4.3 EMISSIONS OF HIGH GLOBAL-WARMING POTENTIAL GASES

4.3.1 SEMICONDUCTOR INDUSTRY: ABATEMENT TECHNOLOGIES

Technology Description

Figure 1. Litmas Blue Plasma Abatement Device

Figure 2. Hitachi Catalytic Oxidation System

Semiconductor manufacturers perform plasma etching and cleaning processes that use gaseous chemicals including perfluorocarbons (e.g., CF_4, C_2F_6 and C_3F_8), nitrogen trifluoride (NF_3), HFC-23 (CHF_3), and sulfur hexafluoride (SF_6). Collectively termed high global-warming potential (GWP) gases, these chemicals are potent greenhouse gases; one metric ton of SF_6 is equivalent to 23,900 Mt of carbon dioxide in terms of its potential effect on global warming. In addition, many high GWP gases 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 the semiconductor industry is to abate the emissions before they reach the atmosphere. Abatement of high GWP gases from the exhaust gas stream in semiconductor processing facilities may be achieved by two mechanisms: 1) thermal destruction and 2) plasma destruction. Thermal destruction technology may be applied to chamber-cleaning and etching processes within a fab (a local point-of-use [POU] application) or fab wide (an end-of-pipe [EOP] application). A POU device controls emissions as they emerge from an individual tool, while an EOP device is installed further "downstream," where it can abate emissions from a group of tools – or the entire fab – prior to the exhaust reaching the stack. Two thermal destruction technologies are being pursued: combustion systems and catalytic systems. In plasma-based systems, plasmas are formed from the effluent stream from etch or clean processes using either radio frequencies (low pressure streams) or microwaves (streams at atmospheric pressure). Destruction of high GWP gases that use plasmas offer system designers a broad range of conditions: oxidizing, reducing, and combinations of oxidizing and reducing conditions.

System Concepts

- In POU applications, thermal-destruction systems may be configured to accept exhaust from multiple etch/chemical vapor deposition chambers. High GWP emissions are oxidized in a natural gas-fired burner or over an electrically heated catalyst before the combustion products are removed by the on-site waste treatment systems.

- Burner and catalytic systems require pretreatment of inlet streams to reduce the loads of unused deposition/etchant gases and particles that can block burners or clog catalysts.
- Hydrofluoric acid formed in thermal destruction systems may be removed via POU scrubbers to prevent exceeding scrubber design limits.
- Plasma abatement technologies rely on the basic idea that larger exhaust molecules are broken into fragments in the plasma and then recombine in new ways, in the presence of other fragments formed from the dissociation of other gases added to the plasma, to form a new set of exhaust gases that may then be removed by existing waste-treatment systems.
- Plasma abatement systems for high GWP gases typically require very little floor space, because they are mounted off the floor directly on the foreline to the dry pump that feeds exhaust to scrubbing systems.

Representative Technologies

- The Edwards TPU 4214 (oxidation with advanced burner technology) is applicable for all high GWP emissions.
- The Hitachi system (catalytic oxidation technology) is applicable to CF_4, C_2F_6, c-C_4F_8, and SF_6.
- Investigators at Texas A&M patented an approach that used radio frequency and microwave surface wave plasmas. They now favor microwave technology that has proven more effective and holds the potential for exploiting low-cost magnetron technology.
- Litmas Inc. has two systems. The first, “Blue,” uses an inductively coupled radio frequency plasma source to transform high-GWP exhaust gases from etchers. The second technology from Litmas, “Red,” transforms the exhausts from plasma-enhanced chemical vapor deposition chambers using microwaves.
- AMAT’s Pegasys™ POU unit integrates cold-plasma abatement technology with popular etchers, which makes the abatement unit transparent to process engineers.

