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F-GASES

Waste Management Guideline for
Solvents and Waste Management Entities

May 2020

Technical Assistance for Increased Capacity for Transposition and Capacity Building on F-Gases

TR2013/0327.05.01-04/001

CFCU CENTRAL FINANCE & CONTRACTS UNIT

GFA CONSULTING GROUP

List of abbreviations

CFC	Chlorofluorocarbon
CO_2	Carbon Dioxide
CREO	Central Database of Equipment Operators
DBR	Database of Business Reports
EOL	End of Life
EU	European Union
F-gas	Fluorinated Greenhouse Gas
FP	Fire Protection
GHG	Greenhouse Gas
GIS	Gas Insulated Switchgear
GWP	Global Warming Potential
HC	Hydrocarbon
HCFC	Hydrochlorofluorocarbon
HFC	Hydrofluorocarbon
HFO	Hydrofluoroolefin
KDS	Mass Balance System
MoEU	Ministry of Environment and Urbanisation
MoTAT	Mobile Hazardous Waste Tracking System
NH_3	Ammonia
ODS	Ozone Depleting Substance
PFC	Perfluorinated Compounds
RAC&HP	Refrigeration, Air Conditioning & Heat Pump
RRR	Recovery, Recycling, Reclaim
SF_6	Sulphur Hexafluoride
TABS	Hazardous Waste Declaration System
TEAP	Technology and Economic Assessment Panel
WEEE	Waste Electrical and Electronic Equipment
WMA	Waste Management Application

Aim of the Guideline

Fluorinated greenhouse gases (F-gases) increasingly contribute to climate change due to their high global warming potentials (GWP). To decrease its greenhouse gas (GHG) emissions, Turkey is working towards updating its national By-Law on F-gases (hereinafter "F-gas By-law") in line with the Regulation (EU) No 517/2014 (hereinafter "EU F-gas Regulation"). This transition requires a phase-down of the use of F-gases, improved monitoring and reporting, enhanced legal structures and increased national and local capacity.

This guideline is prepared to provide guidance on the proper management of the waste F-gases and/or end-of-life equipment containing F-gases. It is aimed at waste management entities to promote the phase-down and waste management of F-gases from relevant equipment, with emphasis on reclamation and destruction of F-gases recovered from refrigeration, air conditioning & heat pump (RAC&HP), fire protection (FP) and gas insulated switchgear(GIS) sectors.

The information in this guideline is grouped into five sections:

- Main Concepts
- Refrigerator Recycling Plants
- Reclamation Facilities
- Destruction Facilities
- Suggested Reading

1 Main Concepts

F-gases have a high global warming potential (GWP) and therefore contribute to climate change when released into the atmosphere. They denote a group of gases including hydrofluorocarbons (HFCs) and perfluorinated compounds (PFCs). HFCs are widely used in refrigeration and air conditioning equipment and also have some applications such as foam blowing agents, aerosols and in fixed fire protection systems and fire extinguishers. Perfluorocarbons (PFCs) are also used in the latter. The very potent greenhouse gas sulphur hexafluoride (SF_6) is mainly used in gas insulated switchgear (GIS) within the electric transmission and network and power plants.

F-gases must be recovered because they must not be vented due to their climate change impact when maintenance requires the removal of the gas from the product or equipment and before decommissioning. Once recovered, F-gases can be reclaimed, recycled or destroyed.

All entities working with F-gases will benefit from an efficient recycling and reclamation process. Given the phase-down objectives, the supply of virgin F-gases will gradually and significantly decrease, leading to price increases and the necessity of an increased share of reclaimed F-gases. Therefore, it is of great significance to recycle or recover F-gases to the extent feasible. Moreover, reclaimed and recycled HFCs will likely not be covered by the phase-down requirements.

The F-Gas By-law states the following basic principles of control in relation to waste F-gases and for end-of-life equipment containing F-gases:

- ! Venting of F-gases is banned (Article 6-1.a).
- ! Acceptance of equipment at recycling or disposal facilities is banned unless F-gases are recovered before sending (Article 6-1.c).
- ! Leak checks of the product or equipment are carried out by users who hold a certificate. Following the establishment of the central database, it is obligatory to enter the information related to leakage controls into the central database (Article 8/6).
- ! Natural and legal persons who conduct recovery, recycling, reclamation or destruction of F-gases are required to register in the database of business records following its set-up and must report on the respective amounts. (Article 10-1.b).*

*According to the new F-Gas Regulation that will be published as a result of transposition of EU F-Gas Regulation 517/2014, equipment operators will be responsible to register to the Central Registry of Equipment Operators (CREO) for electrical switchgear equipment containing 6 kg or more of SF_6; while importers, exporters, users and distributors of F-Gases and equipment containing F-Gases, will be responsible to report annually to the Database of Business Reports (DBR).

