ZVEI:
Die Elektroindustrie

User Guide

Information on the Use, Transport and Disposal of SF_6 and Equipment Filled with SF_6 for the Supply of Electrical Energy

October 2018

Power Engineering Division

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Foreword

SF_6 (sulphur hexafluoride) is a non-toxic, inert insulation gas with high dielectric stability. In electrical engineering today, it is not only used in high and extra high-voltage switchgear but also in other electrical equipment such as medium-voltage switchgear, high-voltage lines, transformers, voltage transformers, particle accelerators, X-ray equipment and UHV transmission lines.

Under the influence of energy, the SF_6 molecule dissociates and can, together with other reacting agents, form substances with toxic or corrosive properties. Therefore, an appropriate risk assessment must be carried out for SF_6 gas taken from electrical equipment and for the electrical equipment from which the SF_6 gas was taken. Legal labelling/marking obligations can, in turn, be derived from the assessed hazard potential, and are extremely important particularly for the handling of the gas itself or the electrical equipment (hazardous substance), for the transport (hazardous goods) by road in accordance with ADR [15] and for their disposal (waste).

The application of the labelling/marking obligations and the necessary measures resulting from them are prescribed by law. The legal basis is complex due to the generality of the statutory provisions and the multitude of substances handled in the numerous different areas of industry, crafts and the private sphere. In the past, this repeatedly gave rise to questions in connection with the transport and disposal of used SF_6 gas and equipment filled with SF_6.

This User's Guide intends to contribute to reducing the complexity of the handling of equipment filled with SF_6 and to provide a simple overview of necessary labelling/marking regulations in the areas of hazardous substances, hazardous goods[1], the extended use and reuse (ReUse Concept) as well as the waste relating to the topic of SF_6 gas and equipment filled with SF_6.

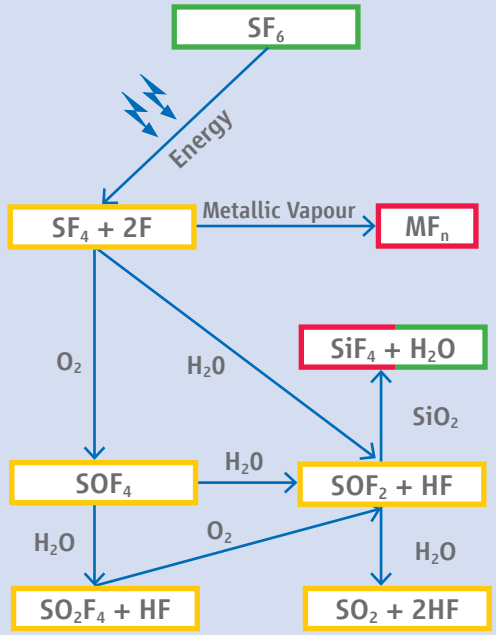
This User's Guide is based on the statutory requirements of the Federal Republic of Germany. Technical aspects, however, are of a general character.

[1] Further regulations are relevant with regard to sea and air cargo transport – this document only takes transport by road into consideration

1. Handling SF_6 Gas

Sulphur hexafluoride gas (SF_6) must be handled with care despite its inert[2] nature. It is important that the emission of SF_6 into the environment is limited to a minimum [1]. On the one hand, leaking SF_6 gas can reduce the oxygen concentration and thus constitute a suffocation hazard. On the other hand, used[3] SF_6 gas can contain decomposition products that are harmful to health. Decomposition products can arise when energy is applied to the SF_6 molecule, for example through electrical discharges. A temperature input, for example as it occurs in the burning ash of a cigarette, can also lead to the decomposition of SF_6 gas.

Fig. 1: Example of a reaction chain of SF_6 under the influence of energy and reaction partners



Source: ZVEI Training documentation for SF_6-Certification pursuant to Regulation (EC) 517/2014

Figure 1 illustrates how possible reactions of SF_6 with moisture (H_2O), oxygen (O_2) and energy lead to decomposition products. The reaction chain shows that in the electrical discharge primarily SF_4 is formed, which, however, immediately reacts with other partners so that finally only SO_2 and SO_2F_2 remain. Hydrogen fluoride (HF) reacts independently thereof to particulate fluorides as soon as it comes into contact with surfaces. The additional hazard potential of these decomposition products must be taken into consideration when handling used SF_6 gas.

Table 1 provides a brief description of the decomposition products shown in Figure 1.

[2] Inert = shows low reaction under normal conditions
[3] Used gas is understood as gas that is not contained in the sealed new gas cylinder

Table 1: Properties of the decomposition products [12]

Chem. Formula	Name	Chemical Stability in air	Final products	Occupational exposure limit (ppm_v[4])	Smell
SF_6	Sulphur hexafluoride	stable		1,000	none
SF_4	Sulphur tetrafluoride	rapid decomposition	HF, SO_2	0.1	acid sour
SOF_2	Thionyl fluoride	slow decomposition	HF, SO_2	1.5	rotten eggs
SOF_4	Sulphur oxide-tetrafluoride	rapid decomposition	SO_2F_2, HF	0.5	sour
SO_2F_2	Sulfuryl fluoride	stable		5	none
SO_2	Sulphur dioxide	stable		1	acid
HF	Hydrogen fluoride	stable		1	sour
SiF_4	Silicon tetrafluoride	Rapid decomposition	SiO_2, HF	3	sour
MF_n	Place-keeper for solid decomposition products (switching dust)	Solid decomposition products are dealt with in 3. "Handling electrical equipment filled with SF_6"			

Source: ZVEI, own depiction

SF_4 (highest hazard potential[5]) and SO_2 (chemically stable and easily measurable) play a particular role for the classification of a SF_6 gas mixture with regard to hazard substances, hazardous goods and waste. According to insights based on technical standards ([4], [7]), the ratio of SO_2 to total amount of all decomposition products in used SF_6 gas is 1 : 4 (SO_2 equivalence). The proportion of all decomposition products in the gas can therefore be determined by measuring the proportion of SO_2. The hazard potential of the total amount of all decomposition products is then assessed with the hazard potential of SF_4 as all other decomposition products, such as SO_2F_2, SOF_4 and HF, have a lower hazard potential.

