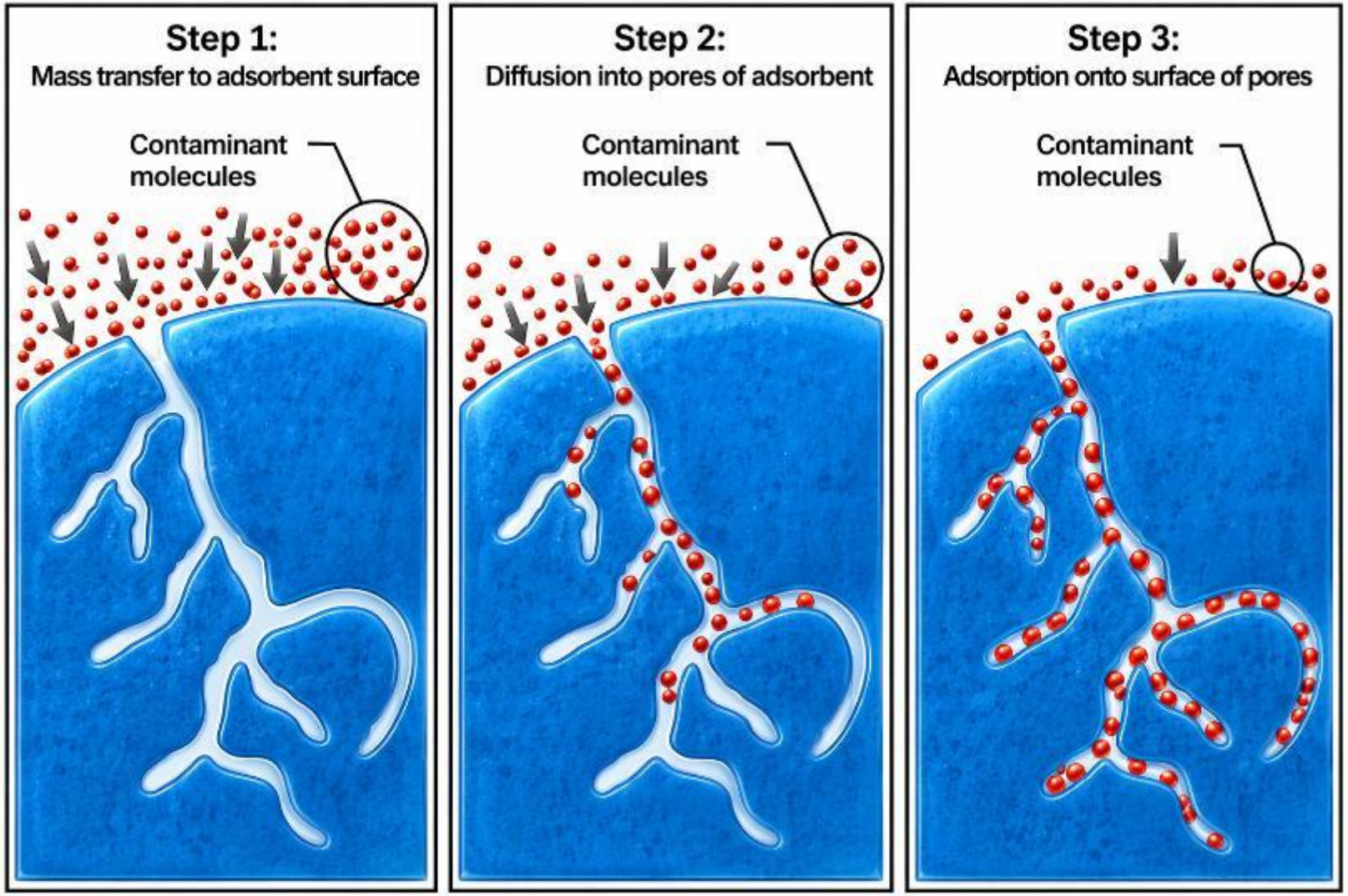
- How do adsorption control technologies operate?
- What are common types of adsorption control technologies?
- How are adsorption control technologies designed?
- What is the typical control efficiency for adsorption?
- How are adsorption control technologies monitored?
- What are common problems with adsorption control technologies?
- How do we ensure compliance?

Adsorption (Dry Scrubber)

- Pollutants in exhaust adhere to (captured) surface of a solid



Chapter 6: Adsorption
Principles of Operation



Absorption (Liquids)

Absorb

- Wet or semi-dry scrubber
- Air pollutant captured by liquids
- Chemical reaction optional
- Wet liquids must be treated for reuse or disposal

Adsorption (Solids)

Adhere

- Dry scrubber
- Air pollutant captured by solids
- Chemical reaction optional
- Solids may be disposed or desorbed for reuse

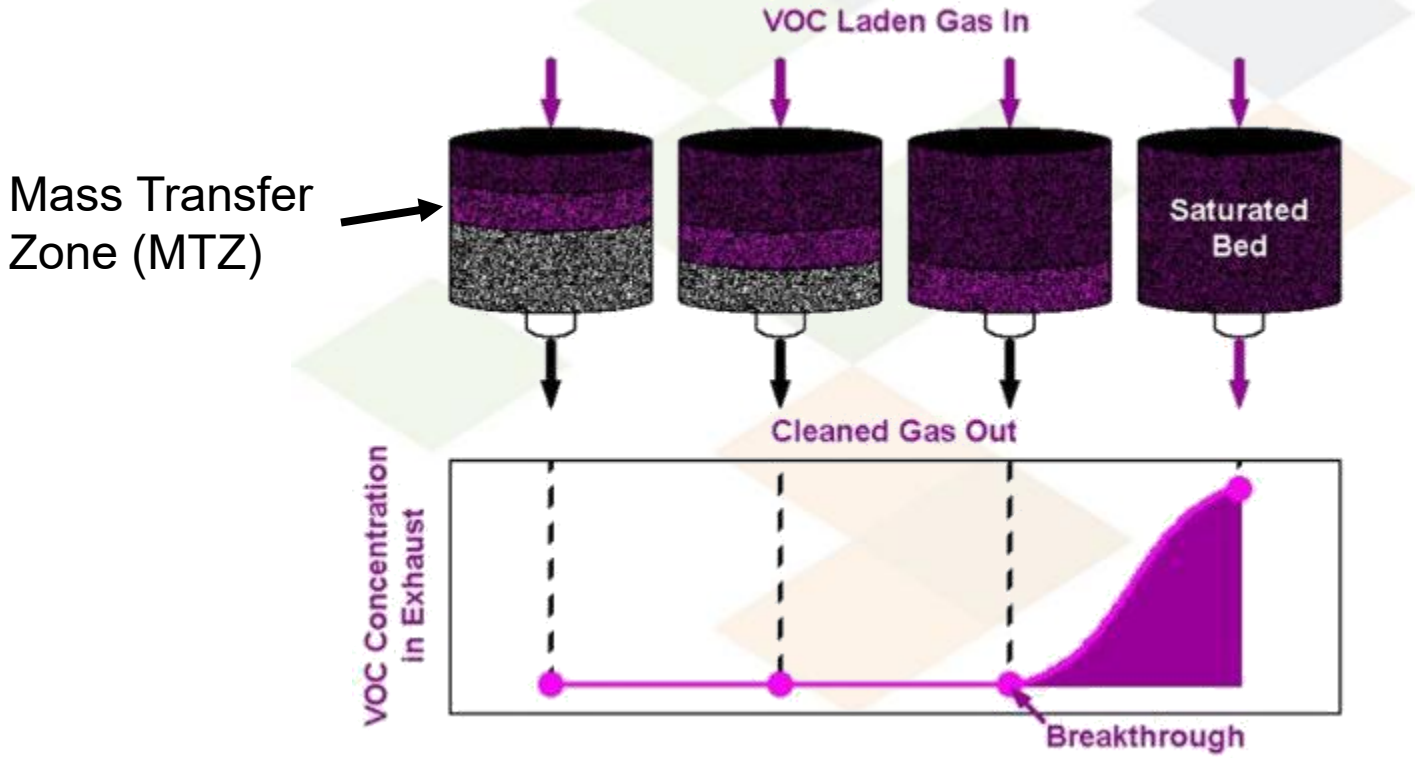
Adsorption (Dry Scrubber)

Pollutants in exhaust (adsorbates) are removed by adhering to solid adsorbent via physical or chemical reaction

1. **Physical (Physisorption)**: Adsorbate (pollutant) weakly bound; reversible (desorption); no new chemicals formed
   - Physical reaction may be reversed onsite or offsite
   - PM control device required only if adsorbate mixed with gas stream
2. **Chemical (Chemisorption)**: Adsorbate (pollutant) reacts with pollutant and is converted into new chemical
   - New chemicals created are usually water, CO_2, and salts that are removed by PM control devices

Saturation

- Adsorbent becomes saturated with pollutant over time
  - When Mass Transfer Zone reaches outlet of bed, breakthrough occurs



Adsorber Breakthrough



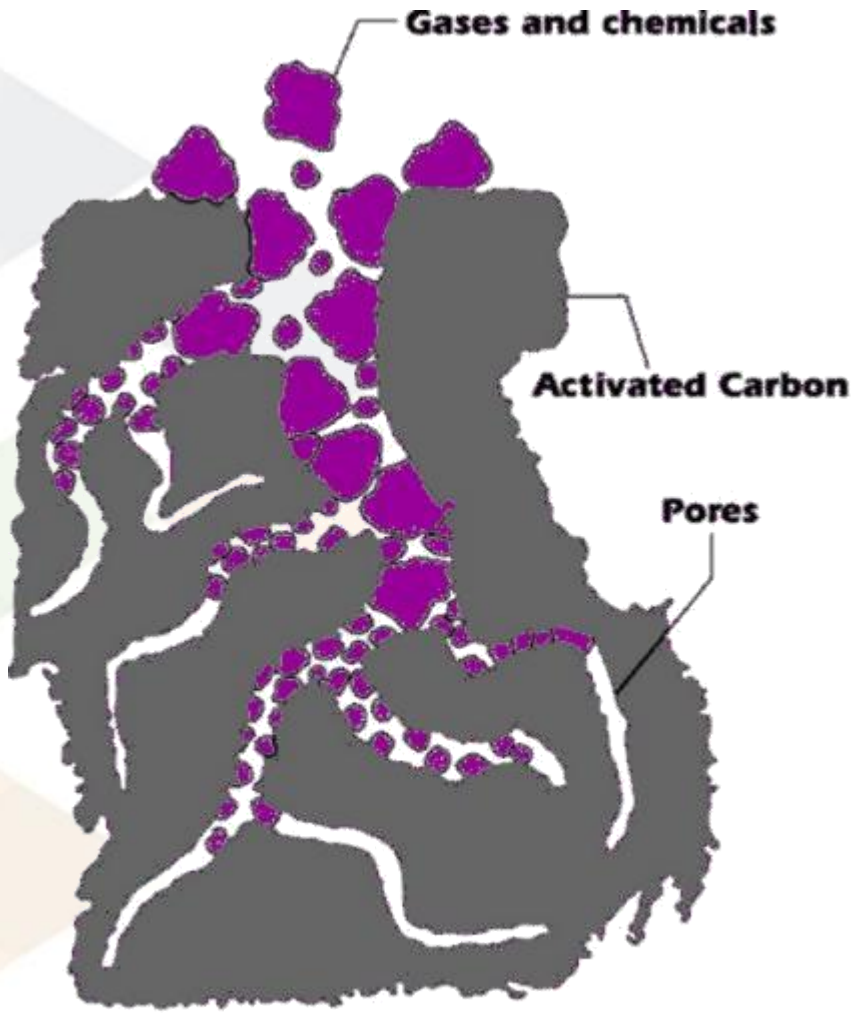
Chapter 6: Adsorption
Video

VOC 4.0 - Adsorption Intro.mp4

3.7 - Carbon Adsorption.mp4

Physical Adsorption

- Adsorbent is placed in bed (packed bed) or a thin layer is applied to support material
- Exhaust gas passes through / over adsorbent
- Air pollutants are removed by the adsorbent
- Process is reversible (desorb)

