Controlling Carbonate Buildup in Pneumatic Hydrate Injection Systems-

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Overview

- Introduction & Summary
- Chemistry and Reactivity Considerations
- Design & Operational Challenges
- ADA Hydrated Lime Injection System Design Approach.

Carbonate Formation in Hydrated Lime Injection Systems

- Hydrated lime reacts with Carbon Dioxide (CO_2) at ambient concentrations.
- Hydrated lime reacts with CO_2 to form calcium carbonate, ($CaCO_3$) and water (H_2O).

$$Ca(OH)_2 + CO_2 \rightarrow CaCO_3 + H_2O$$

- To avoid scale, either remove the CO_2 or control the reaction.

Carbonate Formation in Hydrated Lime Injection Systems (Cont.)

- Targeted Reactions:

$$Ca(OH)_2 + SO_3 \rightarrow CaSO_4 + H_2O$$

$$Ca(OH)_2 + H_2SO_4 \rightarrow CaSO_4 + 2H_2O$$

- To promote optimum acid gas mitigation & reagent utilization - lime reactions *should* occur in the duct.
- *Minimize* $CaCO_3$ formation in conveyance system
  - Deliver more effective reactant to the duct (lime v. carbonate) .
  - Decrease carbonate system scaling.
  - Increases system reliability.

Carbonate Formation in Hydrated Lime Injection Systems (Cont.)

- Carbonate formation is thermodynamically-dependent
  - At ambient temperature and atmospheric concentrations, $CaCO_3$ formation is moderated.
  - Once fluid temp > 95°F the $CaCO_3$ formation increases.
  - Once fluid temp > 120°F the rate of carbonate formation is believed to accelerate

Carbonate Formation in Lime Injection Systems (Cont.)

- Temperature is important in determining the carbonate morphology (speciation).
- $CaCO_3$ can differ in crystalline structure and ‘morphology’.
- Maintaining system temperatures appropriately low keeps $CaCO_3$ formation away from the *bad* polymorphs which minimizes scale production and buildup

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System Design & Operational Challenges

- Operational consideration
  - Motive air source for most pneumatic systems is ambient air that is compressed by a regenerative or positive displacement blower.
  - Compression inefficiencies result in heat being added to the air versus compression work.
- Required reactants (CO_2, $Ca(OH)_2$ and heat) now available and favorable for $CaCO_3$.

System Design & Operational Challenges

- CO_2 is essentially an unavoidable consequence of using ambient air for motive air.
- Inject the lime as lime not carbonate
  - $CaCO_3$ is less reactive that $Ca(OH)_2$.
  - $CaCO_3$ polymorphs *can be* abrasive.
  - $CaCO_3$ polymorphs *can be* sticky which have a greater scaling potential as they dehydrate and/or heat .

System Design & Operational Challenges

- Presence of moisture further complicates conveyance system performance because:
  - $Ca(OH)_2$ is hygroscopic and will absorb water ultimately changes handling characteristics (↑ density).
  - ↑ $CaCO_3$ related abrasion & agglomeration issues.
- These effects seem to be additive and promote component scaling, material accumulation, and eventual system failure.