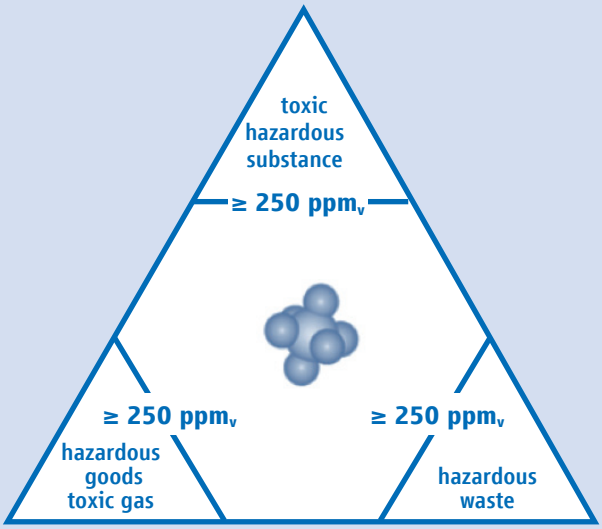
The following sections show the limits for classification of SF_6 gas in its various characteristics as hazardous substance, hazardous goods and waste, determined on the basis of the worst case approach in accordance with the CLP Regulation [2], ADR [15] based on the Orange Book Rev. 20 (UN Model Recommendations on the Transport of Dangerous Goods) and Waste Framework Directive [16]. In addition, they inform the operator on the respective labelling/marking obligations. The values for SO_2 concentration shown in Figure 2 are to be understood as recommendations for dealing with the three different areas of legislation in practice.

The calculated limits for toxic hazardous goods (Attachment 2: Calculation of limits for the classification of hazardous goods) and hazardous waste (Attachment 3: Calculation of limits for the classification as waste) are partly higher than those recommended in Figure 2; therefore, the classification based on the recommended limits provides additional safety in practice.

As a rule, during normal grid operation the operator of electrical equipment can assume that the SF_6 gas contained in it has negligible impurities. Furthermore, the operator can assume that SF_6 gas taken from electrical equipment using a customary commercial servicing device and filled into pressurised gas cylinders or tanks contains SO_2 concentrations of less than 250 ppm_v (see 1.1 SF_6 gas as a hazardous substance) as these SF_6 servicing devices have a filter as a standard feature for absorbing impurities. This should be taken into account when servicing devices are procured. Where higher levels of impurities in the SF_6 gas are suspected – for example, in the case of an operational malfunction (arc fault) of the electrical equipment or neglected maintenance of the servicing device – the SO_2 content in the SF_6 gas should be determined using a customary measuring instrument with electrochemical sensors in the measuring range from 0 ppm_v to 500 ppm_v.

[4] ppm_v = parts per million by volume (1,000 ppm_v = 0.1% of a volume)
[5] The high hazard potential arises through the comparatively large proportion of SF_4, when SF_6 decomposes through energy input. Here SF_4 is to be understood as a place-keeper for all decomposition products as it reacts almost completely with other partners.

Fig. 2: SO_2 values for the classification of SF_6 gas mixtures



Source: ZVEI, own depiction

1.1 SF_6 gas as a hazardous substance

According to the CLP Regulation [2], the generic and specific concentration limits, multiplying factors and general cut-off values mentioned in the Regulation are to be applied for the classification of a mixture containing one or more constituents classified as hazardous. Moreover, where necessary, additive effects must be taken into consideration on the basis of the calculation methods described in Annex I of the CLP Regulation [2].

Application of the calculation pursuant to the CLP Regulation [2] in accordance with Attachment 1 of this document: "Calculation of limits for the classification of hazardous substances", taking the SO_2 equivalence (factor 1 : 4) into account, results in an arithmetic limit of

$$1{,}000\ ppm_V\ SF_4 \times \frac{1}{4} \times \frac{SO_2}{SF_4} = 250\ ppm_V\ SO_2$$

Therefore, according to the CLP Regulation [2], a gas mixture must be marked as "Acute Tox 3 (H331)" if the proportion of SO_2 measured in the SF_6 gas is larger than 250 ppm_v. This value is given in Figure 2 and Table 2.

Besides the criterion as to whether a gas is evaluated as being toxic or non-toxic, according to the CLP Regulation [2] all gases are to be evaluated as hazardous substances with regard to all possible physical hazards and, if necessary, labelled/marked as such.

Table 2: Overview of Hazardous substance labelling/marking

Chemical formula	New SF_6	Used SF_6 without toxic properties	Used SF_6 with toxic properties
Hazardous substance classification	Gas	Gas	Gas + toxic
SO_2 value	0 ppm_V + no other decomposition products	< 250 ppm_V	≥ 250 ppm_V
Labelling of the cylinder shoulder	"green"	"green"	"yellow"

Source: ZVEI, own depiction

1.2 SF_6 gas as hazardous goods

The application of the limit determination according to Attachment 2: "Calculation of the limits for the classification of hazardous goods" taking the SO_2 equivalence results in the following arithmetic limit for the SO_2 concentration:

$$8{,}000\ ppm_V\ SF_4 \times \frac{1}{4} \times \frac{SO_2}{SF_4} = 2{,}000\ ppm_V\ SO_2$$

Nowadays, commercially used portable measuring instruments have electrochemical sensors to measure SO_2 and are available in measuring ranges from 0 ppm_v to 500 ppm_v. Hence, a limit of 250 ppm_v is recommended to determine the hazardous goods character in practice; in Figure 2 this lower value is given as the limit for toxic hazardous goods.

According to ADR [15], the sender is responsible for all labelling/marking obligations. A detailed table for the classification of SF_6 gas can be found in Attachment 4 of this document: "Table for the Classification of SF_6 gas for transport".

Table 3: Overview of hazardous goods labelling/marking

	New SF_6	Used SF_6	Used SF_6 with toxic properties
Cylinder/Container	green: 	Gas	Gas + toxic 
Hazardous goods classification for transport	UN1080 Class 2.2	UN3163 Class 2.2 N.A.G.	UN3308 Class 2.3 + Class 8 N.A.G
SO_2 value	0 ppm_V+ no other decomposition products	< 250ppm_V	≥ 250 ppm_V
Add. Labelling for transport			
Safety plan pursuant to ADR	No	No	Yes