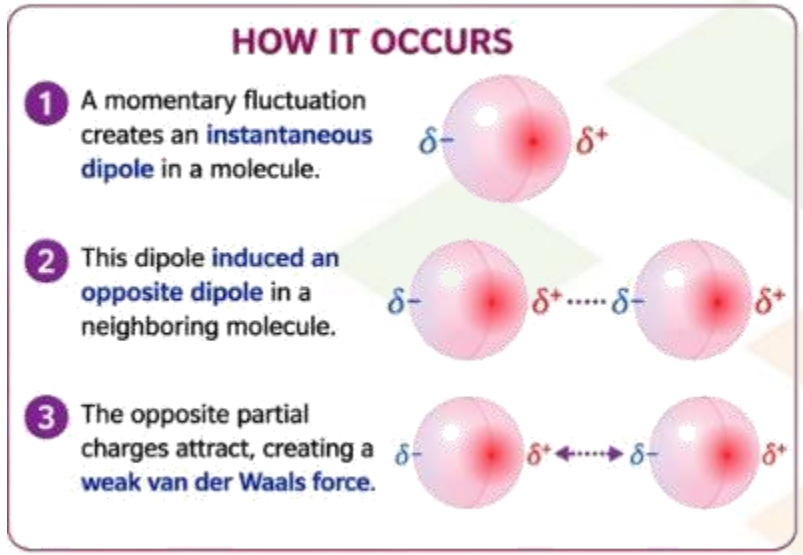


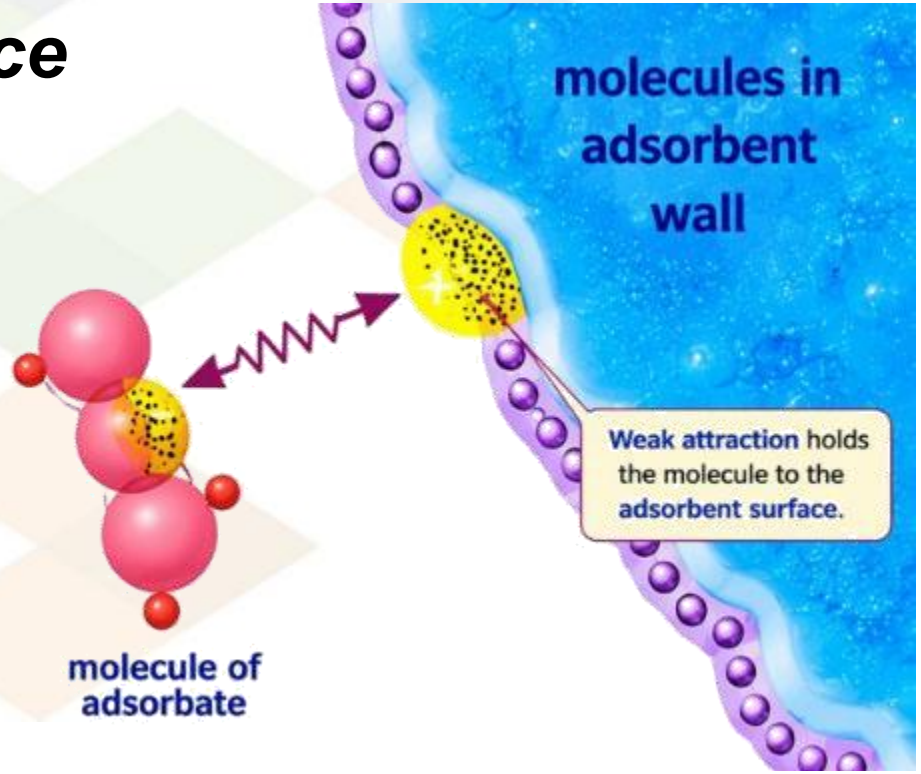
Activated Carbon adsorbs gases and chemicals

van der Waals Force: Weak, temporary molecular attraction

- Caused by slight, momentary shifts in electron clouds, creating brief positive and negative regions

London Dispersion Force





Desorption Options

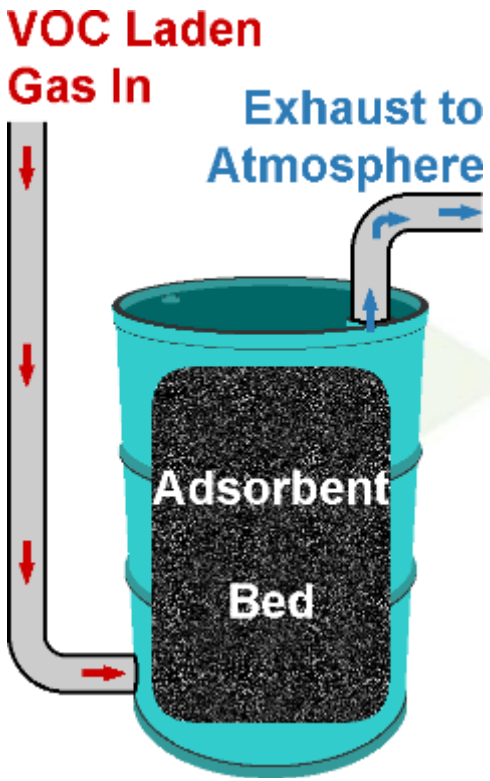
1. Thermal Swing: Raise bed temperature with steam or hot air
   - Cannot be used if exhaust is too hot or contains steam
2. Pressure Swing: Vacuum drawn on bed
   - Reduced heating / cooling time for bed
   - Higher operating / construction costs
3. Inert Purge Gas Stripping: Push unreactive gas through beds
   - Lowers partial pressure near pollutants in adsorbent, causing pollutants to enter inert purge gas stream
4. Displacement: Introduction of stronger adsorbate
   - Stronger adsorbate displaces pollutants in adsorbent

Chemical Adsorption (Chemisorption)

- Chemical bonding between adsorbate (pollutant) & adsorbent
  - Irreversible chemical reaction between adsorbate and adsorbent
  - Used to neutralize acid gases (CO_2, HCl, H_2S, SO_X, and NO_X)
- Chemicals adsorbent used depends on pollutant and exhaust gas conditions
  - Limestone ($CaCO_3$), hydrated / slaked lime ($Ca(OH)_2$), quicklime (CaO)
  - Sodium bicarbonate ($NaHCO_3$)
  - Magnesium Oxide (MgO)

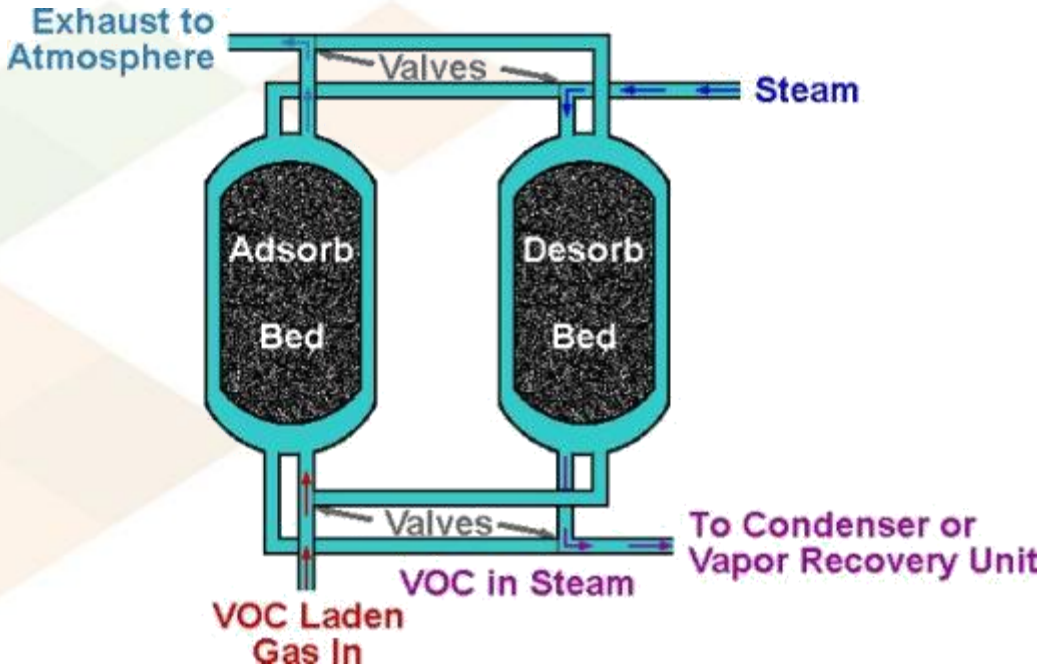
Non-regenerative Adsorbers

1. Fixed Bed
2. Injection



Regenerative Adsorbers

1. Fixed Bed
2. Rotary (Moving) Bed
3. Fluidized Bed



1. Fixed Bed:

- Used to control VOC
- Can be regenerated within control by steam or hot air
- Continuous operation requires multiple (>1) beds

2. Rotary (Moving) Bed:

- Uses carbon bed more effectively
- Can be regenerated within control by steam or hot air
- May be filters impregnated with activated carbon / zeolites

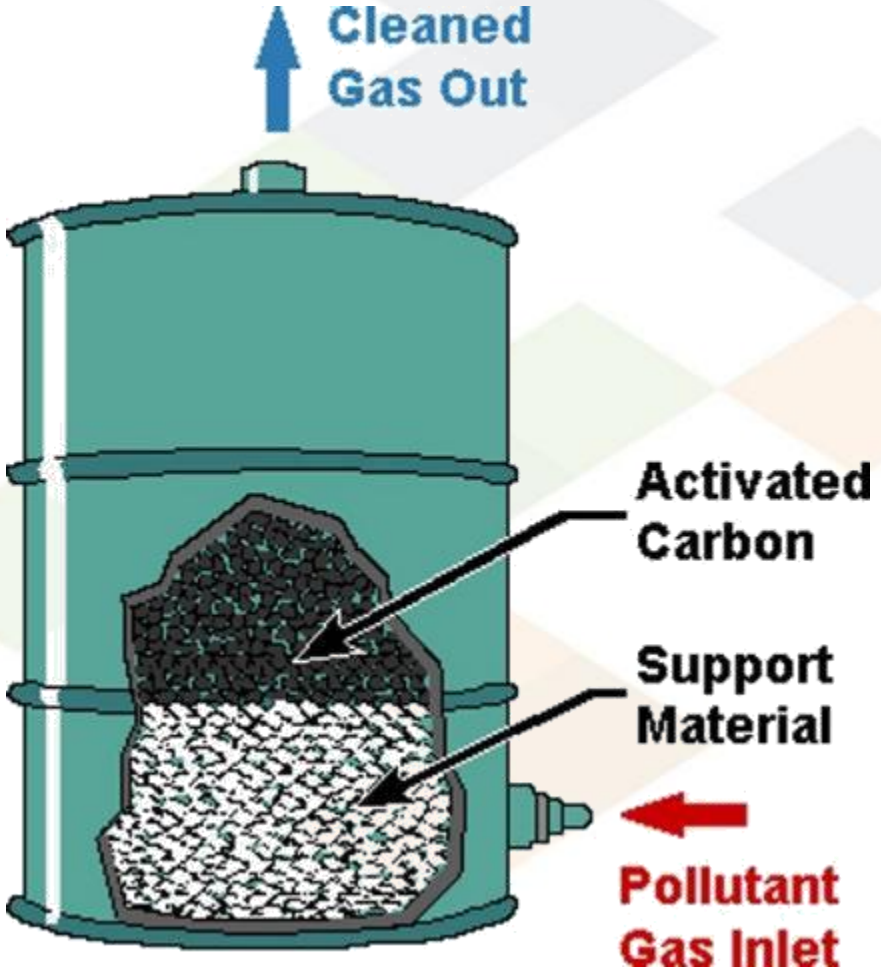
3. Fluidized Bed:

