Silane Abatement – Things to Watch For

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SESHA Phoenix Miniconference

22 April 2008

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Overview

- Some abatement considerations
- Silane properties
- Methods of abatement
- Other gases in the process
- Some specific solutions
- Summary

Some Practical Considerations

- Must treat for products, not just reactant gases
  - Plasma reactors are the worst for side reactions
- Different processes require different solutions
  - There is no one-size-fits-all solution for exhaust management
- Matter can neither be created nor destroyed
  - Exhaust products won't just "go away"
    - Will get solids, liquids, or gases out of abatement device.
- Some scrubbers will cause more harm than good
  - F_2 can be dangerous (may form OF_2 the presence of water)
- Must look at process and pump and abatement AS A SYSTEM, not as independent components

It is the stated goal of exhaust gas management to prevent downtime. This is done by conversion of effluent into a less hazardous form OR into a more easily handled form.

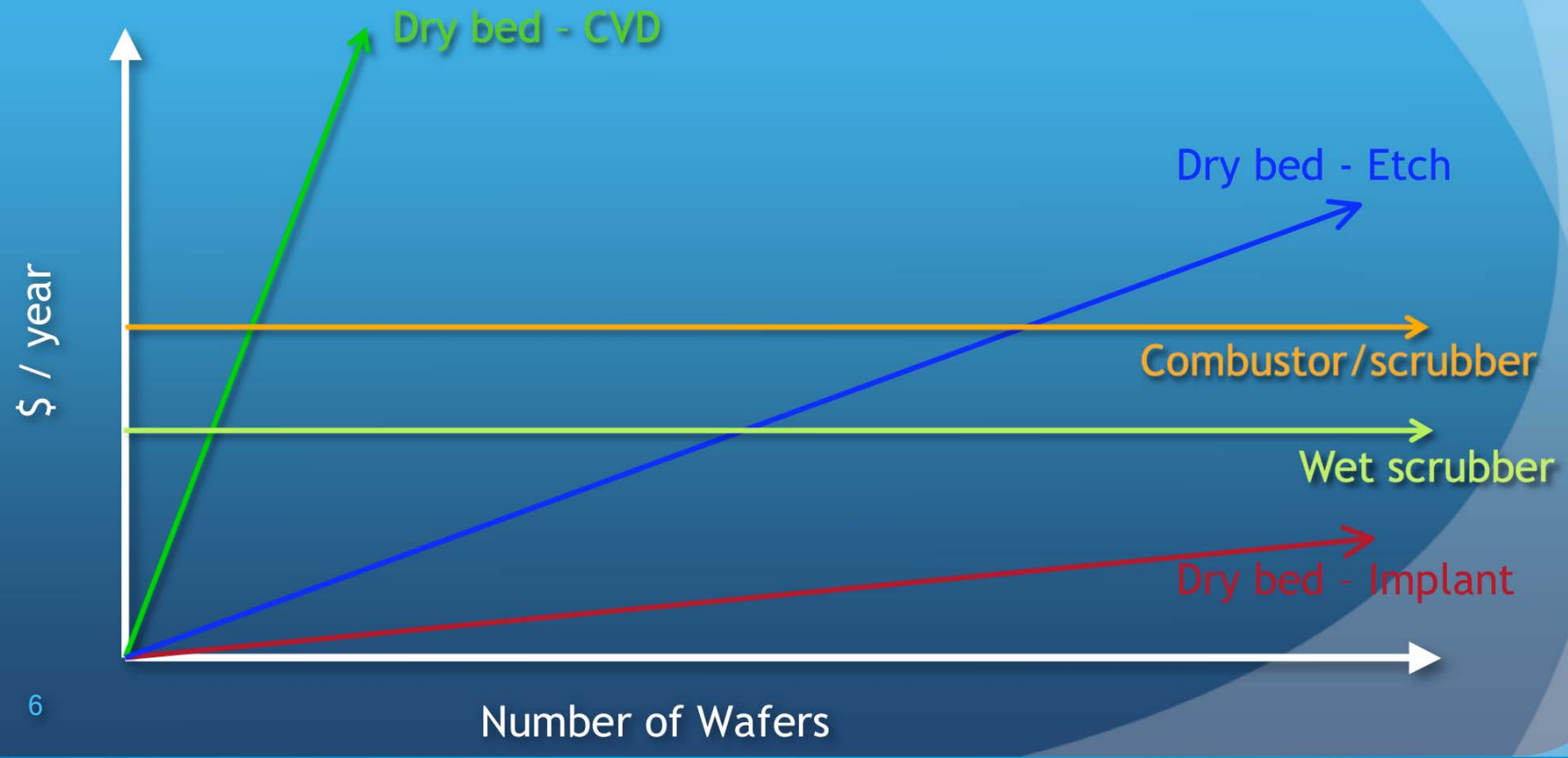
- Silane is pyrophoric and dangerous when not given the respect it demands. Conversion to SiO_2 dramatically reduces the hazard.