Current Research, Development, and Demonstration

RD&D Goals

- To lower high GWP emissions from waste streams by more than 99%, while minimizing (1) NO_x emissions to levels at or below emissions standards, (2) water use and burdens on industrial wastewater-treatment systems, (3) fabrication floor space, (4) unscheduled outages and (5) maintenance costs.
- To apply plasma technology to develop a cost-effective POU abatement device that lowers exhaust stream concentrations of high GWP gases by two to three orders of magnitude from etchers and plasma-enhanced chemical vapor deposition chambers; and transforms those gases into molecules that can be readily removed from air emissions using known scrubbing technologies.

RD&D Challenges

- Optimal combustion conditions to achieve destruction efficiencies for all high GWP gases, minimal energy consumption, and water use.
- In low-pressure applications, convincing skeptical process engineers that back-streaming from the plasma system does not threaten etch-process performance.
- Achieving more than 99% destruction efficiencies for all high GWP gases, particularly CF_4 and SF_6.
- Develop a cost-effective POU abatement device that lowers exhaust-stream concentrations of high GWP gases by two to three orders of magnitude, and transforms these gases into molecules that can be removed with current scrubbing technologies.

RD&D Activities

- Evaluations/reviews of approximately 13 thermal-destruction systems have been completed. Evaluations and demonstrations performed under fabrication operating conditions with Litmas and Texas A&M plasma systems produced favorable results.

Recent Progress

- The Edwards TPU 4214 (oxidation with advanced burner technology) achieves more than 99% destruction efficiency.
- The Hitachi system (catalytic oxidation technology) achieves destruction efficiencies of more than 99% for CF_4, C_2F_6, c-C_4F_8 and SF_6.

- Litmas Inc. reports emission reductions from 97% to 99% for its “Blue” POU device.
- AMAT’s capacitively coupled device (Pegasys II™) claims typically more than 95% reduction in emissions.
- Recent reports indicate that the surface wave device offers emissions reductions of more than 99% for a large range of tested waste streams.
- The Pegasys and Litmas radio frequency POU units appear affordable, with reasonable capital and operating costs, assuming that the existing hydrofluoric acid scrubber system (including ductwork) can handle the increase in hydrofluoric acid from these abatement units.
- The AMAT and Litmas radio frequency POU units have a small footprint, are easy to install, and are applicable to 200- and 300-mm etch tools.

Commercialization and Deployment Activities

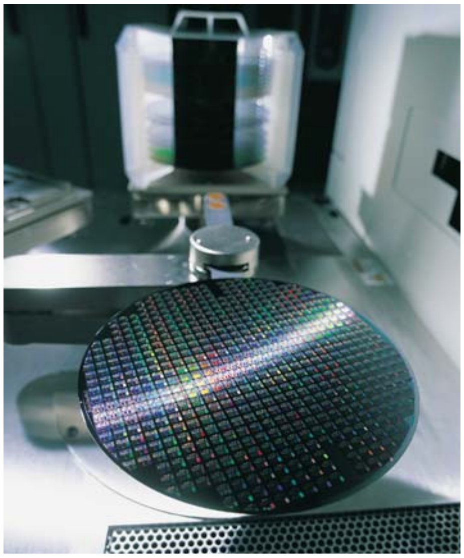
- The Edwards TPU 4214 is the only thermal-destruction device in commercial use and represents a favored POU solution for chemical vapor deposition cleaning processes.
- AMAT’s and Litmas’ systems are commercially available and reported in use.
- AMAT’s (Pegasys II™) interfaces with AMAT’s 200 and 300mm dielectric oxide etchers.
- Litmas’ “Blue” technology has successfully completed long-term impact tests on etch process performance.
- Litmas’ “Red” technology reported by Litmas to be in use on plasma-enhanced chemical vapor deposition chambers.
- There are no reports of commercial application of the surface wave plasma device. Research continues at Texas A&M.

Market Context

- Thermal and plasma destruction technologies can have broad applicability across the semiconductor industry.

4.3.2 SEMICONDUCTOR INDUSTRY: SUBSTITUTES FOR HIGH GWP GASES

Technology Description



PFCs, HFCs, NF_3, and SF_6 are used to construct intricate semiconductor products on silicon wafers such as this one. (Reprinted with permission of Greenleaf Publishing.)