- Gas stream causes turbulence between pollutants and adsorbents
- Separate adsorption and desorption processes

Non-Regenerative Adsorber:

- Exhaust gas passes through adsorbent
- Air pollutants (adsorbates) are adsorbed
- Clean exhaust gas exits stack
- Spent adsorbent must be disposed of:
  - Can be regenerated offsite (higher temperatures); or
  - Disposed of as a solid waste (landfill)
- Service life generally equivalent to ≤50% of saturation capacity
- Commonly used for controlling VOC emissions from tanks, odor control, and landfill gas treatment

Fixed Bed Non-Regenerative Adsorber



Chapter 6: Adsorption Controls

Non-Regenerative Adsorbers





Dry Sorbent Injection (DSI)

- Sorbent injected into exhaust stream
  - Adsorption occurs in flue / duct
- Desorption not conducted
  - Activated carbon + pollutant removed by PM controls
  - Spent adsorbent contaminated and cannot be regenerated



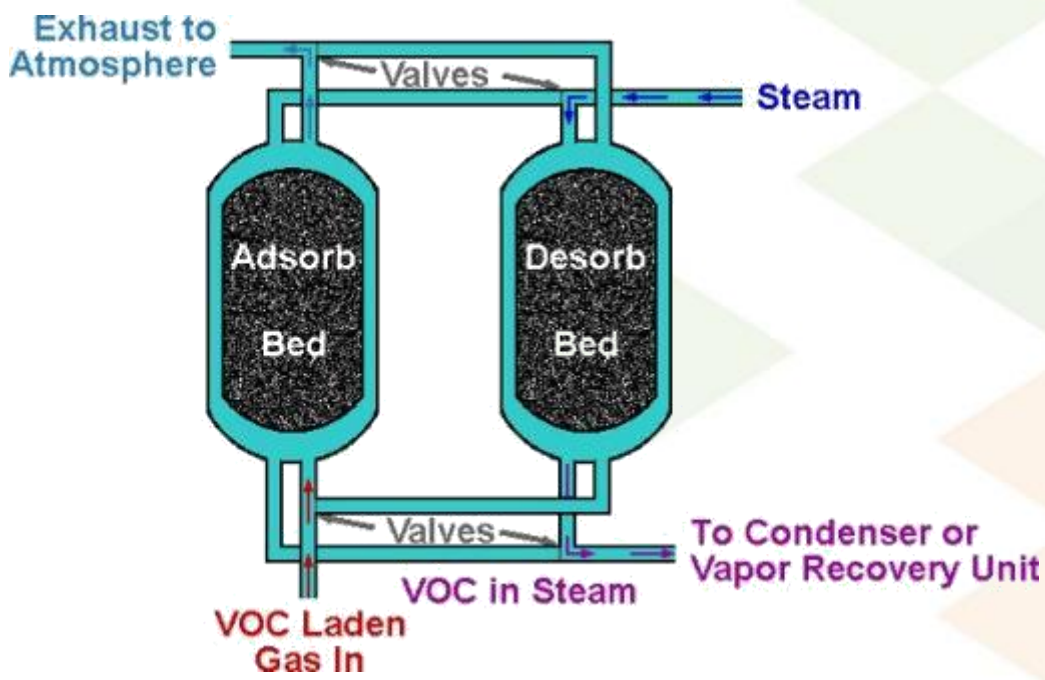
Regenerative Adsorber (Concentrator):

- Adsorbents with only physical binding to adsorbate can be desorbed via heat (regeneration) onsite

1. Adsorption Cycle: Concentrator collects air pollutants at variable concentration & flow
2. Desorption Cycle: Regenerates adsorbent using hot air or steam, followed by a cool down before adsorption cycle
   - Emits air pollutants at constant concentration and flow into secondary control device (concentrator or thermal oxidizer)
   - Pollutant “heel” builds up in adsorbent (even with desorption), reducing available adsorbent for collection (eventually leads to breakthrough)

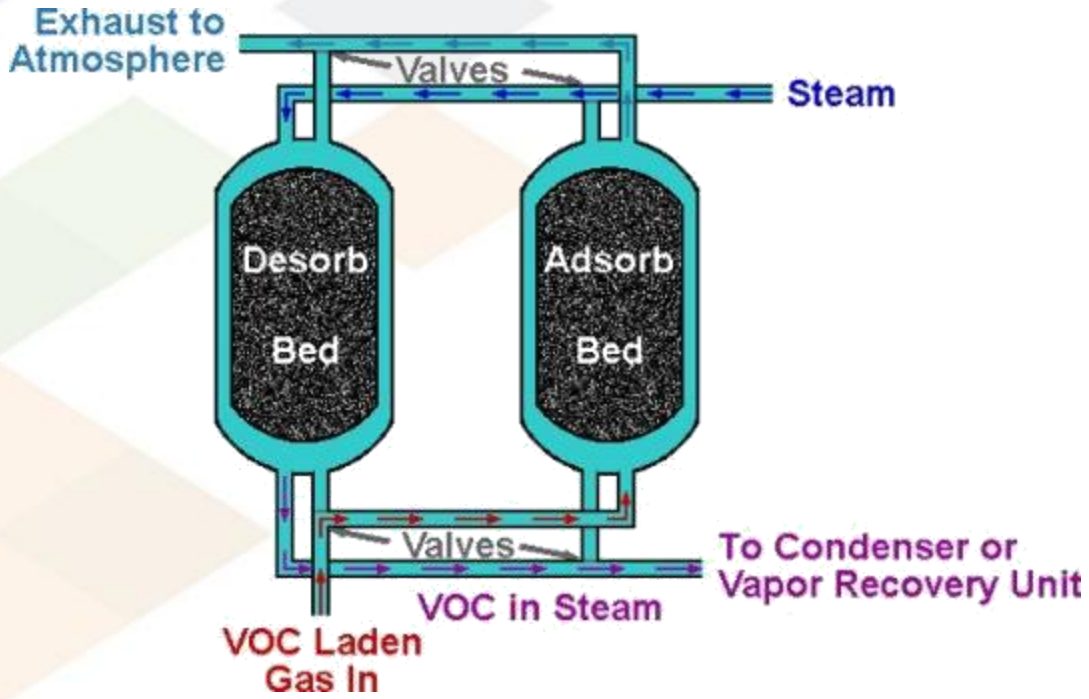
Fixed Bed Regenerative Adsorber

Left Adsorb / Right Desorb



Fixed Bed Regenerative Adsorber

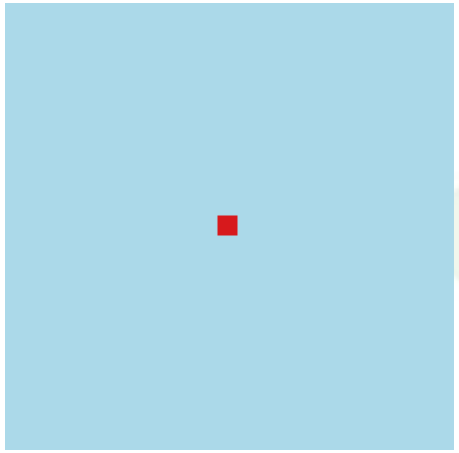
Left Desorb / Right Adsorb



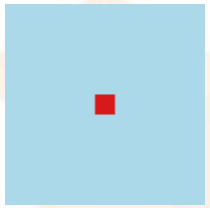

Fixed Bed Regenerative Adsorber
Fixed Bed Adsorber
Fixed Bed Adsorber
Condenser

Concentrator

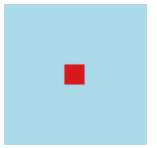
- Adsorbers desorb pollutants at a consistent flow rate
  - Condensers operate more efficiently with higher pollutant concentration
  - Reduce thermal oxidizer size (less natural gas)



