

# LINDE TECHNOLOGY

Issue

*FEATURED TOPIC: THE CO<sub>2</sub> MANAGERS*

#1.  
10

*SEPARATING CARBON DIOXIDE*  
Clean flue gas in the power plant

*CONVERTING CO<sub>2</sub>*  
Raw materials from the algae farm

*REDUCING GREENHOUSE GASES*  
Green solar cell production

*ELECTRIC MOBILITY*  
Getting closer to hydrogen infrastructure

*MEDICINE*  
Heliox relieves shortness of breath

*FOOD*  
Specialty gases against pests

*INNOVATIVE TECHNOLOGIES FOR CLIMATE PROTECTION*

## *THE CO<sub>2</sub> MANAGERS*



THE LINDE GROUP

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### **Climate protection through CO<sub>2</sub> management:**

*the featured topic shows examples of innovative  
technologies which guarantee a comprehensive,  
effective and secure management of carbon  
dioxide – thereby contributing to the protection of  
the environment and of generations to come.*

#1.  
10

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# EDITORIAL

*Dear Readers,*

The world economy is still coping with the impacts of the most difficult crisis in decades, and struggling to restabilise the global finance system. This crisis has shown that growth alone does not constitute a practical foundation for life. Only a sustainable and substantial growth secures the future of coming generations. Therefore, climate protection is our highest priority. In such a predicament, the question isn't whether we can afford climate protection, but rather: can the world's population afford climate change?

Real innovations are needed now – products and processes which make renewable energies economically usable and significantly lower the consumption of natural resources. But we also need technologies which help to reduce, or completely prevent, climate-destructive emissions as well as waste. In the end, that pays off both ecologically and economically.

Despite all efforts to promote renewable energies, fossil sources of energy will still remain the most dominant resources for securing global energy provision for decades to come. The near future thus demands a comprehensive, efficient and secure management of carbon dioxide. Our company has already been contributing to this goal with innovative technologies, as the featured topic of this issue illustrates with diverse examples. Coal-fired power plants are emitting less carbon dioxide thanks to CO<sub>2</sub> scrubbing, solar cells can be produced in a climate-friendly way and CO<sub>2</sub> from industrial waste gases can even be used to create biofuels and chemical base substances. We also offer comprehensive solutions for supplying industrial branches which rely on CO<sub>2</sub> as a raw material. Over and above, we are pressing further ahead with the expansion of the hydrogen supply for future low-emission mobility: with the initiative 'H<sub>2</sub> Mobility', for example, we have made great strides towards establishing a nationwide hydrogen infrastructure in Germany.

The technological challenges presented by climate protection are so complex that they can only be overcome by qualified experts. The engineers and technicians at Linde are here to contribute – to CO<sub>2</sub> management, just as to other future-oriented applications in the field of energy and the environment.

I hope you enjoy reading this issue.

Professor Dr Wolfgang Reitzle  
Chief Executive Officer of Linde AG





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## FEATURED TOPIC

## THE CO<sub>2</sub> MANAGERS

*With innovative technologies, the engineers and technicians of The Linde Group are helping to make the transition to new forms of energy production and use as climate-friendly as possible.*

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*Pharmaceutical production:  
under clean room conditions,  
F. Hoffman-La Roche produces  
so-called monoclonal anti-  
bodies for cancer treatment.*

*Oxygen supply for the pharmaceutical industry*

# *PROTEIN SYNTHESIS IN THE CLEAN ROOM*

The pharmaceutical industry swears by biotechnology. Experts from Linde-KCA-Dresden GmbH have planned a new production centre which will produce antibodies for cancer treatment: highly complex process technology under sterile conditions.





Biotechnology aids healing: pharmaceutical researchers are developing effective medications using the most modern methods from molecular biology and genetics. Innovative medicines are being produced with the help of genetically modified cells, enabling entirely new therapeutic approaches. The biotechnological process for propagating such cells on an industrial scale demands highly complex facilities with extensive control and supervision. At their headquarters in Basel, Switzerland, the pharmaceutical group F. Hoffmann-La Roche has built a new production centre for so-called monoclonal antibodies, which are used in oncology against many different

types of cancer. Linde-KCA-Dresden, a subsidiary of The Linde Group, acted as the main contractor for the planning of this new construction. The total protein production, with multi-stage fermentation and downstream processes, is installed in pharmaceutical clean rooms with exactly specified air qualities. For fermentation the cell production and protein synthesis require high-purity oxygen, which is supplied on-site from the Swiss Linde-subsidiary PanGas. The production centre's innovative project concept also persuaded the renowned International Society of Pharmaceutical Engineering (ISPE) – in 2009 they awarded the project the distinction of 'Facility of the Year'.

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**LINKS:**

[www.linde-kca.com](http://www.linde-kca.com)

[www.roche.com](http://www.roche.com)

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[www.roche.com/de/biotechnology.htm](http://www.roche.com/de/biotechnology.htm)

# NEWS

USA:

## BIOGAS LIQUEFIER IN OPERATION

The largest facility for producing biogas from landfill gas is now running: already in the first weeks of production, a plant connected to a landfill in California has generated 750,000 litres of carbon-neutral biogas. The renewable fuel source is the project of a joint venture between Waste Management, the largest waste service company in America, and The Linde Group, who has taken over the building and operation of the facility. With the help of the most modern gas purification and liquefaction technology, 50,000 litres of liquid gas will be converted from landfill gas: an output that can provide fuel for 300 waste transporters. Biogas from landfills is absolutely climate-neutral – in contrast to natural gas, which is delivered by pipelines. During combustion it will release only as much carbon dioxide as the organic waste material had previously absorbed. With more liquefaction facilities like this, Waste Management wants to sustainably improve its fuel efficiency by around 15 percent by 2020. “We’re using valuable energy from landfill waste and relieving the burden on the en-

vironment at the same time,” says Duane Woods, Senior Vice President of Waste Management’s Western Group. And Pat Murphy, President of Linde North America, is also pleased with the project: “Linde is proud to be generating clean and green energy for the inhabitants of California with this facility.” The CO<sub>2</sub> emissions are expected to be decreased yearly by 30,000 tonnes (see also ‘Propelled by waste’, Linde Technology 2/2008).



MOBILITY:

## PROFESSOR DR WOLFGANG REITZLE RECEIVES THE ‘YELLOW ANGEL’

Hydrogen as an environmentally friendly fuel for cars – this is the long-standing and committed goal of Professor Dr Wolfgang Reitzle, CEO of Linde AG. In January’s ADAC awards ceremony the ‘Yellow Angels’, he received the distinction of ‘Personality of the Year 2010’. The German automobile club thereby recognised his exceptional achievements in the fields of traffic, mobility and automobiles. Already in the 1990s, Prof. Reitzle had developed early

prototypes for hydrogen-powered cars. “I am sure that series production vehicles will soon appear which in five to ten years will be strongly represented in metropolitan areas,” he said during the awards ceremony. It will take even greater efforts from the industry to achieve this end (see also ‘Full speed ahead with hydrogen’, page 10).





