

# CO<sub>2</sub> IMPURITIES

Captured CO<sub>2</sub> from an (industrial) activity (such as the CO<sub>2</sub> that will be handled by the CO<sub>2</sub> distribution hub) may contain impurities, which would have practical impacts on CO<sub>2</sub> transport and storage systems and also potential health, safety and environmental impacts. These impurity levels may be very heterogeneous and in order to be able to combine these sources in one system it will be required to establish one common CO<sub>2</sub> specification. Any impurity levels exceeding these specifications should be removed at the emitter. There are many literature references that provide typical CO<sub>2</sub> stream compositions from the three main capture processes. From this data a typical composition list, which is presented in Table 1, is developed.

The major impurities in CO<sub>2</sub> are well known, but there is little published information about the impact of any trace impurities in the feed gas such as heavy metals. CO<sub>2</sub> from post-combustion solvent scrubbing processes normally contains low concentrations of impurities. Many of the existing post-combustion capture plants produce high purity CO<sub>2</sub> for use in the food industry. CO<sub>2</sub> from pre-combustion physical solvent scrubbing processes typically contains about 1–2 % H<sub>2</sub> and traces of H<sub>2</sub>S and other sulfur compounds.

Integrated gasification combined cycles (IGCC) plants with pre-combustion capture can be designed to produce a combined stream of CO<sub>2</sub> and sulfur compounds, to reduce costs and avoid the production of solid sulfur. The CO<sub>2</sub>-rich gas from oxy-fuel processes contains oxygen, nitrogen, argon, sulfur and nitrogen oxides and various other trace impurities. This gas will normally be compressed and fed to a cryogenic purification process to reduce the impurities concentrations to the levels required to avoid two-phase flow conditions in the transportation pipelines [2].

**Table 1:** Indicative compositions of CO<sub>2</sub> stream by % vol.

<b>Compounds</b>	<b>Post-combustion capture at power plant</b>	<b>Pre-combustion capture at power plant</b>	<b>Oxy-fuel combustion at power plant</b>
Nitrogen (N <sub>2</sub> )	0.18 % vol.	0.2 % vol.	2.0 % vol.
Oxygen (O <sub>2</sub> )	100 ppmv	trace	1.2 % vol.
Argon (Ar)	20 ppmv	1.0 % vol.	0.8 % vol.
Carbon monoxide (CO)	10 ppmv	0.13 % vol.	trace
Hydrogen (H <sub>2</sub> )	trace	1 % vol.	trace
Methane (CH <sub>4</sub> )	100 ppmv	200 ppmv	–
Sum of non-condensables (Ar, CH <sub>4</sub> , H <sub>2</sub> , N <sub>2</sub> , O <sub>2</sub> )	0.2 % vol.	1.2 % vol.	4 % vol.
Nitric oxides, as NO <sub>2</sub>	5 ppmv	11 ppmv	721 ppmv
Sulfur oxides, as SO <sub>2</sub>	0.84 ppmv	–	1.3 % vol.
Carbonyl sulfide (COS)		1.7 ppmv	
Hydrogen sulfide (H <sub>2</sub> S)		100 ppmv	
Chlorine (Cl)	0.85 ppmv	17.5 ppmv	0.14 % vol.
Mercury	0.00069 ppm	0.000068 ppm	0.0035 ppm
Arsenic	0.055 ppm	0.0033 ppm	0.0085 ppm
Selenium	0.017 ppm	0.01 ppm	0.026 ppm
Ash	11.5 ppm	1.2 ppm	75 ppm

The impurities influence the characteristics (density, critical pressure) of the CO<sub>2</sub> stream. The impurities N<sub>2</sub>, Ar, CH<sub>4</sub> and H<sub>2</sub> lower the density of a CO<sub>2</sub> stream, resulting in a higher pressure drop. Also, the critical pressure will increase, meaning higher pressures are needed to prevent the occurrence of a two-phase flow. Especially hydrogen has a significant influence.

Some of these impurities are (highly) flammable (CO, H<sub>2</sub>, H<sub>2</sub>S, CH<sub>4</sub>) and/or toxic (CO, NO<sub>2</sub>, SO<sub>2</sub>, H<sub>2</sub>S, Cl, COS). However, the CO<sub>2</sub> stream will not be flammable since the concentration of the impurities is very low and therefore flammable effects will not be considered in the safety study. Toxic impurities could increase the toxicity of the CO<sub>2</sub> stream compared to a pure CO<sub>2</sub> stream. Nevertheless, the CO<sub>2</sub> stream will be considered as pure CO<sub>2</sub> and the impurities will not be considered in the safety study. The reason is that it is expected that the used probit, is conservative enough to take into account the possible higher toxicity of the small concentration of toxic impurities [1]. However, some information on the influence of the impurities on the toxicity of the stream is given in paragraph 3.3.

In the CO<sub>2</sub> liquefier the impurities are concentrated as the flow moves through the cold box through the vent to the atmosphere. This vent flow typically consists of 50/50 % vol. impurities/CO<sub>2</sub>.

The only issue identified here is the excess oxygen that stems from an oxy-fuel process (reducing environment) which, if mixed with CO<sub>2</sub> from pre-/post-combustion capture (oxidizing environment) sources, may lead to a flammable mixture at the liquefier's vent. If these CO<sub>2</sub> flows are to be combined in one system it is advised to remove the oxygen directly at the source. All other impurity concentrations are so low that it is not expected to give rise to any chemical reaction in the chain's equipment. Also a condensate flow from the liquefier is not to be expected: most impurities concern light components or are at such low partial pressure due to their low concentration that these all end up in the vent stream. No issues have been identified, regarding the reactivity between the components in the CO<sub>2</sub> stream, upstream the CO<sub>2</sub>liquefier other than H<sub>2</sub>O and CO<sub>2</sub> forming an acid (H<sub>2</sub>CO<sub>3</sub>), which may attack the materials of construction.

It is advised to study the impurity combinations on a case by case basis, especially since the capture technologies are developing at a fast pace. A specific example that could give rise to problems for instance, is a capture process that shows relatively high H<sub>2</sub>S and SO<sub>x</sub> levels in the CO<sub>2</sub> flow. A so-called Claus reaction then could result in formation of elemental sulphur which then would manifest itself as yellow particle dust in the vapor flow which may clog up filters etc. downstream. However, this reaction requires elevated temperatures (300 °C) and an aluminum based catalyst to show significant reaction kinetics.

The highest temperature in the chain is at the compressor intercoolers, but typically limited to 150 °C while aluminum is only to be expected in the liquefier cold box, operating at –50 °C.

A thermodynamics model and equation of state to use for calculating the chain's components has to be selected. It is of paramount importance to have consensus on this in order to guarantee that the parties involved in the whole chain calculate, model and simulate with the same “reality”. From an engineering point of view the following Equations of State (EOS) allow for reliable equipment design:

- For wet CO<sub>2</sub> streams the Soave-Redlich-Kwong Equation of State with the Sour option, and Lee-Kessler enthalpy method specification (Sour SRK-LK).
- For Dry CO<sub>2</sub> streams The Peng-Robinson equation with Strylek and Vera modification and Lee-Kessler enthalpy method specification (PRSV-LK).

Source: <http://hub.globalccsinstitute.com/publications/co2-liquid-logistics-shipping-concept-llsc-safety-health-and-environment-she-report/32>