- F_2 is converted to HF. HF is also very hazardous, but it is less corrosive, and can be scrubbed and treated in the acid drain.

- $AlCl_3$ or NH_4Cl are condensible solids that block pipework. Heated pipework prevents condensation and enables POU abatement to eliminate the effluent.

Cost per Wafer (Excluding CapEx)

- **Cost / wafer depends on:**
  - Gases used in process
  - Facilities used / consumed by scrubber



Silane Properties

- Silane is the primary Si source in semiconductor manufacturing
- Chemical formula SiH_4, molecular weight 32 g/mol
  - 0.7 g/liter
  - 1 liter of SiH_4 produces 2.7 g SiO_2
  - Lower flammable limit (LFL) 1.0% (UFL 96%)
  - Lower explosive limit (LEL) 1.4%, UEL 96%)
  - BP -112° C
  - Insoluble in water
- Not water-scrubbable
- Forms solids upon combustion

Silane Properties

- Flammability
  - Pyrophoric – burns in air > 1% concentrations
- Toxicity
  - TLV 5 ppm (6.6 mg/m^3)
- Solids
  - 2.7 g SiO_2 per liter of SiH_4
- Cross-reactivity
  - Reducing agents react violently with oxidizers (F_2, NF_3)

Typical SiH_4 Flows

- W CVD deposition 40-50 sccm
- PECVD oxide – nitride deposition: 150 – 300 sccm
- Epitaxial deposition 200 – 500 sccm
- Polysilicondepostion 300 – 2,000 sccm
- FPD, solar panel up to 40 slm (Gen-8)

Use of Silane in Thermal Processes

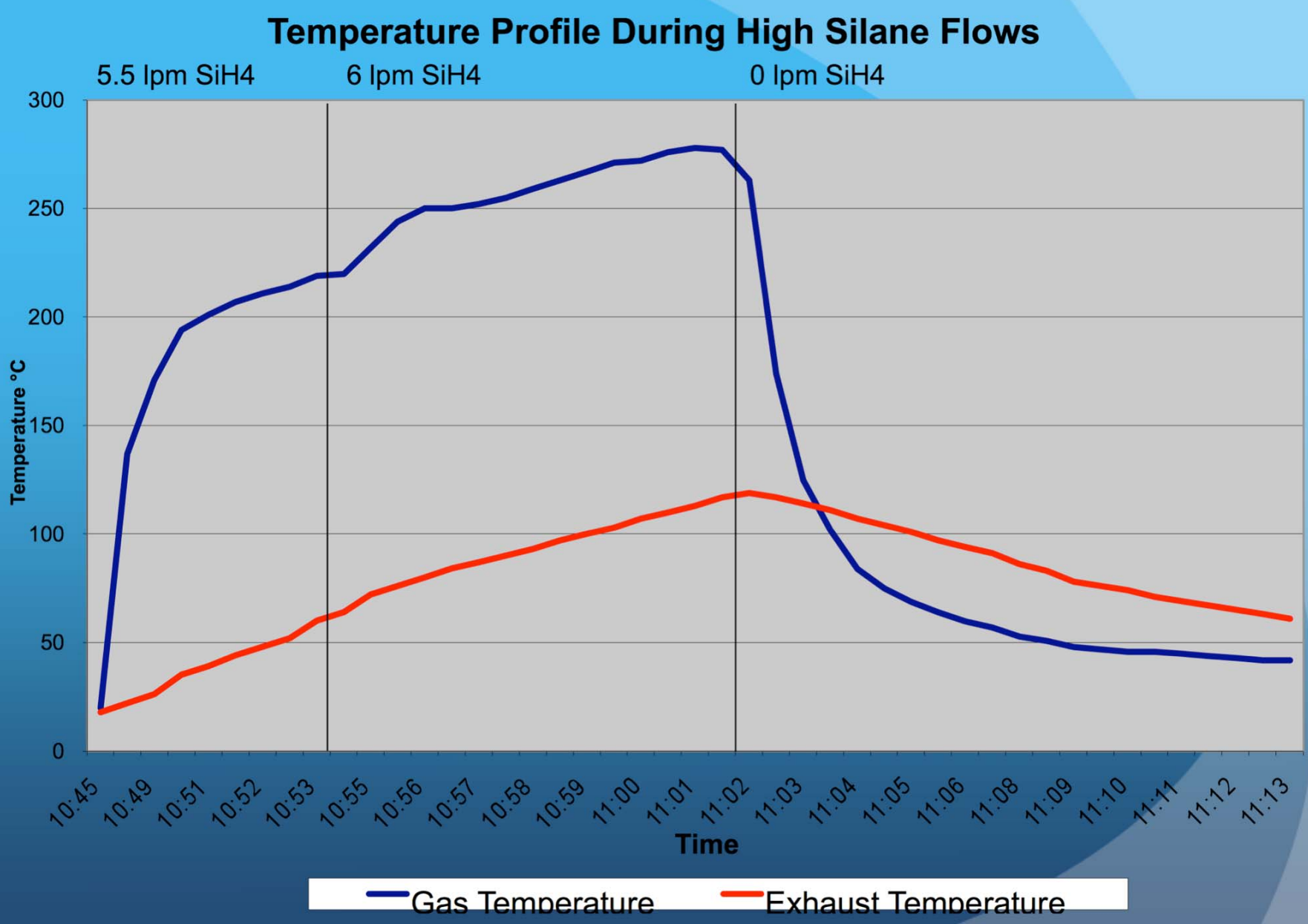
- SiH_4 is silicon precursor; thermal decomposition forms Si and H_2
  - Poly – polycrystalline growth; 400° – 600° C
    - HCl cleans
  - Epi- single crystal growth; 800° – 1200° C, high H_2 flows
    - HCl cleans
  - Utilization of SiH_4 is poor in thermal processes
- Silane is not the main hazard with epi
  - High H_2 flows
    - Flammable, LFL 4% in air
  - Polychlorosilane and silicic acid byproducts in pipework
    - Explosive, shock-sensitive

