

“ Hope you had a Wonderful **Holiday** Season and welcome to the New Year “

## Issue Focus: CO<sub>2</sub> Manufacture and Treatment

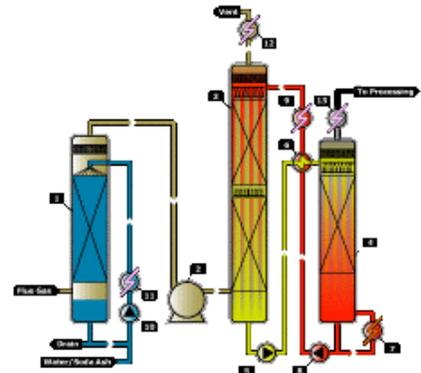
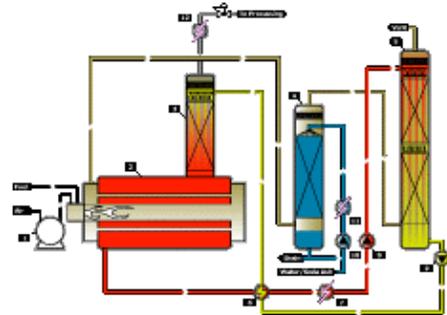
- Attached to this issue of T-B is our focus on Carbon Dioxide. We are highlighting three “in-plant” systems:
  - 1) CO<sub>2</sub> manufacture from a complete system, including the boiler
  - 2) CO<sub>2</sub> manufacture (stripping the CO<sub>2</sub> from flue gases) from an existing boiler
  - 3) beverage plant treatment of carbon dioxide enroute to the filling operation.

### The targets: Costs, Quality, Sustainability

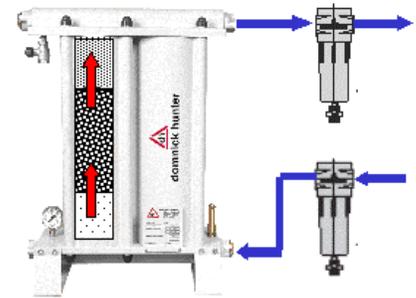
**The Wittemann Company:** If we can combine our need for heat and carbon dioxide so that co-generation is the effect, it can have a dramatic impact on plant costs: In supplying heat for plant use we are generating high quality CO<sub>2</sub>, or in producing CO<sub>2</sub>, we generate heat for our production needs or for facility purposes.

Where plants use pasteurizers, retorts, hydrostatic sterilizers, warmers, bottle washers or other significant heat exchange usage equipment, this is of high potential. It also dramatically impacts industry efforts on managing sustainability.

The recovery equipment, whether recovering CO<sub>2</sub> from an existing boiler, or a complete system for CO<sub>2</sub> manufacture, in addition to the above, also addresses reducing CO<sub>2</sub> emissions released into the atmosphere

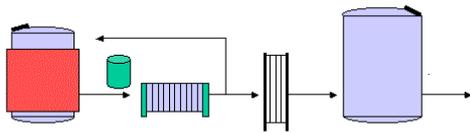


*domnick hunter: For CO2 treatment at the plant: Protecting the quality of carbon dioxide used in the product and in the process equipment used for production purposes is a critical responsibility for all beverage plants. The right technology, ease of servicing and maintenance, and an effective QC/QA protocol are important issues.*



## **Sugar Treatment:**

*Future issues of “Tech-Briefs” will address sugar treatment as practiced with good success in “International” beverage plants. Good success refers to quality (from an sensory, microbial and analytic POV) and cost savings. Treatments range from “tight” filtration, use of powdered activated carbon and diatomaceous earth, hot and cold filtration (often with pH adjustment), and ion exchange.*



*The use of automated and bulk syrup batching or continuous feed (granulated and liquid) and ingredient addition gives better control, more consistent quality and a cleaner and less labor intensive work area.*

## **Wastewater Treatment (or Reducing Surcharges)**

*F & B plants are encountering significant problems and costs in disposing of their wastewater. On a world-wide basis, the importance of being in local and national regulatory compliance is critical especially for food and beverage businesses operating on an International basis. Whether it is simple pH adjustment, increasing surcharges ... or being pointed toward a complete WWT system ... the implications are clear; 1) significant capital expense, 2) an added operational cost burden or high (and they will always increase) surcharges. See “wastewater page on website.*

*Where possible, building a wastewater facility should be avoided. There are a number of alternatives that can render a plants wastewater more acceptable to normal discharge. Also, very often a less costly system (aerobic or anaerobic) will give treatment advantages and reduced operating costs.*

## **Water Treatment**

*Coagulation systems (Lime based for alkalinity reduction) have been a mainstay of beverage water treatment for many years. Dependable, capable of addressing numerous water conditions and easy to control. For years, capable of delivering a water of superior characteristics and quality.*

A few problems:

- With surface water supplies, the incoming water can have the precursors for trihalomethanes. The high pH of the system and the available chlorine would generate THM's, often to the full potential.
- Lime based coagulation systems generate significant inorganic sludge. Potential for concern with plant discharge (mainly suspended solids ... no BOD/COD issues).
- For a number of products, TDS and specific ions must be reduced either to make such as "Purified" water, or requiring lower sodium. Coagulation systems cannot produce this type of water without help.