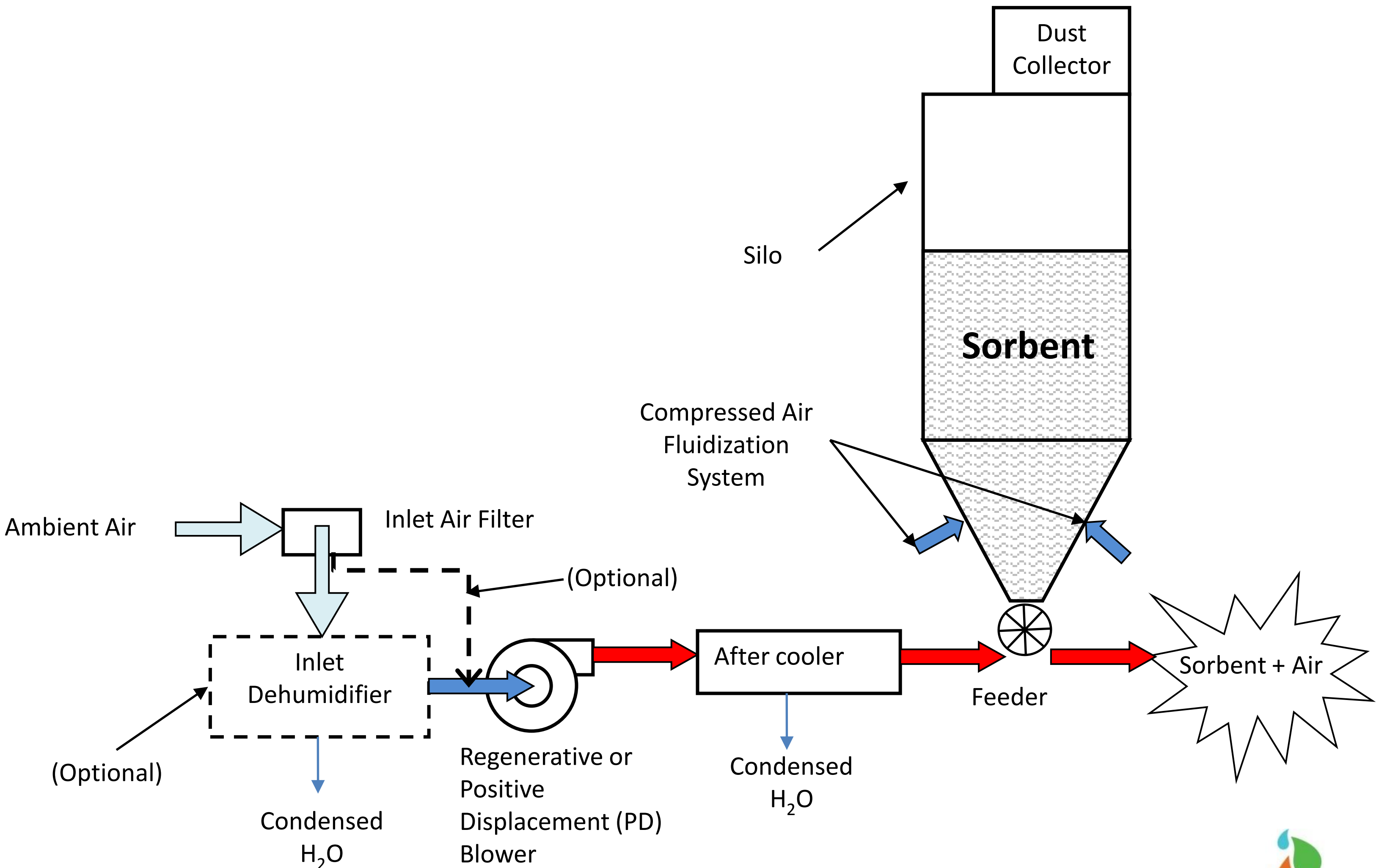
System Design & Operational Challenges

- System design that promotes the targeted chemistry and limits the by-product chemistry.
- CO_2 issue is part of the ambient air but we can eliminate its impact by reducing heat input.
- Distribution considerations.

Hydrate Systems

- Two general Hydrated Lime Injection System (HLIS) configurations:
  - 1st based on an equipment arrangement that works well for a lot of applications
  - 2nd based on a new equipment configuration through Mississippi Lime Company (MLC).
- ADA configuration is designed to address the $Ca(OH)_2$ reactivity issues.