## CHINA:

*RESEARCH IN THE MIDDLE KINGDOM*

In Shanghai, Linde has founded the third research and development centre worldwide for new technological processes for gases applications. With this the company is emphasising its position in China and in the entire Asia-Pacific region. The technology centre should especially help industrial companies and research institutions to develop future-oriented green technologies. For Linde's industrial gases business, the countries of the Asia-Pacific region are continually growing key markets. "The more quickly this region develops, the more robustly the companies will search for advanced and sustainable gas solutions," says Steven Fang, responsible at Linde for the Greater China Region. Linde has already agreed to cooperate with Nanjing Iron and Steel Company (NISCO), Sinopec Research Institute of Petroleum Processing (RIPP) and the University of Tsinghua. Projects are planned for waste water treatment and reducing CO<sub>2</sub> emissions, among others. The development of hydrogen technologies for China will also play a large role.



## RENEWABLE RAW MATERIALS:

*NEW CENTRE BRIDGES DEVELOPMENT GAP*

Chemical companies worldwide are working to replace crude oil with renewable raw materials. In order to serve as a raw material source on an industrial scale, plant substances must be available at constant quality and at affordable prices. A new chemical-biotechnical process centre (CBP) at the chemical site of Leuna, Germany, should now bridge the gap in the development of renewable raw materials between laboratories and industrial implementation. 23 industrial companies and 15 universities and research institutions plan to participate in the project. The Linde subsidiary

Linde-KCA-Dresden was chosen as general contractor for the planning, supply and construction of the entire technical facility. The CBP should make it easier to bring innovative products from raw materials to industrial implementation in the future, by way of biocatalysts and scaling the necessary procedures. To this end, Linde-KCA-Dresden will construct seven process plants. The first should already be transferred to the Fraunhofer Society and their partners by November 2011.

## GERMANY:

*HYDROGEN FOR BERLIN*

In Berlin a new hydrogen filling station from the Clean Energy Partnership (CEP) is going into operation. Linde provides the liquid hydrogen for the filling station from Germany's only industrial hydrogen liquefaction plant, located in Leuna. In the long-term, the new filling station should supply 40 passenger cars with liquid as well as with gaseous hydrogen. The hydrogen delivered in liquid form is stored without refrigeration in a reinforced insulated tank developed by Linde. Hydrogen gas is generated on-site by electrolysis. The electrolyser is powered with electricity from renewable energies, and can be very quickly and flexibly adapted according to need. The hydrogen is stored at 1,000 bar in a newly developed pressure vessel. The fuelling system communicates with the storage plant as well as with the tank of



the vehicle to be filled – and can thereby generate the required pressure for the gas pumps, at either 350 or 700 bar. The surplus hydrogen drives a fuel cell which provides the filling station with power and heat.

*Industry initiative helps build up H<sub>2</sub> infrastructure*

# FULL SPEED AHEAD WITH HYDROGEN

More than a century after the automobile was invented, mobility is being redefined. Currently, all strategies focus in particular on bringing costs quickly under control. Hydrogen is emerging as a promising option: Linde engineers are advancing H<sub>2</sub>-enabled mobility with innovative technologies that bring greater cost efficiencies to the expanding H<sub>2</sub> infrastructure.

Green Mobility – an important megatrend for our century. However – at least for private transport – there are still a multitude of concepts competing for dominance: simple battery-powered cars, fuel cell drives, biofuel combustion engines, hydrogen and synthetic fuels. It is not as yet clear what the future will hold. The automotive industry is at a crossroads similar to that of a hundred years ago, when steam engines fought against electric motors, petrol and diesel engines for recognition as the most successful propulsion technology – we all know the results. This time, according to many experts, it is unlikely that one single technology will be seen as the solution to the challenge. Indeed, it seems likely that the differing designs will each find their niche in a separate application field. City buses require a different design than heavy duty long distance vehicles, or vehicles designed for individual recreational mobility in the city or country.

Both politics and industry have set their hopes on electric mobility. Although battery-powered cars fit for mass production will already be on the streets by the year's end, a number of design features stand in need of improvement.

There is still no comprehensive solution for concerns of range, costs and infrastructure. Alongside purely electric vehicles, fuel cells are becoming of growing importance to the field of electric mobility – and so is hydrogen. "Hydrogen-powered vehicles will play an important role in providing low-emission electric mobility. The concepts of simple battery-powered cars and fuel cell vehicles complement each other well; each will have their individual application," says Markus Bachmeier, Head of Hydrogen Solutions at Linde. He ought to know:

**FUEL CELLS  
AND BATTERIES  
WORK TOGETHER  
PERFECTLY  
IN A CAR.**

as a mechanical engineer and business economist, he spent long years working for the automotive industry before starting with Linde in 2008.

The automotive industry is proving him correct. In mid-2009 Daimler, Ford, General Motors, Honda, Hyundai, Kia, Renault, Nissan, and Toyota signed a memorandum of understanding, agreeing to introduce commercial fuel cell vehicles to the market starting in 2015. "In 2010, there is no longer any question whether H<sub>2</sub> drives will be implemented. The real question now is economic efficiency. The variety of individual models already being put on the road worldwide by the automotive industry is past count," says, for example, Bettina Mayer, editor-in-chief of the business publication 'Automobil Produktion'.

At the end of 2009, production had already started on a limited series production of Mercedes Benz B-Class F-Cells. The first mass-produced fuel cell passenger car, by Mercedes Benz, has a range of around 400 kilometres thanks to the 700 bar hydrogen tank built into the sandwich floor. The electric motor is comparable in power to a two-litre petrol engine, and the fuel cell drive uses approximately three litres of fuel per 100 kilometres (converted to diesel equivalent measures). The first of a total of 200 vehicles are currently being delivered to customers in Europe and the USA. Mercedes Development Manager, Thomas Weber, expects affordable market prices for the car by 2020. "If we manufacture more than one hundred thousand units, the fuel cells won't cost any more than a high-tech electric hybrid diesel," he told the Süddeutsche Zeitung.





*Clean mobility: using fuel cells and hydrogen, the first B-Class F-Cell mass produced by Mercedes Benz can travel around 400 kilometres on one tank.*



*H<sub>2</sub> in the city centre:* Vattenfall is building a new hydrogen filling station in Hamburg, within a confined space in the harbour city centre. The filling station will be fully integrated with the existing architecture (large image). Ionic compressors will be used for filling up with high-pressure hydrogen. Innovative technology is used to fill up vehicles at the new filling station in Stuttgart (above right) and at the Linde Hydrogen Center in Unterschleissheim, near Munich (below right).



## One tank, 693 kilometres

Honda, too, has had hydrogen vehicles on the road for some time now. In California the FCX Clarity, equipped with a 100 kilowatt electric motor, has been available for lease since the summer of 2008. The range per tank: about 460 kilometres. And even the development engineers from BMW, currently working on a hydrogen combustion engine, see H<sub>2</sub> as the long-term alternative for sustainable, individual mobility. According to the company, they are concentrating on developing a 'cryo-compressed hydrogen storage system' – a huge leap forward for H<sub>2</sub> motor technology.