The move has been to membrane systems, where needed, or to minimum treatment where the incoming supply is already of high quality.

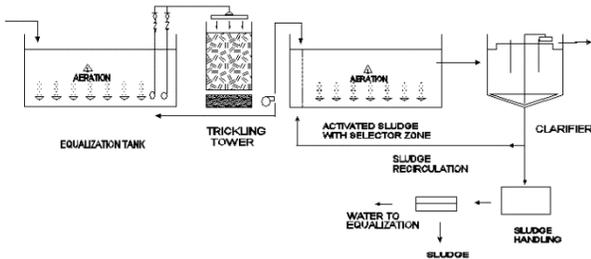
There are a number of ways to upgrade coagulation systems to address the problems either on a temporary or permanent basis. Contact Tri-Lake group for help.

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### Question for this issue ...

1. Does the loss of THM removal capacity in a carbon bed relate to the carbon's capacity for this small molecule organic or to the temperature/pressure of the steam stripping process? The following are the approximate boiling temperatures of the different THM species:

Chloroform	142 - 144° F.	(61 - 62° C.)
Bromodichloromethane	194° F.	(90° C.)
Dibromochloromethane	246° F.	(119° C.)
Bromoform	300 - 302° F.	(149 - 150° C.)



Your suggestions on topics to be covered in Tech-Briefs are appreciated.

Tri-Lake has considerable experience on operating conditions and processing needs in North America and most "international" markets.

We are available as consultants, training assistants, trouble-shooters or for special projects, production and training manuals, research, seminars or audits/surveys.

Fee schedule is available on request.



## Carbon Dioxide (CO<sub>2</sub>)

CO<sub>2</sub> has many commercial uses with new applications continually being created. While CO<sub>2</sub> may be used in either a vapor, liquid, solid or supercritical state in a given application, it is typically converted into liquid form at approximately 250 to 300 psig (17.6 - 21.1 kg/cm<sup>2</sup>) for economical storage and transportation.

CO<sub>2</sub> vaporizers convert bulk liquid CO<sub>2</sub> to vapor which can be utilized in applications such as the carbonation of beverages (pin point carbonators), increasing the hardness of desalinated water, or the pH adjustment of process or effluent streams.

Bulk liquid CO<sub>2</sub> can be utilized as a low temperature heat transfer fluid or as a part of a cascade mechanical refrigeration system.

Solid CO<sub>2</sub> or "dry ice" is often used for food freezing. It is produced by expanding bulk liquid CO<sub>2</sub> to near atmospheric pressure and compacting the resultant solid in a dry ice press. The vapor CO<sub>2</sub> or "revert gas" produced along with the solid CO<sub>2</sub> when the liquid is expanded is typically recovered in a revert system and returned to the bulk storage tank.

Supercritical CO<sub>2</sub> is produced by taking bulk liquid CO<sub>2</sub> and increasing both the temperature and pressure above their respective critical values. Numerous separation and cleaning applications take advantage of the solubility and / or low surface tension properties of supercritical CO<sub>2</sub>.

## **CO2 EXTRACTION FROM FLUE GAS**

### **1) Introduction**

Flue gas extraction systems remove in excess of 95% of the CO<sub>2</sub> contained in dilute, oxygen bearing exhaust / flue gas streams from steam boilers, turbines or electric generators. These systems, available upward of 6 metric tons per day, are designed around a uniquely energy efficient solvent that has greater CO<sub>2</sub> carrying capability than other chemical solvents, is oxygen tolerant, and, in fact, protects internal surfaces from corrosion.

The CO<sub>2</sub> produced meets Food and Beverage grade requirements (ISBT Standards).