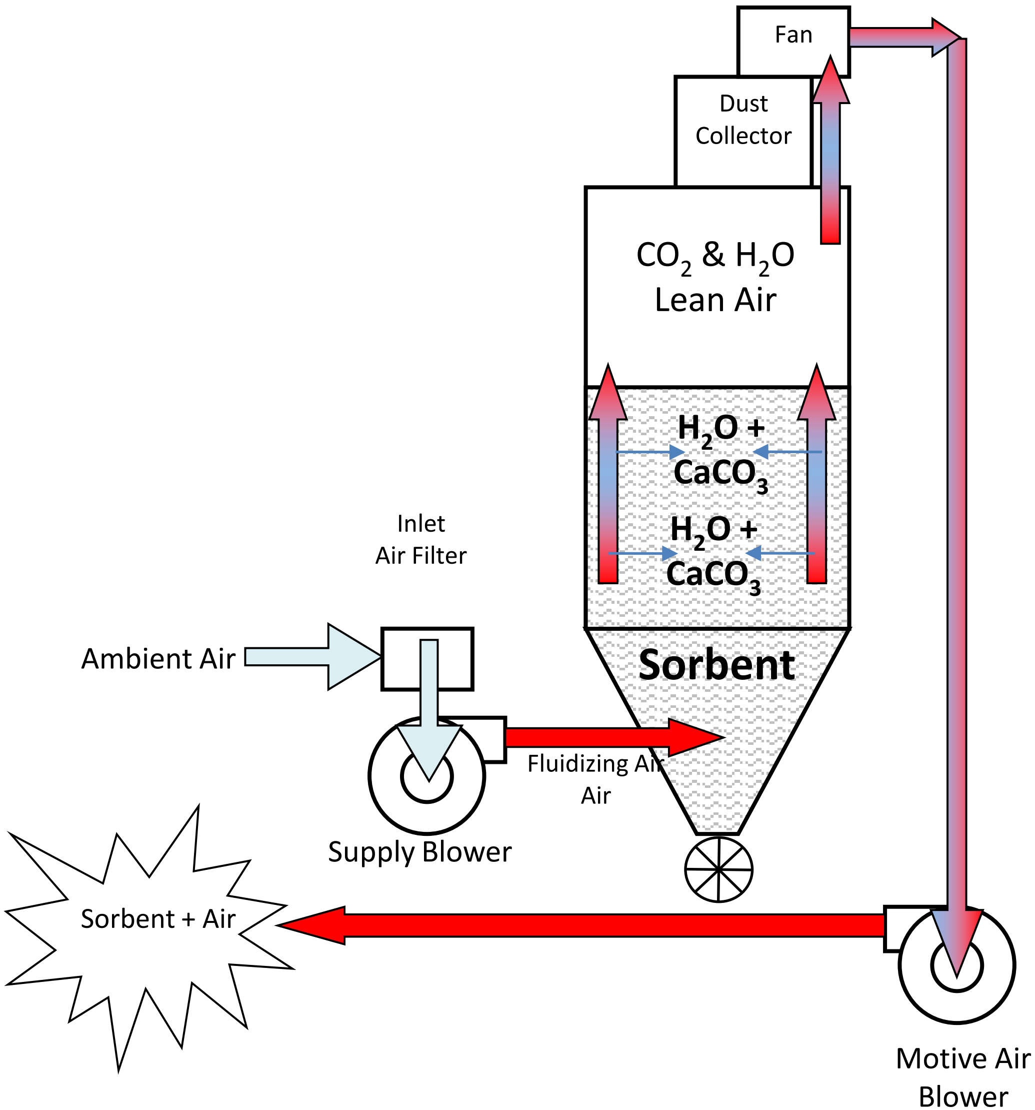
Hydrate Delivery System Design Option 1



Hydrate Delivery System Design Option 1 (Cont.)

- Recent operating experience with this equipment arrangement suggests:
  - Inlet dehumidifiers are not always effective.
  - After cooler downstream the blower seems to have the most impact.

Hydrate Delivery System Design Option 2 – MLC (Cont.)



Hydrate Delivery System Design Option 2 – MLC (Cont.)

- While this design has demonstrated performance improvements – by chemistry this approach possesses limitations.
- For the CO_2 to be scrubbed the air supplied by the fluidizing system needs to be hot.
  - Speciation becomes a concern.
- CO_2 removal likely dependent on the silo material level.

Hydrate Delivery System Design Option 2 – MLC (Cont.)

- $CaCO_3$ still produced - according to MLC the expected occlusion duration is ~220 days.
- Another limitation this approach is CO_2 removal would most likely be variable with the material level in the silo.

Hydrate Delivery System Design Option 3 – ADA

- CO_2 & heat are issues with previous approach.
  - Scale prevention should include temperature and moisture control of the entire conveyance system.
- ADA approach involves 3 design criteria:

  1.) maintaining the conveyance air at lower temperatures 2.) reducing moisture levels in the conveyance air, and 3.) appropriate conveyance velocities.
- The ADA design philosophy can be summarized as: '*keep it cool, keep it dry, keep it slow*™.'