Japan is also promoting H<sub>2</sub> technology. Toyota, for example, plans to bring a fuel cell hybrid car onto the market in 2015. The company is implementing a substantial programme in the USA to help them along this path. More than 100 Toyota FCHV-adv cars will be used in the coming three years in New York and California by private companies, universities, and government agencies. These vehicles have a formidable range: during a test run requested by the US Department of Energy, the FCHV-adv was able to reach a generous 693 kilometres on one tank.

This is a success that must be built upon: "Constructing a comprehensive infrastructure of filling stations is now the decisive next step in the process," says Irv Miller, Vice President Environmen-

tal and Public Affairs at Toyota Motor Sales USA. Linde Manager Bachmeier agrees: "In the last ten years, we have concentrated on technical feasibility in particular. That problem has since been solved. The challenge now – not just for Linde – involves systematically lowering investment costs and also the total costs along the entire hydrogen production and distribution chain."

The first hydrogen infrastructure centres, such as the filling stations constructed under the Clean Energy Partnership (CEP) in Berlin and Hamburg, are already in place. "Germany is thus on the cutting edge of hydrogen technology in Europe," says Bachmeier. The industry initiative 'H<sub>2</sub> Mobility' plans to capitalise on this edge. For the first time ever, a great number of major companies from various sectors have committed themselves to hydrogen development. Daimler, EnBW, OMV, Shell, Total, Vattenfall, and the Nationale

## GERMANY IS ON THE CUTTING EDGE OF HYDROGEN TECHNOLOGY FOR ALL OF EUROPE.

Organisation Wasserstoff- und Brennstoffzellentechnologie (German National Organisation for Hydrogen and Fuel Cell Technology, or NOW) have already decided, along with Linde, to participate in the programme – and additional partners are welcome. These companies want to combine forces to test the construction of a nationwide infrastructure for supplying hydrogen within Germany, which would then promote mass production of electric cars with fuel cells. The 'H<sub>2</sub>



Mobility' initiative envisions two stages: phase I will involve members examining options for the construction of a nationwide hydrogen filling station network as well as developing an economically-sustainable joint business plan. They plan to build an additional 25 hydrogen filling stations by 2011.

### New cryo pump for high-pressure hydrogen

Linde's engineers are already offering two powerful and highly efficient technologies for fuelling with high-pressure hydrogen. These are the ionic compressor and a newly developed cryo pump, which converts liquid hydrogen to gaseous high-pressure hydrogen. This pump will be placed in a hydrogen filling station belonging to the CEP project in Berlin at the beginning of 2011. There, it will prove its performance capability under strenuous everyday conditions. Hamburg, the second hydrogen capital of Germany (after Berlin), is also making great strides in H<sub>2</sub> technology. Vattenfall is building a modern H<sub>2</sub> filling station within a confined space in the middle of the harbour city. In this filling station, which will be fully integrated into the existing architecture, the ionic compressors will be put to work.

"This is a great example of our H<sub>2</sub> designs being ready for the market, even in city centres," explains Henning Tomforde, responsible for Marketing and Market Development at Linde Hydrogen Solutions. Tomforde says that one of the basic requirements for making hydrogen economically efficient is the capacity of a filling station. "The

price per kilo is the deciding factor." For example, a B-Class F-Cell consumes approximately a kilogramme of H<sub>2</sub> per 100 kilometres. "If we work from the current price of approximately eight euros per kilogramme of hydrogen, then we are already close to diesel prices," says the business economist. "Once the demand for H<sub>2</sub> rises, the costs will sink even further."

In Hamburg, the companies want to test a concept for the sustainable creation of hydrogen. Wind energy helps power the electrolysis which in turn produces the hydrogen. "We simulate the cycles whereby wind energy plants supply power," Bachmeier explains. 'Green Hydrogen' is likewise an important topic for Linde Hydrogen Solutions. This results in a variety of approaches. "We are engaged in talks with wind energy plant manufacturers as well as firms from the solar energy sector," says Tomforde.

### H<sub>2</sub> from biogenic raw materials

Linde is also independently researching a variety of innovative procedures designed to manufacture hydrogen from biogenic raw materials. One example is the demonstration plant which the company is currently constructing at the chemical site of Leuna, Germany, for use producing hydrogen from glycerine. Raw glycerine, which accumulates during the production of biodiesel, is particularly suited to the manufacture of hydrogen. The 'green' liquid hydrogen manufactured at Leuna is planned for use in buses and passenger cars in Berlin and Hamburg, among other applications. "If a fuel cell car is powered by H<sub>2</sub> produced from renewable sources, it emits 90 percent less CO<sub>2</sub> than a diesel-powered vehicle. Even if you use conventionally manufactured hydrogen, made from natural gas, you've already reduced emissions by 30 percent compared to diesel," says Bachmeier. Linde currently assumes they will need to build 1,000 filling stations to reach the goal of nationwide coverage for Germany. "That would be enough to solve the chicken-and-egg problem between the necessary infrastructure construction and the mass production of hydrogen-powered cars," says Linde's engineer, who is already anticipating the technological requirements. Bachmeier: "We are making incredible progress. Just a few years ago, we were aiming for seven minutes filling time. Today we can fill the B-Class F-Cell in just under three minutes. And it can use that fuel to drive 400 kilometres." As he says this, he takes the fuel nozzle in his hand and fills up the hydrogen-powered car for the next trip.

LINK:

[www.linde.com/hydrogen](http://www.linde.com/hydrogen)



## THE CO<sub>2</sub> MANAGERS

*Clean future  
in sight:  
The Linde Group's  
CO<sub>2</sub> managers  
show the ways of  
handling carbon  
dioxide  
responsibly.*

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## CO<sub>2</sub> WORLD IN FLUX

*The energy supply of the future should be free of greenhouse gas emissions. With innovative CO<sub>2</sub> management technologies, the engineers and technicians of The Linde Group are already making their contribution for a climate-friendly transition to new forms of energy production and use.*

Carbon is the raw material of our existence: without it there would be no organic life on the earth. The element is central to the energy supply of animals and plants. Nonetheless, climate change is bringing an end to the age of carbon – scientists worldwide are seeking alternatives to oil, coal and gas combustion. But despite all efforts to promote renewable energies, fossil sources of energy will remain the dominant resources of the global energy supply for decades to come.

The transition to regenerative energy sources and climate-friendly mobility requires safe and cost-effective CO<sub>2</sub> management above all. Coal-fired power plants, for example, harm the climate. But Linde engineers are already doing their part so that power plants emit significantly less carbon dioxide than before: with innovative

approaches for reducing CO<sub>2</sub> emissions to procedures separating it from flue gas, up to storing gases harmful to the climate. But the reduction of greenhouse gas emissions isn't the only thing at the top of Linde's CO<sub>2</sub> managers' agenda. Their goal is also the environmentally friendly, beneficial use of greenhouse gases, which still today invariably accumulate in industrial processes as waste gas. Or the optimisation of distribution paths for CO<sub>2</sub>, which the food industry, for instance, urgently requires.

The featured topic in this issue shows manifold examples of how the CO<sub>2</sub> managers from Linde are ensuring that greenhouse gases are reduced, safely stored or even used in an environmentally friendly manner – worldwide and cost-effectively.



