Maintaining CO_2 Quality in Bulk CO_2 Storage Vessels

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May 4th 2016, Fort Myers, Florida

Maintaining CO_2 Quality in Bulk CO_2 Storage Vessels

NVOR in Mini Bulk Tanks (MBT)

- Properties of NVOR
- Causes for NVOR Build-Up in MBT
- Evaluation of NVOR Contaminant

Transfer of this Knowledge to Larger Scale Vessels

- What is the same, what is different?

How to Maintain the CO_2 Quality

- Influencing Factors
- Best Practices Summary

Background & Definitions

Non-Volatile Residue (NVR):

- Grand total of suspended and dissolved particulate matter, including NVOR. Examples of NVR include, but are not limited to: rust, dirt, adsorbent bed fines (ex. charcoal, silica gel), filter fibers, transfer material / process wear particles.

Non-Volatile Organic Residue (NVOR):

- All forms of organic semi-volatiles and non-volatiles compounds (e.g. oils, greases, plastic and elastomeric leachates).

General Properties of NVOR:

- Low Vapor Pressure
- Soluble or Suspended Organic Impurities in Liquid Phase CO_2. Myth: NVOR is insoluble and floats to bottom.
- Solubility in extracting solvents (ex. hexane, $MeCl_2$)

Potential Sources of NVOR

Overview

Compressor
Oils

Elastomeric Hoses and Tubing

O-Rings and
Elastomeric Parts

Piping & Hardware
Assembly Aids

Feed Gas Bio-Oil
Residues

Basic Analytical Methods

Simple Snow Cone Screening - Qualitative Test

Pass
No Visible NVR / NVOR

Fail
60 ppm w/w NVOR

Snow Screening

- A solid CO_2 (snow) sample is collected and allowed to sublime.
- The interior of the sample container is examined.
- Results are reported as Pass / Fail. If no NVR/NVOR is observed the result is reported as "Pass".

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Basic Analytical Methods

Simple Snow Cone Screening - Qualitative Test

Specification Limit
5 ppm

Pass
2 ppm

At low levels (2 ppm w/w) NVOR can be visually detected.

