

**CIGRE GUIDE FOR SF<sub>6</sub> GAS MIXTURES.  
APPLICATION AND HANDLING IN ELECTRIC POWER EQUIPMENT**

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**ABSTRACT**

This paper presents an outline of the handling and recycling of SF<sub>6</sub> mixtures in electrical power equipment. It is based on the CIGRE Guide for SF<sub>6</sub> mixtures and addresses the application fields of SF<sub>6</sub> mixtures in electric power equipment, their insulation and switching performance, the evaluation of their environmental advantage, and the processes and equipment for their environmentally responsible handling and recycling. As the handling of SF<sub>6</sub> mixtures is similar to that of unmixed SF<sub>6</sub> in many respects, the reader is referred to the CIGRE SF<sub>6</sub> recycling guide, which describes the handling of unmixed SF<sub>6</sub>.

**1. INTRODUCTION**

Due to an exceptional combination of physical and chemical properties, SF<sub>6</sub> has become an indispensable insulation and switching medium for electrical power transmission and distribution equipment, in which it has been successfully used for more than three decades. However, SF<sub>6</sub> turned out to be a strong greenhouse gas. This prompted an intense search for equivalent substitution gases with the disappointing result that the "second best" gas suited for electrical equipment would be air [1]. As air has a much lower functional performance than SF<sub>6</sub> it would require a complete and much larger re-design of the equipment, entailing the use of more materials with a correspondingly increased environmental impact (e.g., [2]).

The only environmentally rational policy, therefore, is to reduce the quantity of SF<sub>6</sub> required per function and to minimize SF<sub>6</sub> emissions. Whereas SF<sub>6</sub> quantity reduction is a cost-driven feature of the equipment development process, emission reduction requires a dedicated effort in the form of investments in gas handling equipment, service logistics, and personnel instruction. The major lines along which SF<sub>6</sub> emissions are being reduced are:

1. Reduction of leakage from operating equipment. This is mainly achieved by repairing or retrofitting strongly leaking (mostly old "first generation") equipment. Newer equipment normally has very low leakage rates (typically less than 0.2% per year). Here, early leak detection of weakly leaking compartments by advanced gas monitoring systems is the most promising strategy (e.g., [15]).
2. Comprehensive implementation of responsible SF<sub>6</sub> handling throughout the electric industry
3. Improvement of the efficiency of gas handling equipment and processes.

This strategy has been followed by the electric industry in the last years and now starts to have an impact on global SF<sub>6</sub> emissions: A recent publication by the Max Planck Institute for Chemistry [10] states that "*....the annual (global) emissions of SF<sub>6</sub> have declined by 27% from 1995 to 1998,*" and it is concluded from background data that "*... a major part of the reduction must come from the magnesium industry and electrical applications.*"

**2. APPLICATIONS OF SF<sub>6</sub> MIXTURES IN ELECTRIC POWER EQUIPMENT**

SF<sub>6</sub> mixtures are presently applied or considered for application in two major fields, primarily to enable switchgear operation at low ambient temperatures and to save SF<sub>6</sub> in large insulation systems. In both cases, the performance of the mixture is inferior to that of unmixed SF<sub>6</sub>. This

has the general consequence that *existing equipment must always be de-rated or redesigned when pure SF<sub>6</sub> is to be replaced by a mixture.*

### 2.1 Enabling switchgear operation at low ambient temperatures

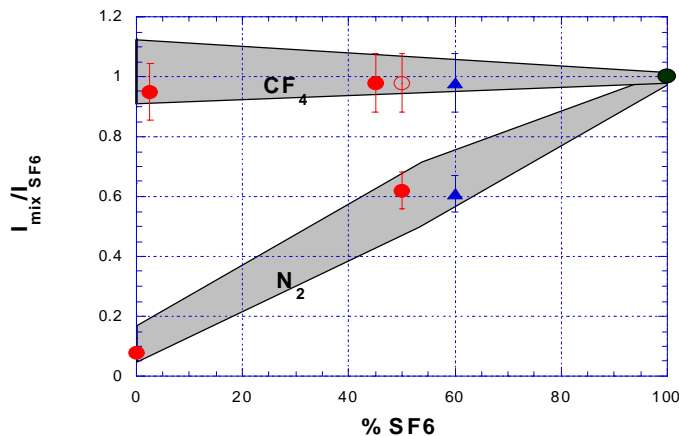
At very low (arctic) ambient temperatures, condensation (liquefaction) of SF<sub>6</sub> would reduce the performance of the equipment and therefore has to be avoided. This is done by reducing the SF<sub>6</sub> partial pressure to a sufficiently low value. The corresponding loss in switching and insulation performance is compensated, as much as possible, by adding a non-liquefying gas, for which N<sub>2</sub> or CF<sub>4</sub> are used. Both gases do not liquefy down to -50°C and are compatible with the technical boundary conditions in electric power equipment; i.e., they are nontoxic, chemically stable, and are not decomposed by arcing.