*The cleaner: in the Vattenfall pilot plant at Schwarze Pumpe, the Oxyfuel process helps with CO<sub>2</sub> capture.*

*New technologies for CO<sub>2</sub> capture*

# CLIMATE PROTECTION AND COAL POWER

Despite all of the efforts to promote renewable energy, fossil fuels will still remain the most important resources for global energy provision for decades to come. However, coal-fired power plants with almost zero CO<sub>2</sub> emissions are within tangible reach. Several concepts are being tested, most of which also count on the know-how of Linde engineers: innovative approaches to reducing CO<sub>2</sub> emissions during combustion are just as helpful as efficient procedures for CO<sub>2</sub> separation from the flue gas.

Image source: Vattenfall  
Author: Bernd Müller

Nobody really wants it anymore, but globally we can't do without it: coal's image has hit rock bottom. Heated in cauldrons and chased through chimneys, black gold is a prime contributor of carbon dioxide emissions and thus to climate change. The Intergovernmental Panel on Climate Change's (IPCC) numbers sound dramatic: CO<sub>2</sub> emissions from burning fossil fuels have risen every year around three and a half percent since 2000 – due if for no other reason to development in China, where a new coal-fired plant starts up every week. The German energy agency, dena, has calculated that in Germany by 2030 a profound shortage of installed power plant capacity of almost 12,000 megawatts will force the construction of new plants fired by fossil fuels. It will take around twelve additional large power plants if this energy gap is to be filled. Thus in Germany, where coal is responsible for around a quarter of primary energy, the energy mix could move even further in the direction of coal.

Instead of less there will therefore be more carbon dioxide (CO<sub>2</sub>) expelled into the air during the next decades – that is unless technological breakthroughs appear on the horizon that could prevent this. And these are being tested at this very moment. Power plant operators summarise this under the term 'Carbon Capture and

Storage' (CCS). The concept: CO<sub>2</sub> is separated before or after burning in the power plant and then forced into the earth, for example into former natural gas repositories or in rocks containing brine where it remains in containment for thousands of years.

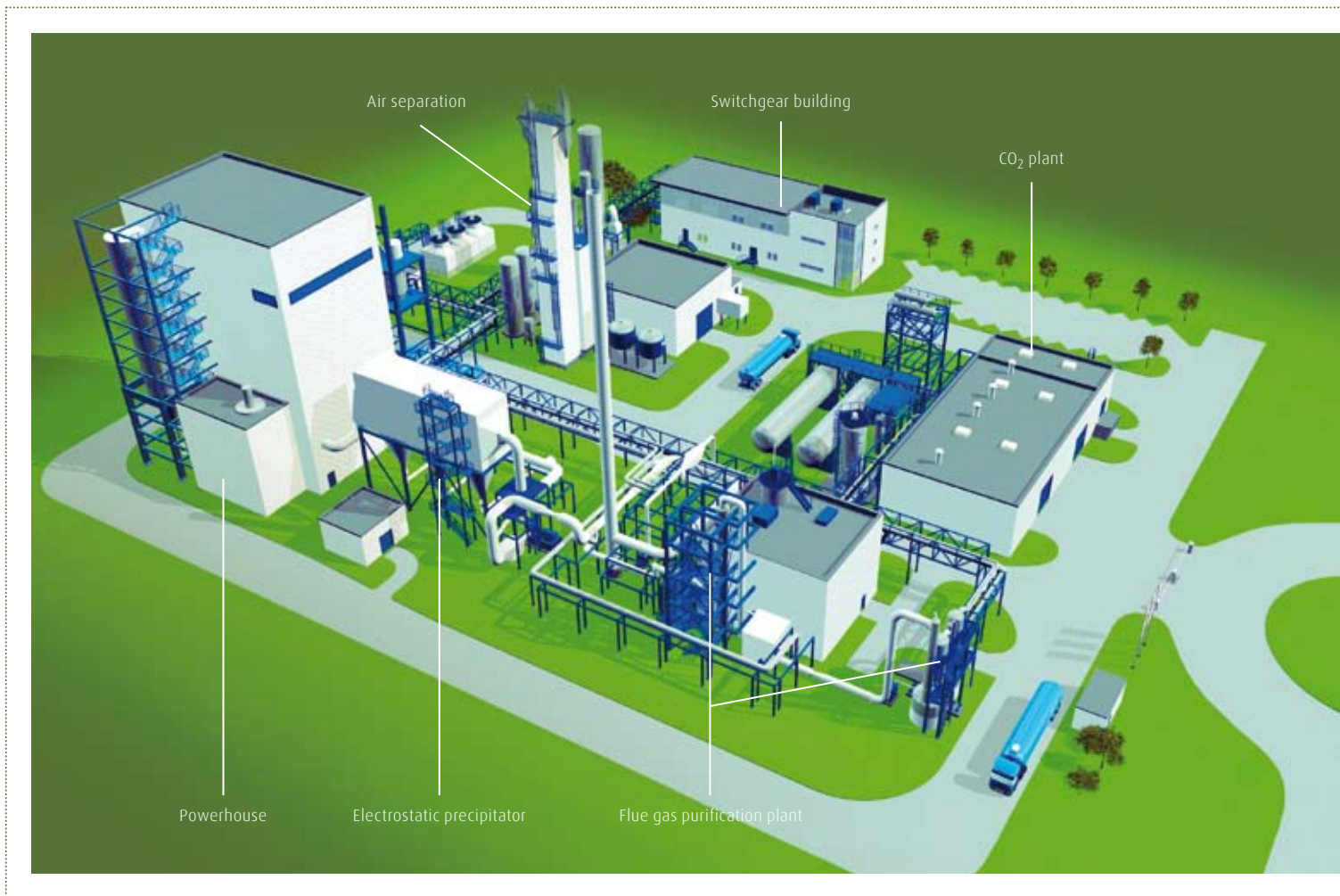
Methods to collect the environmentally detrimental gas in the power plant are currently being examined in the industrial district of Schwarze Pumpe in Brandenburg, Germany, where the energy company Vattenfall operates a pilot facility. Here the way CCS should finally operate in large-scale power plants can be acted out on a small scale. The facility burns 5.2 tonnes of brown coal per hour and in the process creates nine tonnes of CO<sub>2</sub> at a capacity of 30 megawatts. The CO<sub>2</sub> is then so thoroughly purified that it could be used to carbonate mineral water – a whole swimming pool in an hour. However, since that much water would be impossible to drink, the CO<sub>2</sub> is instead liquefied and brought in tanker vehicles to the Altmark, south of Salzwe-

del, where it is to be forced 3,500 metres deep down into an almost exhausted natural gas field. Down below it is used by the French company GDF Suez to boost gas production. Another storage variant is being investigated by the GFZ Helmholtz Centre Potsdam in Ketzin, Brandenburg, where the climate gas is being compressed into a

*CARBON DIOXIDE  
SO PURE, YOU  
COULD ALMOST  
USE IT TO  
CARBONATE  
MINERAL WATER.*







600 metre deep saline aquifer – a sandstone layer filled with saturated brine.