Semiconductor manufacturers perform plasma etching and cleaning processes that use gaseous chemicals including perfluorocarbons (e.g., CF_4, C_2F_6 and C_3F_8), nitrogen trifluoride (NF_3), HFC-23 (CHF_3), and sulfur hexafluoride (SF_6). Collectively termed high global-warming potential (GWP) gases, these chemicals are potent greenhouse gases; one metric ton of SF_6 is equivalent to 23,900 Mt of carbon dioxide in terms of its potential effect on global warming. In addition, many high GWP gases 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 the semiconductor industry is to substitute a different chemical or process for the high GWP gases. Replacing high GWP gases with environmentally benign substitutes for chemical vapor deposition clean and dielectric etch processes is a preferred option when viewed from the perspective of EPA's pollution prevention framework. Alternatives to the high GWP gases, such as SF_6, CF_4, C_3F_8, c-C_4F_8, and C_2F_6, are sought. To significantly lower emissions of high GWP gases, investigators seek gases that do not have high GWPs (and, if they do, are eliminated during the production process) and do not form byproducts with significant GWPs, particularly CF_4 and CHF_3. Important etch process performance criteria are etch rate, etch profile, etch selectivity, and control of the critical dimension. In this option, investigators seek alternative highly fluorinated compounds that either are not high GWP gases themselves or are highly utilized during plasma etching and do not form byproduct high GWP emissions.

System Concepts

- Replacements are not favored if they increase cleaning times (which adversely affects fabrication productivity), form high GWP byproducts such as CF_4 and CHF_3, or pose new health and safety hazards.
- In dielectric etch processes, fluorine is required to etch the desired features into the dielectric materials, and carbon is required to passivate newly etched surfaces by gas formation of C_xF_y polymers that are then deposited to retard etching. Generally accepted models state that the boundary between net etching and deposition is a function of the fluorine:carbon ratio in the discharge. Plasmas rich in fluorine favor etching over deposition and those rich in carbon favor deposition over etching.

Representative Technologies

- Replacing C_2F_6 with C_4-compounds, e.g., switching to c-C_4F_8 and c-C_4F_8O
- Replacing C_2F_6 with NF_3 using *in situ* plasma cleaning.
- Replacing C_2F_6 with a remote fluorine source that dissociates NF_3 in an upstream plasma source.
- Replacing C_2F_6 with ClF_3.
- Hydrofluorocompounds, unsaturated fluorocompounds and iodofluorocompounds are attractive etch gas candidates because they have lower GWPs.
- C_3F_8 is a potential drop-in replacement for C_2F_6 in some chemical vapor deposition clean and etch processes because its high utilization during etch may offset its high GWP.
- Using NF_3, a high-GWP gas with high process utilization, in mixtures of a noble gas with unsaturated hydrocarbons of varying degrees. Examples of unsaturated hydrocarbons are ethyne or acetylene (C_2H_2), ethylene (C_2H_4), propyne (C_3H_4) and ethane (C_2H_6).

Current Research, Development, and Demonstration

RD&D Goals

- To identify the *chemical* and *physical* mechanisms that govern chemical vapor deposition chamber cleaning and etching with perfluorocarbons and non-perfluorocarbons as well as govern process performance so that emissions of high GWP gases may be significantly reduced without either adversely affecting process productivity or increasing health and safety hazards.

RD&D Challenges

- Developing conceptual models that guide the identification of candidate substitutes and substitute classes.
- Finding substitutes that do not form CF_4 (or other high-GWP gases such as CHF_3).
- Finding substitutes that do not require costly process requalification.

RD&D Activities

- Evaluations at the Massachusetts Institute of Technology (MIT) simulated process conditions, and at semiconductor facilities (with participation of equipment manufacturers and gas suppliers) actual representative process conditions (AMD, Motorola, and Texas Instruments).
- Discovery of the *in situ* dilute NF_3 cleaning process.
- Development of the remote NF_3 cleaning process.