Basic Analytical Methods

ISBT Method 8.0 Procedure A – Quantitative Test

Difference weight after sublimation of snow

Snow-filled
1L NVR Can

Scale

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Field Study

ALI Lab Data - MBT Samples to Date

To date 31 MBT samples tested. % ISBT NVOR failures = 29%

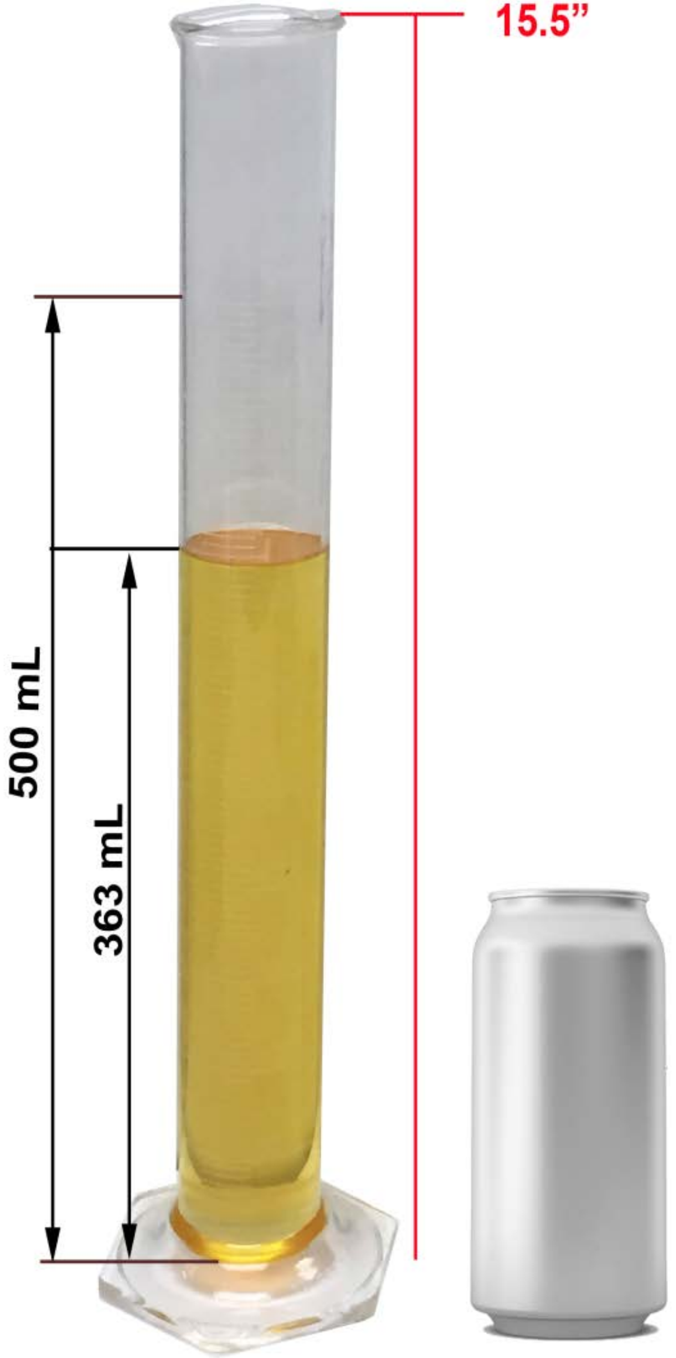
NVR Concentration (ppm)	NVR Description	NVOR Concentration (ppm)	NVOR Description	THC (ppm)
860	Pale, yellow oil and fine, dark paricles.	810	Pale, yellow oil.	7.3
8.3	Yellow oil and various, dark particles.	7.1	Yellow oil.	1.0
11	Various, black particles and clear, yellow oil.	10	Clear, yellow oil.	1.3
230	Dark, yellow oil and black particles.	210	Dark, yellow oil.	0.6
44	Fibers, yellow oil and black particles.	35	Clear oil and light, yellow oil.	--
92	Dark, yellow oil and black particles.	84	Yellow oil.	4
14	Dark, yellow oil residue and black particles.	10	Dark, yellow oil.	--
45	Fine, black particles and clear oil.	31	Clear oil.	6.5
32	Various, black particles, yellow oil and fibers.	29	Some yellow oil and clear colorless oil.	0.2

ISBT NVOR Limit for Bev-Grade CO_2 = 5 ppm w/w
ISBT NVR Limit for Bev-Grade CO_2 = 10 ppm w/w

Field Study

- An NVOR content of 800+ ppm w/w is equivalent to 291 g = 363 mL NVOR in an 800 lb MBT

800+ ppm w/w NVOR



Field Study

Calculations - MBT NVOR Build-up

- 1 year, NVOR = 7 ppm w/w
- 4 yrs, NVOR = 28 ppm w/w
- 8 yrs, NVOR = 56 ppm w/w
  with a NVOR load of 26 ml in the 800 lb MBT

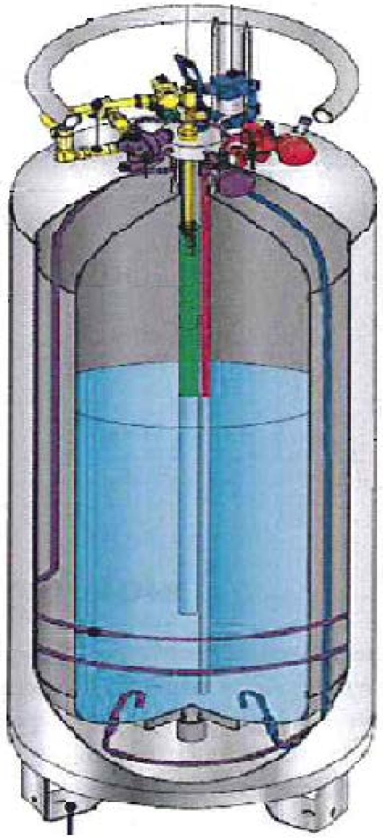
Assumptions:

- All MBT loads @ calculated 1 ppm NVOR
- 150 – 800 lb LCO_2 typical MBT capacity
- MBT Top-off 1X / month @ ≈ 40% remaining fill (0.6 tank capacity)
- Most of oil retained in LCO_2 phase of MBT
- No MBT Drainage for: 1, 2, 4, 8 yrs
- Typical oil density = 0.8 g/ml
- Conversions: 1 US Ton = 2,000 lb = 90,800,000 g =90,800 kg.
  1 lb = 454 g, 1 µg = 1 x 10^{-6}g

Known Causes of High NVOR

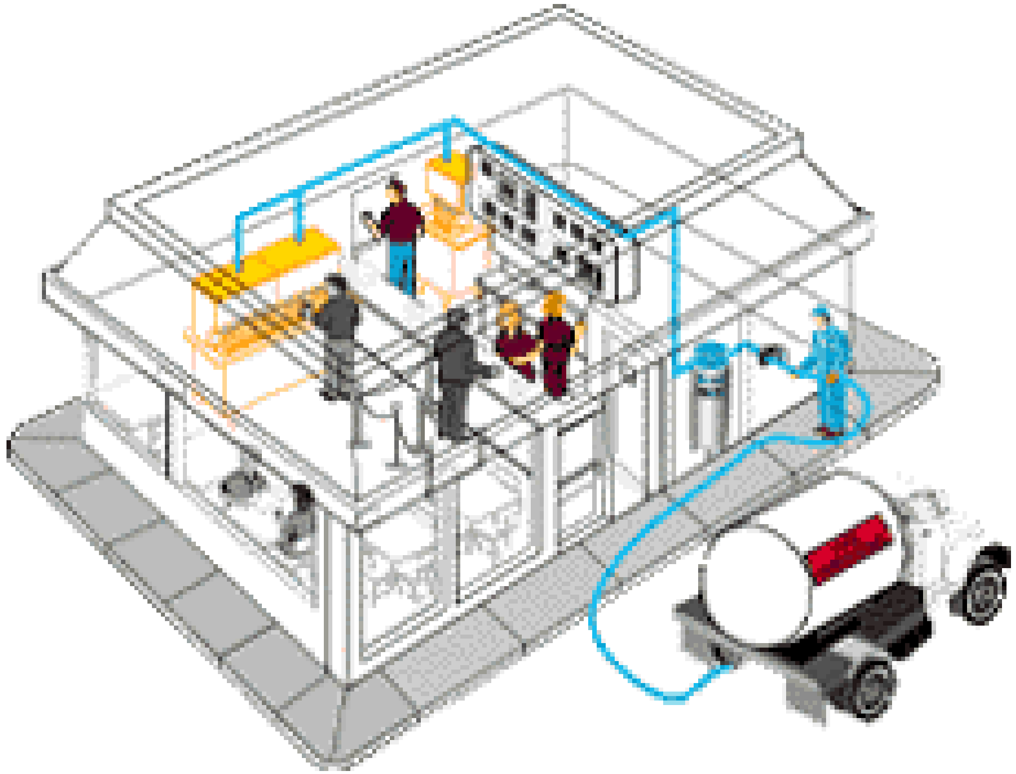
Fountain Mini Bulk Tank Current Practices

- Some MBT manufacturers have no recommended tank drain / tank cleaning schedules – or customers ignore their recommendations
- Some MBT manufacturers have no recommended practices concerning periodic LCO_2 quality screening
- Many current MBT models have no drain port
- It is common to use the vapor phase from MBT



Knowledge Transfer

From MBT to large scale storage vessels



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Contamination in Bulk Tanks is rare, but it happens.