Source: ZVEI, own depiction

2. SF_6 Gas in the Circular Economy

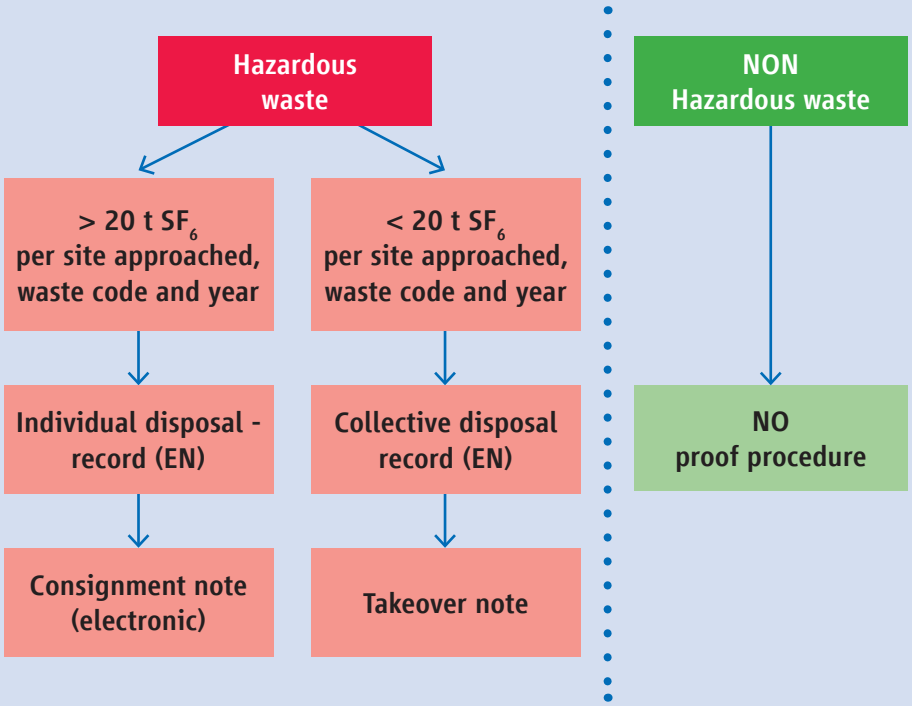
In principle, there are two ways of keeping used SF_6 gas in the material cycle, based on the EU Circular Economy strategy or the principle of waste avoidance or high-quality waste recycling: on the one hand, as waste for recycling and, on the other hand, as a product for reuse. The German Waste Management and Product Recycling Act / (Closed Cycle Management Act) (Kreislaufwirtschaftsgesetz (KrWG) [8]) permits both methods; reuse according to Sec. 3(21) KrWG is a form of waste avoidance pursuant to Sec. 3(20) KrWG.

2.1 Used SF_6 gas as waste

The decision as to whether used SF_6 gas is waste must be taken by its holder, as a rule the operator of the electrical equipment. It must be regarded as waste if the holder wants to dispose the gas without a new usage immediately replacing the previous usage (Sec. 3(3) KrWG [8]).[6]

Furthermore, in this case the Closed Cycle Management Act (KrWG) [8] distinguishes between "non-hazardous waste" and "hazardous waste". The waste producer – as a rule, the operator of the equipment that originally contained the SF_6 gas – is obliged to provide proof in accordance with the German Ordinance on Waste Recovery and Disposal Records (Nachweisverordnung) [10] as soon as hazardous waste is present. The corresponding requirements are shown in Figure 3.

Fig. 3: Record-keeping for waste delivered to the disposer or the gas producer – in deviation from this, amendments are possible – see explanations on "Notice of Exemption" in this chapter



Source: ZVEI, own depiction

[6] The last limitation is not necessarily fulfilled as the previous holder has no usage for the SF_6 gas, but it can normally be used in other electrical equipment for the original purpose without much treatment.

Waste must be classified with a six-digit waste code pursuant to the German Waste Catalogue Ordinance (Abfallverzeichnis-Verordnung –AVV) [9]). A "*" (asterisk) added to the waste code means that the waste is hazardous waste. The waste codes are to be taken from the AVV [9] and are listed in Table 4 for gases in pressurised gas cylinders or tanks.

Table 4: Waste code in connection with gases in pressurised vessels

Waste code	Waste description
16 05	Gases in pressurised vessels and used chemicals
16 05 04*	Gases containing hazardous substances in pressurised vessels (including Halons)
16 05 05	Gases in pressurised vessels with the exception of those falling under 16 05 04

Source: ZVEI, own depiction

Table 4 shows that (used) SF_6 gas in pressurised gas cylinders or tanks can be classified as waste number 16 05 04* or 16 05 05. Therefore decisions on SF_6 must be taken on a case-by-case basis. The AVV is the national implementation of the European Commission Decision 2.000/532/EC and describes the hazardous characteristics, which, in turn, are based on limits from the CLP Regulation [2] mentioned in 1.1 "SF_6 gas as a hazardous substance". Hence, the classification of the SF_6 gas can be done on the basis of the SO_2 measurement using the limit for hazardous substances.

Attachment 3 "Calculation of the limits for the classification as waste" illustrates that a concentration limit value of 35,000 ppm_v is permissible according to the Waste Framework Directive [16], but for reasons of simplification a limit of 1,000 ppm_v is suggested. Therefore, as described in 1.1, "SF_6 gas as a hazardous substance", the limit for SO_2 as a detector gas is as follows:

$$1{,}000\ ppm_V\ SF_4 \times \frac{1}{4} \times \frac{SO_2}{SF_4} = 250\ ppm_V\ SO_2$$

This value is shown in Figure 2 and Table 5 (waste labelling/marking).

Table 5: SF_6 gas as waste

	New SF_6	Used SF_6 (non-hazardous waste)	Used SF_6 (hazardous waste)
Waste code	16 05 05	16 05 05	16 05 04*
SO_2 value	0 ppm_V + no other decomposition products	< 250 ppm_V	≥ 250 ppm_V
Obligation to provide proof	No	No	Yes

Source: ZVEI, own depiction

If the operator has taken the SF_6 gas from electrical equipment that is intact and filled the gas into pressurised gas cylinders or tanks, the waste code 16 05 05 is to be used as normally the waste is not hazardous. The limits according to Annex III of the Waste Framework Directive [16] are not exceeded (see 1. "Handling SF_6 Gas"). The limits can only be exceeded in highly exceptional cases (e.g. arc faults). In that case, the waste code 16 05 04* for hazardous waste is to be used and additional obligations to provide proof in accordance with Sec. 50(1) KrWG apply, if no exemption according to Sec 26 KrWG exists. It must be noted that the labelling/marking obligations for hazardous substances and hazardous goods must be observed, irrespective of the waste classification (hazardous / non-hazardous).

In Germany, operators and manufacturers of SF_6 gas are obliged pursuant to Art. 4(2) of the German Chemicals – Climate Protection Ordinance (ChemKlimaschutzV) [17] to take back SF_6 gas (manufactured by them) within the scope of their product responsibility according to Sec. 23 KrWG [8]. If these companies taking back the SF_6 gas have been granted a notice of exemption valid across the federal states, i.e. throughout Germany, pursuant to Sec. 26 KrWG [8], they can directly accept used SF_6 as waste with the waste code number 160504* (hazardous) or 160505 (non-hazardous) and use it – officially approved. This simplifies or replaces the otherwise necessary proof procedure for hazardous waste pursuant to KrWG [8], and the amount taken back no longer has to be reported or offered to the waste management authorities of a federal state. This is reported annually to the relevant state authority by the company taking the gas back. The waste producer receives a taking-over certificate for the returned SF_6. In combination with a copy of the notice of exemption[7], the taking-over certificate serves as documentation, both for the waste producer and the company taking back the SF_6.

