In focus...

F-Gas reclaim, regeneration and destruction

Avoiding greenhouse gas emissions from spent refrigerants and specialty gases

By Stephen B. Harrison, sbh4 consulting

F-Gases are fluorinated hydrocarbons. Many, such as halocarbon 14, or CF_4 are used extensively in semiconductor processing. Others are used for industrial, commercial, and domestic refrigeration applications.

R404A, which is a blend of three different F-Gas molecules, is used in commercial refrigeration to enable the chilled and frozen food supply chains. Difluoromethane, or R32 which has the formula CH_2F_2, is gaining favour as a refrigerant gas in domestic and commercial air conditioning units.

F-Gases are also commonly used for mobile air conditioning in buildings and cars. For example, R134a and R1234yf are the two main automotive air conditioning gases that have been used in recent years.

Heat pumps can support the energy transition from fossil fuel heating to the use of renewable electricity. They use F-Gases in their circuits to capture low-grade heat from ambient air and upgrade that to usable warmth in our homes, hotels, and offices.

Global warming potential and environmental concerns

The release of F-Gases to the air represents wastage of a valuable chemical. Furthermore, many are extremely potent greenhouse gases (GHGs) with high global warming potential (GWP). Their intentional release to atmosphere is prohibited and highly regulated in most countries. This has led to the development of sophisticated reverse supply chains for F-Gas recovery and re-processing.

In some refrigeration applications, F-Gases can be replaced by so called 'natural refrigerants' such as propane, carbon dioxide and ammonia. Natural refrigerants have lower GWPs than most F-Gases and are therefore considered to have some environmental benefits.

However, in some applications these 'natural refrigerants' are less efficient than their equivalent F-Gas refrigerant and the electrical power requirement for the refrigeration equipment running on the natural refrigerant is increased. In turn, this puts stress on the power grid and can result in extensive greenhouse gas and pollutant emissions from fossil fuel power generation. Therefore, it is likely that F-Gases will co-exist in parallel with the emerging natural refrigerants.

Onsite F-Gas regeneration in the refrigeration sector

The circular economy means re-using materials and reprocessing chemicals. The idea is to minimise the use of energy and conserve limited resources. The hierarchy of waste management advocates re-use and recycling ahead of destruction. The refrigerant distribution sector has implemented this circular approach for decades.

Recovery and regeneration of F-Gases is common practice in the refrigeration sector. Many refrigerant gas distributors and wholesalers offer gas cylinders so that refrigeration contractors can collect spent refrigerant gases from industrial and commercial refrigeration systems. In many cases, these F-Gases can be cleaned or re-processed for subsequent re-use.

The most basic form of refrigerant gas recovery takes place during maintenance of the refrigeration equipment. No waste material is transferred from the site where the service is taking place. The refrigeration contractor will use clean cylinders provided by a refrigerant gas distributor to decant the refrigerant gas into whilst the refrigeration equipment is serviced.

When the mechanical repairs to the refrigeration system are complete, the refrigerant gas is returned to the system. If required, additional fresh refrigerant gas can top-up the system up to the required level. The empty 'decant' cylinders are then returned to the refrigerant gas distributor to be cleaned up so that they can be used again for a similar purpose.

As an enhancement to the above decant process, the refrigerant can be cleaned up on site whilst it is withdrawn from the system. Refrigerants become contaminated with lubrication oils from the compressor and moisture during use. These reduce the efficacy of the refrigerant blend. Rust particles from pipework can also accumulate in the refrigerant. Nitrogen and other inert gases also contaminate the refrigerant gas.