Large particles

Small particles, oil, grease, dust

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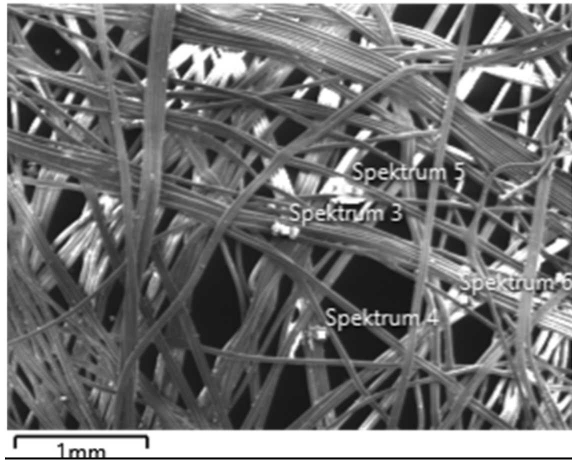
What is it in detail?

Classes of material detected, additional to "O"

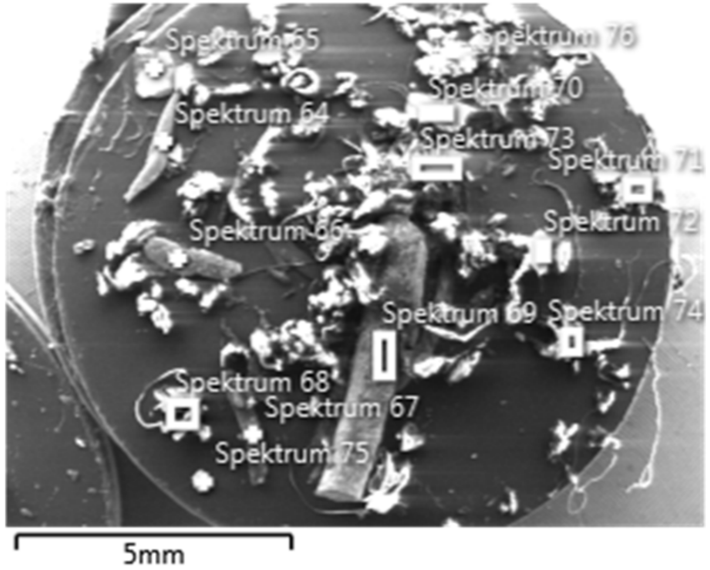
- **Cr Ni Fe** – Iron alloy like carbon steel / chrome nickel steel
- **Cu Sn Zn** – Copper alloy like copper / brass
- **AL Si O** – Mol sieve adsorbent
- **C** – Activated carbon

Method used: SEM/EDX analysis
SEM: Scanning electron microscope
EDX: Energy-dispersive X-ray spectroscopy

Elektronenbild 1



Elektronenbild 10



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Origin of these particles

CO_2 production plants

- **Activated carbon filters** – particles, carbon
- **Mol sieve** - particles, aluminosilicate
- **Carbon steel** – rust
- **Compressor** – oil
- **Installation, maintenance, repair** – gaskets, polytetrafluoroethylene (PTFE), cuttings, dirt

Rail tank cars and road tanker

- **Filling** – dirt, particles in hoses
- **Material deterioration** - paint
- **Carbon steel** – rust
- **Installation, maintenance, repair** – gaskets, polytetrafluoroethylene (PTFE), cuttings, dirt

CO_2 storage vessels

- **Tank inlet** – dirt, particles
- **Build in vaporizers** – accumulation of contaminants
- **Process cross contamination** - e.g. in breweries
- **Carbon steel** – rust
- **Installation, maintenance, repair** – gaskets, polytetrafluoroethylene (PTFE), cuttings, dirt

What is the load we have to handle?