100 VOC : 50,000 Air
(2,000 ppm)

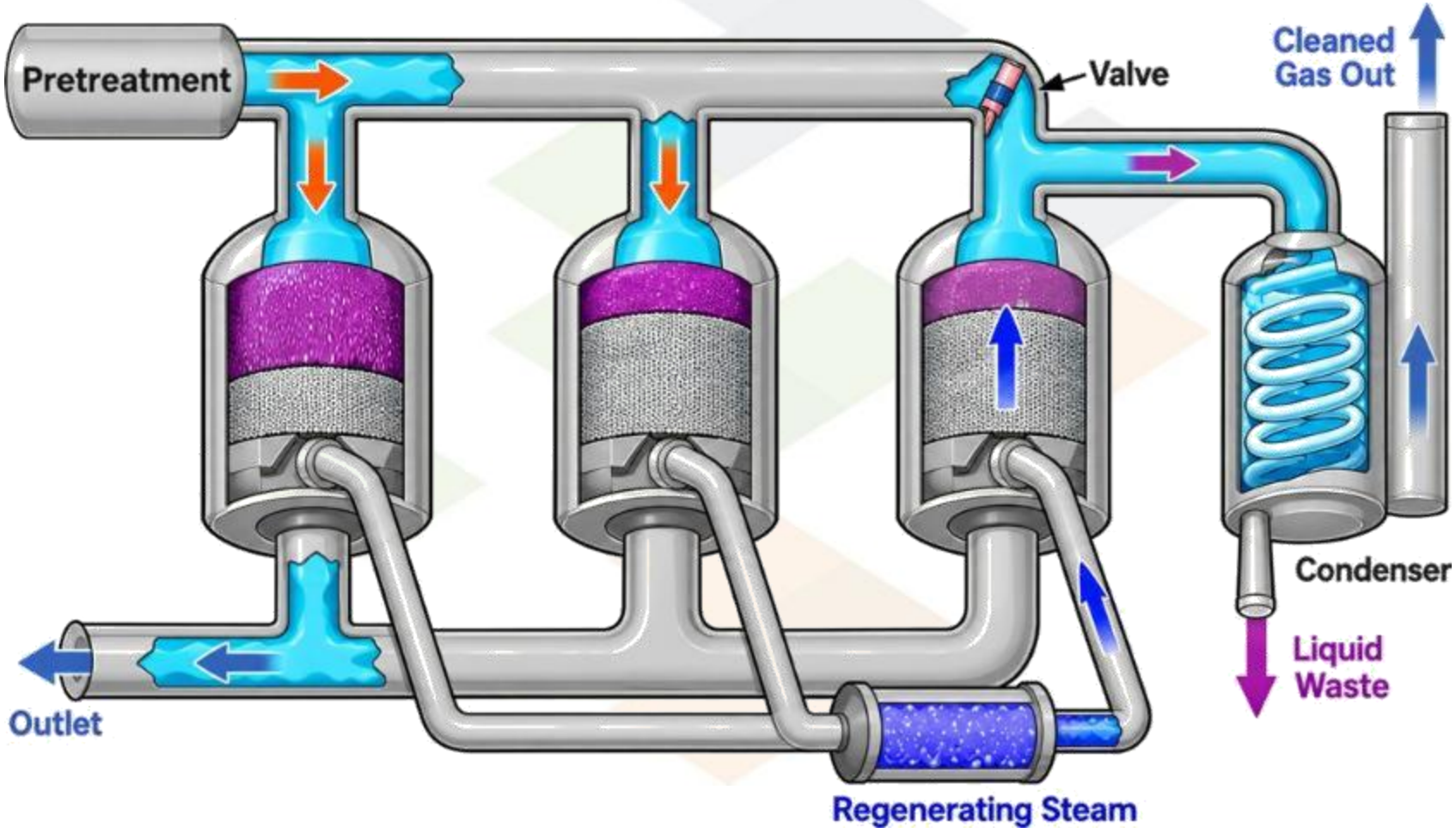


100 VOC : 10,000 Air
(10,000 ppm)

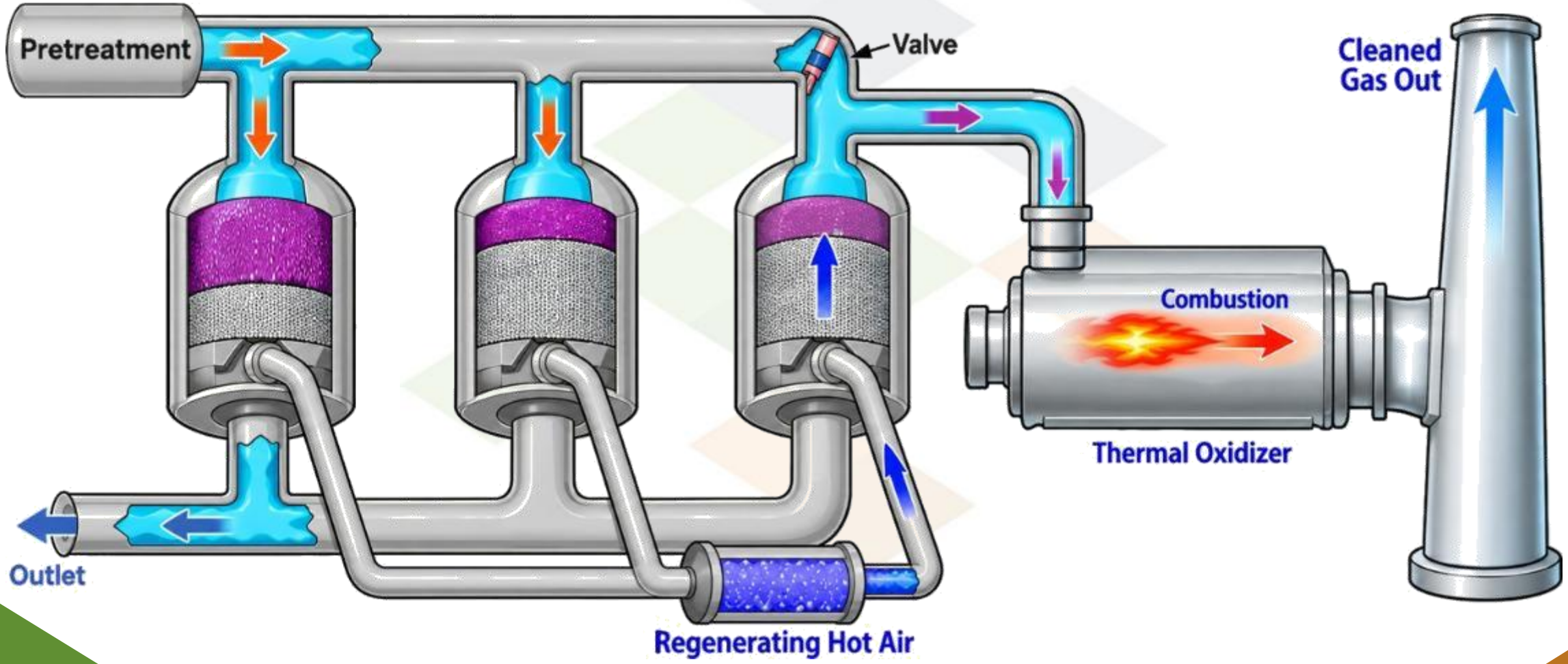


100 VOC : 5,000 Air
(20,000 ppm)

Regenerative Desorption with Condenser Recovery

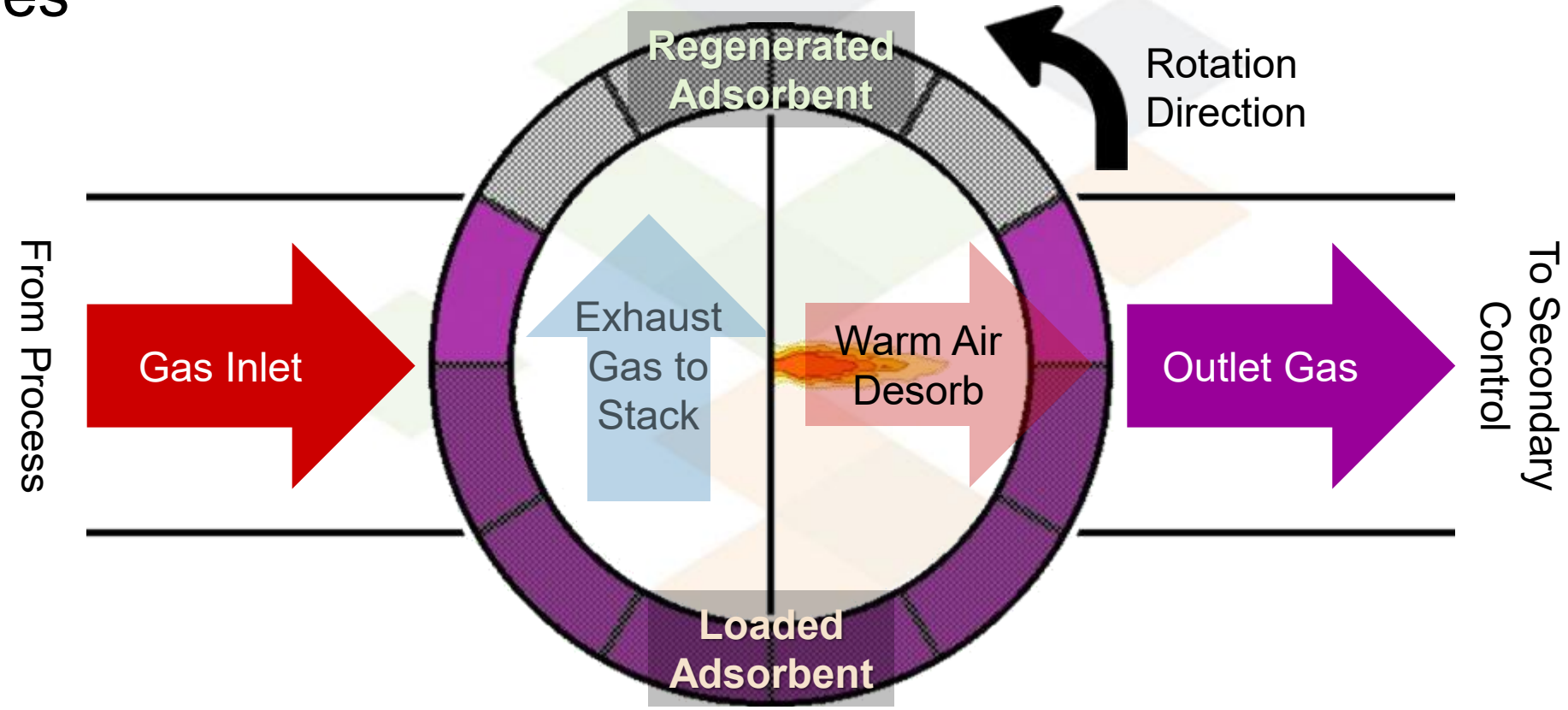


Regenerative Desorption with Thermal Oxidizer

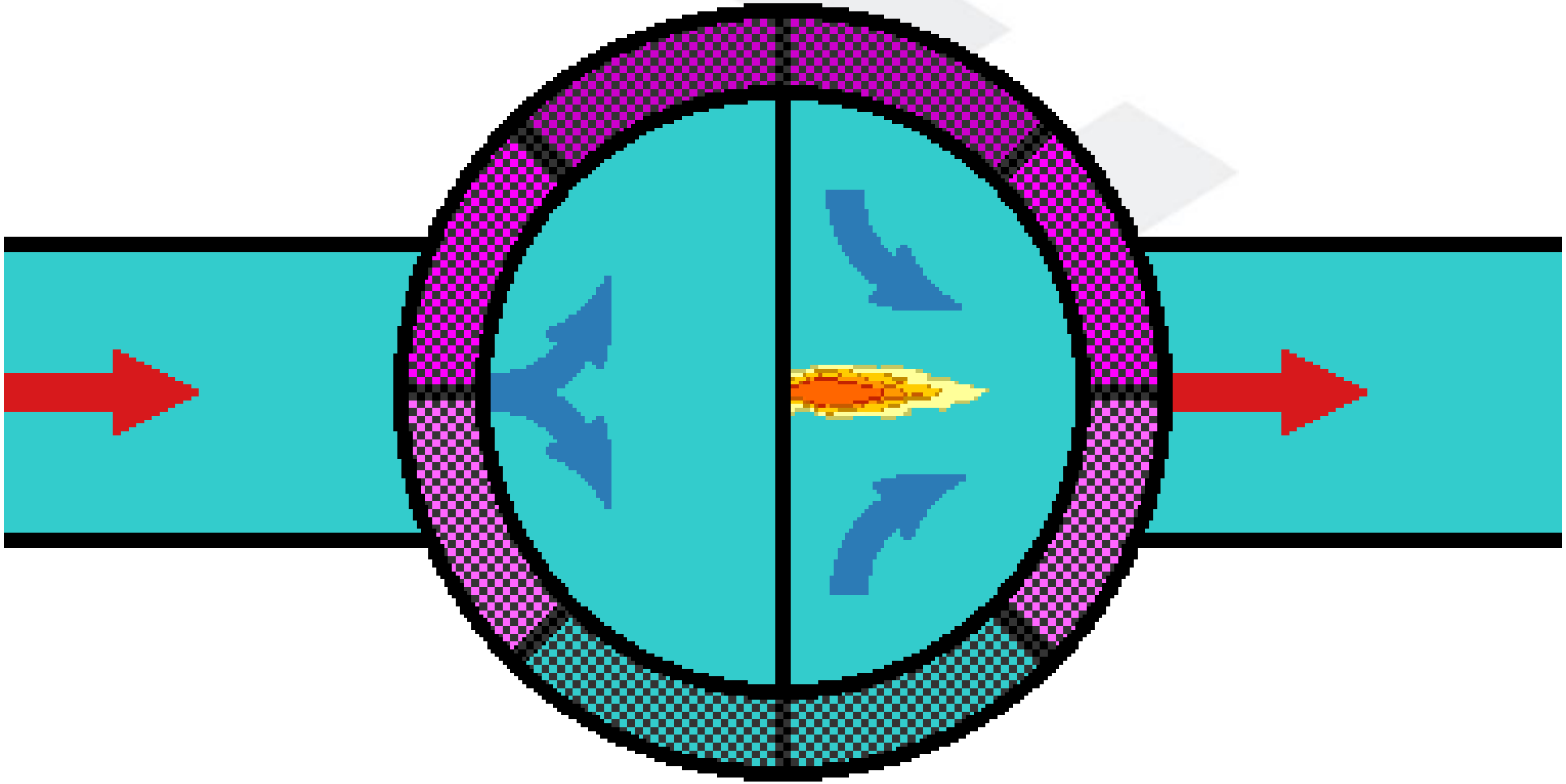


Rotary Bed Regenerative Adsorber

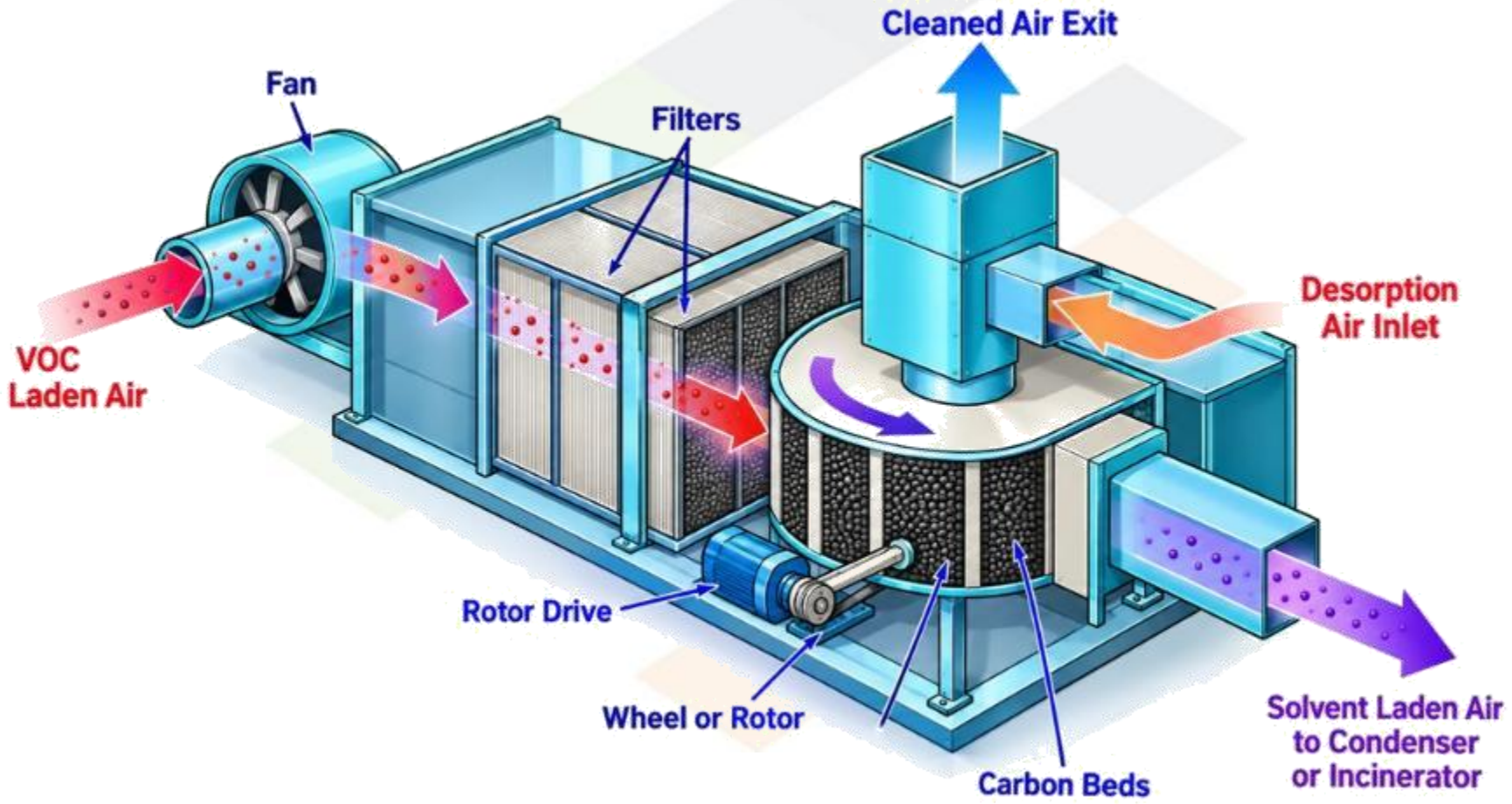
- Adsorbent wheel rotates between adsorption & regeneration zones



Rotary Bed Adsorption / Desorption



Rotary Bed Regenerative Adsorber