### **2) Process Description**

- Flue gas consisting of carbon dioxide, water vapor, nitrogen, and oxygen is piped to a flue gas cooler / scrubber where it is cooled to the required temperature and scrubbed of impurities.
- The flue gas then enters the flue gas blower to increase the pressure and minimize backpressure on the boiler
- The cooled, clean and compressed gas passes through the absorber tower. There, carbon dioxide is absorbed into Econamine FG – A solvent designed to absorb CO<sub>2</sub> from vapor streams bearing upwards of 1% oxygen. The remaining products of combustion are vented to atmosphere from the top of the absorber.
- The Econamine FG solution, now rich in absorbed carbon dioxide, is then pumped to a stripper tower where heat from a reboiler is used to boil off the carbon dioxide in gaseous form at a controlled pressure.

### **3) System and Feed Gas requirements**

- The feed gas must ideally contain at least 8 vol % CO<sub>2</sub>
- The feed gas must be available at a steady and sustained rate, 24 hours per day

- The maximum allowable content of SO<sub>2</sub> in the feed gas is 10 ppm / vol.
- The particulate loading of the feed gas must be less than 10 ppm / wt.
- Excess steam must be available at a pressure greater than 3.4 Bar, and at a rate of approximately 2 kg steam per 1 kg CO<sub>2</sub> recovered.

#### **4) CO<sub>2</sub> Specifications and Guidelines**

Final quality of produced carbon dioxide will meet specifications and guidelines as recommended by the International Society of Soft Drink Technologists.

Flue gas extraction technology allows a company to become self-sufficient in the production of food and beverage grade CO<sub>2</sub>, while eliminating the typical problems associated with purchased CO<sub>2</sub> such as price, inconsistent availability, and quality. The process is energy efficient and the technology is proven, as evident by the many installations in operation around the world.



**A Wittemann Direct Fired CO<sub>2</sub> Manufacturing Plant  
Installed in a large Multi-Line Beverage Plant in the Philippines**



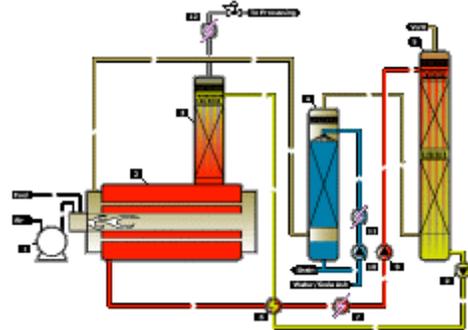
## CO<sub>2</sub> PRODUCTION (Direct Fired and Flue Gas Recovery)

Under some circumstances and in certain areas of the world there is an insufficient supply of high quality CO<sub>2</sub> to meet the needs of the market. In the early 1960's the Wittemann Company responded to this need by developing a line of reliable and efficient flue gas extraction and direct fired CO<sub>2</sub> production systems. These systems are employed on most continents of the world, primarily to meet the CO<sub>2</sub> demands of the soft drink industry.

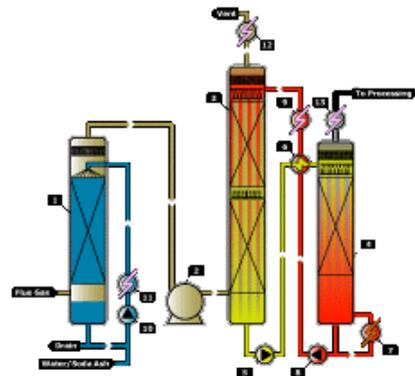
Wittemann understands the need for CO<sub>2</sub> equipment to meet and exceed the latest CO<sub>2</sub> quality specifications. Wittemann CO<sub>2</sub> Production Systems are designed to perform by providing proven purification techniques that minimize nitrogen and oxygen in the final product and eliminate NO, NO<sub>2</sub> and other harmful impurities. The result is up to 99.99% pure CO<sub>2</sub> guaranteed to meet product specifications.

**Direct fired** systems are self contained systems

designed to produce a flue gas specifically for CO<sub>2</sub> production. Robust component selections and an extensive use of Stainless Steel throughout the solvent system and anywhere saturated CO<sub>2</sub> is present ensures a long, trouble-free life.



**Flue gas extraction** technology removes in excess of 95% of the CO<sub>2</sub> contained in flue gas streams from existing (or new) steam boilers, turbines and electric generators. These systems are designed around a uniquely energy efficient solvent that has greater CO<sub>2</sub> carrying capacity than other chemical solvents, is oxygen tolerant, and actually protects internal surfaces from corrosion.



## **KEY SYSTEM FEATURES:**

### **Direct Fired - Key System Features:**

The Wittemann Stripper Tower is an integral part of the reboiler maximizing availability of solvent steam for stripping duty, promoting complete stripping of CO<sub>2</sub> from rich MEA steam and avoiding additional stripping action in the reboiler - a condition which promotes corrosion.

The Wittemann Absorber Tower with counter current MEA flow improves CO<sub>2</sub> absorption and promotes fuel-savings and cost effective CO<sub>2</sub> production.