Recent Progress

- Use of C_3F_8 will reduce high GWP emissions, in terms of carbon dioxide equivalent, by 60% relative to the standard C_2F_6 process.
- A switch to C_4 -fluorocarbons reduces emissions by 90% relative to the standard C_2F_6 process.
- Industry familiarity with the use of fluorocarbon compounds, excellent process performance and chemical cost savings make these alternatives attractive options. c-C_4F_8 is already in widespread fabrication use for high-density plasma oxide etching, reducing the usual procedures for chemical and supplier qualification by the industry.
- NF_3 dilute clean process reduces high GWP emissions by 85% relative to the standard C_2F_6 process.
- Remote NF_3 cleaning process reduces high GWP emissions by more than 99% relative to standard C_2F_6 process.

Commercialization and Deployment Activities

- C_3F_8 is reported in commercial applications at fabricating facilities owned by AMD, Motorola, and Texas Instruments.
- IBM and Novellus have commercialized and deployed dilute NF_3 cleaning processes.
- AMAT and ASTeX have deployed remote NF_3 cleaning processes.
- The etch gas research underway, and completed thus far, is described as proof-of-concept. There are no reports of commercial use.

Market Context

- Identification of a cost-effective PFC substitute could have wide applicability in the semiconductor industry.

4.3.3 SEMICONDUCTORS AND MAGNESIUM: RECOVERY AND RECYCLE

Technology Description

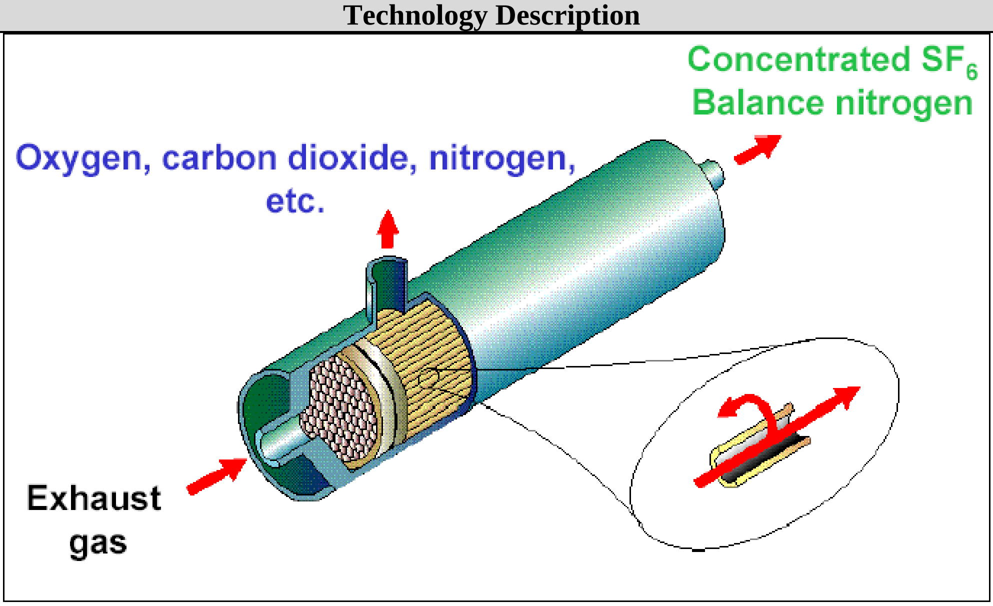


Figure 1. Diagram of Air Liquide's high GWP membrane separation technology.

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 SF_6 are recovered, concentrated, and "bottled." On-site bottled PFCs may be either mixtures or highly purified. Captured SF_6 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 SF_6 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, CHF_3, and SF_6, and up to 75% for CF_4.
- 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 C_2F_6, CF_4, and SF_6, when NF_3 and CHF_3 were first removed. Recovery efficiencies for NF_3 and CHF_3 varied between 30% and 60%, with CHF_3 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 C_2F_6-containing mixture – an offer that includes repurification of C_2F_6 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.