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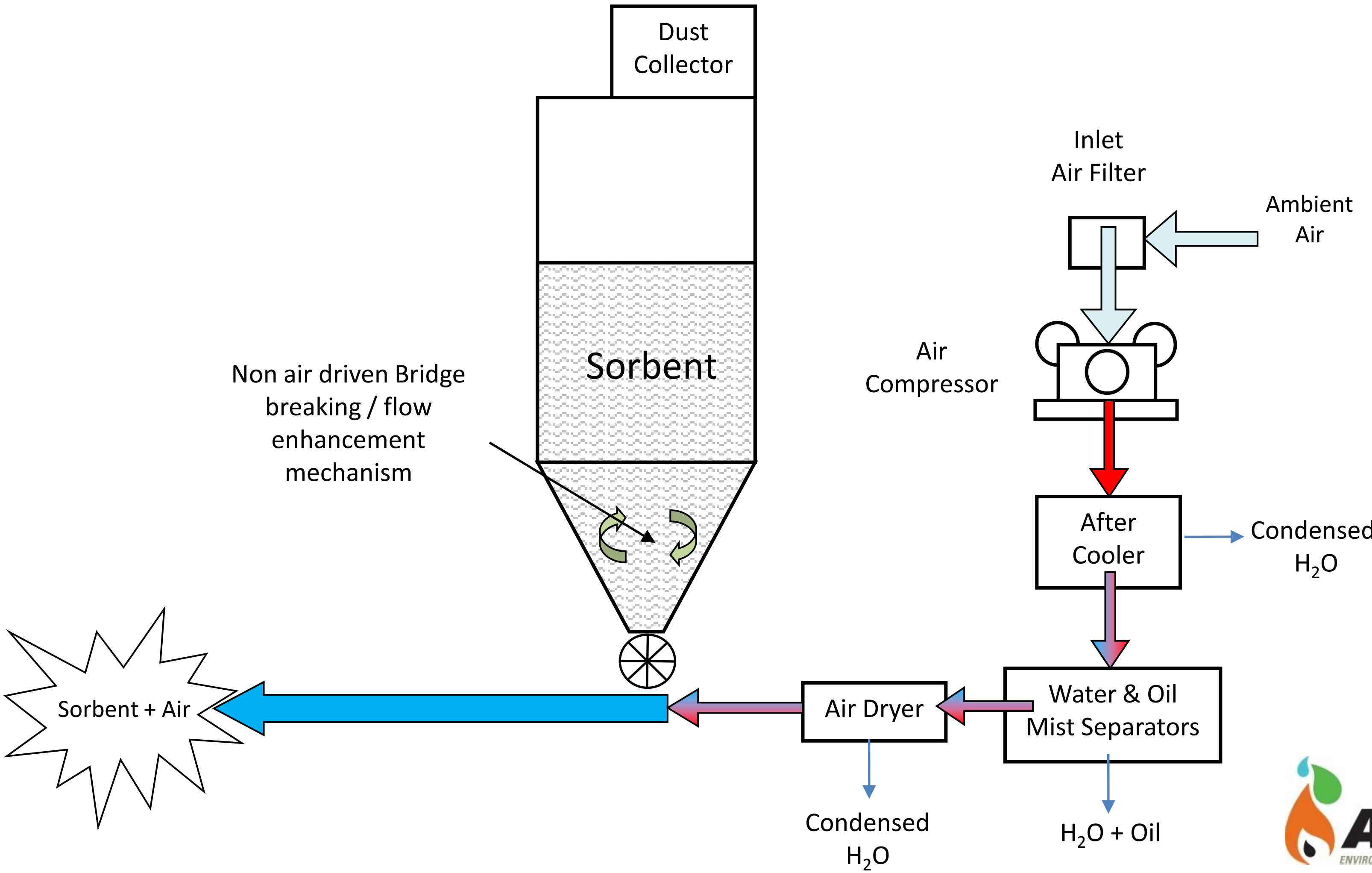
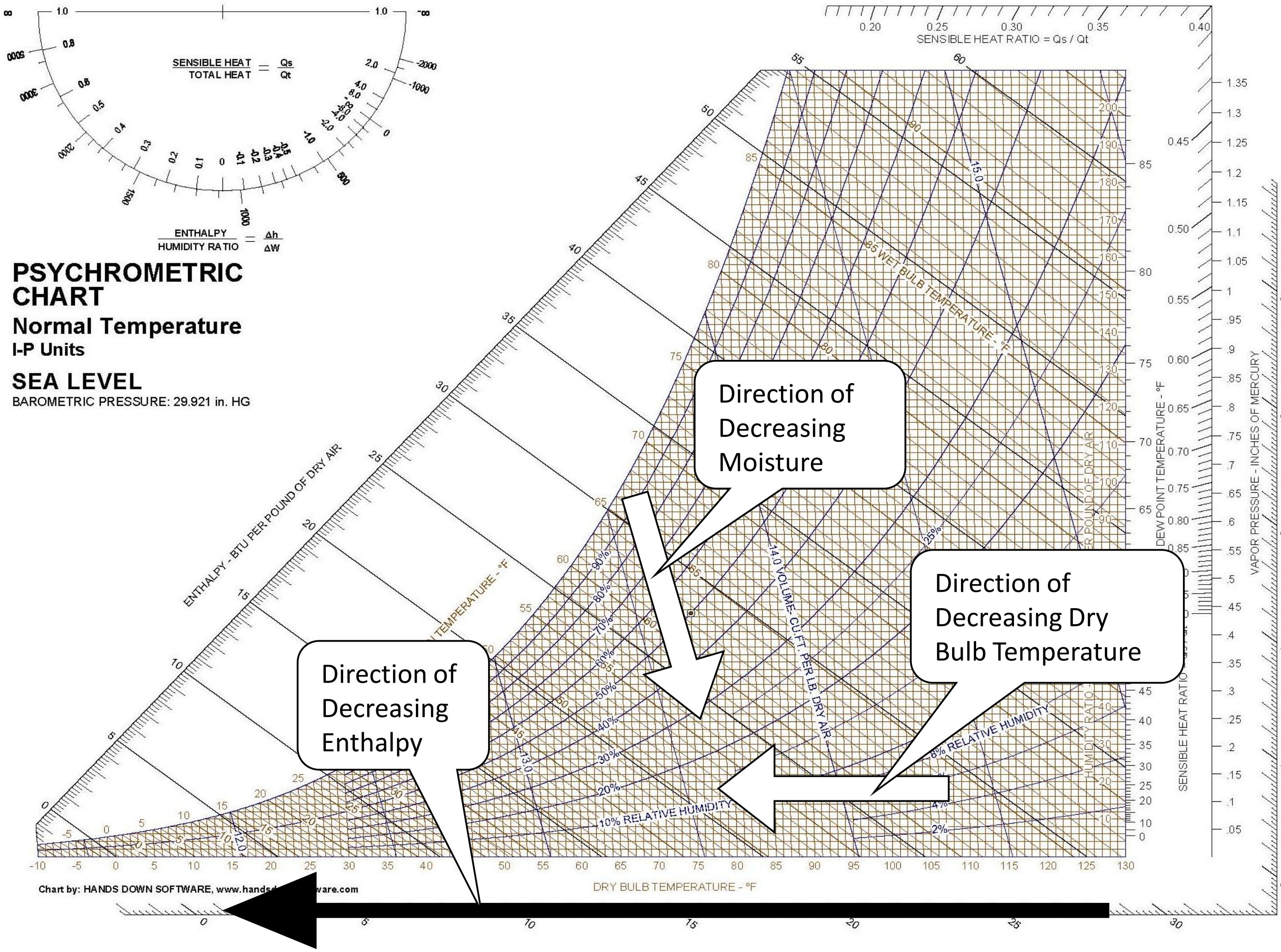
Hydrate Delivery System Design Option 3 – ADA