Use of Silane in Plasma Processes

- Plasma processes form SiO_2, Si_3N_4, SiC (fluorine-based cleans)
  - Oxide – SiO_2 growth; with O_2 or N_2O
  - Nitride – Si_3N_4 growth; with NH_3
    - LP Nitride; DCS/NH_3, thermal
  - Carbide; SiC growth with trimethylsilane or tetramethylsilane
- Silane is typically well-utilized in plasma-based processes
  - However may see other solid byproducts …

Methods of Abatement – Mix with Air

- Since silane burns in air, what could be easier?
- Strictly speaking, this is effluent conditioning, not abatement
  - Other gases (NH_3, C_2F_6, PH_3) not abated at all
- Ideal for gas pads, some low-flow poly applications
- Typically very high air usage
  - > 30 cfm on the low end to hundreds of cfm
- Solids often end up in duct


Temperature Profile During High Silane Flows
5.5 lpm SiH4
6 lpm SiH4
0 lpm SiH4
Temperature °C
300
250
200
150
100
50
0
10:45
10:49
10:51
10:52
10:53
10:55
10:56
10:57
10:58
10:59
11:00
11:01
11:02
11:03
11:04
11:05
11:06
11:08
11:09
11:10
11:11
11:12
11:13
Time
Gas Temperature
Exhaust Temperature

Abatement – Electric Combustion

- Electrically-heated tube typically followed by a wet scrubber
  - CDO (Metron), HOx (Edwards)
- SiH_4 requires O_2 to oxidize; these units add air (CDA or fab air) to the heated zone
- SiO_2 buildup in combustor tube is virtually guaranteed
  - CDO has utilized mechanical scrapers over the years with limited success
  - HOx employs water spray that works very well when properly-configured

Combustor Filled with SiO_2

Abatement – Fuel Combustion

- Typically CH_4 or H_2 are used for fuels
  - CH_4 is a superior fuel for abatement
- Many companies utilize this technology for general abatement
- SiH_4 is usually completely abated
  - Inadequate O_2 may lead to sticky beige $SiO_{<2}$
  - SiO_2 is still a problem, both on sidewalls and at inlets to combustor
  - SiO_2 is not effectively water-scrubbed; buildup of fine particulate in duct is common