The test facility in Schwarze Pumpe works according to the Oxyfuel principle – one of three possible concepts for a reduced-CO<sub>2</sub> power plant. An air separator removes the nitrogen from the air before it enters the boiler. Thus the coal is burnt using a mixture of oxygen and CO<sub>2</sub>. The advantage: the flue gas volume is smaller since there is no nitrogen; the high temperature allows a high efficiency and the CO<sub>2</sub> is easy to collect.

#### 4,600 tonnes of oxygen per day

The small power plant serves as a mere stepping-stone for larger projects. Vattenfall is planning the next step in Jämschwalde in Brandenburg, where the second largest power plant in Germany is situated with six coal-fired power-generating units of 500 megawatts. An Oxy-fuel power plant with a power capacity of at least 250 megawatts is to be built here by 2015. 4,600 tonnes of oxygen per day will be required here with an accumulation of 5,650 tonnes of CO<sub>2</sub>. Jämschwalde is one of six projects to be supported as part of the EU's CCS programme which has a total funding budget of 1.05 billion euros.

Vattenfall receives 180 million euros for Jämschwalde – it is the sole project of its kind in Germany. Of the seven projects in the EU, two will utilise the Oxyfuel procedure and one will utilise the IGCC concept (Integrated Gasification Combined Cycle). This prepares almost any combustible carbon-based fuel for use in a gas turbine and is already in use today in chemical factories. The other projects are using the post-combustion procedure by extracting the CO<sub>2</sub> from the flue gas after combustion.

Linde is applying to be a partner of some of the EU projects supported so far. It has not yet been decided for which one the company will be selected. However, Dr Gerhard Beysel, who is the Manager of Business Development for Air Separation Plants at Linde Engineering in Munich, is optimistic: "Thanks to our partnership with Vattenfall at Schwarze Pumpe, we have achieved a technological advance."

One example are the dynamic load change tests that Linde has carried out in the testing facility. Large cryogenic air separation units in the chemical industry or steel manufacture supply a continuous amount of oxygen by extreme cooling and liquefying of air which is then separated by evaporation at different boiling points – com-

## ← OXYFUEL FOR SCHWARZE PUMPE

### CLEANER WITH OXYGEN

On the grounds of the industrial district of Schwarze Pumpe, Vattenfall Europe has built a pilot facility for capturing CO<sub>2</sub> by the Oxyfuel process in close proximity to the Schwarze Pumpe power plant. The Vattenfall pilot plant is fired with brown coal and has a thermal output of 30 MW. The plant generates no electricity, rather it distributes process steam to plants in the Schwarze Pumpe industrial district.

Its technological basis is the Oxyfuel process, wherein coal is burnt in an atmosphere of pure oxygen and CO<sub>2</sub>. The resulting flue gas is therefore undiluted by nitrogen in the air, consisting primarily of CO<sub>2</sub> and water vapour. The water vapour is condensed out with little effort, so that a highly concentrated stream of CO<sub>2</sub> remains. The CO<sub>2</sub> can then be compressed and transported to the storage system.

Following from the results and insights gained in Schwarze Pumpe, there are now plans to build a demonstration plant in Jämschalde with a thermal output of about 250 MW. With this power plant, the technology used here shall be made ready to enter large-scale production.



*Overview of all processes: an employee of the Vattenfall pilot plant reviews the data from individual process steps.*



*Pilot plant under control: with a modern process control system, the Oxyfuel process can be closely monitored.*

parable to alcohol distillation. The capacity of a power plant wavers according to energy demand, which up until now was no problem with typical air-ventilated facilities. In contrast, oxygen production in Oxyfuel power plants must follow power generation – otherwise too much of the valuable gas goes unused and wasted. “The load alternations have worked and were actually much faster than expected,” says Beysel. The measures include the entire design of the facility – even the process control system has been accelerated.

Air separation at low temperatures has been perfected over many decades and would supply plenty of oxygen, even for big Oxyfuel power plants. One production line creates up to 100,000 cubic metres of oxygen per hour. However, oxygen production also has its disadvantages: previous calculations indicated that oxy-

gen production in an Oxyfuel power plant devour a third of investment costs and even almost a quarter of the facility’s own energy requirements. Through CCS, the overall efficiency is reduced by up to ten percent, which is due to a considerable extent to the oxygen provision. For this application, which does not require high-purity oxygen,

**100,000 CUBIC METRES OF OXYGEN PER HOUR OF AIR SEPARATION.**

the procedure concept of cryogenic air separation has therefore been adapted so as to achieve energy savings of some 25 percent compared to conventional procedures.

However, the power plant operators also hope for new processes that are to supply oxygen with minimal energy and cost requirements. Otherwise a modification of modern power plants to incorporate CCS technology would set the power plant parks back to the efficiency level of the sixties. The so-called CAR process inspires hope, however. The abbreviation stands for Ceramic Auto-thermal Recovery. Air is channelled at temperatures of 600 to 800 degrees Celsius via a bed of perovskite pellets. Perovskite – a class of mixed metal oxides, for example LSCF, which contains oxides of lanthanum, strontium, cobalt and iron – can accommodate astonishingly large amounts of oxygen at this heat while nitrogen and other trace gases stream by unobstructed. When the mineral oxygen reservoir is full, CO<sub>2</sub> or steam is channelled through the bed that elutes the oxygen and transfers it to the power plant’s combustion chamber. CAR has a number of advantages: it uses low

pressure and oxygen production can be finely adjusted. The disadvantage: due to the high temperature, CAR requires additional energy that must be supplied by a fuel gas, which is added to the air and keeps the thermic process stable.

In a project for the USA Department of Energy in 2006, Linde built a CAR testing facility that supplied 0.7 tonnes of oxygen per day. The tests proved that the energy requirements are around 30 percent less than with a cryogenic air separator – the investment costs were even almost halved. However, the planned demonstration power plants with CO<sub>2</sub> separation would have to forget about these advantages, as the oxygen yielded at the testing facility did not reach the set target. Instead of two percent, the perovskite only accumulated 0.5 percent of its own weight in oxygen – too little for a large-scale technical operation. Indeed, the oxygen capacity could be increased, but at a cost to material stability and service life. The planned second phase of the project, the construction of a facility with ten tonnes of oxygen per day and its combination with a coal burner, was therefore postponed in 2008. “We are still convinced by the potential of the CAR process. However, we have determined that further basic research of the material composition is necessary,” explains Krish Krishnamurthy, who is responsible for energy innovations in the Innovation Management department of Linde. These activities are now in progress at the University of Arizona and by manufacturers of perovskite, amongst others.

### Testing post-combustion treatment

Oxyfuel power plants, which burn coal using pure oxygen, are the most advanced example of future CO<sub>2</sub>-free power plants. However, not everything that is technically feasible will win through. In opposition to the approach with Oxyfuel and IGCC, where CO<sub>2</sub> separation precedes combustion, stands the classical post-combustion facility in which the carbon dioxide is separated after combustion. A flue gas scrubber is located before the chimney that extrudes the CO<sub>2</sub> from the waste gas. An important advantage: nothing changes at the power plant, nor during the combustion process – even older facilities can be modified.

