

Figure 1. Diagram of Air Liquide's high GWP membrane separation technology.

The magnesium and semiconductor industries use and emit significant quantities of high global-warming potential (GWP) gases (e.g., SF_6 , CF_4 , C_2F_6 and C_3F_8). High GWP gases such as perfluorocarbons (PFCs) and SF_6 are potent greenhouse gases; one metric ton of PFCs is equivalent to 6,500-9,200 Mt of carbon dioxide in terms of its potential effect on global warming; SF_6 is the equivalent of 23,900 Mt of carbon dioxide. In addition, these compounds have extremely long lifetimes in the atmosphere (3,000-50,000 years). For the past 15 years, through international efforts to decrease ozone-depleting substances in the atmosphere, industry has been engaged in activities to reduce emissions and find alternatives. One method of decreasing the emissions of high GWP gases from these industries is to recover and recycle these chemicals. Three recovery-and-recycle technologies are being investigated and evaluated: membrane separation, cryogenic capture, and pressure swing absorption.

System Concepts

- These technologies may be designed to treat exhaust streams from large magnesium firms and semiconductor processes.
- All recovery-and-recycle technologies require exhaust pretreatment to remove corrosives (such as hydrofluoric acid) and particles and moisture from the exhaust gas stream.
- The remaining PFCs and/or SF₆ are recovered, concentrated, and "bottled." On-site bottled PFCs may be either mixtures or highly purified. Captured SF₆ may be reused on-site for magnesium melt protection.

Representative Technologies

- Praxair/Ecosys and Edwards: cryogenic capture.
- Air Liquide and Air Products: membrane separation.
- MEGASORB and BOC: pressure swing.

Current Research, Development, and Demonstration

RD&D Goals

• To develop and demonstrate a cost-effective, universally applicable recovery-and-recycle technology (all fabrication facilities and all high GWP gases) that can yield "virgin"-grade high GWP gases for semiconductor fabrication or magnesium plant reuse or sufficiently pure high GWP gases for further use or purification elsewhere.

RD&D Challenges

- Development of a method for universal pretreatment.
- Capital and operating costs are high relative to other alternatives to reduce emissions, and only appear justifiable when recovery-and-recycle systems are applied to large portions of waste streams of large fabricating facilities or plants.
- As other high GWP emission-reducing technologies are considered and implemented, the viability of recovery-and-recycle systems and further investigation of those systems is reduced. This occurs because as high GWP gas concentrations in waste streams become lower, the technical challenges for separation and repurification increase as does the cost.

RD&D Activities

- Six systems have been tested at fabrication facilities, which demonstrated that cryogenic capture and membrane separation show promise.
- Air Liquide's membrane technology underwent an extended a successful evaluation at a U.S. primary magnesium producer demonstrated 41% reduction in SF₆ emissions.
- DuPont is investigating the requirements for collecting, repurifying, and/or disposing of C_2F_6 .

Recent Progress

- The Praxair/Ecoys (cryogenic capture) system has shown emission-reduction capabilities of up to 99% for C_2F_6 , CHF₃, and SF₆, and up to 75% for CF₄.
- The Edwards (cryogenic capture) system has shown capture efficiencies that exceed 90%.
- Both the Air Liquide and the Air Products systems (membrane separation) have capture efficiencies of 96%-98% for C₂F₆, CF₄, and SF₆, when NF₃ and CHF₃ were first removed. Recovery efficiencies for NF₃ and CHF₃ varied between 30% and 60%, with CHF₃ being as low as about 30%.
- The MEGASORB and BOC systems (pressure swing) have shown low capture efficiencies, approximately 1% for the BOC system.

Commercialization and Deployment Activities

- Both cryogenic capture and membrane separation technologies have received encouraging press reports from chip manufacturers. However, there are no published reports of commercial use.
- Unpublished reports indicate that Intel is using Air Products' membrane separation technology in at least one fabricating facility.
- DuPont has expressed its intention to provide to the industry a disposition offering for recovered C₂F₆containing mixture – an offer that includes repurification of C₂F₆ to virgin-grade specifications and, potentially if necessary, off-site destruction.

Market Context

• Recover-and-recycling technologies are only applicable for large facilities, such as large fabs, primary magnesium producers, or very large magnesium-casting companies.