Wittemann designs and manufactures its reboiler specifically for MEA service. Our two-pass, dry-back design allows operation at near stoichiometric combustion - most important when trying to combat the potentially corrosive effects of MEA in the presence of oxygen.

Extensive low pressure purification yields high purity CO<sub>2</sub> as well as extending the life of downstream mechanical equipment by protecting it from entrained impurities and sludge.

The system employs three (3) stainless steel vessels -- two (2) large diameter, bubbler-type KMnO<sub>4</sub> Scrubbers (this makes more KMnO<sub>4</sub> solution available for impurity removal and minimizes the frequency of change-out) followed by a third vessel that combines a carbon bed support with a special purifying medium, WittFill, to remove the various products of combustion and compounds formed during MEA degradation.

### **Flue Gas Recovery - Key System Features:**

Recovers in excess of 95% of the CO<sub>2</sub> contained in the flue gas. This is accomplished without compressing the flue gas above the level required to pass it through the absorber and without removing the oxygen present.

This system design now allows users of CO<sub>2</sub> to become self-sufficient in their requirements or even have surplus CO<sub>2</sub> that they can sell in the market for other users (additional revenue in their pocket).

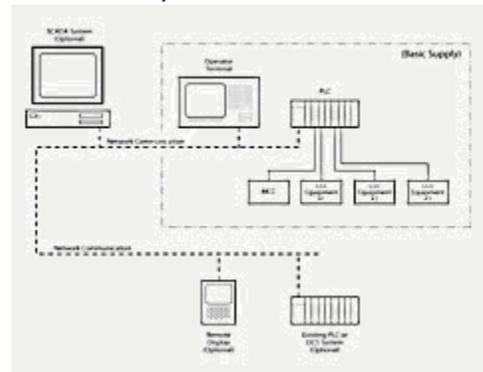
Economine FG solvent is the key to economical recovery of CO<sub>2</sub> from flue gases. Developed by a large USA chemical company, this solvent is uniquely energy efficient, has much greater CO<sub>2</sub> carrying capacity than other solvents

and is oxygen tolerant. In fact, this solvent actually protects the surfaces it contacts from corrosion.

By recovering the CO<sub>2</sub> from the flue gas, you are reducing the CO<sub>2</sub> emissions to atmosphere. This could be a potential source for tax credits from the government of your country.

## Microprocessor Control

To put all this technology at your fingertips, Wittemann systems are controlled by a sophisticated, yet simple to configure and operate microprocessor control system. At the heart of the system is a microprocessor that receives critical operating data, then outputs control information to the plant for optimal performance and efficiency. Supplied software provides important features, such as data logging, reports, graph plotting and equipment runtime tracking. The system is designed with flexibility in mind and can be connected to a local computer or remotely connected via modem.



PLC Control System

Contact:

# CO<sub>2</sub> Production System

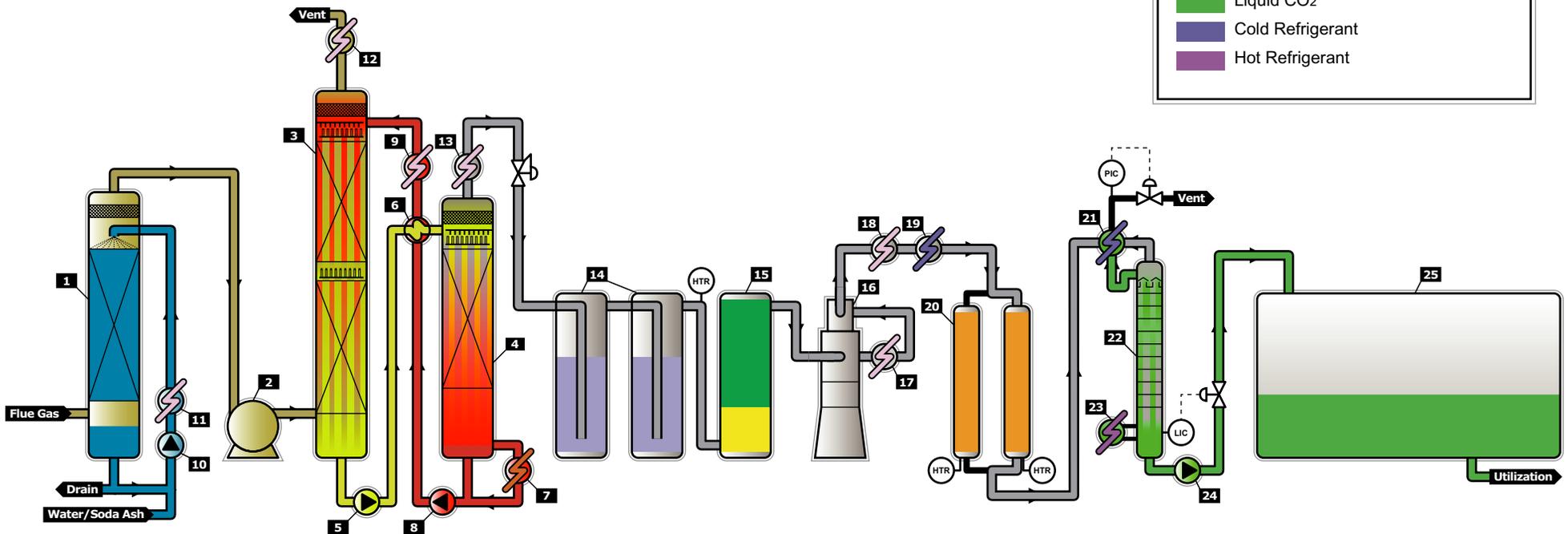
## - Flue Gas Recovery

### Components Legend

- |                                     |   |
|-------------------------------------|---|
| 1. Direct Contact Cooler / Scrubber | 14. KMnO <sub>4</sub> Bubblers              |
| 2. Flue Gas Blower                  | 15. WittFill Tower                          |
| 3. Absorber Tower                   | 16. CO <sub>2</sub> Compressor              |
| 4. Stripper Tower                   | 17. Intercooler                             |
| 5. Rich Pump                        | 18. Aftercooler                             |
| 6. Lean / Rich Exchanger            | 19. High Pressure Precooler                 |
| 7. Reboiler                         | 20. Dual Tower CO <sub>2</sub> Dryer        |
| 8. Lean Pump                        | 21. CO <sub>2</sub> Condenser               |
| 9. Trim Cooler                      | 22. Liquid CO <sub>2</sub> Stripping Column |
| 10. Recirculation Pump              | 23. Reboiler                                |
| 11. Recirculation Cooler            | 24. Product Pump                            |
| 12. Absorber Vent Cooler            | 25. Liquid CO <sub>2</sub> Storage Tank     |
| 13. Product Cooler                  |   |

### Fluids Legend

- Flue Gas
- Monoethanolamine (MEA) - Lean
- Monoethanolamine (MEA) - Rich
- Saturated Steam
- Vapor CO<sub>2</sub>
- Potassium Permanganate (KMnO<sub>4</sub>)
- WittFill
- Water-Soda Ash / Condensate
- Cooling Water
- Activated Carbon
- Desiccant
- Liquid CO<sub>2</sub>
- Cold Refrigerant
- Hot Refrigerant