4.3.4 ALUMINUM INDUSTRY: PERFLUOROCARBON EMISSIONS

Technology Description

Primary aluminum production is the largest source of emissions of perfluorocarbons in the United States. Mitigation technologies and measures cannot only reduce emissions, but they also can improve process efficiency. (Reprinted with permission of Greenleaf Publishing.)

Aluminum is produced through the electrolytic reduction of alumina (AL_2O_3). The electrolytic Hall-Héroult process was adopted in the late 19th century, and continues as the process in commercial use today. Producing aluminum by the conventional electrolytic cell process requires a large amount of energy and produces significant emissions of greenhouse gases. The Hall-Héroult process results in direct emissions of CO_2, due to the consumption of the carbon anode, and also perfluorocarbon emissions. Within the electrolytic bath, the alumina is dissolved in a mixture of molten cryolite (Na_3AlF) and aluminum fluoride (AlF_3). Perfluorocarbon emissions are formed as intermittent byproducts within the aluminum smelting pot as the result of operational disturbances called anode effects. Anode effects occur when there is an over-voltage disturbance of the smelting process and are triggered when alumina levels in the pot decline below a critical level. During these events, the fluorine from the cryolite bath reacts with the carbon anode to form tetrafluoromethane (CF_4) and hexafluoroethane (C_2F_6). Primary aluminum production is the largest source of emissions of perfluorocarbons in the United States. Greenhouse gas emission reduction measures not only reduce perfluorocarbon and other greenhouse gas emissions, but they also can improve process efficiency. The United States is one of the largest global producers of primary aluminum and, as of 2000, there were 11 U.S. companies that produced primary aluminum.

System Concepts

- Current efforts to reduce perfluorocarbon emissions from primary aluminum production focus on using the most efficient smelting processes to reduce the frequency and duration of anode effects. Perfluorocarbon reduction potential varies by smelter technology with point-feed technology the most efficient – and Søderberg technology the least efficient. Another concept, now in the research and development phase, involves replacing the carbon anode with an inert anode. Doing so would completely eliminate process-related perfluorocarbon and CO_2 emissions.

Representative Technologies

- Currently available perfluorocarbon mitigation technologies and practices include computerized controls and point-feeder systems, as well as improved operating practices that minimize the frequency and duration of anode effects and associated emissions. When using the Hall-Héroult process, perfluorocarbon emission reductions could be achieved through retrofitting existing cells, converting older technologies, and using advanced technologies. Emerging technologies include use of the inert anode mentioned above.

Technology Status/Application

- Computerized controls, point-feeder systems, and improved operator practices vary in their cost-effectiveness and ability to reduce emissions. Further research regarding anode effects could yield additional cost-effective emissions reductions. The Department of Energy, through its Industries of the Future strategy, supports research and development of the inert anode. Being noncarbon, the inert anode would eliminate PFC emissions. Laboratory, pilot-scale, and commercial-scale testing of inert anodes is currently underway.

A commercially viable design is expected by 2005. Commercialization can be expected by 2010-2015. Use of the inert anode technology will most likely be in conjunction with wetted cathode technology as part of an advanced technology cell. The advance technology cell is a combination of an inert anode, which would not be consumed during electrolysis, and a cathode with a stable surface, which would reduce electricity requirements.

Current Research, Development, and Demonstration

RD&D Goals

- If successful, the nonconsumable, inert anode technology would have clear advantages over conventional carbon anode technology, including energy efficiency increases, operating cost reductions, elimination of perfluorocarbon emissions, and productivity gains.

RD&D Challenges

- A number of critical technology barriers prevent the aluminum industry from the targets it has identified for inert anode technology. These challenges represent the difference between present-day carbon anode technology and the current state of nonconsumable anode technology. Challenges include:
  - Demonstration of "viable" inert materials for use in fabricating the anodes, including fabricating candidate materials in large sizes, and the means for scaling up the fabrication processes.
  - Basic knowledge of the operation of nonconsumable anodes.
  - Validation of the potential for full-scale process improvement.
  - Computer modeling to address retrofitting issues.