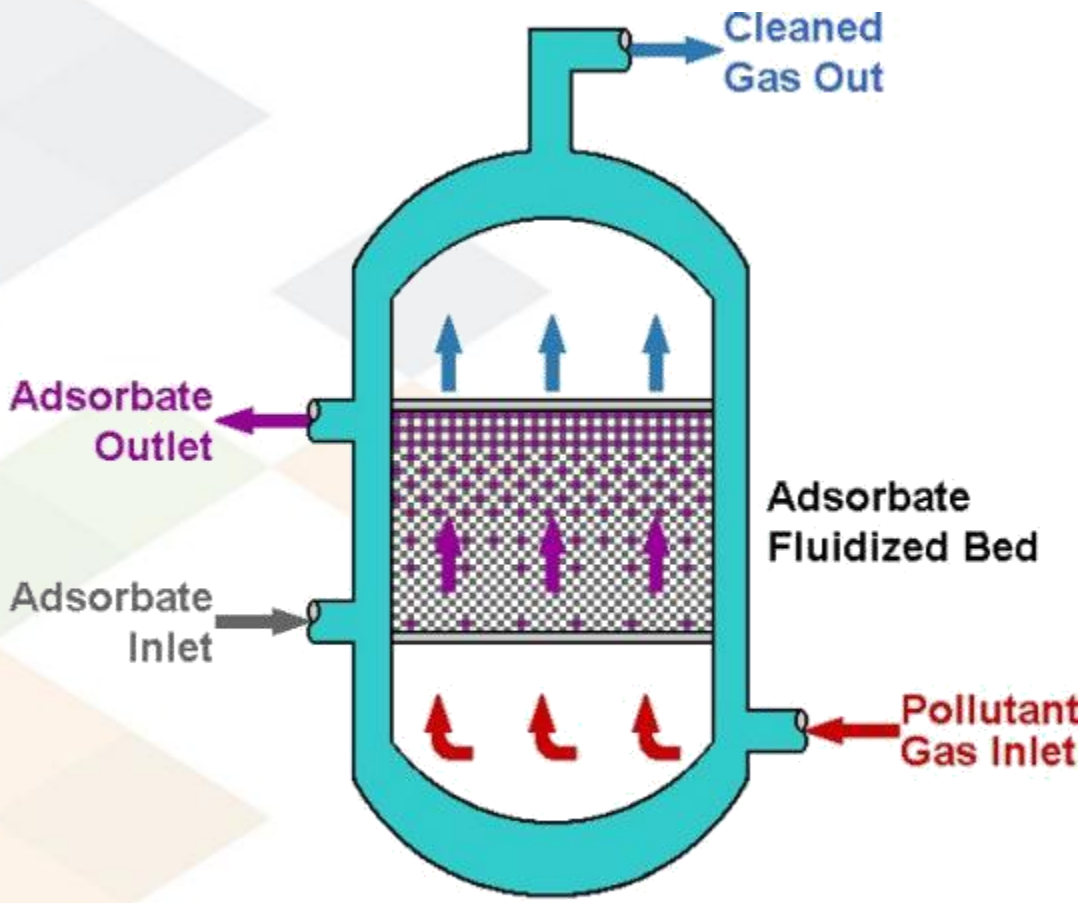


Chapter 6: Adsorption Controls



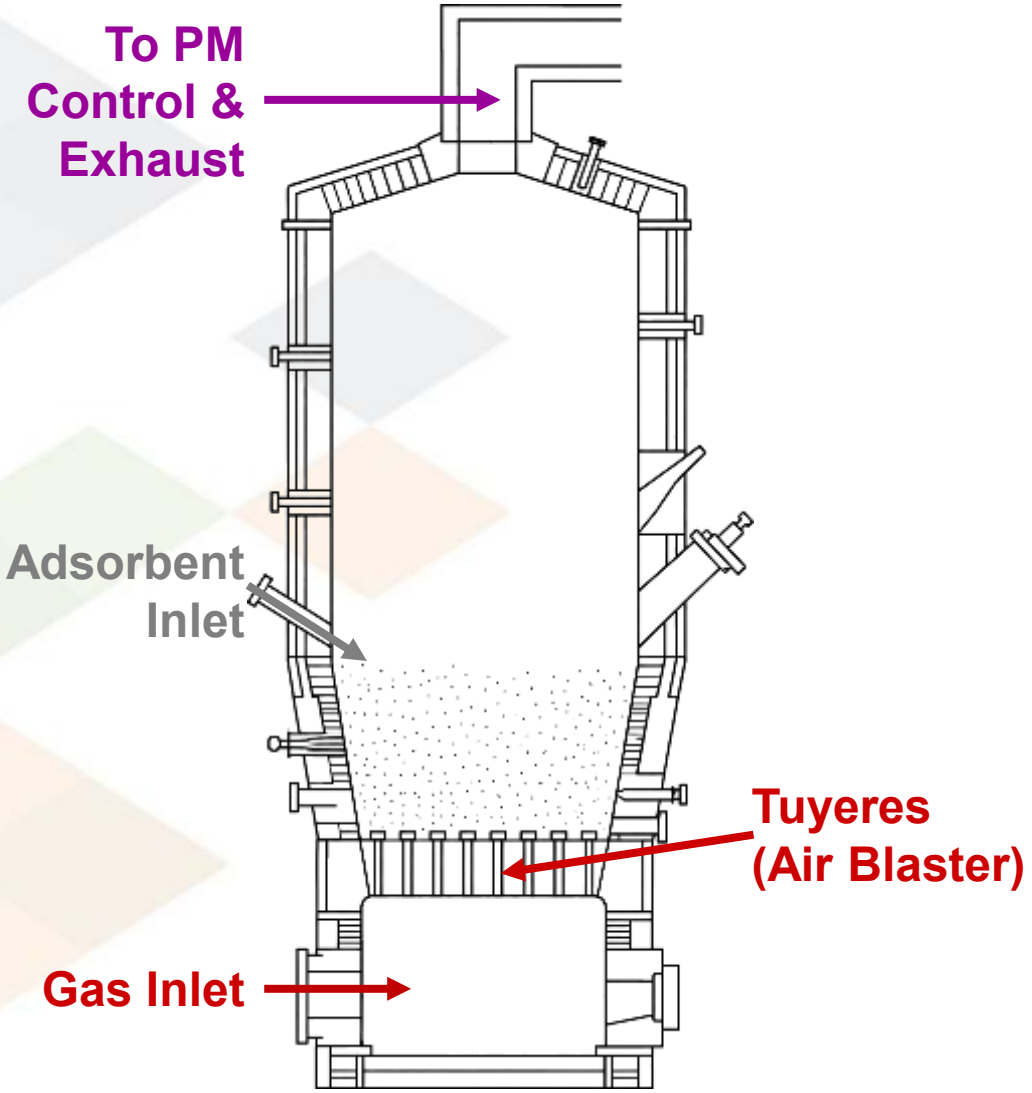
Fluidized Bed Regenerative Adsorber

- Adsorbent added & churned with air, acting like a fluid
- Turbulence assists in interaction between adsorbate and adsorbent
- PM control separates spent adsorbent from exhaust stream for regeneration



Fluidized Bed Regenerative Adsorber

- Tuyere: Blasts streams of exhaust gas, causing solid adsorbents to fluidize
- PM Control: Removes spent adsorbent
- Regenerator / Desorber: Regenerates adsorbent for reintroduction to adsorber