Hydrate Delivery System Design Option 3 – ADA (Cont.)

- Using cool dry expanded compressed air has some distinct advantages:
  - Constant volume.
  - Since alkaline sorbents are hygroscopic, air moisture content is principal to overall system performance and for enduring operation.
- Related to air dryness & moisture content is the ability of the dry air to be a superior insulator
  - Since the compressed air system provides dryer air, it has less ability to carry & transfer heat to its surroundings
  - Consequently the air cannot transfer heat to the hydrate further facilitating scale prevention.

Hydrate Delivery System Design
Option 3 – ADA



Hydrate Delivery System Design Option 3 – ADA (Cont.)

- Dry compressed air is supplied to the air supply side at the metering point.
- Near the manifold, the compressed air expands to the design pressure of the dilute phase pneumatic conveyance system
  - The precisely metered air is allowed to expand adiabatically.
  - This expansion achieves a net cooling effect which further facilitates reducing system temperature.

Hydrate Delivery System Design Option 3 – ADA (Cont.)

- When conveying at slower velocities material tends to more closely follow the bulk air flow.
- Slow conveying velocities are key to preventing excessive material impingement and therefore abrasion erosion of injection components.
- To allow continued & reliable operation at lower velocities, ADA developed a manifold which allows material to follow conveyance air and assure the designed distribution is maintained.

Hydrate Delivery System Design Option 3 – ADA (Cont.)

- ADA system success attributed too:
  - Avoiding the formation of the harder aragonite carbonate species.
  - Using lower conveying temperatures.
  - Slower conveying velocities to minimize material self-heating, impingement, and turbulence.
- Post-mortem inspection of the injection system internals following testing-scale operations has not revealed component wear.

Summary

- Accounting for chemistry is critical to system performance.
- The choices are to control...
  - the reactants or
  - the reactions
- ADA's approach is to hydrate injection is

"Keep it cool, keep it dry, keep it slow"™

Thank You

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