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■ WHITE PAPER

## Gas mixtures and mixing of gases

## Part 2

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## 1. Introduction

In this second part of the guide to Alternative Gases you will get a brief overview of the basic physical properties of gases and gas mixtures. It will also show the latest possibilities of the production and use of alternative gas mixtures during commissioning of gas-filled units or after service and maintenance works as well as the advantages and disadvantages of the procedures listed.


## 2. Overview "Gas mixtures and mixing of gases"

## Physical properties

Due to their physical properties, pure $\mathrm{SF}_{6}$ and Synthetic Air are always present in a homogeneous, gaseous state under usual ambient conditions for gas compartments ( $>-50^{\circ} \mathrm{C}$; $<20$ bar $_{\text {abs }}$ ). We speak of a homogeneous state when the medium has only one aggregate state (gaseous, liquid or solid) and there is no partial liquefaction. Partial liquefaction means that in a closed, gas-filled compartment (switchgear, pressure tank etc.) partial liquefaction of one or several components occurs due to an increase in pressure or decrease in temperature, resulting in a change in the composition of the gas phase of the mixture. At room temperature pure C5 is liquefied at atmospheric pressure
and $\mathrm{C4}$ at slight overpressure (> 250 kPa ) (Figure 1). At a temperature of $20^{\circ} \mathrm{C}$, C 5 has a vapour pressure of approx. $78 \mathrm{kPa}\left(=0.78\right.$ bar $\left._{\text {abs }}\right)$, which means that a decrease in temperature at constant pressure or an increase in pressure at constant temperature results in partial liquefaction. Both gases, as single components, cannot have a higher pressure at room temperature. Mixing with other gases is thus necessary to achieve a higher pressure for filling gas compartments. For this purpose nitrogen $\left(\mathrm{N}_{2}\right)$ which cannot be liquefied at room temperature and carbon dioxide $\left(\mathrm{CO}_{2}\right)$ are used as filling gas. $\mathrm{CO}_{2}$ can be liquefied at room temperature, but the required pressure is 5.73 MPa ( $=57.3$ bar $_{\text {abs }}$ ), which is higher than the pressures used in gas-insulated equipment.


Figure 1: Vapour pressure curves of pure $\mathrm{SF}_{6}, \mathrm{C} 4$ and C 5 in the temperature range from $-40^{\circ} \mathrm{C}$ to $45^{\circ} \mathrm{C}$. This curve describes the pressure at which a substance liquefies dependent on the temperature. In the area below the curve, the substance is gaseous, above the curve it is liquefied.

The limit values of the liquefaction are shifted to lower temperatures or higher pressures by mixing C4 and C5 with the carrier gases (Table 1). Once homogenised, the mixtures are stable at constant ambient conditions in the operating medium. By temperature reduction, as is the
case for pure gases, partial liquefaction of single components might occur, so that there is no longer a consistent mixing ratio within the equipment and the insulating capacity of the gas mixture is reduced.

| Properties of the gas mixtures |  |  |  |  |
| :---: | :---: | :---: | :---: | :---: |
| Common trade names |  | $\mathrm{g}^{3}$ (GE) | AirPlus (ABB) | CleanAir (Siemens) |
| Gas mixtures in use | Pure $\mathrm{SF}_{6}$ | $\mathrm{C4}:<6.3 \%$ with $\mathrm{CO}_{2}$ | C5: < 15 \% in Synthetic Air | CA: ~ $20 \% \mathrm{O}_{2}$ in $\mathrm{N}_{2}$ |
|  | $\mathrm{SF}_{6}$ with $\mathrm{N}_{2}$ or $\mathrm{CF}_{4}$ | $\mathrm{C4}:<6.3 \%$ with $\mathrm{O}_{2} / \mathrm{CO}_{2}$ | $\mathrm{C5}:<15 \%$ in $\mathrm{O}_{2} / \mathrm{CO}_{2}$ | - |
| Minimum operating temperature | Pure $\mathrm{SF}_{6}:<-30^{\circ} \mathrm{C}$ | Depending on the exact mixture: |  | $<-50{ }^{\circ} \mathrm{C}$ |
|  | $\mathrm{SF}_{6}$ with $\mathrm{N}_{2} / \mathrm{CF}_{4}:<-50^{\circ} \mathrm{C}$ | $-30^{\circ}$ | to $-5^{\circ} \mathrm{C}$ | - |
| Global warming potential | $\leq 22800$ | $\leq 500$ | $<1$ | 0 |

Table 1: Overview of Alternative Gases and their mixtures compared to $\mathrm{SF}_{6}$.

