Freezing for pollution prevention

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The eutectic freeze crystallisation (EFC) unit designed and built by Prentec at the Tweefontein Colliery in Mpumalanga, based on research done at UCT's chemical engineering department. Much of the research was funded by the Water Research Commission.

As the need to protect the planet – and the life-support systems on which we depend – is recognised worldwide, tighter restrictions are being imposed on the quantity and quality of effluents and emissions generated by industry. The race is on to find sustainable and cost-effective ways of removing contaminants from these waste discharges. Here, *Quest* reviews some innovative technologies that use freezing for this purpose.

Eutectic freeze crystallisation

Industries producing highly contaminated effluent are required to treat these effluents to a set standard before either releasing them into the environment, sending them to a municipal wastewater treatment works, or reusing them in some way. This typically involves a number of membrane filtration steps, often culminating in reverse osmosis to separate out the dissolved salts, metal ions and other minute particles. In the process, these contaminants are concentrated into a highly saline brine, which presents a disposal problem. Usually brines are discharged into evaporation ponds, but these take up a lot of space and risk contaminating groundwater if the lining fails.

In 2007, researchers in the chemical engineering department at the University of Cape Town began investigating a novel technology to deal with these brines, while also recovering the salts for other purposes. The technology, called eutectic freeze crystallisation (EFC), involves cooling down the brine to its eutectic point – the lowest temperature at which it can exist in the liquid phase. Beyond that, the water in the brine crystallises out as ice, which floats on the surface, and the contaminants crystallise out as salts, which sink to the bottom.

Individual salts can be recovered, because each has its own unique temperature at which it will crystallise out in a particular mixture. During one laboratory experiment using brine from a coal mine, for example, the research team recovered calcium sulphate – more commonly known as gypsum – as well as sodium sulphate. Apart from being the material from which ceiling boards, drywall and plaster are made, gypsum is also used as a fertiliser in agriculture and as a filler in dentistry and orthopaedic surgery. Sodium sulphate is a key ingredient of soaps and detergents, but it is used in the production of paper, glass, textiles and a variety of other materials too.

Prof. Alison Lewis, who leads the team in the department's Crystallisation and Precipitation Research Unit, explains that work on EFC started overseas in the 1950s. Although it was

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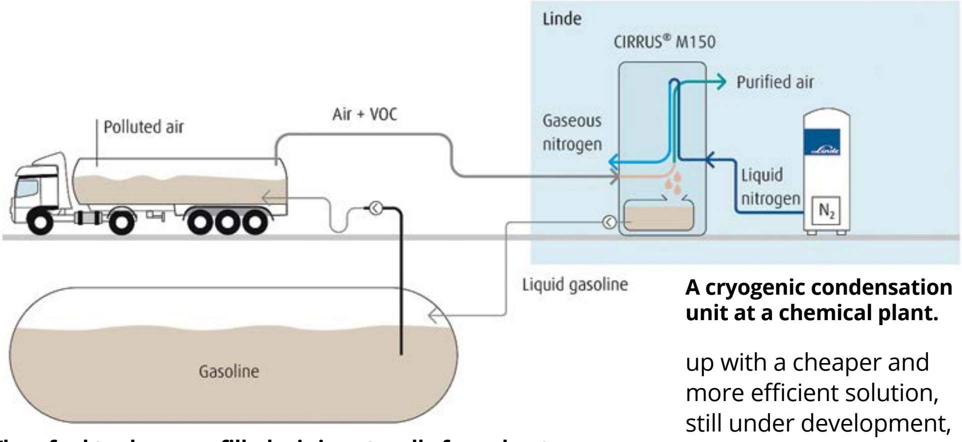
Prof. Alison Lewis (far left) and postgraduate students at the commissioning of the EFC pilot plant at Eskom's Research and Innovation Centre in April 2016.

found to be technically feasible, freezing was too expensive then to make it financially viable. Modern-day compressors have improved the outlook, but capital costs still make it prohibitively expensive. Nevertheless, Eskom commissioned a pilot plant at its Research and Innovation Centre at Rosherville in April 2016, and investigations are continuing. A larger system was also installed in 2017 at Glencore's Tweefontein Colliery, but the feed stream was found to be too dilute for effective use of EFC. It is anticipated that research will resume once the process has been modified to concentrate the brine.

Cryogenic condensation

Many industrial processes also emit volatile organic compounds (VOCs), which are organic compounds – containing carbon – that readily produce vapours at room temperature. These are released as gases into the air, where they may react in sunlight with nitrogen oxides to form ground-level ozone and photochemical smog. Common products such as paints, inks, varnishes, glues and solvents release VOCs, some of which are toxic and carcinogenic. The manufacturing of these and other



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When fuel tankers are filled, air is naturally forced out. In some countries, fuel depots are obliged by emission regulations to prevent these fumes from escaping into the environment. Cryogenic condensation units can treat the fumes by condensing out the volatile organic compounds. These recovered VOCs can then be recycled.