Tests using this post-combustion procedure have been in progress for half a year in Niederaussem in North Rhine-Westphalia, Germany, where the energy producer RWE operates a 1,000-megawatt coal-fired power plant. For the test, a small amount of the waste gas, the equivalent of a two-megawatt power plant, is diverted and channelled through a scrubber. The flue gas ascends upwards through a separation column, while a liquid trickles down from above. The liquid contains amine, a chemical relative of ammonium, which captures large amounts of CO<sub>2</sub>. In a second tower, the CO<sub>2</sub> is expelled again using steam. The liquid is clean once more and arrives back at the scrubber in the closed cycle.

The scrubbing liquid in Niederaussem is provided by the BASF; LKCA-Dresden, a subsidiary of Linde, constructed the scrubbing facility according to the chemical company’s specifications. In January 2010, both companies agreed to market the technology for separation of

### *CO<sub>2</sub> CAPTURE FROM FLUE GASES ASSISTS IN THE RECOVERY OF CRUDE OIL.*

CO<sub>2</sub> from flue gas together – particularly in the Near and Far East, where CO<sub>2</sub> is required for yielding from crude oil fields. In order to be able to equip other power plants with the post-combustion scrubbers,

Linde has formed a project partnership with Mitsubishi Heavy Industries. The Japanese company has developed its own technology based on another scrubbing fluid, which Linde will be offering for various power plant projects currently advertised in the EU. The following is valid for both CO<sub>2</sub> scrubbing procedures: they use a lot of energy due to the regeneration of the scrubbing fluid with hot steam; the efficiency level of the power plant will decrease by around ten percent, as with Oxyfuel. “We still have a lot of work ahead of us,” says Dr Bernd Holling, the Manager of Business Development for Chemical and Gas Plants at LKCA-Dresden.

With pre-combustion, Oxyfuel and post-combustion, power plant constructors have the choice between three strategies for CO<sub>2</sub>-free power plants. As all three procedures display advantages







*Securely transporting and storing: carbon dioxide from the flue gas that accrues in Schwarze Pumpe is taken by tank truck 400 kilometres to the Altmark and there injected into an exhausted natural gas field.*

as well as disadvantages, it might be sensible to combine them in such a way that the disadvantages disappear and only the positive effects remain. It is exactly this approach that RWE npower is following in England. Instead of burning the coal with a mixture of CO<sub>2</sub> and oxygen as in an Oxyfuel plant, this approach considers a mixture of air and oxygen aimed at reducing the nitrogen but not completely removing it. As there is no pure CO<sub>2</sub> present in the waste gas, this must be separated from the remaining gases by use of the scrubber. Future power plant operators would therefore have to erect two facilities; the oxygen plant and the scrubber. "Calculations show, however, that this combination could provide advantages in specific cases in terms of lower energy consumption or operational flexibility," says Krishnamurty. Linde is working closely with RWE npower to develop an optimised process design.

Technologies for CO<sub>2</sub> deposition can make an important contribution in curbing climate change – however, they are not an alternative to regenerative power production. Due to the loss in efficiency levels, more coal would have to be burnt, which does not fulfil

the essence of a renewable energy economy. Aside from that, CO<sub>2</sub>-free power plants are at best only CO<sub>2</sub>-reduced facilities – five to ten percent of the CO<sub>2</sub> caused by combustion is expelled into the atmosphere. Bernd Holling explains, "otherwise the expense would be way too high". CCS is therefore recognised by experts as a mere bridging technology – nevertheless an indispensable one. Manfred Volker Habertzettel, authorised agent for technology, PR and politics at energy provider EnBW also sees it as such: "The separation and storage of CO<sub>2</sub> may be a further waste of resources, but on a global scale we have no alternative."

LINKS:

[www.vattenfall.com/en/ccs/index.htm](http://www.vattenfall.com/en/ccs/index.htm)

[www.encapco2.org/CECD/encap\\_sp5\\_fitch.pdf](http://www.encapco2.org/CECD/encap_sp5_fitch.pdf)

*CO<sub>2</sub> as a basis for the production of bioethanol using blue-green algae*

# MINIATURE FACTORIES FROM THE SEA

Algae are exceptionally gifted chemists and help climate protection. This is because algae such as cyanobacteria, also known as blue-green algae, use CO<sub>2</sub> and sunlight to produce chemicals such as carbohydrates, lipids and amino acids. In special cases they even produce bioethanol, which is a valuable substance for the chemical industry and for the use as fuel or fuel additive. Linde engineers together with algae specialists from Algenol Biofuels are developing technologies in order to provide the green cell factories an optimum feed of CO<sub>2</sub>.

The minute, micron-sized cells which can not be seen without a microscope prefer to breathe in carbon dioxide and to drink salt water – oxygen just incurs as annoying waste. Cyanobacteria, more commonly known as blue-green algae, survive by swallowing up the green house gas CO<sub>2</sub>, and they've been doing this for over 3.5 billion years. As the marine bacteria populated the oceans en masse, energised by means of sunlight harvested by photosynthesis, they decidedly altered the earth's atmosphere. Pearls of oxygen gas bubbled out of the countless cells without pause and blew more and more oxygen into the atmosphere. Even today, we sap the 'waste gas' of cyanobacteria. Today we can be thankful to the green cell factories for having practically produced nearly every second oxygen atom that we breathe in.

Research scientists are interested in the innermost part of the cells: their metabolism. Molecular biotechnology has long since used yeast and other bacteria cells as well as fungi as useful minute chemical plants. Using bio-based catalysts, the enzymes, they can produce numerous substances: raw materials for the chemical industry and fuel, building blocks for pharmaceuticals or nutrients and vitamins for animal feed. In addition, these mini-factories are particularly friendly to the environment. Even cyanobacteria which are living both in marine as

well as land environments are interesting for industry. Scientists from the company Algenol Biofuels, for example, studied and modified the metabolism of the cells and stimulated them specially to produce bioethanol. The alcohol can thus serve as fuel or raw material for the chemical industry.

The advantage of the green mini-factories is that they only need a salty broth of nutrients, sunlight and CO<sub>2</sub> to survive. "Each carbon atom in an algae cell comes from the CO<sub>2</sub> in the air which is absorbed by the algae after dissolving in the seawater," explains Dr Mathias Mostertz, biotechnology engineer and Green Power Manager at Linde AG's Innovation Management department. In order to cultivate cyanobacteria in very large amounts, the living conditions must be optimal: they swim in so-called photobioreactors. They obtain their primary nutrition from air, enriched with carbon dioxide. "An enhanced carbon dioxide feed has the same effect as fertiliser on blue-green algae," says Mostertz.