Calculations – Storage Vessel NVOR Build-up

Beverage plant:

2000 t of CO_2 @ 1 ppm NVOR per year 2 kg NVOR per year

28 ppm w/w NVOR in a 70 t storage vessel

CO_2 manufacturing plant:

100.000 t of CO_2 @ 1 ppm NVOR per year 100 kg NVOR per year

50 ppm w/w NVOR in a 2000 t storage capacity

Remember the Mini Bulk Tank calculation:

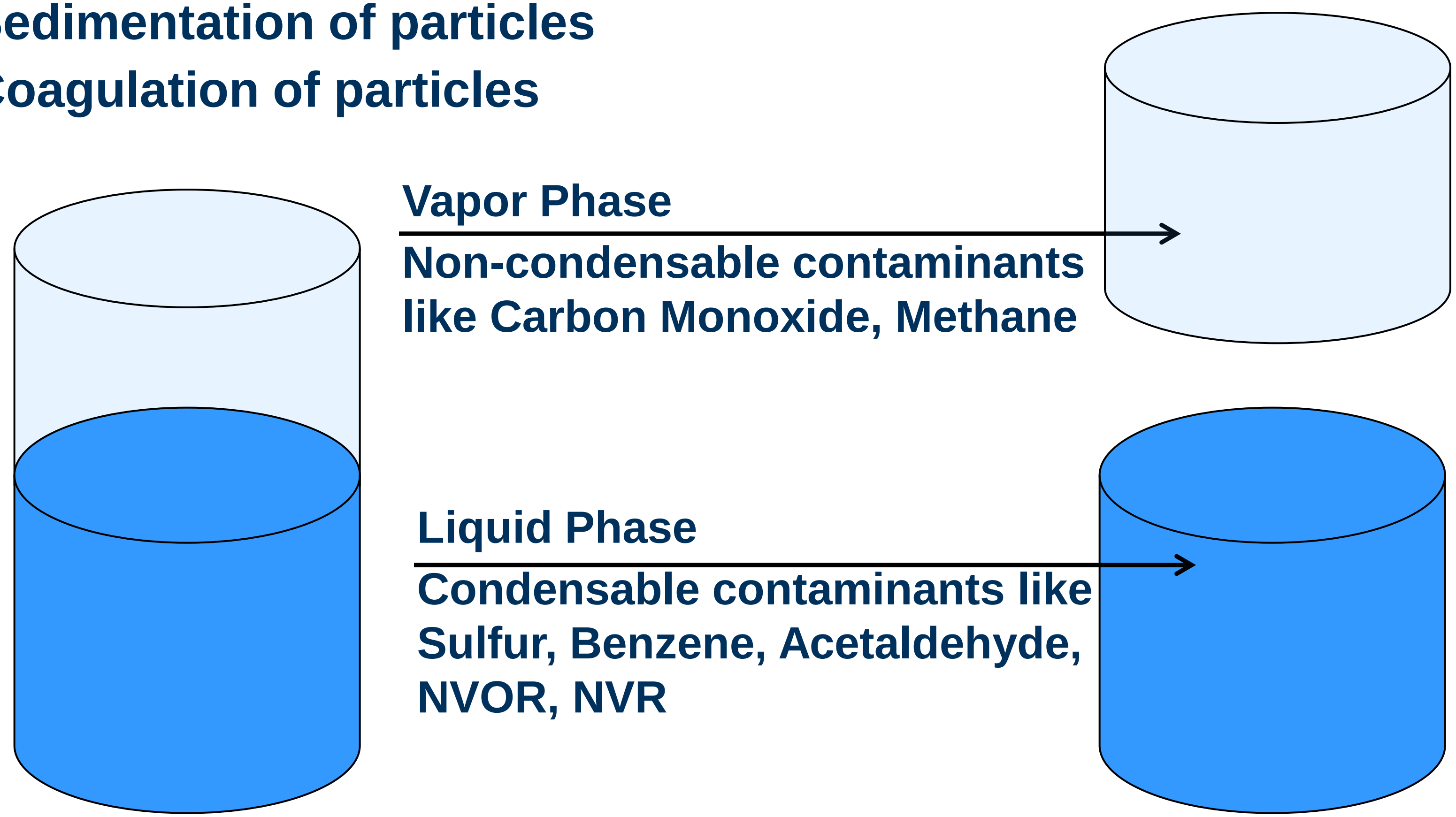
7 ppm w/w NVOR increase per year

The load in conventional storage vessels is even higher than in MBT!
What makes the bulk process more safe?

Storage Tank as a Purification Step

What happens during normal operation, it is not only about NVOR?