In addition, a monitoring scheme of F-gas amounts used in Turkey is being developed as a part of the F-gas regulation. It will be operational once the Database of Business Reports (DBR) is launched. Waste appliances containing F-gases are covered by the waste electrical and electronic equipment (WEEE) regulation with take-back obligations for end-of-life equipment containing F-gas.

Some of the terminology for waste F-Gases may differ from the general waste management terms. To make the distinction, concepts related with waste F-Gases used in this guideline are explained in the box below.

F-gas By-law defines Recovery, Recycling, Reclamation (RRR) and Destruction (Article 5)

Recovery: Removing F-gas in any condition from a system and storing it in an external container.

Recycling: Reuse of a recovered F- gas following a basic cleaning process to reduce contamination (usually by filling it back into the same system).

Reclamation: Processing recovered F-gas to match the equivalent performance of a virgin substance and verifying by analysis of the F-gases that new product specifications have been met.

Destruction: Transformation or decomposition of gas or fluid in one or more substances which are not fluorinated greenhouse gases anymore.

Collection Infrastructure

The development of reclamation and destruction capacities only makes sense, when a robust collection system for equipment and F-gases is set up simultaneously. For F-gases, this means that technicians need to have easy access to collection points and questions around the issue on who pays for the collection and destruction are solved. In many EU member states a so-called reverse logistic system is implemented via gas distributors, obliging them to take back used F-gases. Such systems are sometimes linked to a deposit and (partial) refund system, where the amount refunded is linked to the quality of the returned F-gas. Collecting substances separately in clean cylinders is thus good practice and a precondition for reclamation with reasonable effort.

Waste F-gases should be reclaimed and reused where possible. See Figure 1 and Figure 2 for flow charts of recovery, recycling and reclaim (RRR) and destruction. In case that it is not feasible to do so, F-gases must be sent in bulk to waste disposal facilities with specific licence for F-gas destruction.[1]

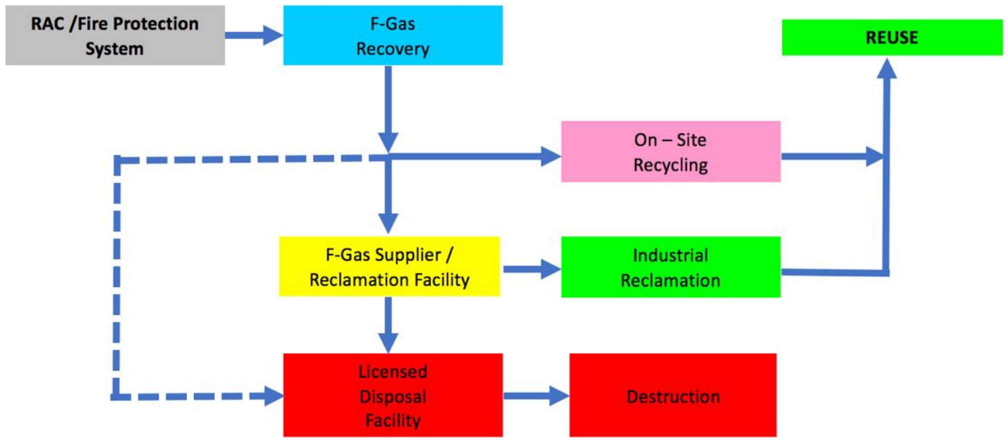
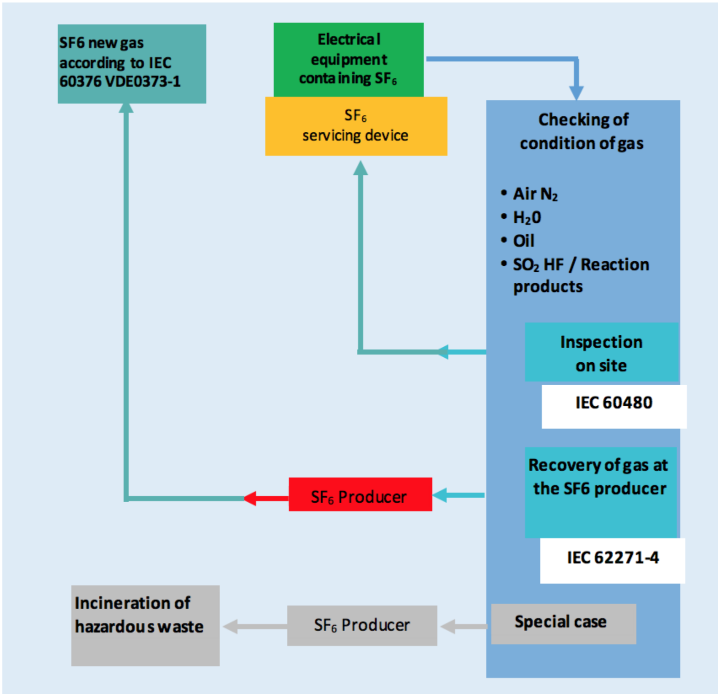