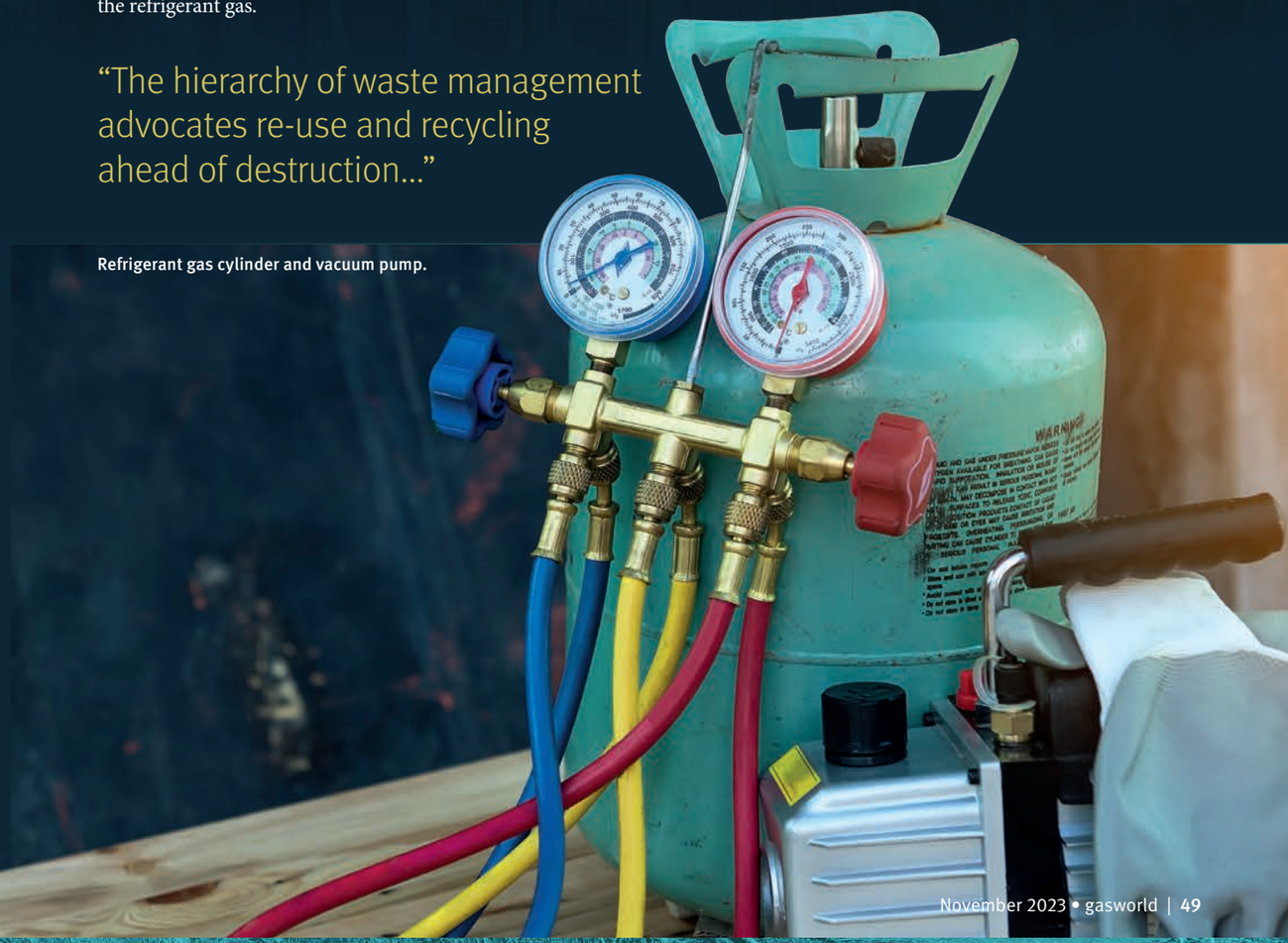
> "The hierarchy of waste management advocates re-use and recycling ahead of destruction..."

Hudson Technologies, based in the US, has innovated specialised equipment to remove inert gases, oils, particles, and water from the refrigerant gas before it is returned to the refrigeration equipment. Using the clean refrigerant requires less electricity and the operating cost savings for the operator can be significant.

Automotive repair shops can use portable versions of this type of equipment to regenerate refrigerant gases from car air conditioning systems. An example is the RRDQ-V1 offered by Daikin. Heating and ventilating engineers can also use similar on-site refrigerant regeneration equipment to clean up F-Gases in stationary air conditioning systems.

F-Gas recovery and re-processing

If the refrigerant gas cannot be regenerated on-site, the F-Gas may need to be recovered and transferred to a central location for more sophisticated re-processing. In this case, the refrigeration contractor would recover the refrigerant



Refrigerant gas cylinder and vacuum pump.

Refrigeration engineer installing a Daikin system.

gases from the system into empty cylinders that they have obtained from a refrigerant gases distributor. These recovery cylinders containing the 'old' refrigerant gas are then returned to the distributor for re-processing.

The simplest form of re-processing involves oil and water separation, inert gas removal and particulates filtration. This level of regeneration can be performed using readily available refrigerant processing equipment such as PCU's Refrigerant Recycling Systems. Many refrigeration wholesalers or distributors can purchase and operate such equipment since it is affordable and simple to use. The distributor benefits from the possibility to re-sell the reclaimed refrigerant gases: an embodiment of the circular economy.

The peak of the refrigerant recovery and regeneration technology is distillation of recovered refrigerant gas mixtures. Many refrigerants, such as the popular R404A, R407C and R410A are blends of more than one F-Gas molecule. During use the composition of the refrigerant gas blend drifts from the optimum composition meaning that the refrigeration system performance and efficiency are compromised.