1. Continuous distillation
2. Sedimentation of particles
3. Coagulation of particles



Storage Tank as a Purification Step

The central question to be answered is:

How do impurities accumulate and where do they go?

Influencing factors

1. **Vertical versus horizontal tank**
   - chance to get lowest point purged
2. **Foam insulated versus vacuum jacketed**
   - Distillation increases with heat gain
3. **Withdrawal**
   - liquid, vapor or a mixture
4. **Outlet at which height of the tank**
   - low point versus stand pipe
5. **Definition lowest tank level in operation**
   - entrain of sediment
6. **Pressure management during loading**
   - vent versus top loading
7. **Purging possibilities**
   - tank, pressure building vaporizer, product vaporizer
8. **Final filtration**

Storage Tank as a Purification Step

Maintain Quality in the Storage Vessels by:

1. Avoid accumulation of impurities
2. Get them out of the system

Possible reasons for high failure rate in MBT:
Vapor phase withdrawal and no purge!

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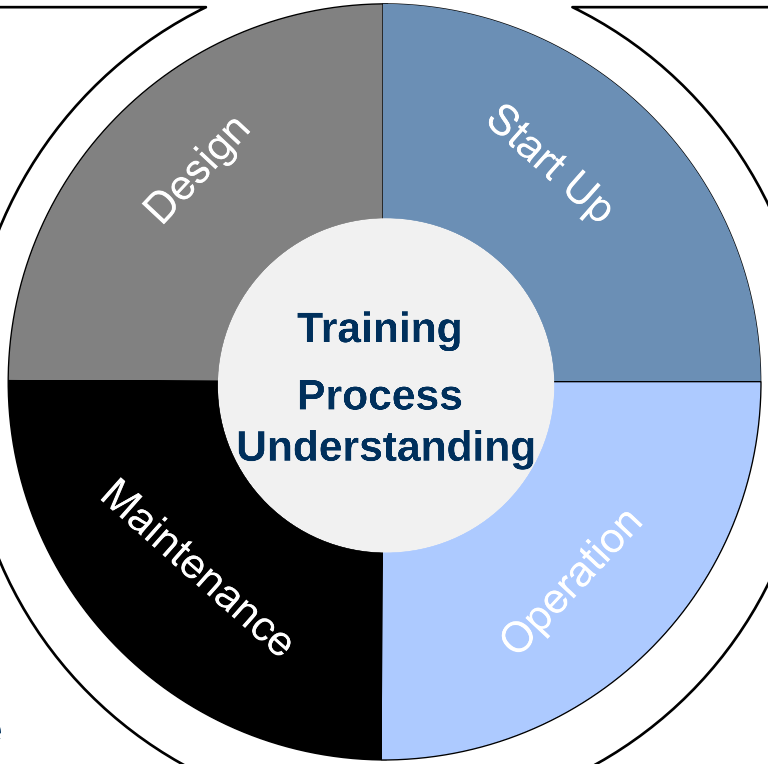
CO_2 Storage Tank Best Practices

Design
- Vertical, vacuum jacketed
- No built in components
- Austenitic or stainless steel
- Low point purge option
- Back pressure protected

Start Up
- Purging procedure
  - Clean
  - Dry
  - Rust free
- Define minimum tank level



Maintenance
- Liquid purge
- Subsequent snow sample
- Vapor purge
- Filter service
- Opt.: Vaporizer liquid purge

Operation
- Turnover of liquid product
- Turnover of gas phase
- Tank level to avoid entrainment of sediment
- Filtration after vaporizer

Checklist

1. **What is reality in your plant?**
   - How is your tank designed – started up - operated - maintained
   - product turnover - purging options and routines

2. **Have you faced any issues with CO_2 quality?**
   - Would you know if you had issues?

3. **Process understanding is key**
   - CO_2 tank as a “purification step”, where do the impurities go?

4. **Set up your specific program**
   - Is there a risk for CO_2 Quality in your system?
   - If yes, how to mitigate these risks?

Questions?

Thank you!

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