Figure 1. Flow chart of RRR and Destruction for RAC&HP and FP Equipment



Source: Solvay Fluor

Figure 2. Flow chart of RRR and Destruction for Switchgear with SF_6

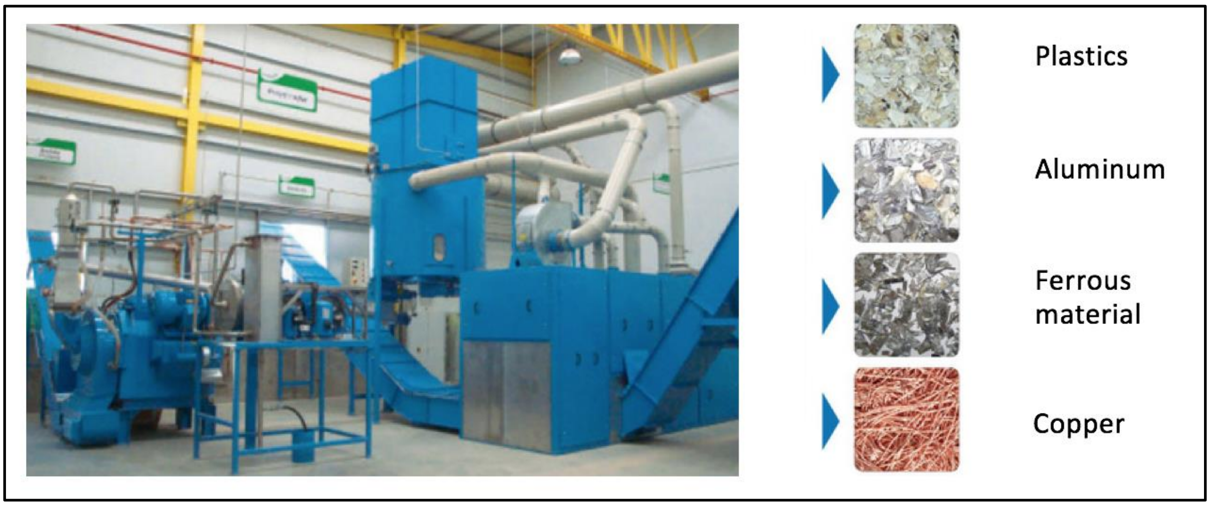
[1] In Turkey there is currently no reclamation facility for F-gases. There are two facilities running tests on SF_6 recycling. One large hazardous waste facility in Turkey accepts F-gases for destruction. However, this facility seems to have limited capacity on treating F-gases in their plant, as they also set F-gases abroad for destruction.

2 Refrigerator Recycling Plants

The state-of-the-art treatment for waste refrigerators and freezers is a 2-staged approach, where in the first stage the refrigerant is recovered by automated pumps and in the second stage, the refrigerator casing is shredded in an encapsulated system, enabling the recovery of the blowing agent released by shredding the insulation foam. The shredded particles are sorted to several fractions, e.g. metal (aluminum, ferrous material, copper), plastic and foam, which are usually recycled. This treatment avoids the release of F-gases to the atmosphere and is compulsory in the European Union.