Chapter 6: Adsorption Controls



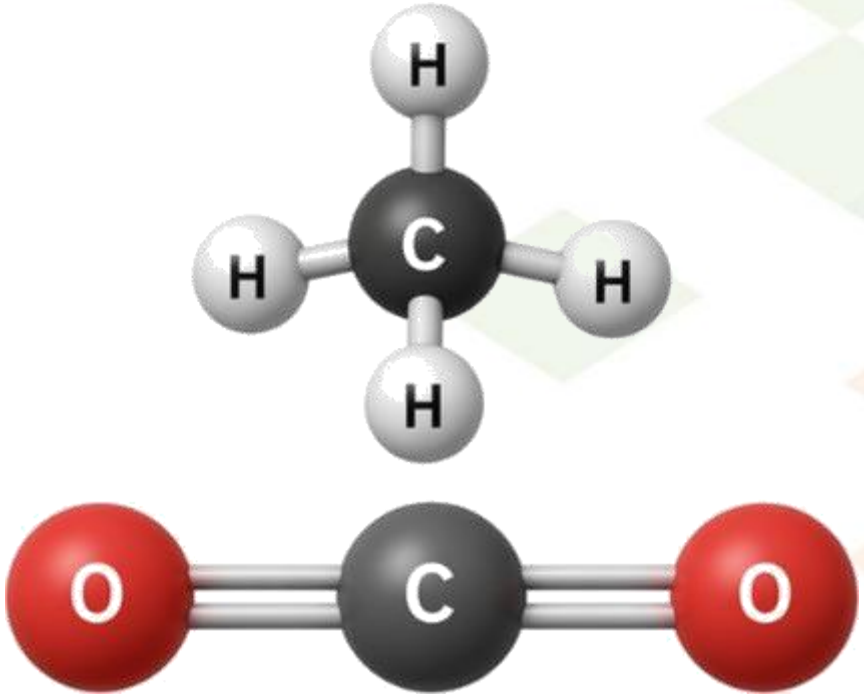
Chapter 6: Adsorption
Video

Fluidized Bed Model

Fluidized Bed Video

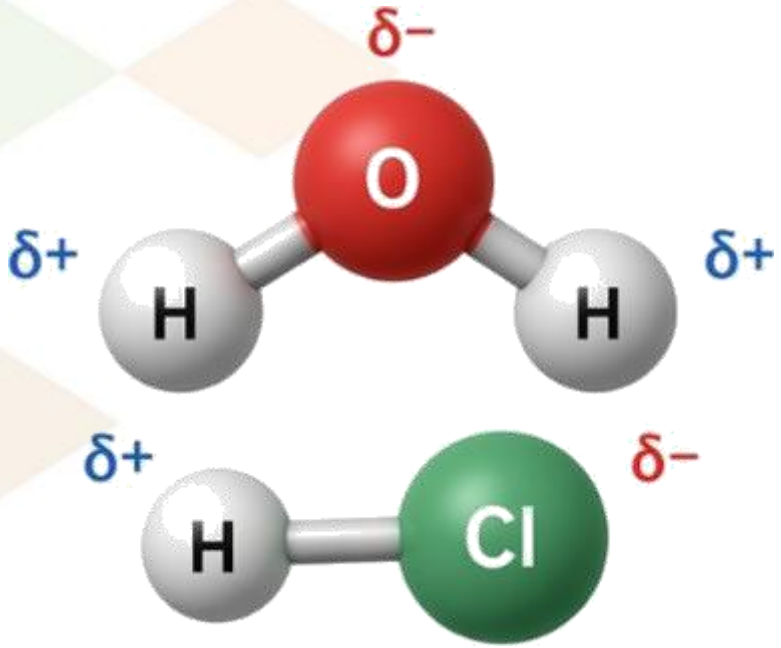
Non-Polar Compounds

- Electrons shared equally by chemical bond
  - No areas of excess charge



Polar Compounds

- Electrons shared unequally by chemical bond
  - Positive/negative charge areas

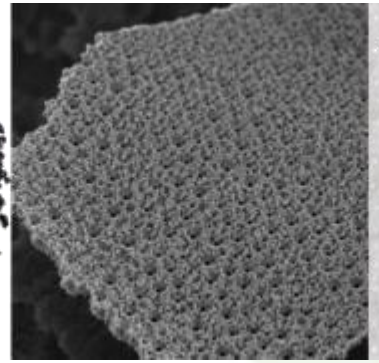


Non-Polar Adsorbers

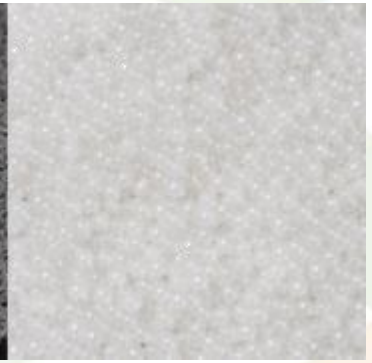
- VOC
- CO_2



Activated Carbon



Metal-Organic Frameworks



Polymer Resins

Polar Adsorbers

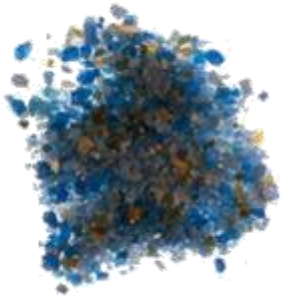
- Specific VOC
- Acid Gases



Activated Alumina



Molecular Sieve (Zeolite)



Silica Gel (SiO_2)

Activated Carbon

- Made from wood, coal, oil products, or plant materials
  - Heated to between 750-1,110ºF in an oxygen free environment
  - Carbon is oxidized ("activated") by reacting with steam, air, or CO_2
  - Can be used as offsite carbon regeneration (removes "heel")
- Most common and cheapest adsorbent



Chapter 6: Adsorption Design Considerations

VOC Suitable for Activated Carbon	Boiling Point °F(°C)	Molecular Weight	Water Soluble?	Flammable Liquid?	LEL % Vol.
Aliphatic					
Heptane	209 (98.4)	100.2	No	Yes	1.2
Hexane	156 (68.7)	86.2	No	Yes	1.2
Pentane	97 (36.1)	72.2	No	Yes	1.5
Naphtha	288 (142)	-	No	Yes	0.92
Mineral Spirits	381 (194)	-	No	Yes	<1.00
Stoddard Solvent	379 (193)	-	No	Yes	1.1
Aromatic					
Benzene	176 (80.0)	78.1	No	Yes	1.2
Toluene	231 (110.6)	92.1	No	Yes	1.1
Xylene	292 (144.4)	106.2	No	Yes	0.9

Chapter 6: Adsorption Design Considerations

VOC Suitable for Activated Carbon	Boiling Point °F(°C)	Molecular Weight	Water Soluble?	Flammable Liquid?	LEL % Vol.
Ester					
n-Butyl Acetate	259 (126.1)	116.2	No	Yes	1.7
Ethyl Acetate	171 (77.2)	88.1	Yes	Yes	2.5
Halogenated					
Carbon Tetrachloride	170 (76.7)	153.8	No	No	N/A
Ethylene Dichloride	210 (98.9)	85	No	Yes	6.2
Methylene Chloride	104 (40.0)	84.9	Yes	No	13
Perchloroethylene	250 (121.1)	165.8	No	No	N/A
Trichloroethylene	189 (87.2)	131.4	No	No	N/A
Trichloroethane	165 (73.9)	133.4	No	No	N/A

Chapter 6: Adsorption
Design Considerations

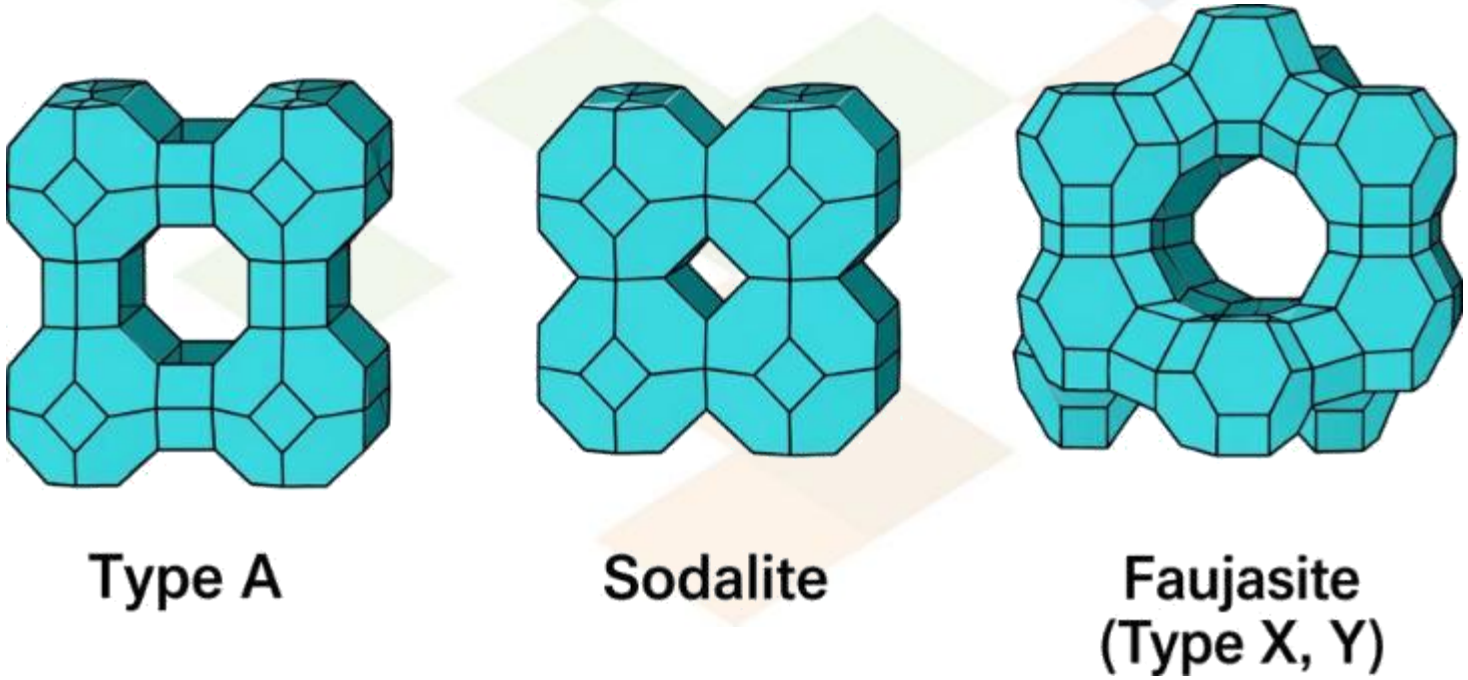
VOC Suitable for Activated Carbon	Boiling Point °F(°C)	Molecular Weight	Water Soluble?	Flammable Liquid?	LEL % Vol.
Ketones					
Acetone	133 (56.1)	58.1	Yes	Yes	2.6
Diacetone Alcohol	293 (145.0)	116.2	Yes	Yes	N/A
Methyl Ethyl Ketone	174 (78.9)	72.1	Yes	Yes	1.8
Methyl Isobutyl Ketone	237 (113.9)	100.2	Yes	Yes	1.2
Alcohols					
Butyl Alcohol	241 (116.1)	74.1	Yes	Yes	1.4
Ethyl Alcohol	173 (78.4)	46.1	Yes	Yes	3.3
Propyl Alcohol	205 (96.1)	60.1	Yes	Yes	2

VOC Generally Not Suitable for Activated Carbon

- **Reactive Compounds:**
  - Organic acids
  - Aldehydes
  - Various monomers
  - Various ketones
- **High Boiling Point:**
  - Plasticizers
  - Resins
  - Long chain hydrocarbons ($+C_{14}$)
  - Glycols, phenols, and amines