2.2 Used SF_6 gas in the product cycle

As already mentioned in the previous chapter, the decision as to whether used SF_6 is to be regarded as waste or is still a product is the responsibility of the respective holder of the SF_6 gas, i.e. normally the operator of the electrical equipment. The Closed Cycle Management Act (KrWG) does not limit the possibility of returning used SF_6 gas to the operator or the manufacturer of SF_6 gas for further use before it is declared as waste. This is a measure to prevent waste. The decisive point here is that the SF_6 gas is used for its original purpose, i.e. insulating and switching in electrical equipment (see explanation 2.1. "Used SF_6 gas as waste"). This process, known as a ReUse process, has already been carried out for many years now by the company Solvay Fluor GmbH, a manufacturer of SF_6 gas in Germany.

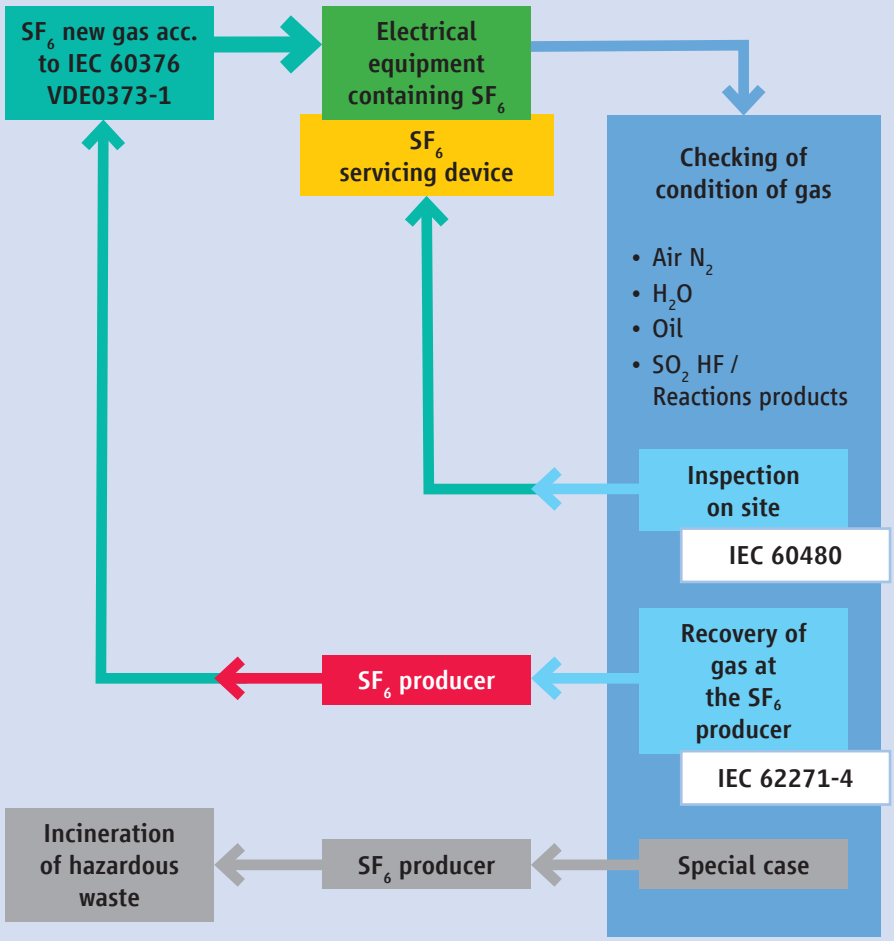
The used SF_6 gas is by all means a hazardous substance and hazardous goods when returned in a pressurised gas cylinder with a relative pressure exceeding 2 bar. The concentration of possibly existing toxic constituents then determines the type of transport for the pressurised gas cylinders or tanks filled with SF_6. It is possible to transport SF_6 gas without a safety plan pursuant to ADR (see Table 3) if the operator has taken the SF_6 gas from undamaged electrical equipment using a customary commercial SF_6 servicing device or has determined a concentration of $SO_2 < 250\ ppm_v$ through measurement. The used pressurised gas cylinders or tanks with green strips should, however, be specially labelled/marked and by no means mixed up with pressurised gas cylinders or tanks used for new SF_6 (according to IEC 60376 [19]) or SF_6 for reuse (according to IEC 60480 [4]). If necessary, the returned used SF_6 gas is analysed again by the accepting company for impurities and reused.

Should the operator extract the SF_6 gas from the electrical equipment with a compression device without a filter or should the SO_2 content exceed $250\ ppm_v$, the gas must be transported in pressurised gas cylinders or tanks with yellow markings and a safety plan must be drawn up.

[7] Solvay Fluor GmbH has had a notice of exemption since 2004, issued by the authorities in Lower Saxony and valid throughout the Federal Republic of Germany, which is renewed every five years.

The ReUse process described corresponds to a closed product cycle as the used SF_6 is directly fed into the production of new SF_6 and then reused in electrical equipment. As illustrated in Figure 4 below, the process is, in principle, comparable with the maintenance of electrical equipment on site. There, the SF_6 gas is recovered and refilled into the electrical equipment following inspection work.

Fig. 4: ReUse Concept



Source: Solvay Fluor

When SF_6 gas is taken back, it is regularly held by the accepting manufacturer or operator of SF_6 gas and becomes their property. A taking-over certificate is issued for the reacceptance. Contaminated SF_6 gas that does not meet the ReUse material specification following an initial analysis is only then declared as waste and designated for final disposal, as shown in Figure 4 (Special Case). The reaccepting company is then responsible for completing the tracing records in accordance with KrWG [8].

3. Handling Electrical Equipment Filled with SF_6

As already introduced in Figure 1 and Table 1 of 1. "Handling SF_6 gas", decomposition products with toxic properties can arise under the influence of energy. The gaseous decomposition products can be extracted together with the remaining SF_6 gas or non-toxic impurities (e.g. air) through filters, using customary commercial SF_6 servicing devices. However, any existing particulate, solid decomposition products remain in the gas compartment of the electrical equipment. An overview of possible particulate decomposition products is shown in Table 6.[8]

Table 6: Properties of the solid decomposition products

Chemical symbol	Name	Occupational limit (AGW) (mg/m^3)
MF_x	Fluoride	1
-	Silver compounds, inorganic	0,01

Source: TRGS 900 [13]

No certain relation can be established between the SO_2 concentration in the SF_6 gas that was taken from the electrical equipment and the existence of switching dust due to attachment effects on metal surfaces and the frequent use of filter materials (absorbers) in the gas compartment of the electrical equipment. Analogous to the considerations taken from the information on SF_6 equipment provided by the DGUV (German Social Accidence Insurance): DGUV Information 213-013 "SF_6-Anlagen und Betriebsmittel", (previously BGI 753), Appendix 4 [11], solid decomposition products can therefore not be ruled out. Hence, the hazard potential of the solid decomposition products in the gas chamber of electrical equipment must be assessed and corresponding labelling/marking carried out.