Table 1 shows some typical values for the maximally admissible SF<sub>6</sub> content in dependence of the lowest ambient temperature (T<sub>min</sub>) at which the equipment has to operate and for several typical filling pressures, measured at ambient temperature T = 20°C. As an example, at a typical circuit breaker filling pressure of 600 kPa, the SF<sub>6</sub> content of the mixture must not exceed 37% when the equipment is to operate down to -50°C.

**Table 1:** Maximal SF<sub>6</sub> content in dependence of the minimal ambient temperature T<sub>min</sub> for some typical filling pressures p<sub>f</sub> (at T = 20°C).

T <sub>min</sub>	p <sub>f</sub> = 400 kPa	p <sub>f</sub> = 600 kPa	p <sub>f</sub> = 800 kPa
-30°C	100%	85%	65%
-40°C	85%	57%	43%
-50°C	57%	37%	28%

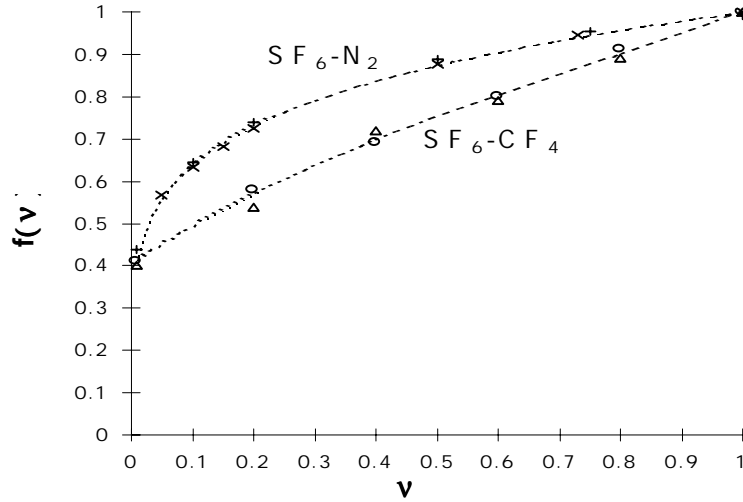
The degree to which the admixed gas reduces the switching and insulation performance of the gas are shown in Figures 1 and 2 in normalized form. Figure 1 shows the relative switching performance under short line fault conditions, which is normally the most critical switching case. It is seen that N<sub>2</sub> strongly reduces the switching performance, whereas



**Figure 1:** Normalized short line fault switching performance of SF<sub>6</sub> mixtures with N<sub>2</sub> and CF<sub>4</sub> as a function of the SF<sub>6</sub> volume concentration v.

CF<sub>4</sub> performs similar to SF<sub>6</sub> in this respect.

Figure 2 shows the insulation performance. Here,  $N_2$  is superior to  $CF_4$  because it exhibits a stronger dielectric synergy; i.e., an over-proportional influence of the  $SF_6$  [3]. For a 50%  $SF_6$  mixture, the admixture of  $N_2$  results in a 28% better insulation performance than  $CF_4$ . Which of the two gases has to be chosen depends on the specific performance requirements of the equipment.  $SF_6 - N_2$  and  $SF_6 - CF_4$  mixtures have been in use in arctic regions for more than two decades.



**Figure 2:** Normalised dielectric strength  $f(v)$  of  $SF_6$  mixtures with nitrogen and  $CF_4$  as a function of the  $SF_6$  volume concentration  $v$ .

## 2.2 $SF_6$ saving in large insulation systems

In large insulation systems, such as gas-insulated transmission lines, in which the gas only has to fulfill the insulation function, there is an interest in reducing the quantity of  $SF_6$  for both cost and environmental reasons. According to Figure 2, an efficient way to obtain such a reduction is using diluted  $SF_6$ -nitrogen mixtures with  $SF_6$  concentrations below 20%. As an example, at an  $SF_6$  concentration of 10%, the dielectric strength of the mixture is reduced only by 35% with respect to pure  $SF_6$ , or, expressed in another way, increased by about 60% with respect to pure nitrogen (0%  $SF_6$ ). This insulation synergy has triggered extensive research [3] and several development projects of gas-insulated transmission lines (GIL) (e.g. [11]).