## Physical Properties of Carbon Dioxide

Property	US Units	SI Units
Molecular Weight	44.01	44.01
Vapor Pressure of Saturated Liquid		
@ 70°F (21°C) [Cylinder]	853 psia	5,875 kPa abs
@ 32°F (0°C)	505 psia	3,485 kPa abs
@ 2°F (-17°C) [refrigerated liquid]	316 psia	2,180 kPa abs
@ -20°F (-29°C)	215 psia	1,482 kPa abs
@ -69.9°F(-56.6°C) [triple point]	75 psia	518 kPa abs
@ -109.3°F (-78.5°C) [dry ice]	14.7 psia	101 kPa abs
Density (Gas)		
@ 70°F (21°C) and 14.7 psia	0.114 lb/ft <sup>3</sup>	1.833 kg/m <sup>3</sup>
@ 0°C (32°F) and 1 atm (101 kPa abs)	0.123 lb/ft <sup>3</sup>	1.977 kg/m <sup>3</sup>
Density (Saturated Liquid)		
@ 70°F (21°C) [Cylinder]	47.6 lb/ft <sup>3</sup>	762 kg/m <sup>3</sup>
@ 32°F (0°C)	58.0 lb/ft <sup>3</sup>	929 kg/m <sup>3</sup>
@ 2°F (-17°C) [refrigerated liquid]	63.3 lb/ft <sup>3</sup>	1,014 kg/m <sup>3</sup>
@ -20°F (-29°C)	66.8 lb/ft <sup>3</sup>	1,070 kg/m <sup>3</sup>
@ -69.9°F(-56.6°C) [triple point]	73.5 lb/ft <sup>3</sup>	1,177 kg/m <sup>3</sup>
Density (Solid Dry Ice)		
@ 14.7 psia and -109.3°F (101 kPa abs and -78.5°C)	97.5 lb/ft <sup>3</sup>	1,562 kg/m <sup>3</sup>
Sublimation Temperature (at 1 atm)	-109.3°F	-78.5°C
Critical Temperature	87.9°F	31.1°C
Critical Pressure	1,071 psia	7,382 kPa abs
Critical Density	29.2 lb/ft <sup>3</sup>	468 kg/m <sup>3</sup>
Triple Point	-69.9°F / 75.1 psia	-56.6°C / 518 kPa abs
Latent Heat of Vaporization		
@ 32°F (0°C)	100.6 BTU/lb	234.5 kJ/kg
@ 2°F (-17°C) [refrigerated liquid]	119.0 BTU/lb	276.8 kJ/kg
@ -20°F (-29°C)	129.7 BTU/lb	301.7 kJ/kg
Latent Heat of Fusion		
@ -69.9°F (-56.6°C) [Triple Point]	85.6 BTU/lb	571.3.0 kJ/kg
Latent Heat of Sublimation		
@ 109.3°F (-78.5°C) [Dry Ice]	245.5 BTU/lb	199.0 kJ/kg
Specific Heat of Gas		
C <sub>p</sub> at 77°F (25°C) and 1 atm	0.203 BTU/lb°F	0.850 kJ/kg°C
C <sub>v</sub> at 77°F (25°C) ant 1 atm	0.157 BTU/lb°F	0.657 kJ/kg°C
Ratio of Specific Heats of Gas		
@ 59°F (15°C)	1.304	1.304
Specific Heat of Liquid		
@ 2°F (-17°C) [refrigerated liquid]	0.489 BTU/lb°F	2.048 kJ/kg°C
Solubility of gas in water, vol/vol		
@ 32°F (0°C) and 1 atm	1.7	1.7
@ 60°F (16°C) and 1 atm	1.0	1.0
@ 32°F (0°C) and 60 psig (414 kPa g)	8.6	8.6
Viscosity (Saturated Liquid)		
@ 2F (-17C) [refrigerated liquid]	0.287 lb/ft h	0.119 x 10 <sup>-3</sup> Pa s

## Typical Food Grade Carbon Dioxide Specifications

### Standard Commercial Quality

Component	Standard
Purity	99.9% v/v min.
Moisture	20 ppm v/v max.
Oxygen	30 ppm v/v max.
Carbon Monoxide	10 ppm v/v max.
Ammonia	2.5 ppm v/v max.
Nitric Oxide / nitrogen dioxide	2.5 ppm v/v max. each
Nonvolatile residue	10 ppm w/w max.
Nonvolatile organic residue	5 ppm w/w max.
Phosphine	To pass test (0.3 ppm v/v max.)
Total volatile hydrocarbons (as methane)	50 ppm v/v max., including 20 ppm v/v total nonmethane hydrocarbons
Acetaldehyde	0.2 ppm v/v max.
Aromatic hydrocarbon	20 ppb v/v max.
Total sulfur content (as S) excluding SO <sub>2</sub>	0.1 ppm v/v max.
Sulfur Dioxide	1 ppm v/v max.
Odor of Solid CO <sub>2</sub> (snow)	No foreign odor
Appearance in water	No color or turbidity
Odor and taste in water	No foreign taste or odor

#### Notes:

- The following standards apply to carbon dioxide as accepted by the beverage industry. CO<sub>2</sub> suppliers should provide the bottler with certification and analysis indicating compliance with these standards.
- Tests are run on vaporized liquid carbon dioxide.
- All values are maxima unless otherwise noted.

# In-Plant CO<sub>2</sub> Treatment



## 1) Introduction

As part of on-going commitment to product assurance carbonated soft drinks beverage producers focus their attention on carbon dioxide (CO<sub>2</sub>) quality.