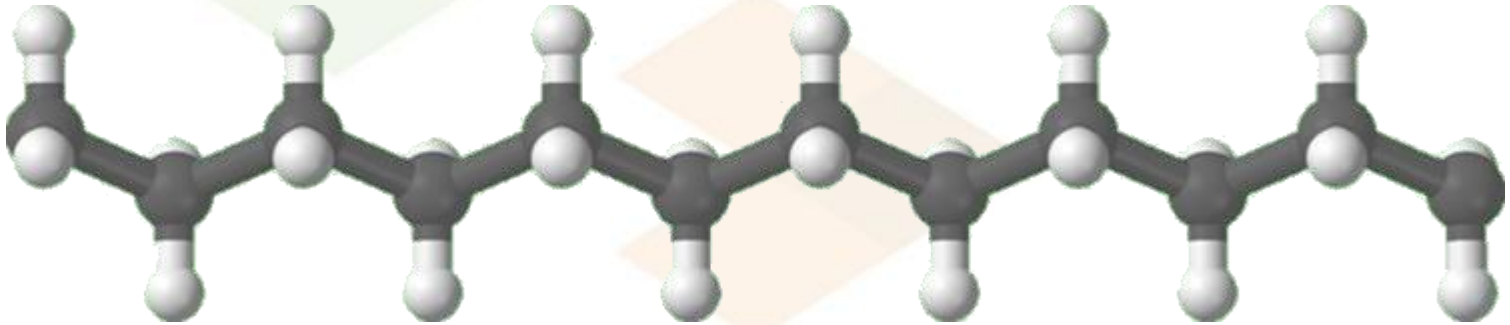
Zeolite / Molecular Sieve

- Crystals with uniform pores that must match pollutant diameter
  - Used in processes to remove moisture and separate hydrocarbons
  - Used for NO_X control



Polymers

- Matrix of small pores and high surface area
- Very high adsorption capacities for select VOC
- Regenerates more rapidly than activated carbon
- High tolerance for water vapor
- Significantly more expensive



Silica Gel

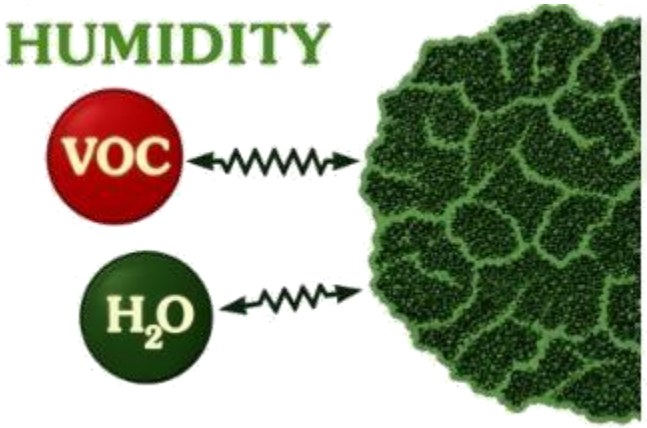
- Primarily used to remove moisture
- Ineffective above 500ºF

Activated Alumina

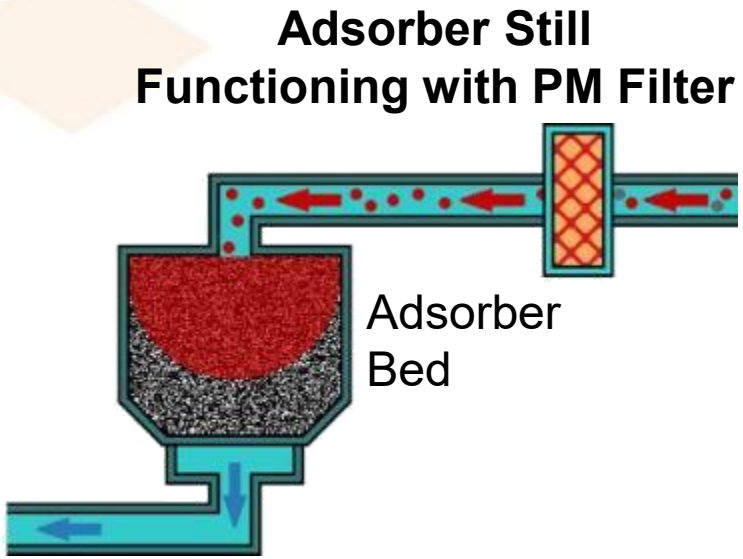
- Primarily used to remove moisture
- Not typically used for air pollution control

Adsorption Capacity

- Pounds of pollutant adsorbed per 100 pounds of adsorbent
  - Adsorbers also adsorb water
  - PM in exhaust stream plugs adsorber, decreasing adsorption capacity







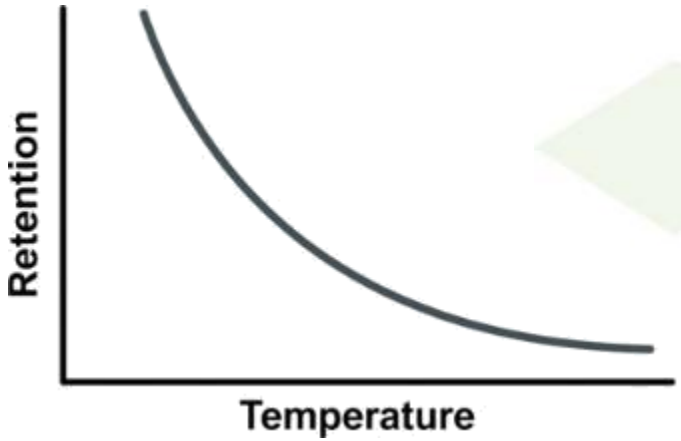
Adsorption Capacity

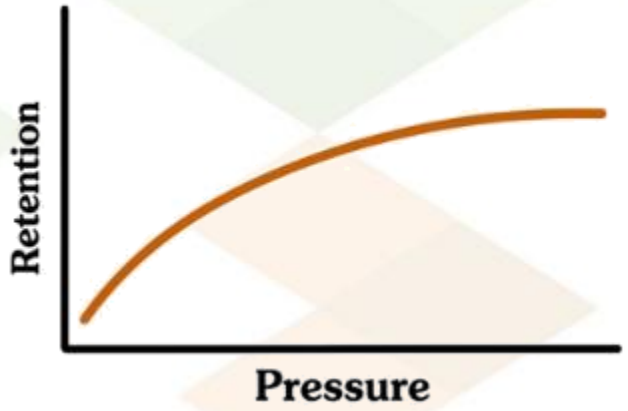
- Breakthrough: Capacity of the bed when vapor not adsorbed is emitted (loss of control efficiency)
- Saturation (equilibrium): Maximum amount of vapor adsorbed per unit of weight at specific temperature and pressure
- Working: Fraction of saturation capacity (0.1-0.5 or 10-50%)

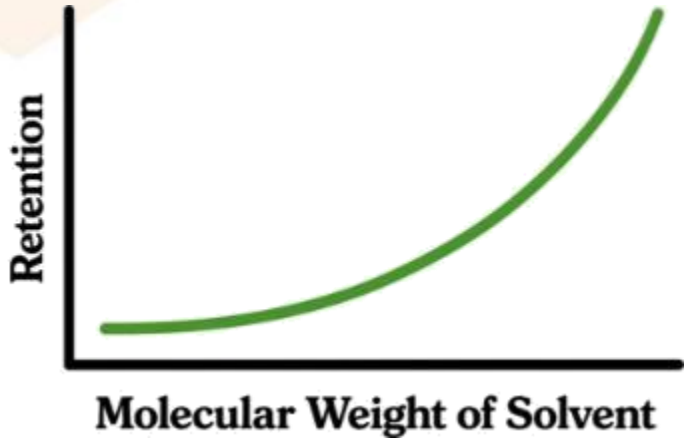
The presence of moisture and/or PM will decrease all these capacities and lead to quick breakthrough.

Adsorption Capacity

- Decreases as gas velocity increases (>20 and <100 feet/min)
- Decreases as temperature increases (adsorber <130ºF)
- Increases as pressure increases
- Increases as molecular weight of air pollutant increases