The  $SF_6$  savings obtainable by using dilution with  $N_2$  can be determined from the normalized synergy curve  $f(v)$  in Figure 2. We consider a coaxial system with diameter  $D$  at fixed pressure. When an  $SF_6$ - $N_2$  mixture is used instead of pure  $SF_6$ , the insulation distances, i.e., diameter  $D$ , have to be increased approximately in inverse proportion to the reduced electric strength  $E$  of the mixture, i.e.,  $D_{mix}/D_{SF6} = E_{SF6}/E_{mix} = 1/f(v)$ . The corresponding  $SF_6$  quantities  $M$  then are related by  $M_{mix}/M_{SF6} = v (D_{mix}/D_{SF6})^2 = v/f(v)^2$  so that the  $SF_6$  savings  $s$  results:

$$s = 1 - M_{mix}/M_{SF6} = 1 - v/f(v)^2 \quad (1)$$

Thus, for a typical  $SF_6$  concentration of 10% ( $v = 0.1$ ,  $f(v) = 0.65$ ) one has  $s = 0.17 = 17\%$ . From the form of the synergy curve in Figure 2, it can be seen that the  $SF_6$  savings are highest at low  $SF_6$  percentages. For a 50% mixture, the  $SF_6$  savings reduce to about 50%.

### 3. ENVIRONMENTAL ADVANTAGE OF SF<sub>6</sub> MIXTURES

In general, the environmental advantage of one technology over another has to be measured in terms of the *total environmental impact of a functional system supplying a specified performance*. In electric power handling, a functional system may be a switching bay in a substation or even a complete regional electrical energy supply system. The performance of such a system would be its power handling capability. The total environmental impact of a functional system composes many contributions such as material consumed, energy dissipated and emissions caused during manufacturing, operational life cycle, and scrapping of the system. SF<sub>6</sub> emissions are thus one contributor among many others. As a consequence, an environmental evaluation of an SF<sub>6</sub> technology has to account for *all* these factors. *An environmental judgement based uniquely on the global warming potential of SF<sub>6</sub> or on SF<sub>6</sub> quantity may be severely misleading.*

In order to quantify the total environmental impact of a functional system and the relative contribution of the SF<sub>6</sub> used in it, a comprehensive *environmental lifecycle assessment (LCA)* is required, which has to be based on a detailed system design so that *all* relevant contributions can be quantified. The procedural features of an LCA have been standardised in the international ISO Standard 14040 [12]. A special form of LCA is a comparative assertion, which compares competing solutions of equal performance. Such a comparative assertion has recently been carried out for an entire regional power supply system with and without the use of SF<sub>6</sub> for insulation [2]. The result was that the use of SF<sub>6</sub> allows the *reduction* of the total environmental impact, in spite of its high global warming potential. A similar comparison between pure and diluted SF<sub>6</sub> insulation is probably under way but has not yet been published, to my knowledge.

### 4. HANDLING PROCEDURES AND CRITERIA

It can be generally stated that *most of the terminology, categories, and safety measures for handling unmixed SF<sub>6</sub>* (as outlined in the CIGRE SF<sub>6</sub> recycling guide [6]) *are also valid for handling SF<sub>6</sub> mixtures*. There are, however, a few mixture-specific differences that will be discussed in the following sections.

#### 4.1 Preparation of mixtures

SF<sub>6</sub> mixtures are available in *premixed* form from gas suppliers or as gas that has been recovered from equipment, purified by a reclaimer, and checked to be suited for reuse. Such a gas can be directly refilled into equipment without special precautions because a gas mixture, once mixed, does not de-mix for thermodynamic reasons.

When mixtures have to be produced by mixing the component gases, special precautions have to be taken to guarantee perfect mixing, particularly when mixing is carried out during filling of electrical equipment. For large volume equipment, a *dynamic mixer* is best suited. It simultaneously injects the component gases through a turbulent jet-mixing zone, their fluxes being controlled so that the correct mixture composition results. A dynamic mixer controlled by an SF<sub>6</sub> percentage meter can also be used to correct the composition of a mixture, if necessary. For small equipment volumes, the component gases can be filled into the equipment “one after the other” provided sufficient time is allowed for their diffusive mixing before the equipment is put in operation. The diffusive mixing time depends on the shape and dimensions of the enclosure and can be quite long [14].