3.1 Electrical equipment filled with SF_6 as a hazardous substance

Solid decomposition products in closed electrical equipment do not pose a hazard as they are contained within a closed casing. Therefore, a classification as toxic hazardous substance is not necessary.

If, however, electrical equipment is opened or the integrity of the gas compartment of the electrical equipment is damaged through a defect, the hazards posed by the solid decomposition products must be assessed. It is clear from the recommended limit in Table 6 that the occupational exposure limit is reached with even small amounts of solid decomposition products.

A visual check for switching dust is therefore not sufficient. Hence, the existence of an amount of solid decomposition products that exceeds the limit must be assumed. At this point, reference is made to the DGUV Information 213-013 (previously: BGI 753) [11].

3.2 Electrical equipment filled with SF_6 as hazardous goods

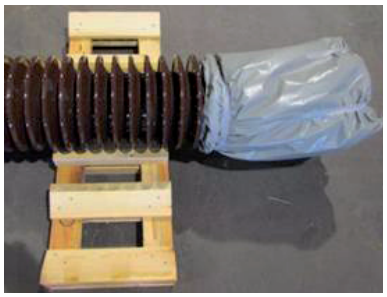
For safety reasons, used electrical equipment filled with SF_6 should generally be considered as hazardous goods in view of the possible existence of switching dust and is therefore to be labelled/marked accordingly for transport (see Attachment 4: "Table for the classification of SF_6 gas for transport"). Labelling/marking with UN Number 3363 means that the hazardous goods are not subject to the provisions of ADR [15] and, apart from this information, (i.e. an accompanying note: "Hazardous goods in machinery or in equipment. Not subject to the provisions of ADR"), no further labelling/marking and no particular measures are required during transport.

The filling pressure of this electrical equipment must also be below 2 bar relative for transport because otherwise ADR [15] is applicable. In addition, the measured SO_2 concentration in the SF_6 gas must be lower than 250 ppm_v[9]; in practice this is the rule.

[8] Sulphur compounds can also be proportionately contained in the switching dusts. There are no limits for them for occupational exposure pursuant to TRGS 900 [13]

The simplification of labelling/marking with UN Number 3363 for the transport of the gas in electrical equipment also only applies if the solid switching dust cannot escape during transport. Open gas compartments in electrical equipment from which the SF_6 gas has already been recovered but which have not yet been cleaned must therefore be closed for transport due to the possible existence of switching dust. The use of concentration has proved to be sufficient for the purpose. Lockable containers can be used as an alternative (see Figures 5 and 6).

Figure 5: Packed ground insulator of a 123-kV circuit breaker/ Packed gas compartment of a 123-kV gas-insulated switchgear



Source: Westnetz

Figure 6: Lockable container Packed medium voltage switch bay

Source: Phönix Elektronik-Recycling

Source: Westnetz

If a neutralisation procedure in accordance with IEC 62271-4 [20] has been carried out and hence the presence of solid decomposition products in the gas compartments can be ruled out, the unfilled electrical equipment can be transported without a problem. Here the obligations already mentioned for labelling/marking or providing proof pursuant to legislation on hazardous goods, transport or waste no longer apply.

3.3 Electrical equipment filled with SF_6 as waste

The decision as to whether filled electrical equipment is waste must be taken by its holder, as a rule the operator of the electrical equipment. It must be regarded as waste if the holder wants to dispose of the gas without a new usage immediately replacing the previous usage (Sec. 3(3) KrWG).

According to the German Waste Catalogue Ordinance [9], the filled electrical equipment is to be declared as shown in Table 7.

[9] Cf. Calculation in Chapter "SF_6 gas as dangerous goods"

Table 7: Waste code in connection with electrical and electronic equipment

Waste code	Waste description
16 02	Electrical and electronic equipment and their components
16 02 09*	Transformers and capacitors containing PCB
16 02 10*	Used equipment containing PCB or contaminated with it, with the exception of equipment falling under 16 02 09
16 02 11*	Used equipment containing chlorofluorocarbons, HCFCs or HFCs
16 02 12*	Used equipment containing free asbestos
16 02 13*	Used equipment containing hazardous constituents with the exception of equipment falling under 16 02 09 to 16 02 12
16 02 14	Used equipment with the exception of equipment falling under 16 02 09 to 16 02 13
16 02 15*	Hazardous components taken from used equipment
16 02 16	Components taken from used equipment with the exception of equipment falling under 16 02 15

Source: ZVEI, own depiction

Table 7 shows that the waste codes 16 02 11*, 16 02 13* (hazardous waste) and 16 02 14 come into consideration for electrical equipment filled with SF_6. Experience shows that if the relevant gas quality can be proved or derived through operational experience, the waste code 16 02 14 can be used as in almost all cases there is no hazardous waste. The limits according to Annex III of the Waste Framework Directive are not exceeded with regard to added amounts of SF_6 gas (also see 2.1. "Handling SF_6 gas as waste").The limits can only be exceeded in highly exceptional cases (e.g. arc faults). In that case, the waste code 16 02 11* or 16 02 13* for hazardous waste is to be used and additional obligations to provide proof in accordance with Sec. 50(1) KrWG apply, if no exemption according to Sec 26 KrWG exists.

If the gas is completely extracted at the operator's installation site, the gas must be handled as described in 2. "SF_6 gas in the circular economy".

The explanations in 3.2 "Electrical equipment filled with SF_6 as hazardous goods" must be observed if the electrical equipment is later handed over to a certified disposal enterprise in view of possible solid decomposition products in the electrical equipment. It must be noted that the labelling/marking obligations for hazardous substances and hazardous goods must be observed, irrespective of the waste classification (hazardous / non-hazardous).

3.4 Electrical equipment filled with SF_6 as a used product

Electrical equipment taken out of service is usually still functional. It can therefore still be used as a used product or returned to the manufacturer for further use, which means that waste is avoided.