Globally, more than 150 firms are dealing with the issue of biofuels from algae. The vision of these companies: extensive algae farms cultivate the mini-factories in seawater and produce the valuable fuel. "The amounts of CO<sub>2</sub> that these algae farms will at some point later need are immense. Farms like these will be up to 20,000

**ALGAE FARMS  
CAN ABSORB  
MASSIVE QUANTITIES  
OF CO<sub>2</sub>  
AND PRODUCE  
BIOETHANOL.**





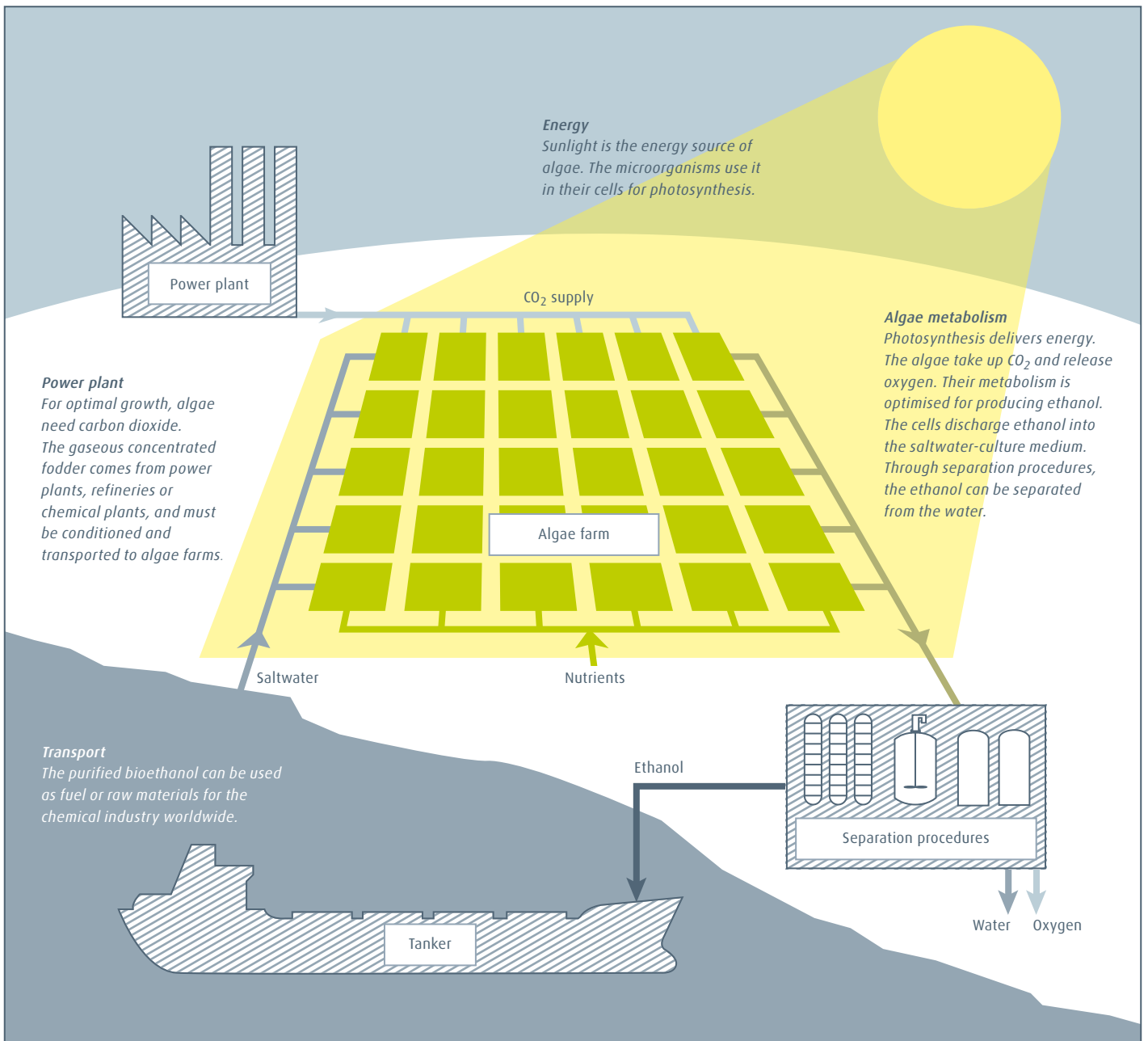
*CO<sub>2</sub> eaters: cyanobacteria, also called blue-green algae, absorb carbon dioxide and exhale oxygen.*



*Green factory: in special plastic containers, the blue-green algae create an ethanol-water mixture with the help of sunlight, CO<sub>2</sub> and a saltwater blend. The concentration of alcohol is further increased by the following physical and chemical procedural steps.*



## BIOETHANOL FROM THE ALGAE FARM ↴



hectares large and would be able to process around two-thirds of the CO<sub>2</sub> emissions from a 1,000-megawatt power plant," continues Mostertz.

### High-efficiency carbon dioxide converters

Their past explains as to why algae are the real CO<sub>2</sub> terminators: since primeval times, the algae have become used to high concentrations of the greenhouse gas. Land-based plants can also filter carbon dioxide from the atmosphere, producing biomass or useful by-products. However, their appetite is already saturated after a much lower dose of CO<sub>2</sub> – just below one tenth of a percent. Additional fertilisation doesn't encourage more growth. "Algae, in contrast, can deal with a ten percent dose of carbon dioxide. This is why they produce two to three times more biomass per time and area than land-based plants," says Mostertz. "As the world's largest supplier in CO<sub>2</sub>, we are trying to support companies such as Algenol with know-how about gases," explains the biotechnology engineer from Linde.

At the end of 2009, Linde started a research cooperation with the American algae experts from Algenol. Within this project, Linde's gas specialists are working on the identification of the most suitable CO<sub>2</sub> sources, and separation, cleaning and transportation of the gaseous algae feed. "First and foremost, the waste gas from coal-fired power plants and refineries comes into question. The aim is to clean the waste gases enough that the microorganisms don't perish," explains Mostertz. This is because each additional step costs energy and affects the CO<sub>2</sub> balance of the entire process, whether it's cleaning, compressing or liquefying the gas. This, however, should come out as significantly carbon reduced or carbon negative in the end in order for the whole process to remain economically and ecologically viable.

The bio-scientists from Algenol deal with the green mini-factories and develop the optimum cyanobacteria. The blue-green algae are natural producers of valuable ethanol in very small amounts. However, the cells only switch their metabolism to alcohol production if they are going hungry or are starving in darkness. The bacteria's emergency plan has been enhanced by researchers using biomolecular methods: they enhance natural enzymes or have inserted enzymes from related organisms and have developed an efficient hybrid-algae with tailored metabolisms that can also produce the desired molecules, even when there is a lot of sunlight. Fed with water and car-

bon dioxide, the algae enzymes process the separate components into sugar precursors. This is then fermented and, much like brewer's yeast, turns to ethanol, which they then secrete into the seawater culture. Using this so-called direct process, researchers are looking to save time and money, as they do not have to destroy or harvest the mini-factories in order to capture the valuable target product. The alcohol can be obtained directly from the green solution during the Algenol procedure. "Our enhanced algae can produce approximately 350 litres of ethanol from one tonne of CO<sub>2</sub>," explains Paul Woods, CEO of Algenol Biofuels.

In contrast to the Algenol technology other algae to fuel companies are taking an indirect approach. They trim the algae to produce a maximal amount of lipids within the algae cell. In order to harvest the lipids, the microorganisms have to be destroyed. Using a combined chemical and mechanical process technology, the obtained extract has to be cleaned and transformed into fuel, such as biodiesel.