#### 4.2 Gas mixture reclaiming

Reclaiming a gas mixture is very similar to reclaiming unmixed SF<sub>6</sub>: The gas recovered from the equipment is purified by pumping it through a set of filters that remove dust, reactive

gaseous decomposition products, and moisture. The cleaned gas is then stored. The only mixture-specific particularity is that SF<sub>6</sub> liquefaction in the storage container must be avoided because this would reduce the SF<sub>6</sub> content in the gas phase over the liquid SF<sub>6</sub> and thus change the mixture composition in an uncontrolled way. SF<sub>6</sub> liquefaction is avoided when the storage pressure is kept below a limit value  $p_{st,max}(v, T_{st})$ , which depends on the SF<sub>6</sub> concentration  $v$  and the storage temperature  $T_{st}$  and can be determined from the vapour pressure curve  $p_{vap}(T)$  of SF<sub>6</sub> as:

$$p_{st,max}(v, T) = p_{vap}(T)/v \quad (2)$$

Typically, at ambient temperature  $T = 20^{\circ}\text{C}$ , one has  $p_{st,max} = 4 \text{ MPa}$  for mixtures with 50% SF<sub>6</sub> and  $p_{st,max} = 20 \text{ MPa}$  for mixtures with 10% SF<sub>6</sub>.

### 4.3 Reuse on-site

Like unmixed SF<sub>6</sub>, SF<sub>6</sub> mixtures can in most cases be reclaimed (i.e., recovered from equipment, purified, and quality-checked) to be reused on-site. A separation of their components, which would require substantial investments in equipment and energy consumption, is not necessary. The quality criteria for reusing a mixture are the same as for unmixed SF<sub>6</sub>. They consist of limit concentrations of reactive decomposition products and humidity and, as a mixture-specific additional criterion, a check of the SF<sub>6</sub> concentration, which has to comply with the specifications of the equipment manufacturer.

Like for unmixed SF<sub>6</sub>, the major environmentally relevant characteristic of the mixture reuse process is the SF<sub>6</sub> release rate  $\lambda$  associated with a handling cycle. It is defined as the ratio:

$$\lambda = \text{SF}_6 \text{ lost to the atmosphere} / \text{SF}_6 \text{ handled} \quad (3)$$

and is essentially determined by the residual recovery pressure down to which the mixture can be recovered from the equipment. Usual SF<sub>6</sub> reclaimers allow to reach  $\lambda \sim 1\%$  typically, as a benchmark value. Recent improvements in pumping technology allow to further reduce  $\lambda$  to below 0.1%.

### 4.4 Further treatment off-site

In the rare case that resulting recovered mixtures are not suited for reuse on-site, they have to be further treated off-site. The criteria and modalities for their transportation are the same as for unmixed SF<sub>6</sub>. The options for further treatment off-site include:

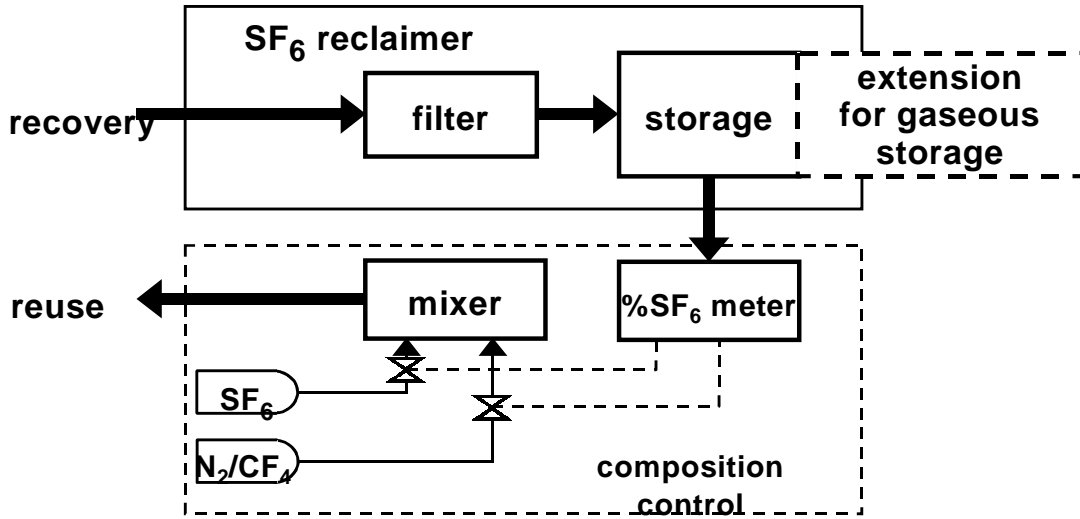
1. Further purification and composition correction to render the mixture reusable
2. Separation of the component gases, particularly SF<sub>6</sub> extraction
3. Final destruction

Processes (1) and (3) are the same as for unmixed SF<sub>6</sub>. Only the separation process (2) is mixture specific and will be further discussed below.