Owing to the "Voluntary self-commitment of SF_6 producers, manufacturers and operators on SF_6 as insulation and extinguishing gas" [14] of May 2005, manufacturers of electrical equipment filled with SF_6 must take the equipment back from the operators after use if it was produced by them. This take back is voluntary, as, unlike SF_6 gas, electrical equipment itself does not fall under the take-back obligation of the Climate Protection Ordinance (ChemKlimaschutzV).

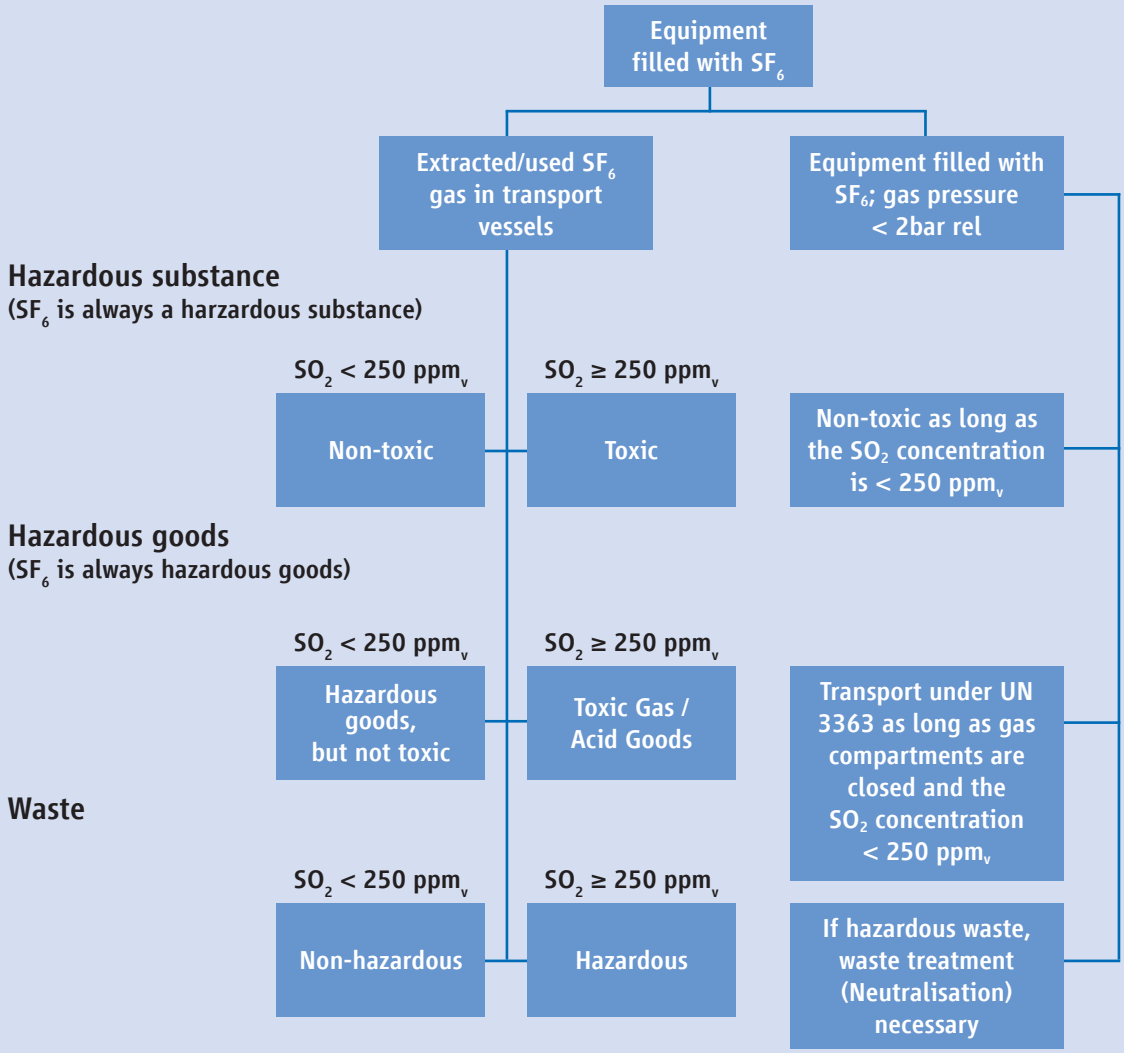
Waste legislation does not apply if electrical equipment filled with SF_6 is returned as a used product. Hence, the question of hazardous or non-hazardous waste does not have to be answered. However, the indications provided in 3.2 Electrical equipment filled with SF_6 as hazardous goods must be observed for the transport.

4. Summary of the Requirements for Handling SF_6 and Electrical Equipment filled with SF_6

The extensive legal requirements for the handling of hazardous substances, the transport of hazardous goods and for waste must be applied for SF_6 gas and electrical equipment filled with SF_6 and necessitate a thorough examination with regard to possible toxic properties. This User's Guide is intended to help all those involved in the handling of SF_6 to understand and implement these requirements.

It is important that for every process concerning both SF_6 gas and electrical equipment filled with SF_6 consideration and labelling/marking take place from the perspectives of (hazardous) substance, hazardous goods and waste. After a consistent and complete consideration, users can assume that they have fulfilled the legal stipulations in the Federal Republic of Germany. In conclusion, Figure 7 shows an overview of the requirements for handling SF_6 gas and electrical equipment filled with SF_6.

Fig. 7: Decision diagram on labelling/marking obligations for SF_6 gas taken from used electrical equipment and for electrical equipment filled with SF_6



Source: ZVEI, own depiction

5. Final Comment

The properties of used SF_6 gas enable its continued use in electrical equipment for a practically indefinite period, on condition that the quality of the gas is in accordance with IEC 60480 [4]. Therefore preference is generally to be given to a continued use of SF_6 gas as a used product.