## Production of gas mixtures

For providing or producing gas mixtures for filling gasinsulated equipment there are the following possibilities:

## Gaseous storage

Alternative Gases can be supplied mixed gaseously and filled directly into the evacuated gas compartments at a constant mixing ratio. For providing gaseous mixtures with the insulating gases C 4 and C 5 , the pressure vessels (gas cylinder or tank) are filled with a low pressure $\left(<20\right.$ bar $_{\text {abs }}$ ) to prevent demixing of the single components at lower temperatures (Table 1). The maximum filling pressure depends on the mixing ratio and the minimum outside temperature on site as well as during transportation. The use in gaseous form is recommended for C4 and C5 for
small gas compartments, since, only a relatively small gas quantity can be stored in the pressure tanks due to the low filling pressure (table 4). Synthetic Air does not liquefy, therefore it is mainly supplied in gas cylinders or gas cylinder bundles at high pressures $(\geq 200$ bar). Prior to the initial filling of the equipment, it must be evacuated by means of a vacuum pump. The filling of gas compartments only requires a gas refilling device (Table 2).

| Advantages | Disadvantages |
| :--- | :--- |
| Certified gas | Relatively small quantities can be stored |
| Small gas compartments can be filled | Partial liquefaction possible when cooling down |
| No service cart necessary (only gas refilling device) | Mixing ratio cannot be changed on site |

Table 2: Overview of the advantages and disadvantages of gaseous storage and withdrawal.

## Partially liquefied storage

When being stored partially liquefied, the gas remains premixed and is stored underhigh pressure. For the mixture, the single components are mixed one after the other or simultaneously and compressed under high pressure, so that partial liquefaction of the single components (C4, $\mathrm{C} 5, \mathrm{CO}_{2}$ ) inside the pressure tank occurs (Figure 2). As a result of this partial liquefaction, the mixing ratio would change considerably in case of direct withdrawal from the
5 pressure tank. Initially, the proportion of non-condensable components, such as nitrogen or oxygen would be highly increased. If the cylinder is recovered to a greater extend, the proportion of previously condensed components such as C4 or C5 would increase.
In liquefied state, substances have a higher density so that, in contrast to gaseous storage, a larger quantity can be stored in the pressure vessel due to partial liquefaction (Table 4). In this case, the stability of the gas mixture during use is independent of the outside temperature (Table 3).

Since single components of the mixture are partially liquefied inside the pressure tank, the mixture must first be homogenised before filling the equipment, that means it must be mixed uniformly. This process requires a specific service cart with integrated heating function. The exact handling during the withdrawal is described in part 3 "Handling of Alternative Gases" of the guide.


Figure 2: DILO mixing unit for mixing up to 4 components

| Advantages | Disadvantages |
| :--- | :--- |
| Large storage quantity | No direct withdrawal possible without service cart |
| Exact predefined gas mixture | Heating by service cart is time-consuming |
| Independent of outside temperature | Mixing ratio cannot be changed on site |

Table 3: Overview of the advantages and disadvantages of partially liquefied storage and withdrawal.