## 5. ON-SITE HANDLING EQUIPMENT

Conventional SF<sub>6</sub> handling equipment for on-site operation (reclaimers) is designed for handling unmixed SF<sub>6</sub> and cannot be directly used for mixture handling. However, the components can be upgraded for this purpose as indicated in Figure 3. The upper part of the diagram shows the main components of a conventional SF<sub>6</sub> reclaimer, namely, a set of filters and a storage container. The pumping devices and gas-quality checking devices have been omitted for simplicity. Upgrading for mixture handling requires the two add-on modifications:

1. The volume of the **storage container** has to be increased such that the mixture can be stored in gaseous form—i.e., below the maximum admissible storage pressure  $p_{st,max}$  according to (2). The most convenient pressure containers for this purpose are standard gas cylinders of the  $N_2$  type, which have relatively low cost, cover the typical storage pressure range, and comply with safety and transport regulations.



**Figure 3:** Upgrading of a conventional  $SF_6$  reclaimer for the handling of  $SF_6$  mixtures

2. A **mixing and composition control block** has to be added (lower part of Figure 3), which measures the  $SF_6$  concentration in the reclaimed gas (" $SF_6$  % meter") and allows to correct it, if necessary, by adding either  $SF_6$  or the admixture gas ( $N_2$  or  $CF_4$ ) via a dynamic mixer.

## 6. FURTHER TREATMENT OFF-SITE

Mixtures that can no longer be reused on-site or are no longer required have to be either separated to recover pure  $SF_6$  or have to be destroyed—i.e., to be re-transformed into environmentally compatible substances to close the eco-cycle.

For *mixture separation*, various physical principles can be considered, such as pressurised cryo-distillation, membrane technology, selective sorption, gas centrifuges, etc. An optimal combination of such processes can usually be tailored to the specific separation task. Whereas cryo-distillation seems to be suited for the separation of mixtures with high  $SF_6$  content, diluted  $SF_6$ - $N_2$  mixtures can be efficiently separated by a combined membrane/sorption technique with an  $SF_6$  loss rate  $\lambda < 0.01\%$  [13].

For *closing the eco-cycle, i.e., final disposal*, of  $SF_6$  and  $CF_4$ , various physical processes are known of which thermal destruction by kiln burning is presently the preferential solution. It is an established technology that is already used for the destruction of other halogenated compounds. In this process, the  $SF_6$  mixture is injected as co-flow into a flame, in which it is heated to above about  $1000^\circ K$ . This causes thermal dissociation of the  $SF_6$  ( $CF_4$ ) molecules so that the fragments can react with the flame combustion products to form sulphur oxides ( $SO_x$ ) and fluoric acid (HF). These reaction products are removed by acid flue gas treatment during which they react with lime (CaO) by which they are transformed into  $CaSO_4$  (gypsum) and  $CaF_2$  (fluorspar). These substances can be reused as raw materials or deposited without problems, as they are naturally occurring minerals.

## 7. SERVICES

For the rapid implementation of an environmentally responsible handling of SF<sub>6</sub> mixtures, a world-wide network of information and services is required. Presently, information can be found on the Web sites of SF<sub>6</sub> producers, SF<sub>6</sub>-handling equipment manufacturers, and SF<sub>6</sub> service enterprises. A CIGRE SF<sub>6</sub> Web site [9] is presently under development, which is intended to serve as a nodal point for such information.

## 8. CONCLUSIONS

1. SF<sub>6</sub> mixtures are presently applied in electric power equipment for two purposes:
  - To enable switchgear operation at low (arctic) ambient temperatures.
  - To reduce SF<sub>6</sub> cost and environmental impact in large insulation systems.
2. The environmental advantage of SF<sub>6</sub> mixtures over unmixed SF<sub>6</sub> has to be assessed quantitatively by a comparative environmental life cycle assertion (LCA), according to the Standard ISO 14040.
3. SF<sub>6</sub> mixtures can normally be reused on-site without separating their components.
4. Conventional SF<sub>6</sub> reclaimers designed for handling unmixed SF<sub>6</sub> can be upgraded for mixture handling.
5. Mixtures that can no longer be reused on-site or are no longer needed can be further treated off-site where they can be:
  - Rendered reusable.
  - Separated to recover the SF<sub>6</sub>.
  - Destroyed by a thermal process to close the eco-cycle.

## 9. REFERENCES

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