RD&D Activities

- DOE is leading the effort in producing inert anode technologies.

Recent Progress

- Use of the most efficient aluminum processing technologies, such as point-feed technology, has resulted in reducing perfluorocarbon emissions from U.S. primary aluminum production by more than 40% since 1990.

Commercialization and Deployment Activities

- High-efficiency smelting technologies (e.g., point-feed technology) and options for retrofitting the Hall-Héroult process are commercially available. A commercially viable inert anode design is not expected to be available until 2005.

Market Context

- Retrofit capability is a key issue with inert anode technology. If the new technology is technically and economically successful – but, ultimately, cannot be retrofitted to existing cells – it will still be considered a success. However, the ability to retrofit would be considered a major benefit, and would improve the technology's economics.

4.3.5 ELECTRIC POWER SYSTEMS AND MAGNESIUM: SUBSTITUTES AND ALTERNATIVES FOR SF_6

Technology Description

Figure 1. Molten Mg with SF_6 cover gas.

Figure 2. Molten Mg without protective cover gas.

Electric Power Systems: Sulfur hexafluoride (SF_6) is a favored insulating agent for high-voltage electric power system equipment because of its dielectric strength and arc-suppression capabilities. Use of other insulating media has been researched and some have been used, especially in medium- and low-voltage applications. Historically, several other media were used (e.g., air, vacuum, oil) before the advent of SF_6, some of which remain in use today in certain applications. Emissions reductions can be achieved through the adoption of currently available "SF_6-Free" technologies (up to 145 kV) as well as through research into alternative gases and on-site recovery systems for such alternative gases and/or mixtures.

Magnesium Industry: Magnesium metal producers and casters use SF_6 mixed with dry air and/or CO_2 as a cover gas to prevent oxidation and burning of the molten metal. About 5% to 20% of the SF_6 is believed to react with the metal surface, preventing oxidation, while the remainder escapes to the atmosphere. The magnesium casting machine operators need to have access to the surface of the magnesium melt. Therefore, a tightly sealed system is difficult to engineer and maintain. Recognizing that some gas will escape, a highly attractive technology option involves use of a gas other than SF_6 with better environmental characteristics. The challenge is to isolate a substitute with low or no global-warming potential that satisfies the magnesium industry's melt protection performance and safety requirements.

System Concepts

- Electric power systems: Purchase/use equipment that relies on insulating agents other than SF_6; Research, design, and development of "SF_6-Free" high-voltage equipment for the U.S. market.
- Magnesium casting: Use a gas for magnesium melt protection that avoids the global-warming concerns associated with SF_6.

Representative Technologies

- Electric power systems:
  - Existing insulating agents other than SF_6 include oil, air, or vacuum insulation; but SF_6 is the predominant choice for high-voltage applications. Despite extensive research efforts, no single gaseous compound has been isolated that serves as a substitute for SF_6 in high-voltage applications. SF_6 remains the insulating medium of choice. Gas mixtures, however, have been used successfully, including mixtures of SF_6/N_2 or SF_6/CF_4 in cold-weather applications.
  - 145kV vacuum interrupter (developed by Japan AE Power)

- Magnesium casting:
  - HFC-134a: The Cooperative Research Centre for Cast Metals Manufacturing (CAST) in Australia is conducting research and development to find a suitable substitute gas for SF_6. Based on the concept that the addition of fluorine into the magnesium oxide surface film is the key mechanism for preventing oxidation of molten magnesium, CAST has developed a process that uses the hydrofluorocarbon gas 1,1,1,2-tetrafluoroethane, otherwise known as HFC-134a.
  - SO_2: Sulfur dioxide provides effective protection of molten magnesium, but its toxicity presents a concern for use in the workplace.