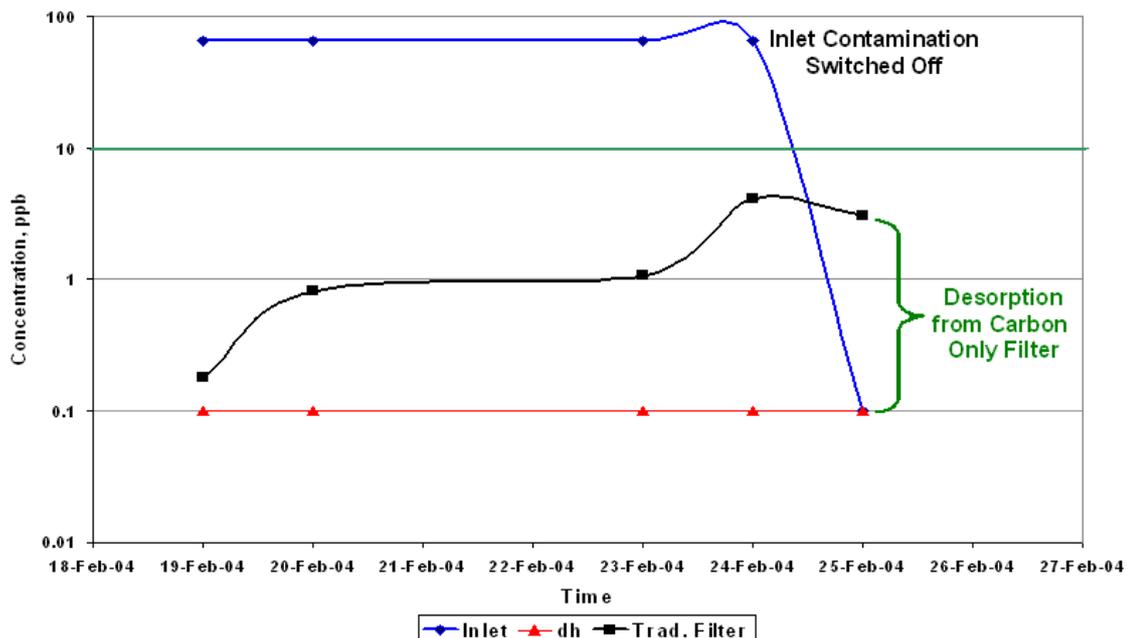
As CO<sub>2</sub> is dissolved into the final beverage it is classed as an active ingredient and must therefore meet stringent quality guidelines detailed by organizations such as the International Society of Beverage Technologists (ISBT).

Most beverage plants producing carbonated soft drinks purchase commercial bulk liquid carbon dioxide (LCO<sub>2</sub>), which is delivered to the site with a Certificate of Analysis (CoA). The LCO<sub>2</sub> is stored under pressure and temperature control until needed, at which time it is evaporated into the gas phase prior to use in the carbonation equipment.

## 2) Traditional In-Plant Treatment Systems

While ensuring beverage grade CO<sub>2</sub> is used in the production of carbonated soft drinks, additional activated carbon towers are traditionally installed at the packaging plant after the evaporator, to give added security. However, the performance of “carbon only” polishing systems cannot be guaranteed.

The graph below shows the independent results of Aromatic Hydrocarbon removal through both a traditional “carbon only” adsorption bed and a **dh** multi-barrier system.



Although the “carbon only” bed will reduce a benzene level, it will not achieve the same performance as a multi-barrier system. Perhaps more interestingly, it can be seen that the final point of data shows that when inlet contamination is removed and a clean CO<sub>2</sub> flow is passed across the adsorption bed, then some of the contaminant is desorbed and re-entrained into the outlet gas stream.

### 3) Potential Impurities & Contaminants

Commercially available carbon dioxide is generally produced as a by-product to another process, such as fermentation and combustion. As such it has the potential to contain a large number of trace impurities. A list of the typical impurities is show below,

Potential Impurity	Combustion	Wells / Geothermal	Fermentation	Hydrogen / Ammonia Production	Coal Gasification	Ethylene Oxide Production
Aldehydes	✓	✓	✓	✓	✓	✓
Benzene	✓	✓	✓	✓	✓	✓
Carbon Monoxide	✓	✓	✓	✓	✓	✓
Carbonyl Sulphide	✓	✓	✓	✓	✓	
Cyclic Aliphatic Hydrocarbons	✓	✓		✓	✓	✓
Dimethyl Sulphide		✓	✓		✓	
Ethanol	✓	✓	✓	✓	✓	✓
Ethyl Benzene		✓		✓	✓	✓
Hydrogen Sulphide	✓	✓	✓	✓	✓	✓
Ketones	✓	✓	✓	✓	✓	✓
Mercaptans	✓	✓	✓	✓	✓	✓
Nitrogen Oxides	✓		✓	✓	✓	✓
Sulphur Dioxide	✓	✓	✓	✓	✓	
Toluene		✓	✓	✓	✓	✓
Volatile Hydrocarbons	✓	✓	✓	✓	✓	✓
Xylene		✓	✓	✓	✓	✓

Source CGA G-6.2 (2000) - Commodity Specification for Carbon Dioxide

An impurity is defined as a trace level of one or more of the above compounds in the CO<sub>2</sub> that have been carried over from the supply source.

In addition to potential trace impurities, and of great concern to the industry, is the potential for trace contaminants being inadvertently introduced to the CO<sub>2</sub> during storage, transportation or evaporation of liquid phase CO<sub>2</sub>.