Appropriate equipment for refrigerator recycling

After cutting off cords and taking out the glass shelves, a conveyor belt transports the waste fridges to the stage 1, where the refrigerant circuit is opened by a drilling device that minimizes leakage and recovers the refrigerant and the oil contained in the circuit. Oil and refrigerants are separated, and recovered refrigerants range from CFC-12 to HFC-134a to HC-600a. They are often collected together in one container and destroyed in a separate step. Due to the flammability of HC-600a, safety measures are needed such as avoiding ignition sources and good ventilation. The conveyor belt then takes the refrigerators into the encapsulated shredder. Possible blowing agents that are released from the insulation foam during the shredding are CFC-11, HCFC-141b or pentane. Since pentane is flammable, the shredding needs to be done under a protective atmosphere. After the shredder the components are sorted. A fridge usually contains about 48% ferrous material, 22% plastic, 20% foam, 5% aluminum and 2% copper[2]. The remainder are the refrigerant, glass shelves, etc. See Figure 3 below.



Source: Adelmann[3]

Figure 3. Refrigerator Recycling Plant

[2] https://eldan-recycling.com/sites/default/files/BR_REFRIGERATOR_1804_EN_high-180409.pdf

[3] Adelmann Recycling Plant For White Ware And Electronic Scrap RPWW/ES
https://www.adelmann.de/lieferprogramm/recyclinganlagen/kuehlgeraete-und-elektroschrott-recyclinganlage-rpwwes.html

To assess the quality of refrigerator recycling, a detailed guideline and testing specifications was issued by the German RAL Quality Assurance Association for the Demanufacture of Refrigeration Equipment[4] in 2007. This document lays down detailed requirements specifically for the recycling of refrigerators and freezers. It includes test specifications and monitoring requirements and establishes minimum recovery amounts of 115 g refrigerant per fridge and 283 g blowing agent from the foam[5].

Recovered F-gas amounts are tracked by the Database of Business Reports (DBR), presently being set up by the MoEU. Entities carrying out recovery (and reclaim or destruction) of F-gases have to report their quantities annually by 31 March for the preceding year.

3 F-gas reclamation

Reclamation facilities are usually situated at gas producers' or gas distributors' sites[6] and separate oil, acid, moisture and hard particle contaminants through special methods that pump the substances into separation chambers. These units generally have average capacities of around 2.5 kg/min. Blended refrigerants are separated into their components by fractionating columns.

Refrigerant reclamation includes treatment of used and recovered refrigerants in order to meet the same specifications that are valid for virgin substances (DIN 8960; AHRI-700).

An analysis as to the viability of refrigerant submitted for reclamation is the first part of the process. The first task is to weigh the cylinder to determine the volume of refrigerant inside. Subsequently, the content of each cylinder is determined by means of hand-held gas analysers or, more accurately, by using a gas chromatographer.

Once the content of the returned cylinder is determined, decisions about the further treatment are to be taken. A variety of treatments is basically possible including e.g. separation or dilution. While theoretically most recovered refrigerants could be reclaimed, time and resource constraints typically apply in practice and determine the extent of processing recovered gases.

The following rules apply at major reclamation facilities in Germany:

- If the purity of the refrigerant is lower than 99% (i.e. more than 1% of a different refrigerant type is contained in the cylinder): Destruction by thermal decomposition
- If the purity of the refrigerant exceeds 99%: Further reclamation steps

Depending on the level of contamination and pressure of the materials, recovered refrigerants are consolidated into different bulk tanks for different reclamation procedures.

The effort required for reclamation depends on the condition of the recovered gas. A collection system that encourages collecting substances separately in clean cylinders can is thus good practice.

As for refrigerants, a common method for reclamation is distillation to make sure that non-refrigerant contaminants (oil, metal shavings, acids, moisture, non-condensables) normally found in recovered

[4] Quality Assurance and Test Specifications for the Demanufacture of Refrigeration Equipment, www.ral-online.org

[5] The given numbers are stated for CFCs, but similar values can be expected HFCs.

[6] At present, no reclamation facility for F-gases is known in Turkey.

refrigerant will be removed. The distillation process itself consists of boiling the refrigerants to assist in separating out the non-condensables and oils. The distillation process takes advantage of the fact that the different refrigerants will have different boiling points. The composition typically needs to be adjusted as often one or more components do not meet the blend specification.