Fuel-fired Combustor

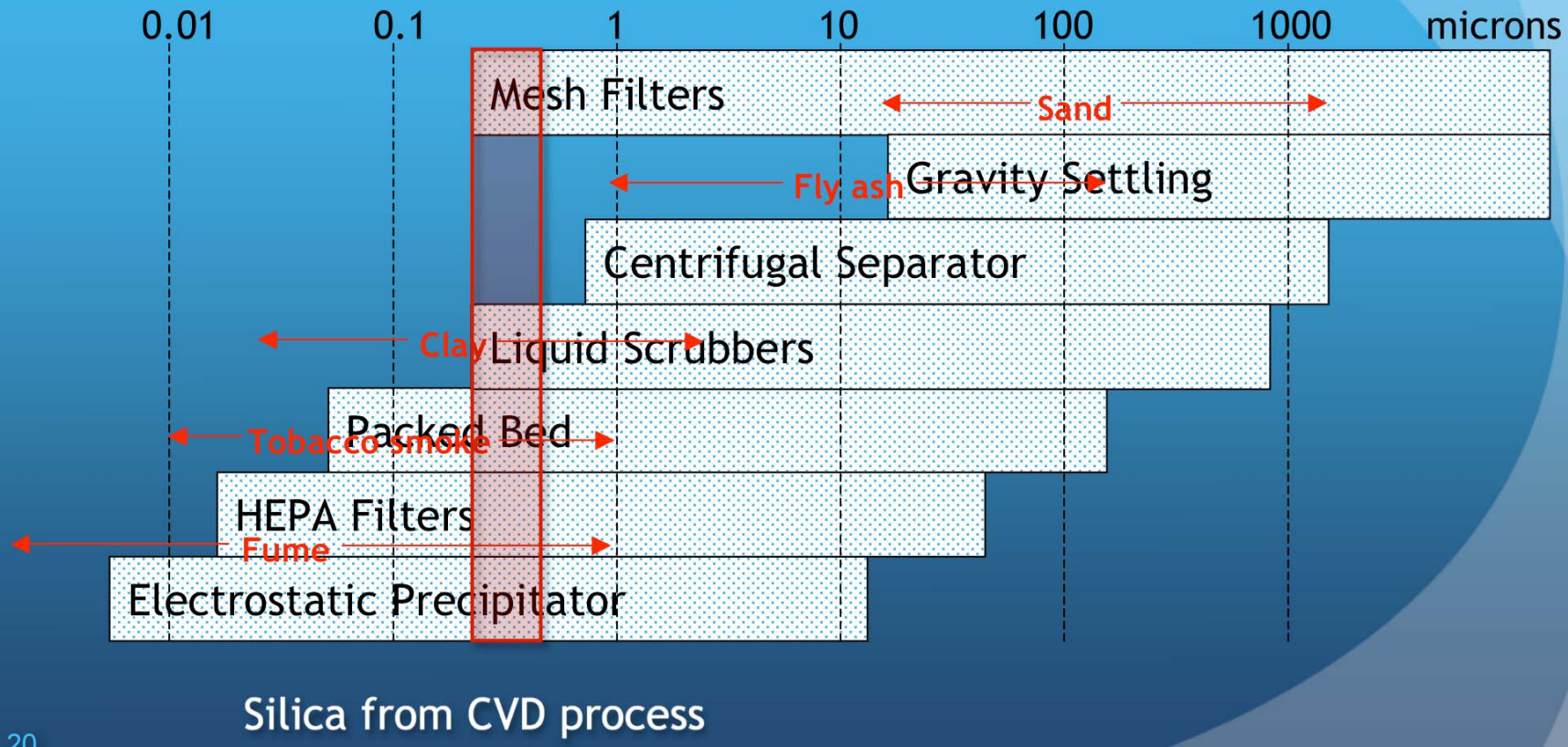
Abatement – Dry Bed or Wet Scrubber

- Dry bed abatement of SiH_4 is effective but very expensive for HVM
  - Superior method for gas pads as SiH_4 is destroyed, not merely diluted, and CoO is good since volume is small
    - Cost-competitive with air-conditioning loads for dilution equipment
- SiH_4 is not water-soluble; scrubbing is ineffective
  - Dosing with oxidants (H_2O_2, NaOCl) is of limited effectiveness
    - Henry's Law and Time-rate function both unfavorable; SiH_4 doesn't spend enough time in liquid phase to react efficiently

Abatement – the Powder

Abatement – the Powder

Fine solids act more like a gas – not easily scrubbed



Silica from CVD process

Wet ElectroStatic Precipitator

Other Gases - Thermal

- Polycrystalline and epitaxial Si are commonly doped
  - B_2H_6, PH_3, AsH_3, GeH_4, SiH_3CH_3
    - Very low concentrations – often 100 ppm in H_2
    - GeH_4 will be in the % range for SiGeepi
  - HCl for chamber etchback – often 20 slm or more
  - H_2 (<10 slm for poly, 40 – 120 slm for epi)
- WCVD; small amount of SiH_4 for WSi adhesion layer; much fluoride from this process
- Dilution is a poor abatement strategy for any of these gases
  - Combustion is the preferred method so H_2 and GeH_4 are destroyed
    - Wet scrubbing required for HCl, HF
    - Solids buildup, residue in pipework may be a concern

Other Gases – Plasma Processes

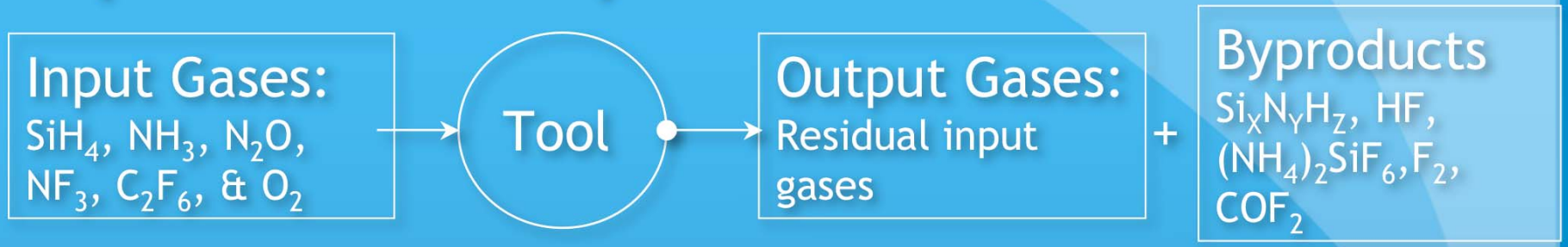
- SiH_4 is rarely the only gas to be used in a process; the other gases must be recognized as well
  - NH_3 (difficult to burn, does not wet-scrub especially well)
  - PH_3, B_2H_6 readily burned, do not wet scrub at all
  - $NF_3 \rightarrow F_2$; easy to abate if done properly
  - N_2O – significant global warmer, but difficult to abate
  - CF_4, C_2F_6, etc., difficult to abate