    IMA Study / SINTEF: The International Magnesium Association (IMA) established an Ad Hoc Committee on SF_6 composed of representatives from IMA, several magnesium casting firms, and an automobile manufacturer. The committee selected a research proposal from SINTEF, the Foundation of Scientific and Industrial Research at the Norwegian University of Science and Technology, to evaluate alternative cover gases for protection of molten magnesium.
  - Novec 612™: 3M™ has commercialized a fluorinated ketone, $C_3F_7C(O)C_2F_5$ (Novec 612™) as a substitute for SF_6.
  - CO_2 "Snow": German researchers are investigating the efficacy of applying solid CO_2 "snow" to protect molten magnesium from oxidation. The CO_2 snow is reported to cool the melt surface and displace ambient air as it expands, thus limiting oxidation.

Technology Status/Application

- Electric power systems:
  - At least one utility is known to use SF_6/N_2 and SF_6/CF_4 gas mixtures for circuit breakers used in cold weather, at transmission and sub-transmission voltage levels (i.e., 500 kV and below);
  - EPRI is testing a "Solid State Current Limiter" - a "SF_6-Free" circuit breaker type device.
- Magnesium casting: HFC-134a and Novec 612™ are reported to provide good molten metal protection in magnesium production and die-casting applications. CO_2 snow protection is being studied at laboratory and pilot scales.

Current Research, Development, and Demonstration

RD&D Goals

- To find substitutes for SF_6 that have comparable insulating and arc quenching properties in high-voltage applications and/or protect molten magnesium – and significantly less or no global-warming potential.

RD&D Challenges

- Electric power systems: To date, no widely applicable alternatives have been found for SF_6. The primary RD&D challenge is to find an acceptable insulating medium for high-voltage applications; alternative gases will most likely requirement equipment modifications.
- Magnesium casting:
  - Characterizing chemical and physical mechanisms that govern protection of molten magnesium through use of cover gas.
  - Selecting effective gas substitutes that not only guard against magnesium burning, but also minimize emissions of greenhouse gases or other pollutants of concern.
  - Isolating the best methods of gas distribution to overcome the potential disturbances associated with magnesium melt turbulence and temperature.

RD&D Activities

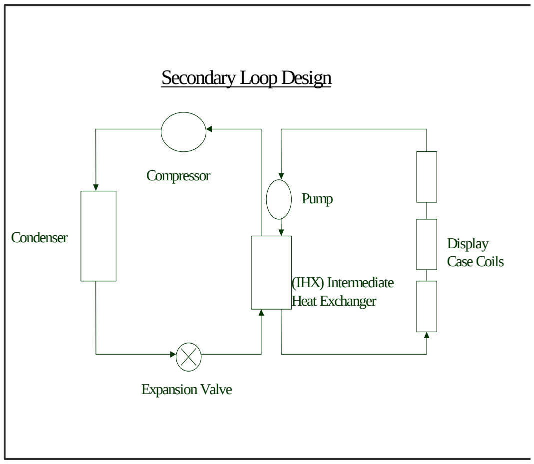
- Electric power systems: The Electric Power Research Institute (EPRI) is investigating a solid-state current limiter that may lead to future equipment designs that do not require SF_6 insulation.
- Magnesium casting:
  - EPA and the magnesium industry are working in a voluntary partnership to eliminate SF_6 emissions
  - SINTEF and CAST continue their work with alternative gases and HFC-134a. Based on their findings regarding solubility of fluorine in molten magnesium, SINTEF is researching the viability of bubbling a fluorine-bearing gas through the melt or adding fluorine in a solid matrix, such as iron fluoride.

Recent Progress
• Electric power systems: Gas mixtures, as discussed above, have been used successfully in cold-weather applications; some equipment and gas manufacturers are devoting R&D resources into alternatives. • Magnesium producers and casting firms report promising results from early production-scale trials of alternative fluorinated cover gases.
Commercialization and Deployment Activities
• 145kV vacuum interrupter commercially available in Japan. • If a substitute gas is found, commercialization and deployment are not expected to represent hurdles. Gas mixtures appear to be readily available to potential users in cold regions where they are applicable. **Market Context** • Electric Power Systems: Circuit breaker equipment used in high-voltage electricity transmission and distribution; “SF_6-Free” power equipment, such as the 145kV vacuum breaker, is 2-3 times more expensive than high-voltage power equipment currently available in the market. • Magnesium Industry: All magnesium production and casting firms that use SF_6 for magnesium melt protection.