Depending on the degree of pollution, additional processes are needed to bring multi-refrigerant mixtures (e.g. R404A, R410A) back to original purity standards.

Once the refrigerant is at the right purity level, it is dried using desiccants to bring its moisture level to the specifications. The process is rather complicated due to the high number of fluorochemical mixtures composed of single component refrigerants and blended refrigerants. If needed, additional quantities of the blend components are added to the cleaned refrigerant mixture to dilute the unwanted component out (below 0.5%). As cost constraints apply, the virgin quantities added would typically range at 1-4%.

Furthermore, it is possible to re-blend substances by adding an adequate amount of the required refrigerant. For example, if the recovered gas consists of a high share of R410A and a small share of R134a it would be possible to add more R134a in order to obtain R407C. This, of course, would only be applied if the resulting blend could be sold (more) easily.

Depending on production cost for virgin substances and efforts needed for reaching high-quality reclaimed F-gases, reclamation can be a business case. For example in Germany, there is a very well-established system in place for SF_6 which is run by Solvay, the manufacturer of SF_6. Contaminated SF_6 that is recovered from equipment is analyzed and either reused together with virgin SF_6 or sent for thermal destruction, depending on the degree of contamination.

4 F-gas Destruction

As mentioned above, RRR should be the first choice of action for all waste F-gases. Destruction should be considered as the last resort, in cases where the gas is too contaminated to be reclaimed or the use of it is completely banned by legislations (as it is the case for most ODS). Figure 4 shows some technical options for the F-gas destruction. The needed capacity for destruction strongly depends on the successful implementation of the mandatory recovery of F-gases and effective collection systems. At present limited quantities of F-gases are destructed at a hazardous waste facility in Turkey while other (small) quantities are exported for destruction.

Local stationary destruction plant	Rotary Kiln / Cement kiln	Mobile Destruction Plant	Export for destruction
• New facility or increase capacity of existing facility • If high amounts of waste F-gases are expected for a longer time period • High investment cost for new facilities	• Adaption by installing a feeder for liquid waste directly to flame • Attractive alternative (lower investment costs) • Destruction rate depends on cement production • Ensure temperatures > 1200°C	• For areas with low urbanisation to avoid extended transport logistics • Can be attractive for a group of countries	• Option for lower amounts of F-gases • Basel convention on transboundary movement of hazardous waste adds bureaucratic burden

Figure 4. Options to Deal with Waste F-gases

Promising options for HFC Destruction

There is currently little data on HFC destruction available, as most refers to Ozone Depleting Substance (ODS) such as CFC and HCFCs. In 2018, Technology and Economic Assessment Panel (TEAP) published a task force report on destruction technologies for controlled substances[7], in which the destruction of HFCs were discussed. Technologies considered as an option for HFC destruction are approved destruction technologies for ODS only. Those options were approved based on a set of criteria, the most prominent being their destruction and removal efficiency (DRE), where TEAP defined > 99.99% as threshold for concentrated sources[8]. In their cases, compatibility is assumed because of the similarities between chlorofluorocarbons (CFC), hydrochlorofluorocarbons (HCFC) and HFCs.

Due to the higher fluoride content of HFCs compared to HCFC, the formation of fluorine containing dioxins has to be carefully avoided by e.g. limiting the amount of HFC input into the destruction process.

Promising options are a porous reactor, because it enables effective and complete destruction reaction and rotary kiln furnaces that are often already used in hazardous waste incineration facilities. The utilisation of municipal solid waste incineration is only advisable for the destruction of foam blocks in state-of-the-art incineration plants to prevent negative environmental impact. If cement kiln operators are open to adjust their plants for HFC destruction, this can be a very cost-effective way of destruction.

[7] TEAP 2018 – Volume 2 Decision XXIX/4 TEAP Task force report on destruction technolgies for controlled substances. https://ozone.unep.org/sites/default/files/2019-04/TEAP-DecXXIX4-TF-Report-April2018.pdf

[8] TEAP 2002 - Volume 3B – Report of the task force on destruction technologies. https://ozone.unep.org/sites/default/files/2019-05/TEAP02V3b%20%281%29.pdf

In a **porous reactor**, HFCs are broken down into usable components such as hydrogen fluoride (HF). The destruction takes place in an oxidizing atmosphere and under a controlled input of natural gas at very high temperatures. The destruction is not taking place in a flame but is supported by the porous and inert matrix with excellent heat transfer properties of the reaction chamber. This means that the HFCs have a longer residence time in the destruction zone compared to the destruction with a flame, allowing for a more complete reaction. The products of the reaction are CO_2, HF and water vapour. The material of the porous matrix is made from graphite, which is resistant to corrosion through the acids[9].