Distillation of refrigerant gas mixtures can yield the pure molecules from which the blends were made. These pure refrigerant gases can be re-blended to any required formulation and re-sold to the market. Installation of such distillation equipment is capital intensive, and its operation and the subsequent refrigerant re-blending requires a high degree of technical expertise.

In Europe, only a few of the leading refrigeration distributors such as A-Gas in the UK and Netherlands, Tazzetti in Italy and BOC Gases in the UK operate such distillation and re-blending equipment. Analysis and certification of the new blend is also required to guarantee the quality of the regenerated product.

> "F-Gases are similarly robust chemicals that require specialised processing at high temperature to ensure they can be disposed of in a sustainable way"

End of life destruction

Some recovered F-gases may be heavily contaminated, or they might be an older chlorinated refrigerant (CFC or HCFC) which is no longer permitted to be used. In these cases, their safe and environmentally friendly destruction is essential. In fiscal year 2021, Daikin Group in Japan destroyed more than 400 tonnes of refrigerant gases through their reclaim and destruction business.

Fluorine, which is used to make F-Gases, is an exceptionally reactive element. When it binds to carbon atoms the bonds are very strong. Fluorinated polymers that are used as plastics and foaming agents are sometimes referred to as 'forever chemicals' since they are very persistent in the environment.

F-Gases are similarly robust chemicals that require specialised processing at high temperature to ensure they can be disposed of in a sustainable way. Plasma is one way of producing very high temperatures and energy to safely destroy F-Gases.

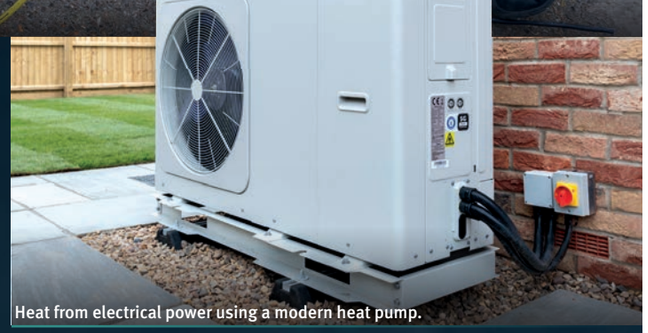
Some waste management facilities and cement kilns are licensed to process hazardous wastes such as F-Gases. A high temperature rotary kiln with a natural gas- or pulverised coal-fired burner is a highly effective means of destroying F-Gases. The F-Gases are introduced in small quantities and are co-incinerated along with the main fuel.

However, where F-Gases are co-incinerated with other waste or fuels, careful monitoring and mitigation of the flue gases must take place to avoid emissions of toxic pollutants. It is possible that dioxins can be formed as the halogens from the refrigerant gas recombine with hydrocarbons. Acid gas emissions must also be avoided. Scrubbers are the most common means to capture and avoid these pollutant emissions.

© GeneralGas | **Solstice N40 (R448A) KryonLight refrigerant gas cylinder.**

Refrigeration engineer installing a heat pump.

"Incineration of F-Gases generates hydrogen fluoride (HF). Other halogens such as chlorine and bromine may also be present..."



Heat from electrical power using a modern heat pump.

A water-tight solution from Selas-Linde: Sub-X® thermal oxidiser

Incineration of F-Gases generates hydrogen fluoride (HF). Other halogens such as chlorine and bromine may also be present in refrigerant gases and these generate similar acidic pollutant gases. To avoid the release of these gases to the atmosphere, a technology known as 'submerged combustion' can be used.

In 2019, seven submerged combustion systems were in use worldwide for hazardous waste destruction. In this process, the gases to be destroyed are introduced directly into a flame or plasma at the top of a vertical cylindrical incineration chamber. Oxyfuel combustion can be used to generate high temperature flames for incineration. Argon plasma is also used to generate the high temperature heat required in this process. The waste F-Gases are converted to carbon dioxide and HF as they are incinerated.

At the base of the cylinder, the gases flow through a quench bath of water. This simultaneously cools the gases and captures the HF. The water with the acidic gases dissolved in it is treated with lime ($CaCO_3$). Fluorite (CaF_2) is formed through the reaction of lime with HF. Fluorite is a natural mineral and the main ore that is used to create F-Gases.

Selas-Linde's submerged exhaust Sub-X® oxidiser is an example of a submerged combustion system which is ideal for F-Gas destruction and other halogenated wastes. It is designed to operate with maximum destruction efficiency (DE) and high operational availability. The Sub-X® mitigates the risk of acid gas pollution during the destruction of aqueous waste. gw