- Bottom line – cannot just treat for silane

Other Gases – Mix and Match?

- As a reducing agent, SiH_4 reacts with oxidizers
  - Explosive reaction with NF_3
    - LFL of SiH_4 is only 0.66% in NF_3
  - Hydrides also react with halogens (Cl_2, F_2)
    - This is why CVD process exhaust streams are never mixed
- Silane is nonreactive towards other hydrides (PH_3, NH_3, GeH_4, etc.)
- Silane is largely nonreactive towards acid gases (HCl, WF_6)

Specific Example: PECVD Nitride



- Safety: SiH_4 is explosive (LFL=1%) and toxic (TLV=5 ppm); NH_3 is toxic and flammable, F_2 is corrosive

- Environmental: HF (TLV=3 ppm) is acid gas; C_2F_6 is a global warmer (GWP=230,000)

- Downtime: Nitride-type solids from deposition step can block inlets, pipework, and reduce vacuum pump lifetime

- Ammonium hexaflurosilicate $(NH_4)_2SiF_6$ from the clean step condenses as a solid to block the pipes

PECVD Nitride: Abatement

Pumping: Run pump with max. N_2 purge to minimize solids buildup

The pipe line between pump and the abatement device may be heated if formation of $(NH_4)_2SiF_6$ causes blockages

Traps may extend uptime for both pumps and abatement

- **Water Scrubber:**
  - NH_3, $(NH_4)_2SiF_6$, HF, solids are removed
  - SiH_4, N_2O, C_2F_6, NF_3, will pass through the unit (SiH_4 minimal)
  - F_2 from NF_3 clean may be a concern - keep pH low
- **Cold Adsorbers / Hot Bed Reactor:**
  - Ensure not only the input gases but also byproducts are abated.
  - PFC gases are not abated
  - Can be cost prohibitive
- **Combustor / Scrubber:**
  - All the gases and byproducts will be combusted - water scrubber will remove HF, residual NH_3
  - Be wary of blockages in the inlet nozzles

PECVD Nitride

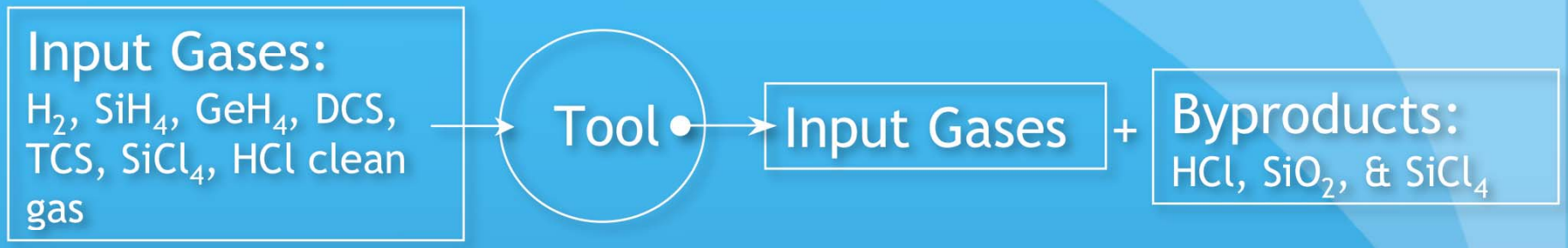
- Input: SiH_4, NH_3, N_2O, C_2F_6, NF_3
- Output: Solids, SiH_4, HF, F_2, NH_3, $(NH_4)_2SiF_6$, N_2O, SiF_4, C_2F_6

	$\underline{NH_3}$	$\underline{SiH_4}$	$\underline{NF_3}$	$\underline{HF}$	$\underline{F_2}$	$\underline{(NH_4)_2SiF_6}$	$^*\underline{SiF_4}$	$\underline{C_2F_6}$
Hot Bed	N	Y	Y	Y	Y	Y	Y	?
Water	Y	N	N	Y	Y	Y	Y	N
Burn	Y	Y	YNY	Y	Y	Y		
Cold Bed	Y	Y	N	?	Y	Y	Y	N
Burn/ Scrub	Y	Y	Y	Y	Y	Y	Y	Y

***$(NH_4)_2SiF_6$ condenses in the pipelines as a solid during chamber cleans and may require heat trace to prevent blockages.**

Recommendation: Combustor/scrubber. Wet scrubber as long as SiH_4 does not exceed 1%. Use of 3MS or 4MS for nitride films requires combustor / scrubber.