Rotary kiln furnaces are mainly used for the incineration of hazardous waste. They are often operated by public waste management authorities, but to great extend also by private entities, in particular in the chemical industry. A modern hazardous waste incineration plant typically comprises a rotary kiln furnace followed by a high temperature post-combustion chamber, a boiler for energy recovery and an air pollution control system for emission control. Rotary kiln incinerators are operated at 1,200°C and a residence time of 2 seconds. The high temperature has to be maintained by several burners fueled by natural gas, propane, oil or high calorific gaseous production residues. The high temperature level makes rotary kiln combustion an appropriate tool for HFC destruction. Gases are easily injected into the feeding line of the main burner and foams can be introduced along with the solid waste via the feeding chute. To avoid HF corrosion of the refractory cladding of kiln and combustion chamber the fluorine input by HFCs has to be limited.

Cement kilns often provide a cost-effective possibility for HFC destruction. Adjustments of cement kilns are easy and relatively cheap. A closed area for the reception and storage of refrigerant cylinders is necessary, where cylinders can be stored at ambient temperature. Further, a dosage area has to be established from where the gases can be injected into the kiln. These can include a water bath to facilitate the extraction of the gas, a system of manifolds and gauges to attach the cylinders to the kiln (via a pressure regulator and automatic control panel), a vacuum pump to fully recover the gas from the cylinder and other items such as filter systems, insulating materials and scales for cylinders. The mass flow and the related overall content of fluorine needs to monitored to prevent adverse influence to the cement quality.

Options for SF_6 Destruction

SF_6 can be destroyed at a thermal process operating at > 1150°C. Under the influence of energy, the SF_6 molecule can form highly toxic or corrosive substances that are harmful to health. The thermal destruction methods described above are applicable in principle, except for cement kilns.

[9] Brandt, M.; Aubel, T.; Hasender, R.; Härtel, G.; Franz, M. (2006). Porenbrenner spaltet FCKW. Chemie Technik November 2006.

5 Suggested Reading

- By-law on Fluorinated Greenhouse Gases (Official Journal No. 30291, dated 04.01.2018)
- By-law on Waste Management (Official Journal No. 29314, dated 02.04.2015)
- By-law on Waste Electric and Electronic Equipment (Official Journal No: 28300; dated 22.05.2012
- Waste Management Web Application https://ecbs.cevre.gov.tr
- Users Manual on Waste Declaration System https://cevreonline.com/atik-beyan-sistemi-kullanim-kilavuzu/
- Communique on the Transport of Waste by Road (Official Journal No: 29301; dated 20.03.2015)
- Regulation (EU) No 517/2014 of the European Parliament and of the Council of 16 April 2014 on Fluorinated Greenhouse Gases and Repealing Regulation (EC) No 842/2006
- TEAP 2018 – Volume 2 Decision XXIX/4 TEAP Task force report on destruction technologies for controlled substances https://ozone.unep.org/sites/default/files/2019-04/TEAP-DecXXIX4-TF-Report-April2018.pdf
- TEAP 2002 - Volume 3B – Report of the task force on destruction technologies. https://ozone.unep.org/sites/default/files/2019-05/TEAP02V3b%20%281%29.pdf
- Adelmann Recycling Plant For White Ware And Electronic Scrap RPWW/ES https://www.adelmann.de/lieferprogramm/recyclinganlagen/kuehlgeraete-und-elektroschrott-recyclinganlage-rpwwes.html
- Brandt, M.; Aubel, T.; Hasender, R.; Härtel, G.; Franz, M. (2006). Porenbrenner spaltet FCKW, Chemie Technik, November 2006.
- https://eldan-recycling.com/sites/default/files/BR_REFRIGERATOR_1804_EN_high-180409.pdf
- Quality Assurance and Test Specifications for the Demanufacture of Refrigeration Equipment, www.ral-online.org
- The SF6-ReUse-Process, Solvay Fluor https://www.solvay.com/sites/g/files/srpend221/files/tridion/documents/SF6-ReUse-Process.pdf

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