Liquid CO<sub>2</sub> is transported by road and/or rail with often between 3 – 6 transfer points before reaching the beverage plant. During each transfer and / or storage stage, potential contaminants could be introduced from tankers, transfer hoses and pumps.

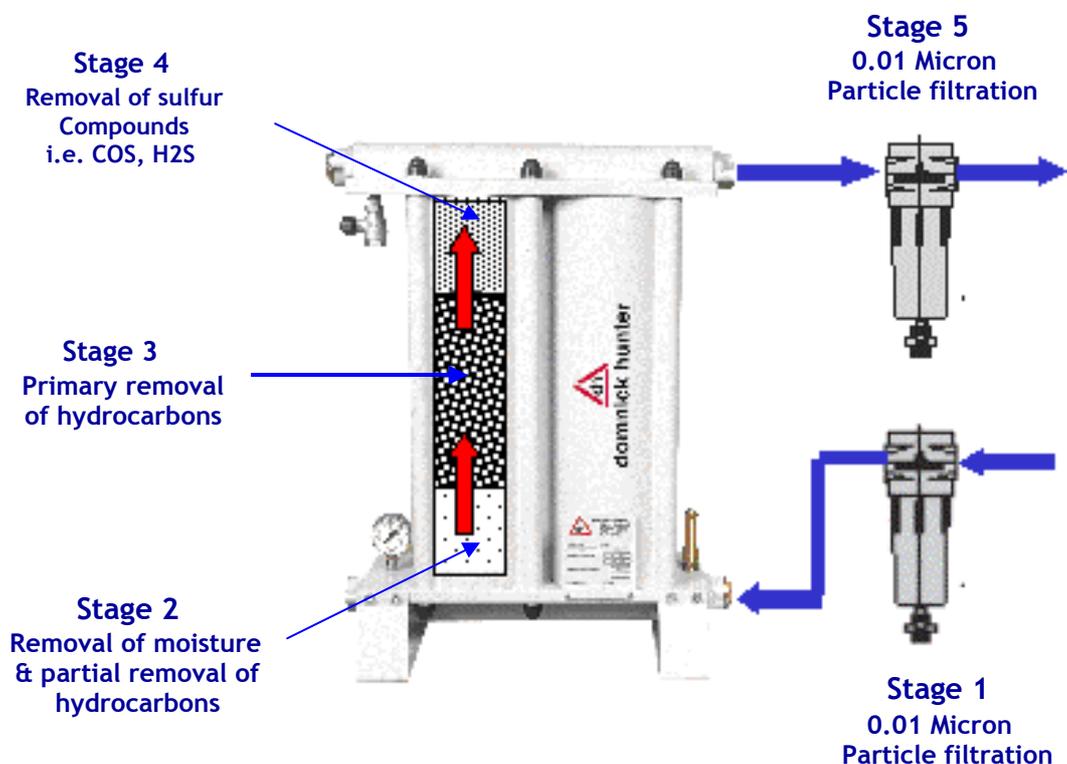
Typically a gas supplier will issue a COA (Certificate of Analysis) stating that the CO<sub>2</sub> is “beverage grade” quality. The analysis is often done at the front end of the transportation stages, therefore is no guarantee of the final quality of the gas that is delivered to the plant.

#### 4) The Multi-Barrier Polishing Systems Approach

Independent testing has also shown that not only do carbon based polishing systems have the potential to re-release impurities back into the downstream gas supply, but that they are also not equally effective at removing the wide range of possible impurities or contaminants that may be present.

Since the potential impurities range from moisture, volatile and aromatic hydrocarbons, to aldehyde and sulphur compounds, it’s not surprising that “carbon only” systems will have a limited performance.

In order to combat the potential range of impurities **domnick hunter** has developed a 5-stage PCO<sub>2</sub> purification system designed to offer carbon dioxide quality incident protection due to its unique 3-layer adsorption bed design. The adsorption materials used were carefully selected and independently tested for their ability to preferentially adsorb potential impurities and contaminants, thus ensuring optimum removal efficiency of the system during its operational life.



## Summary

With over 900 systems operating around the world the PCO<sub>2</sub> multi-barrier carbon dioxide quality approach has become the preferred choice for the soft drinks industry. While giving maximum quality protection the PCO<sub>2</sub> systems offer an economical solution with easy maintenance due to the use of pre-loaded adsorption cartridges.

For more information on Multi-Barrier Purification systems for safeguarding CO<sub>2</sub> supplies contact Gary Robson at domnick hunter - (800) 345-8462 or [gary.robson@domnickhunter.com](mailto:gary.robson@domnickhunter.com) [www.domnickhunter.com](http://www.domnickhunter.com)