Si and SiGeEpitaxy



- Safety: Hydrogen is explosively flammable (LFL 4%)
  - Viscous "honey" in exhaust line is unstable – may explode
  - Acid gases generate HCl - corrosive
  - GeH_4 is highly toxic

- Environmental: Particulates, HCl cannot be vented to atmosphere.

- Downtime: Solids can block exhaust line.
- Require exhaust pressure stability if tool operated at atmospheric pressure

Si and SiGeEpitaxy

N_2 purge that is at least equal to H_2 flow is strongly recommended after the vacuum pump.

There is no substitute for adequate leak testing with H_2 processes!!!

- **Combustor (Strongly recommended)**
  - Removes hydrides and H_2, but combustor technology must be adequate for safe H_2 removal
  - Associated scrubber to remove particulates and HCl - water treatment
- **Wet scrubber (not recommended)**
  - Removes HCl, DCS, TCS, SilTet.
  - Presence of H_2: an explosion hazard as this is not removed by the scrubber; ATEX directives forbid wet scrubbers on epi
- **Dry Absorber**
  - Typically cost-prohibitive for high gas flows seen in epi process

Si and SiGeEpitaxy

- Input: H_2, SiH_4, GeH_4, DCS, TCS, $SiCl_4$, HCl
- Output: Process gases, SiO_2, GeO_2

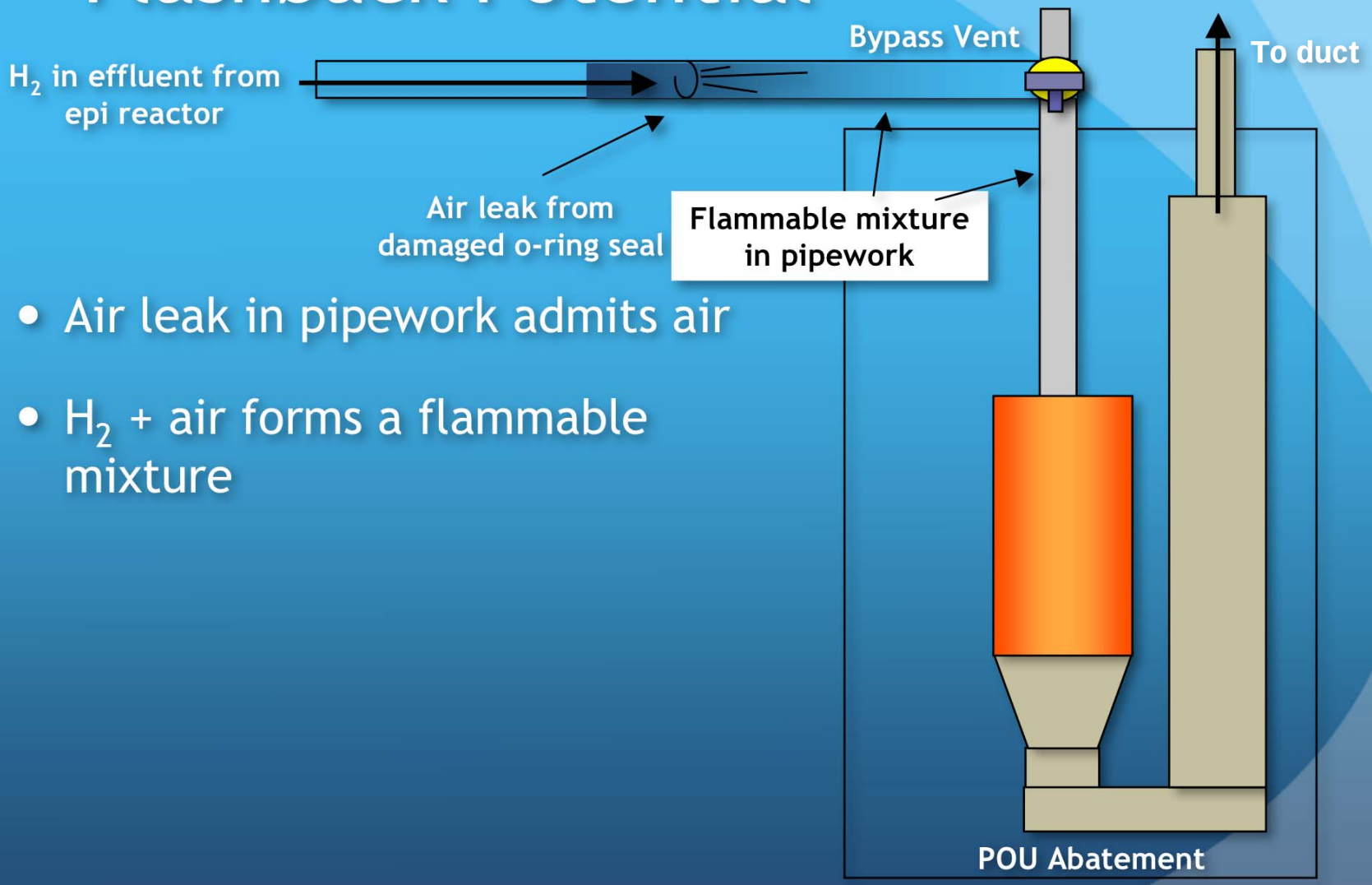
	H_2	SiH_4	DCS	TCS	$SiCl_4$	GeH_4	HCl
Hot Bed	N	Y	Y	Y	Y	Y	Y
Water	N	N	Y	Y	Y	N	Y
Burn	Y	Y	?	?	?	Y	N
Cold Bed	N	Y	Y	Y	Y	Y	Y
Burn/Scrub	Y	Y	Y	Y	Y	Y	Y