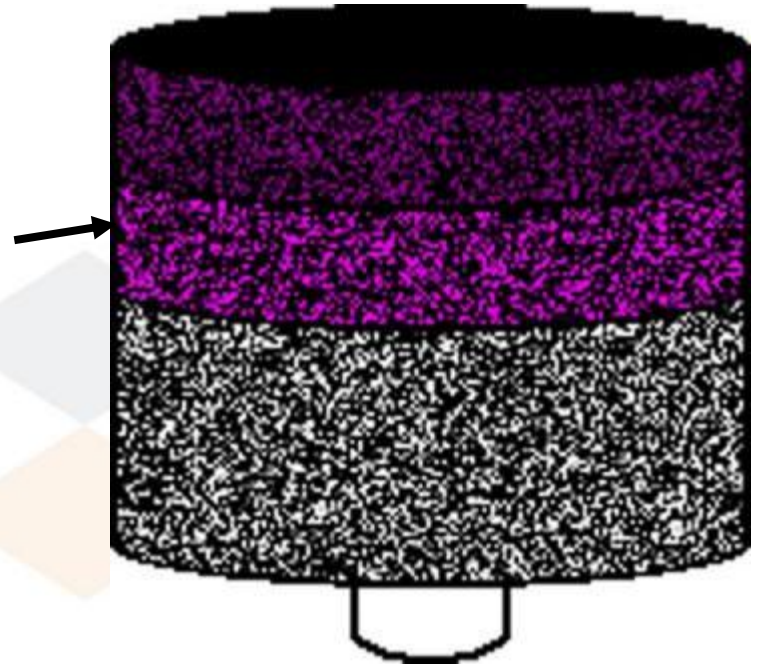


Adsorption Capacity

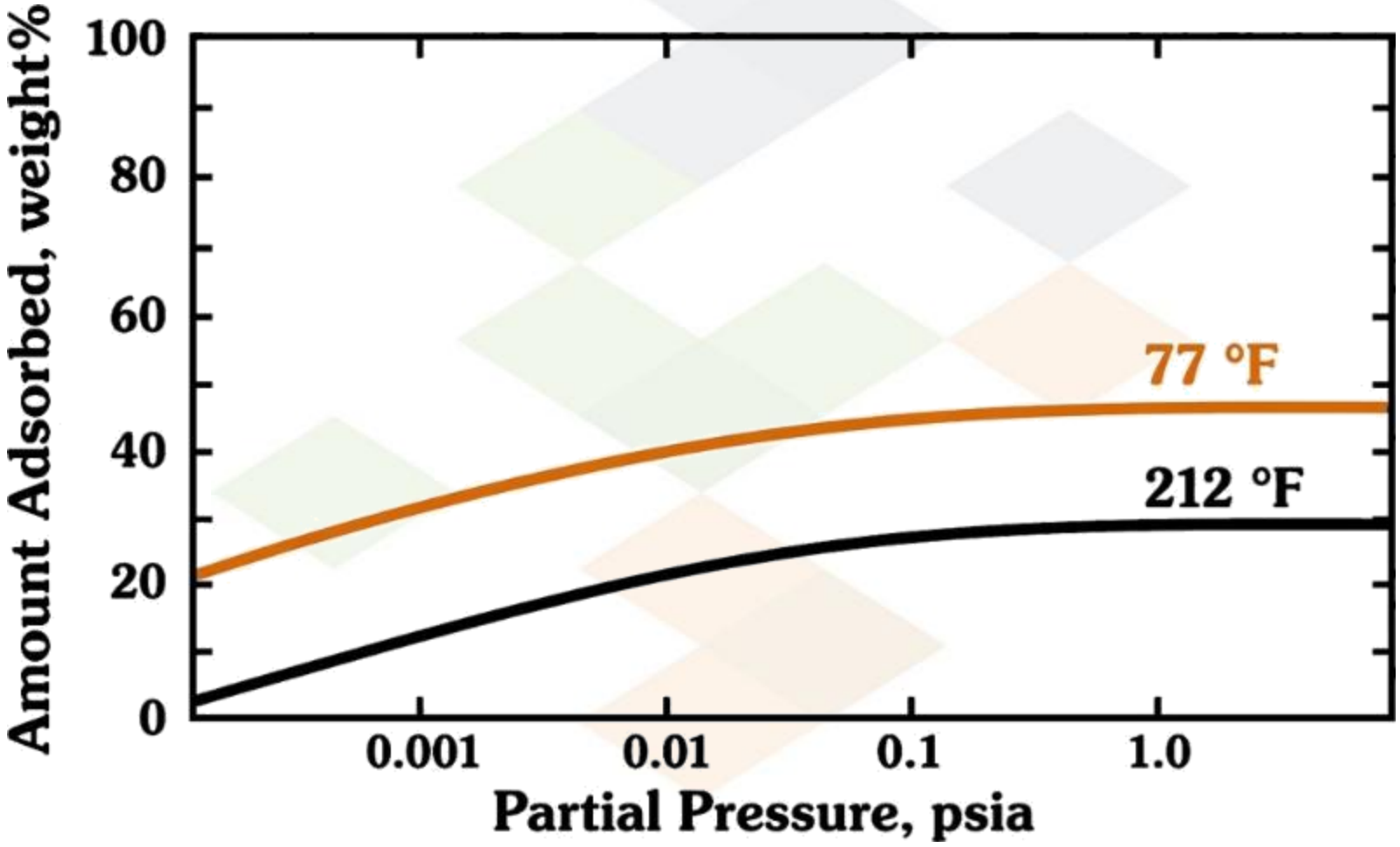
- Maximum amount of vapor that can be adsorbed at operating conditions
  - Isobar: Constant pressure
  - Isostere: Constant concentration (loading)
  - Isotherm: Constant temperature (most common)

Adsorption Capacity

- Mass Transfer Zone (MTZ)
  - Adsorbent particle size
  - Gas velocity
  - Pollutant concentration in exhaust gas
  - Fluid properties of gas stream
  - System temperature
  - System pressure
- May increase pressure differential as adsorbent bed becomes saturated



Adsorption Capacity Isotherm



Desorption Options

- What to do with the desorbed pollutants?
  - Thermal / pressure swing exhaust can be condensed (reclaimed) or incinerated in thermal oxidizer
  - Inert gas from purges is now contaminated with desorbed pollutants and needs treatment (condenser / thermal oxidizer)
  - Displacement extracts adsorbed pollutants but bed is still saturated (unusable)
  - If moisture is in the exhaust gas, it is in the desorbed gas

Physical Adsorption (Physisorption)

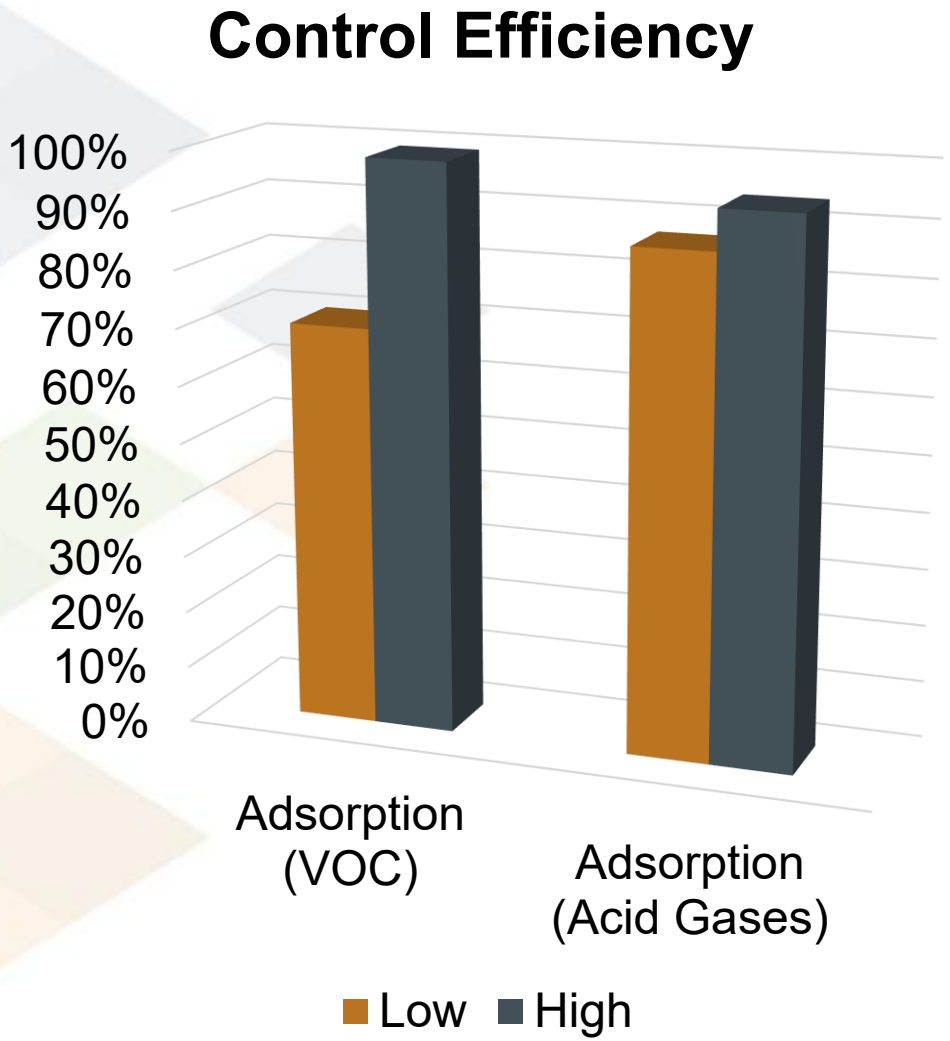
- Slightly exothermic
  - Releases a little heat
- Electrostatic attraction
  - van der Waals Forces
- Onsite desorption (regeneration) possible
- Adsorbate (pollutant) recovery possible

Chemical Adsorption (Chemisorption)

- Significantly exothermic
  - Releases significant heat
- Chemical reaction
- Desorption very difficult
  - Additional chemical reactions
- Adsorbent (pollutant) recovery impossible

Control Efficiency

- 70-99% for VOC
- 87%-94% for acid gases
- Control efficiency separate from TO or condenser on regenerative units
- Breakthrough: Reduced control efficiency occurs at bed saturation (just before breakthrough)



Parametric Monitoring

1. Outlet Concentration
2. Moisture Content
3. Temperature
4. Regeneration Cycle Timing
5. Pressure Differential







Operating Problems

- **Fire!**
  - Saturating adsorbent with VOC makes adsorbent more flammable
  - Activated carbon is already flammable
  - Desorb temperatures (when bed is already saturated) are higher
- Exhaust gas temperature cannot exceed desorption temperature
  - Pollutants will be desorbed as they are adsorbed – no control efficiency
- Saturation: adsorbent must be replaced before breakthrough
  - Non-regenerative: no more adsorption capacity
  - Regenerative: air pollutants are not fully desorbed; a “heel” of air pollutants remains that increases with each desorption cycle

Chapter 6: Adsorption
Operating Problems

- Channeling: exhaust air creates tunnels in adsorbent
  - Air pollutant must contact fresh adsorbent or no control efficiency
- Change in air pollutants in exhaust stream
  - Fouling of adsorbent
  - Change in polarity may affect adsorption rate
- Water in exhaust stream is also adsorbed, decreasing adsorption rate for air pollutants
- Disposal of adsorbent
- Secondary control:
  - Thermal oxidizer or refrigerated condenser
  - PM control for DSI

Chapter 6: Adsorption
Operating Problems

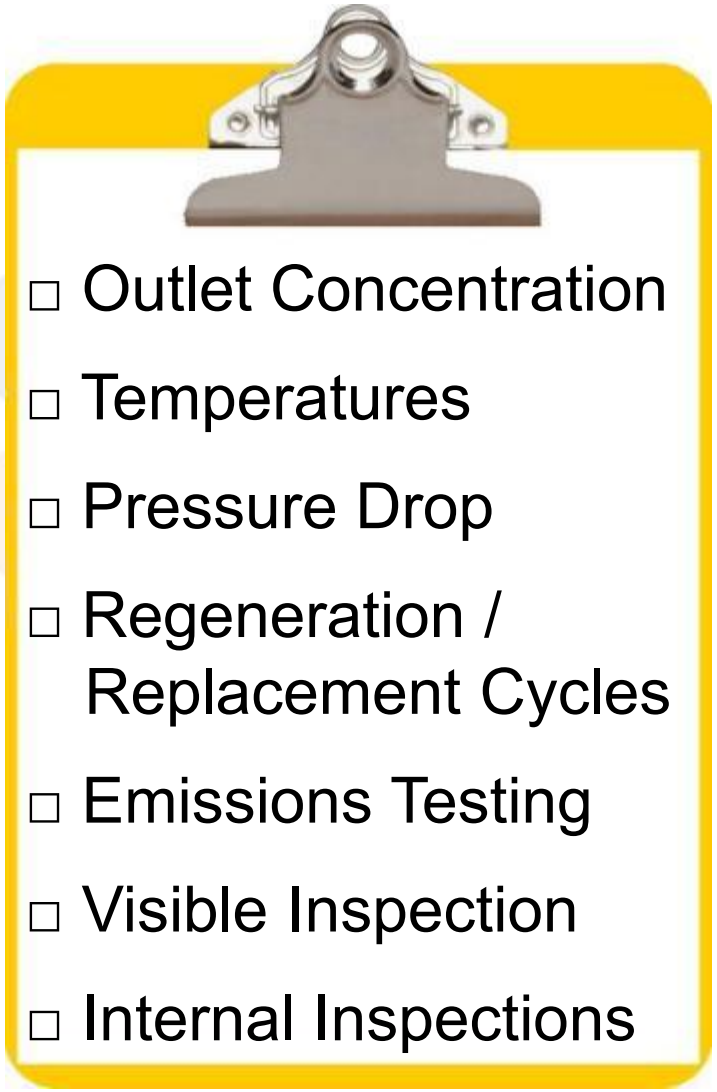
- PM in exhaust stream reduces control efficiency
  - Blinding: PM >3 micrometers ($PM_{3.0}$) covers surface of adsorbent
  - Liquid droplets act like PM, covering surface of adsorbent
  - Liquid droplets can cause bed fires, due to higher heat generated when adsorbed
  - May place PM pre-filter and entrainment separator (mist eliminator) before adsorber
- High boiling point VOC and high molecular weight VOC may be too strong to desorb and can react chemically with carbon
- When cleaning regenerative beds with steam, have to dry the bed (hot air only), as saturates bed

Chapter 6: Adsorption
Video

4.1 - Adsorption Problems.mp4

Inspection Parameters

- Outlet air pollutant concentration
  - CEMS
- Inlet / Bed / Outlet temperatures
- Pressure Differential
- Regeneration cycle
- Adsorbent replacement cycle
- Internal Inspection report
- **Secondary Air Pollution Controls!**



Chapter 6: Adsorption
Recap

In this chapter, we discussed:

- How adsorption control technologies operate
- Common types of adsorption control technologies
- Key design considerations for adsorption control technologies
- Typical achievable control efficiencies
- Monitoring methods for adsorption control technologies
- Common problems with adsorption control technologies
- Ensuring compliance