For gaseous and partially liquefied storage, the pressure tank is filled with the mixing ratio defined in the customer specification. The gas mixtures are analysed and a corresponding certificate indicating the exact composition of the mixture is issued. The mixing ratio can no longer be changed on site.

| Comparison of storage capacity | 6 \% C4 and $94 \% \mathrm{CO}_{2}$ | 6 \% C5 and $94 \% \mathrm{CO}_{2}$ | Synthetic Air $\left(20 \% \mathrm{O}_{2} \text { in } 80 \% \mathrm{~N}_{2}\right)$ |
| :---: | :---: | :---: | :---: |
| gaseous |  |  |  |
| 50 I cylinder, $\mathrm{T}=20^{\circ} \mathrm{C}$ | 5.1 kg | 1.6 kg | 11.8 kg |
| 600 I tank/cylinder bundle, $\mathrm{T}=20^{\circ} \mathrm{C}$ | 61.3 kg | 19.1 kg | 141.6 kg |
| Filling pressure, $\mathrm{T}=20^{\circ} \mathrm{C}$ | 46.9 bar | 13.5 bar | 200 bar |
| liquefied |  |  |  |
| 50 I cylinder, $\mathrm{PH}=300 \mathrm{bar}$ | 28.3 kg | 30.6 kg | Not applicable |
| 600 l cylinder, $\mathrm{PH}=70$ bar | 79.3 kg | 85.6 kg | Not applicable |

Table 4: Comparison of the maximum storage capacities of liquefied and gaseous mixtures of Alternatives Gases.
$\mathrm{PH}=$ Test pressure of the pressure tank. For synthetic air, a filling with 200 bar at $20^{\circ} \mathrm{C}$ has been used as a calculation basis. Liquefaction of the mixture at this temperature cannot occur. For calculation of the liquefaction point, the ideal gas equation was used.

## Mixing on-site (Use of gas mixing units)

When using gas mixing and filling units, the gas mixture is generated with individual gases directly in the gas-filled unit. Thus, gas mixtures with different mixing ratios can be produced. This method requires the delivery of the single components as well as a mixing unit calibrated for
the gases, temperatures and desired concentrations used (Figure3). Due to the worldwide availability of the common carrier gases such as $\mathrm{N}_{2}$ and $\mathrm{CO}_{2}$, they can be purchased locally, so that only the transport of the insulating gas would be necessary. To increase the pressure of the produced mixture, a compressor is connected downstream. Small and large gas compartments can be filled by using different mixing units (Table 5).

| Advantages | Disadvantages |
| :--- | :--- |
| Mixing ratio adjustable | Transport of the individual gases necessary |
| Carrier gases can be purchased locally | Availability of a mixing unit for target concentrations |
| Large and small gas compartments can be filled | Regular calibration of the mixing unit required |

Table 5: Overview of the advantages and disadvantages when using gas mixing units.


Figure 3: Schematic diagram of a gas mixing and filling unit for the direct filling of gas compartments from single components.

The production of a preset mixture (gaseous or partially liquefied) is carried out by different procedures. The most common procedures for Alternative Gas mixtures are weight-based (gravimetric), pressure-based (manometric) or volume-based (volumetric) processes. Depending on the method of production, different specifications are used for the exact composition of the mixtures (mol-\%, vol.-\%, etc.). The composition by mol- $\%$ is directly traceable to the international system of units, as it is independent of pressure and temperature and is used worldwide, independent of the environment. ${ }^{1}$

There are various possibilities for mixing and providing Alternative Gases. Depending on the application, all processes have the advantages and disadvantages described above and are highly precise in order to comply with the manufacturers' specified filling accuracy.

The next edition of the guide will focus on the proper handling of Alternative Gases. Furthermore, the technical possibilities for process-safe use and interchangeability of the different types of gases are discussed.

## 3. List of literature

(1) Michael M. Walter, Diana Leguizamon, Louis Maksoud, Thomas Berteloot, Yannick Kieffel, John Owens, Ang Xiao, Jason Bonk, Mike Delorme. Low temperature behaviour and dielectric performance of Fluoronitrile/CO2/02 mixture. Cigre 2020.

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| SF GAS |  |  |
| :--- | :--- | :--- | :--- |
| ALTERNATIVE |  |  |
| GASES |  |  |$\quad$| INDUSTRIAL |
| :--- |
| GAS EQUIPMENT |$\quad$| HIGH PRESSURE |
| :--- |
| PRODUCTS |

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