Water scrubbers remove acid gases but not flammables.
Combustor needs fuel and water scrubber to remove DCS, TCS, $SiCl_4$

High H_2 flows require much O_2 and are difficult to burn cleanly.

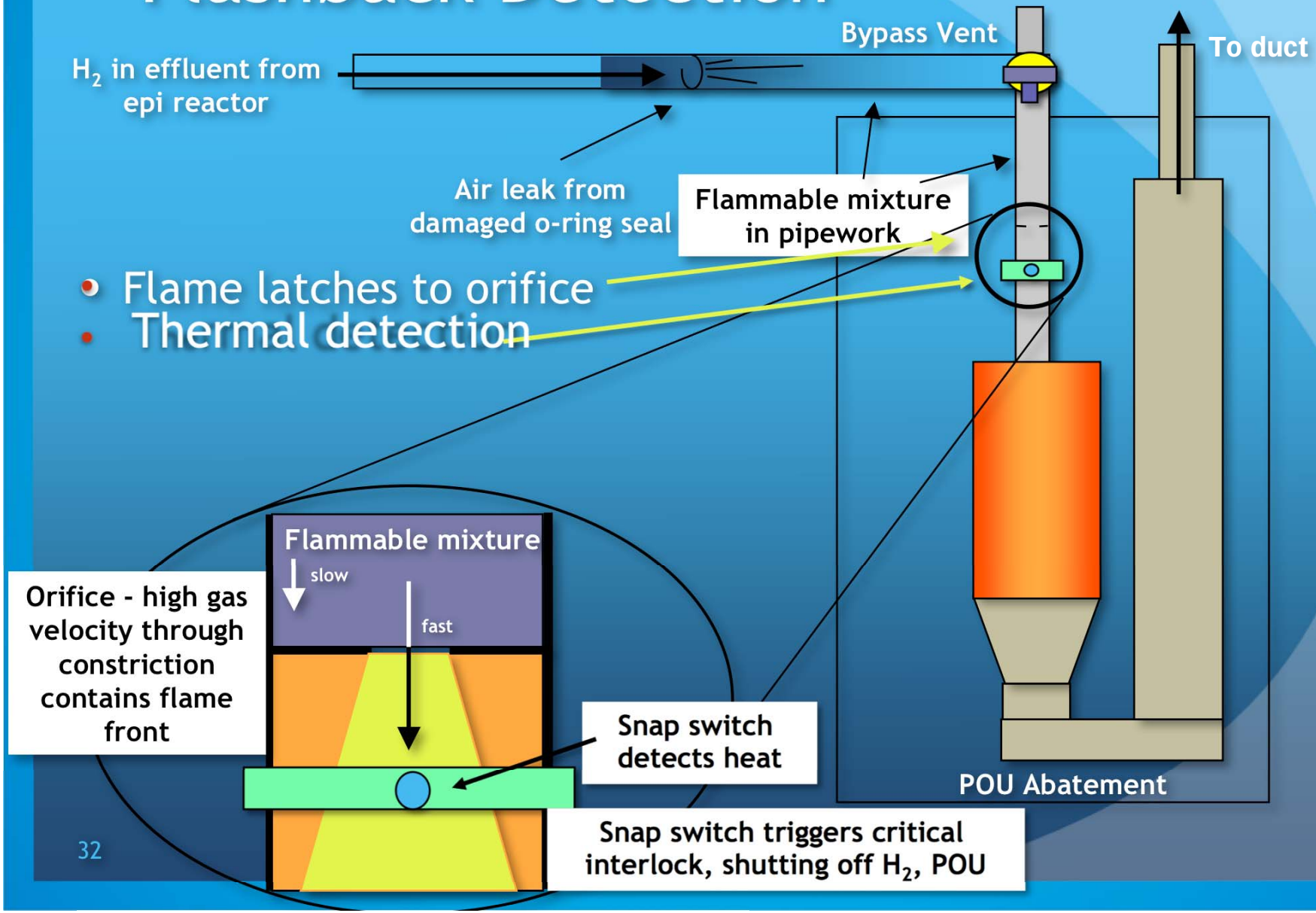
Recommendation: Combustor or combustor/scrubber