List of References

[1] Regulation (EU) No 517/2014 of the European Parliament and of the Council of 16 April 2014 on SF_4 fluorinated greenhouse gases and repealing Regulation (EC) No 842/2006 (F-Gases Regulation)

[2] Regulation (EC) No 1272/2008 of the European Parliament and of the Council of 16 December 2008 on classification, labelling and packaging of substances and mixtures, amending and repealing DirectivesSF_4 67/548/EEC and 1999/45/EC, and amending Regulation (EC) No 1907/2006 (CLP Regulation)

[3] Ridder, Klaus; Holzhäuser, Jörg: ADR 2017. Landsberg am Lech: EcoMed Sicherheit, 32 Edition 2017

[4] IEC 60480:2004 (DIN EN 60480:2005-08), Guidelines for the checking and treatment of sulfurSF_4 hexfluoride (SF_6) taken from electical equipment and specification for ist re-use

[5] Act on the Implementation of Measures of Occupational Safety and Health to Encourage Improvements in the Safety and Health Protection of Workers at Work (Arbeitsschutzgesetz, ArbSchG)

[6] German Ordinance on Industrial Safety and Health (Betriebssicherheitsverordnung – BetrSichV)

[7] CIGRE Brochure 234, SF_6 Recycling Guide – Revision 2003

[8] German Closed Cycle and Waste Management Act (Kreislaufwirtschaftsgesetz (KrWG))

[9] Ordinance on the European Waste Catalogue (Abfallverzeichnisverordnung – AVV)

[10] Ordinance on Waste Recovery and Disposal Records (Nachweisverordnung – NachwV)

[11] DGUV (German Social Accident Insurance) Information 213-013 (previously: BGI 753). Note: currentlySF_4 (as of: April 2018) being revisedSF_4

[12] Kurte, R.: Infrarotspektrometrische Spurengasbestimmung in für elektrische Schaltanlagen verwendetem Schwefelhexafluorid. Dortmund: Dissertation der TU Dortmund, 03.04.2002 (Infrared spectometric trace gas determination in sulphur hexafluoride used for electrical switchgear)

[13] Technische Regel für Gefahrstoffe 900, Arbeitsplatzgrenzwerte (TRGS 900) (Technical Rules for SO_2 Hazardous Substances 900, occupational exposure limit (TRGS 900)) . Edition: January 2006 BArBl. SO_2 Issue 1/2006 pp. 41–55, last revised and supplemented: GMBl 2015 pp. 1186–1189 [N0. 60] ofSF_4 06.11.2015

[14] Voluntary self-commitment of SF_6 producers, manufacturers and operators of electrical equipment > 1 kVSF_4 for the transmission and distribution of electrical energyin the Federal Republic of Germany on SF_6 as anSF_4 insulation and extinguishing gas

[15] ADR = Accord européen relatif au transport international des marchandises dangereuses par routeSF_4 (English: European Agreement Concerning the International Carriage of Dangerous Goods by Road)

[16] Directive 2008/98/EC of the European Parliament and of the Council of 19 November 2008 on waste andSF_4 repealing certain Directives (Waste Framework Directive) including amendments to Annex III, effectiveSF_4 from 05.07.2018 pursuant to Council Regulation EU 2017/997

[17] German Ordinance to protect the climate against the effects of the entry of certain fluorinatedSF_4 greenhouse gases (Chemicals – Climate Protection Ordinance (Chemikalienklimaschutzverordnung – SF_4 ChemKlimaschutzV))

[18] Safety data sheet "Used Sulphur Hexafluoride" pursuant to Regulation (EC) No 1907/2006

[19] IEC 60376:2018, Specification of technical grade sulphur hexafluoride (SF_6) and complementary gasesSF_4 to be used in its mixtures for use in electrical equipment

[20] IEC 62271-4:2013 (DIN EN 62271-4 (VDE 0671-4)), Handling procedures for sulphur hexafluoride (SF_6) SF_4 and its mixtures

Attachments

Attachment 1: Calculation of limits for the classification of hazardous substances

The example on acute toxicity below shows how the classification can be carried out based on information on the substances in a gas mixture with a worst case approach (see 1. Handling SF_6 Gas) and using the criteria from Annex I of the CLP Regulation [2]. The procedure of self-classification for further hazard classes must be analogous.

The so-called ATE value of the SF_6-SF_4 mixture (estimated value of acute toxicity) must be determined for the classification of the pure sulphur tetrafluoride substance (SF_4) as "Acute Tox. 1 (H330)". This is calculated according to the following formula:

$$\frac{100}{ATE_{mix}} = \sum \frac{c_i}{ATE_i}$$

The example on acute toxicity below shows how the classification can be carried out based on information on the substances in a gas mixture with a worst case approach (see 1. Handling SF_6 Gas) and using the criteria from Annex I of the CLP Regulation [2]. The procedure of self-classification for further hazard classes must be analogous.

Attachment 2: Calculation of the limits for the classification of hazardous goods

In accordance with Chapter 2.2.2.1.5 [3] of ADR 2015, the limit for the determination of the hazardous-material property can be determined from the $LC50_{1h}$ value of a substance. The following applies for SF_4 (Chapter 4.1.4.1 P200):

SF_4 $LC50_{1h}$: 40 ppm_v

The limit for the mixture of SF_6 and SF_4 can be estimated under the following assumptions:

1. All possible other constituents in the gas have physiological and chemical properties similar to SF_4 and the same or a higher $LC50_{1h}$ value (worst-case approach).
2. The mixture has an $LC50_{1h}$ value exceeding 5.000 ppm_v and can therefore be transported as non-toxic (Packing group 3).

This results in the highest permissible level of impurities with toxic substances:

$$\frac{LC50_{1h,\,SF4}}{5{,}000\ ppm_v} = 8{,}000\ ppm_V\ SF_4 = 0{,}8\ Vol.\ \%\ SF_4$$

Attachment 3: Calculation of the limits for the classification as waste

On the basis of the calculated values in Annex I: Calculation of Limits for the Classification of Hazardous Substances, our gas mixture must be regarded as Acute Tox 3 "toxic by inhalation", i.e. with the H331 coding.

A cut-off value for the assessment of toxicity in mixtures can be found in Annex III of the Waste Framework Directive [16], HP 6 „acute toxicity". The mixture can be classified as non-hazardous waste without further examination of the Waste Framework Directive if the value for the additive in the mixture is lower than 0.1 per cent (1,000 ppm_v). If it exceeds the limit value of 0.1 per cent, the maximum permissible concentration in the mixture must be determined on the basis of Table 5 in Annex III of the Waste Framework Directive, depending on the respective coding. In the case of H331 Acute Tox 3, a maximum value of 3.5 per cent (35.000 ppm_v) would be permissible. However, for reasons of simplification, a concentration limit of 1,000 ppm_v is adhered to in this guide.