Afrox/Linde

A cryogenic condensation unit at a chemical plant.

chemicals for both home and industrial use accounts for some of the emissions of VOCs, but any burning of fuel – including petrol, diesel, coal, natural gas and wood – releases VOCs. This means that power plants, refineries, smelters, factories, vehicles and even veld fires all contribute to atmospheric levels of VOCs.

Since VOCs pose a threat to human health and the environment, air quality legislation typically includes standards for VOC emissions with which facilities must comply. Cryogenic condensation is a cost-effective way of reducing VOC emissions. By cooling the exhaust gas stream with liquid nitrogen, and hence lowering the vapour pressure, the volatile components condense and then freeze.

Depending on the composition of the exhaust stream and the selected temperature, which can be adjusted by controlling the flow rate of the liquid nitrogen inside the cryogenic condensation unit, VOCs can be recovered as either liquids or solids. These can then be stored for safe disposal, reuse or sale. Recovery performance is typically better than 99%, so even stringent emission standards can be met. The liquid nitrogen used for cooling does not come into contact with the exhaust stream, so it does not become contaminated. In the process it is fully vaporised into nitrogen gas, and can either be released into the air (remember that 78% of air is made up of nitrogen) or captured for reuse in other processes within the facility.

Cryogenic condensation systems can cope with fluctuating flow rates and VOC concentrations in mixed exhaust streams, and they do not produce any harmful by-products because the process relies simply on phase change. Modular systems of different sizes are available, so cryogenic condensation is even used for controlling VOC emissions from tanker trucks and ships.

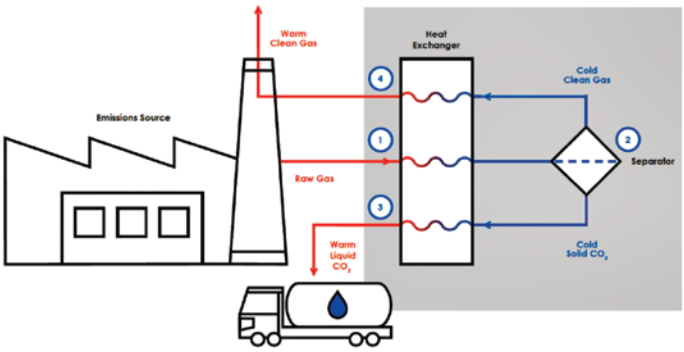
Cryogenic carbon capture

Coal-fired power plants are a major source of emissions of carbon dioxide (CO_2), the primary greenhouse gas contributing to global warming. Various technologies exist to reduce these emissions, but a chemical engineering professor at Brigham Young University in Utah, USA, came up with a cheaper and more efficient solution, still under development, called cryogenic carbon capture (CCC).

Prof. Larry Baxter's CCC technology freezes the CO_2 out of the exhaust gas as dry ice – the solid form of CO_2. By cooling the CO_2 to approximately −140°C, the gas transforms into the solid without passing through the liquid phase, which is known as desublimation. The dry ice is then separated from the non-condensible gases, typically nitrogen. Both the dry ice and the cold nitrogen are used in recuperative heat exchangers to assist in cooling down the incoming waste stream. During the recuperative step, the dry ice melts, forming liquid CO_2 that is delivered at ambient temperature. This so-called 'captured' CO_2 can be used in many applications, including biofuels production.

The CCC technology has the potential to reduce carbon emissions from coal-fired power plants by 95–99% at half the cost and energy of alternative carbon capture technologies. In addition, the process removes other pollutants such as sulphur oxides, nitrogen oxides and mercury. The remaining gas is nearly pure nitrogen, and can be safely released to the atmosphere.

Prof. Baxter co-founded a start-up with his son to commercialise the CCC technology. Sustainable Energy Solutions has to date been funded mainly by government grants, as the technology would help the USA reach its targets for emissions reduction. Promising results were achieved in tests conducted at a power plant during 2019, and the intention is to scale up to a pilot plant soon.



Sustainable Energy Solutions

The CCC process (1) cools a dirty exhaust gas stream to the point that the CO_2 freezes, using mostly heat recuperation, (2) separates solid CO_2 as it freezes from the clean gas, (3) melts the CO_2 through heat recuperation and pressurises it to form a pure liquid, and (4) warms up the clean, harmless gas before releasing it to the atmosphere.

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