Flashback Potential

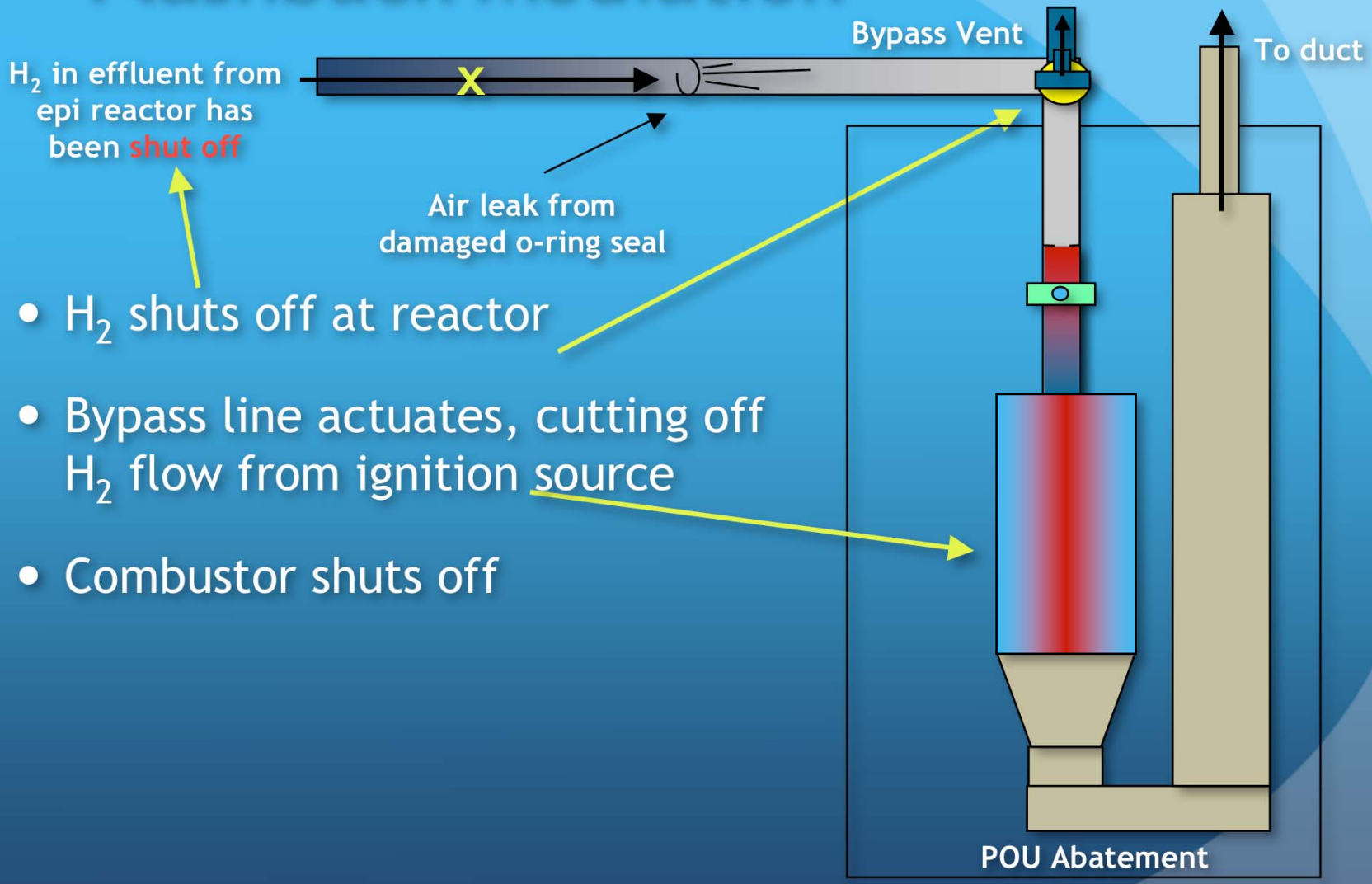


- Air leak in pipework admits air
- H_2 + air forms a flammable mixture

Flashback Detection



Flashback Mediation



- H_2 shuts off at reactor
- Bypass line actuates, cutting off H_2 flow from ignition source
- Combustor shuts off

Summary

- Silane as a pyrophoric requires special attention
  - Must not allow flammable mixtures into ductwork
- The amount of silane makes a big difference as to the abatement approach
  - Mixing with air is seldom the best solution
  - Solids must be managed at the expense of uptime
- The other gases in the process also must be considered
  - Mixing with oxidizers must be avoided at all costs
  - Other flammables, corrosives must also be addressed