4.3.6 SUPERMARKET REFRIGERATION: HYDROFLUOROCARBON EMISSIONS

Technology Description

Distributed refrigeration technology can be seamlessly integrated into a store.



Secondary-Loop Refrigeration, where an extra pump and internal heat exchanger are added to the equipment used in a conventional design.

To comply with the U.S. Clean Air Act, supermarkets are phasing out the use of ozone-depleting refrigerants. As substitutes, the industry is using hydrofluorocarbons (HFCs), which are potent greenhouse gases. To ensure that food products are kept cold, the typical supermarket design pumps these HFC refrigerants through miles of piping and thousands of joints. Historically, annual emissions of 35% to 50% of the 2,000- to 4,000-pound charge have occurred. As old stores are replaced and new ones built, new technologies can drastically limit greenhouse gas emissions.

System Concepts

- Better equipment design and store layout can lead to a reduction in the amount of refrigerant needed for a given amount of product cooling.
- Additionally, replacing the complex miles of piping with either distributed cooling systems or a single centralized refrigeration plant can reduce the percent of refrigerant emitted annually.

Representative Technologies

- *Distributed Refrigeration* is a technology that puts refrigeration equipment closer to the food display cases, eliminating the need for excessive refrigerant piping throughout the store to reach a mechanical room sited away from the food.
- *Secondary-Loop Refrigeration* segregates refrigerant-containing equipment to a separate, centralized location, and uses a benign fluid to transfer heat from the food display cases.

Technology Status and Applications

- Both concepts have existed for some time but have seen very little adoption in the highly competitive, low-margin supermarket business.
- Only a handful of secondary-loop systems have been installed in the United States, primarily for “medium-temperature” (e.g., dairy products) portions of supermarkets. Very few “low-temperature” (e.g., frozen foods) systems exist in the world.
- Both technologies centralize refrigerants to one or a few locations. This allows for economical installation of leak-detection equipment to alert system operators when HFC refrigerant emissions occur.

Current Research, Development, and Demonstration

RD&D Goals and Challenges

- Continuously improve energy-use performance of these new technologies, investigating various designs, control strategies, and operational techniques.

- Investigate ways to reduce installation and operational costs of new technologies.
- Demonstrate applicability and advantages in various locations, store sizes, and product mixes.
- Educate store designers and builders regarding new technologies and how these technologies can be integrated into new or retrofitted stores at a net savings.

RD&D Activities

- EPA has built a facility to test secondary-loop refrigeration systems. Additional funding from DOE has been provided to support the research and test related products.
- Various manufacturers and supermarkets are conducting their own proprietary research on these technologies.

Recent Progress

- Existing systems have proved relatively easy to operate and maintain. Minimal refrigerant leakage has provided an economic benefit for the storeowner as well as an environmental benefit for society.
- Under the U.S./Australia Climate Action Partnership, the possibility of building and monitoring a typical and secondary-loop store is being explored. This will allow verification of potential benefits.

Commercialization and Deployment Activities

- The most opportune time to implement these technologies is during new store construction or during major overhaul and retrofit of existing stores. There are more than 30,000 supermarkets in the United States, and this is likely to grow with a growing population. Because many stores are currently switching from ozone-depleting refrigerants, there is a high potential to introduce these new technologies quickly if technical, economical, and educational challenges are met.

Market Context

- High competition in design and construction of supermarkets creates unwillingness to explore newer, unfamiliar technologies despite potential benefits.
- Low-margin business creates “chicken-and-egg” situation where supermarkets are unwilling to install new technologies until the benefits are proven, but benefits cannot be proven until supermarkets install new technologies.