[10] ATE = Acute Toxicity Estimate

Attachment 4: Table for the classification of SF_6 gas for transport

Implementation in practice – classification of SF_6 for Transport

Table 8: For the classification of SF_6 in pressurised gas cylinders or vessels

Type of hazardous goods acc. to ADR[4]	UN #	Technical Classification (Gas Class)	Technical Description acc. to ADR	SO_2 Test acc. to ADR[4]	Cylinder shoulder	Technical Requirements
Hazardous goods (Substance)	1080	Technical SF_6	SULPHUR HEXA-FLUORIDE (liquefied inert gas)	0 ppm_v	green	• meets IEC 60376 "New Gas" • single-digit traces of SO_2 possible
Hazardous goods (Substance)	3163	Used SF_6 for reuse	LIQUEFIED GAS N.A.G[3] (Gas with by-products)	< 250 ppm_v[5]	green	• if < 12ppm_v SO_2 meets IEC 60480 "Used Gas" • Specimen danger label 2.2 (green label with gas cylinder) acc. to ADR classification up to < 250ppm_v SO_2 permitted[2]
Hazardous goods (Substance)	3163	Used SF_6 for reuse – special filter process necessary	LIQUEFIED GAS N.A.G[3] (Gas with by-products)	< 250 ppm_v[5]	green	• if > 12ppm_v SO_2 • small amount of toxic impurities require filtering before filling the vessels • Specimen danger label 2.2 (green label with gas cylinder) acc. to ADR classification up to < 250ppm_v SO_2 permitted[2]
Hazardous goods (Substance) with high hazard potential[1]	3308	Used SF_6 for reuse or disposal • Take-back by gas producer • Qualified laboratory test necessary in order to assess the gas quality	LIQUEFIED GAS, TOXIC, CORROSIVE N.A.[3] (Gas containing toxic and corrosive decomposition products)	≥ 250 ppm_v[5]	Yellow with stainless steel valve	• Special vessel with stainless steel valve • Secure storage until collection required • Qualified assessment of the gas quality can only be done through a thorough laboratory test • In Germany, as in all ADR states, a security plan acc. to ADR 1.10 is required • Acc. to the German Sicherheitsüberprüfungsfeststellungsverordnung (security screening ordinance) additional security screening is required

Source: Siemens

Table 9: For the classification of SF_6 in electrical equipment

Type of hazardous goods acc. to ADR[4]	UN #	Gas Class	Description acc. to ADR	SO_2 test acc. to ADR[4]	Pressure[5] Gas Class A&O	Technical Requirements
Hazardous goods in machines / equipment	3363	Technical SF_6 / used SF_6 for reuse or disposal	Accompanying note required: "Hazardous goods in machinery or in equipment". Does not fall under the provisions of ADR[4)]	< 250 ppm_v[5] or corresponding value based on experience	Pressure < 2 bar (200kPa) at 20 °C	• SF_6 Exemption from hazardous goods regulations if the pressure in the enclosure, (e.g. pressure vessel) **is below 2 bar (200kPa)** at a temperature of 20 °C. • This exemption does not apply acc. to the Allgemeinen Deutschen Seeversicherungsbedingungen (ADS) (General German Marine Insurance Conditions)

Source: Siemens

[1] Pursuant to ADR1.10.3 Provisions for high consequence dangerous goods
[2] From 249 ppm_v onwards toxic and corrosive must also be marked/labelled separately pursuant to CLP classification of hazardous substances.
[3] not otherwise specified; a collective term to which such substances and mixtures can be assigned
[4] ADR – European Agreement Concerning the International Carriage of Dangerous Goods by Road
[5] µl per litre = ppm_v

Attachment 5: Limit for SF4 in a mixture pursuant to CLP [2] for occupational health and safety[11]

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Per E-Mail

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Dortmund, 24.08.2018
GZ: 5.0-720 34/04/2015.2495
5.0-720 34/04/2018.1699

Your enquiry dated 30.09.2015

Dear Dr Kurte,

You enquired about the limit for sulphur tetrafluoride (SF4, CAS-No 7783-60-0, EG-No 232-013-4) in a mixture with regard to the classification pursuant to CLP (Regulation (EC) No 1272/2008). With your enquiry, you sent us a Safety Data Sheet (SDS) for a mixture consisting of 98% nitrogen and 2% sulphur tetrafluoride.

According to Article 4(1) of the CLP Regulation, manufacturers, importers and downstream users must classify substances or mixtures in accordance with Title II of the CLP Regulation before placing them on the market. This classification by the distributors at their own responsibility is also known as self-classification. If a harmonised classification in accordance with Annex VI of the CLP Regulation already exists, this classification is to be observed. The “harmonised classification and labelling for certain hazardous substances” is listed in Annex VI of the CLP Regulation. There is no harmonised classification according to CLP for the substance you mention, i.e. sulphur tetrafluoride.

With regard to substances for which no harmonised classification exists, the manufacturer or the importer is obliged to carry out a self-classification of the substance in accordance with Article 4(1) CLP Regulation. This (self-) classification for the substance sulphur tetrafluoride is shown in Section 3 of the SDS transmitted by you. Stated there:

[11] Letter was provided by Helpdesk in German. The english translation is not authorized by Helpdesk.

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Chemical name	Classification
Sulphur tetrafluoride	Compr. Gas Liquef. Gas; H280 Acute Tox 1; H330 STOT SE 3; H335 Skin Corr 1A; H314
Compr. Gas; H280	Compr. Gas; H280

Insofar as you have no reasonable doubts regarding the classification of the substance (or the mixture), it can be assumed that the information in the SDS is correct.

According to the CLP Regulation, the generic and specific concentration limits, multiplying factors and general and specific concentration cut-off values mentioned in the Regulation are to be applied for the classification of a defined mixture containing one or more constituents classified as hazardous. Moreover, where necessary, additive effects must be taken into consideration on the basis of the calculation methods described in Annex I of the CLP Regulation.

The following example on toxicity shows that the classification can be carried out with the criteria in Annex I of the CLP Regulation, based on information regarding the constituents of a mixture. The procedure of self-classification for further hazard classes must be analogous.

In view of the classification of the substance sulphur tetrafluoride given in the SDS as Acute Tox. 1 (H330), you are obliged to determine the so-called ATE value (estimated value acute toxicity) for the classification of the mixture. This value is calculated according to the following formula:
$100/ATEmix = \sum ci/ATEi$
In the safety data sheet at hand, the manufacturer has done so, and the calculated value is shown in Section 11.1. The ATE for the mixture is 1000ppm and the mixture is therefore classified as Acut Tox 3 H331 and labelled with the “skull and crossbones” pictogram (GHS06). You will find information on classification and labelling in Section 2 of the SDS.
The classification of mixtures containing the other substances you mentioned is done as in the example above with sulphur tetrafluoride.

You will find further information on the topic at hand in the “Guidance on the compilation of safety data sheets” provided by the European Chemicals Agency (ECHA).
https://echa.europa.eu/de/guidance-documents/guidance-on-reach

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Please contact the German Federal Ministry of Transport and Digital Infrastructure (BMVI) regarding any questions on transport law and labelling for transport.

The Ministry's internet address is:
https://www.bmvi.de/DE/Themen/Mobilitaet/GueterverkehrLogistik/Gefahrgut/gefahrgut.html

Yours sincerely,

Kristof Seubert

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