### Optimally dosing algae fodder

Algenol cultivates the valuable green mini-factories in special photobioreactors: these are made from a flexible plastic film that allows sunlight to shine through, providing the bacteria with an energy source. The oblong bags are filled up to almost a quarter with the algae/saltwater mixture. The vapour space above is used to harvest the valuable product ethanol. Here's how: the sun heats up the inside of the closed reactors so strongly that the obtained ethanol/water mixture vaporises. In the night, due to the colder ambient air temperature the ethanol/water vapour condenses. Fine grooves on the inner side of the specially developed plastic skin allow the condensate to be captured. This liquid contains approximately one percent of ethanol. Following a proprietary Algenol physical and chemical procedure, the water is separated out step-by-step and the ethanol concentration increases.

Since the algae 'inhale' CO<sub>2</sub>, but also 'exhale' oxygen, the amount of these gases have to be controlled. "In order for the microorganisms to function at an optimal level, we have to regulate both gases precisely," explains the biotechnology engineer.

During the entire chain of procedures, all economic and ecological aspects, such as energy costs and carbon dioxide balance, have to be evaluated. In doing so, a lot of questions arise for the

### FOSSILISED ALGAE

Cyanobacteria belong to the oldest still living organisms that use sunlight as an energy source and perform photosynthesis. It is in this way that they can reproduce and generate energy-rich products such as starch, sugar or lipids. Thanks to them, the earth is now surrounded by an oxygenated shell, the atmosphere. Depending on the

composition of the pigments, to which chlorophyll also belongs, the blue-green colouration changes. The cyanobacteria owe their name to the blue pigment phycocyanine. On countless beaches one can find fossils of blue-green algae, so-called stromatolites (photo left).



*Algae farm in the desert: the immense algae farms of the future could arise in regions not usable for normal agriculture. The computer simulation shows the planned testing facility for an algae farm in the Sonoran Desert in Mexico.*



CO<sub>2</sub> managers: how much does the amount of CO<sub>2</sub> and its transport cost? How much energy is required for cleaning and compression of the power station's waste gases? How can I set up an efficient supply of gas to bioreactors – without causing large pressure drops in the pipeline systems? "This is an extremely iterative process," says the Linde manager. "Most of the technology for each step exists. However, for the algae project we have to optimise and readjust these processes," states Mostertz.

### Bonding CO<sub>2</sub> durably

The goal of the algae experts is an ambitious one: they want to produce up to 9.3 litres of ethanol per square metre (10,000 gallons per acre year). "In our current test facilities, the yield was up until now a good 5.6 litres per square metre per year (6,000 gallons per acre year)," explains Woods. "By working together with Linde, we expect to find a cost-effective supply of CO<sub>2</sub>," Woods continues. "We are thereby not only reducing the amount of greenhouse gases in the atmosphere, but also supplying a sustainable raw material for bio-fuels and green chemistry," states the Algenol CEO.

Furthermore it must be recalled that ethanol's natural characteristics also instantly translate into benefits as a fuel for mobility. First, the process recycles the CO<sub>2</sub> emission by burning the fuel and then reabsorbing it to make a new gallon of ethanol. The second benefit is that it displaces a comparable amount of fossil fuels which

were not used the first or second time. This strictly implies a carbon-negative production process. Using the ethanol as building block for plastics production leads to a permanent sequestration of the CO<sub>2</sub> unless the plastic is burnt.

The advantages of blue-green algae in contrast to biofuel production from grain are unbeatable: not only do they eat up more carbon dioxide from the atmosphere, but they also produce more ethanol. Corn plants, for example, just about manage to produce a 0.37 litre of ethanol per square metre (400 gallons per acre year). In addition, algae cultivation does not stand in competition with the food industry.

Since no freshwater is required, areas unsuitable for normal agriculture can be used: a future commercial facility for an algae farm is, for example, planned in the Sonoran Desert in Mexico, on the border to the United States. Cyanobacteria may only be one piece of the jigsaw puzzle in the battle against climate change, but they have already helped at least once in revolutionising life on earth.

LINKS:

[www.algenolbiofuels.com](http://www.algenolbiofuels.com)  
[www.ucmp.berkeley.edu](http://www.ucmp.berkeley.edu)



## SHORT INTERVIEW

# “WE ARE VERY EXPERIENCED CO<sub>2</sub> MANAGERS”

Energy, mobility, society – climate change calls for not just different technologies but real innovations, as in the case of CO<sub>2</sub> management. ‘Linde Technology’ spoke with Dr Andreas Opfermann, Head of Innovation Management for The Linde Group.



## ↳ WHAT CAN YOU EXPECT FROM COOPERATIONS LIKE YOURS WITH ALGENOL BIOFUELS LLC?

Here we are connecting the fields of energy/resources with climate protection. If we can realise the technology and economy for such projects, it won't just be a contribution to resource conservation and climate protection, but will also open huge new markets for us. We already have a wide range of experience in the classical use of CO<sub>2</sub> as an industrial gas, as well as in handling CO<sub>2</sub> in the climate protection field. An example is the OCAP project (editor's note: see page 37).

## ↳ WILL THERE BE MORE OF THIS TYPE OF COOPERATION?

The world today has become so complex that when it comes to major new developments, collaborating with partners is the best approach. We have a clear profile and our core competencies, but we want to expand these strengths together with different partners in new fields like energy and climate protection. In the future, too, we will react both strategically and flexibly to changing circumstances – especially in the field of energy. Thereby Linde can build on a unique wealth of experience around the subject of CO<sub>2</sub> management. We are very experienced CO<sub>2</sub> managers.

## ↳ WHAT MAKES LINDE ESPECIALLY STAND OUT IN CO<sub>2</sub> MANAGEMENT?

In this field, Linde can truly apply their strengths in the combination of Gases Division and Engineering Division. In the Gases Division we are the largest CO<sub>2</sub> supplier worldwide. The management of megaprojects is a special strength of our Engineering Division. And precisely this combination generates technological and economically innovative approaches necessary for such ambitious projects as Carbon Capture and Storage (CCS), Green Mobility and alternative energy production. Most climate protection projects are driven by technological developments in those fields where we have already been strong for many years, operating worldwide and researching together with cooperation partners – hydrogen as fuel, for example.

## ↳ HOW DO YOU ASSESS THE SUBJECT OF HYDROGEN FOR THE FUTURE?

Still extremely positive. We have made enormous progress in the past years. Fuel cell vehicles offer all of the benefits of electrical mobility, combined with wide range and fast refueling. Now the goal is to reduce the costs of H<sub>2</sub> down the entire chain of production, distribution and use, enabling the widespread use of hydrogen as fuel. And the conditions for this have never been as good as today.



*Spanish electricity factory:  
the solar cells for the Parque  
de Solar Arnedo in Spain were  
produced with the help of  
Linde gases.*

*Improved CO<sub>2</sub> balance from thin-film solar cells*

# SUN CATCHERS, EXTRA GREEN

Image source: Linde AG  
Author: Tim Schröder

The solar industry boom was surely hindered by the economic crisis, but new factories for photovoltaic devices are nonetheless springing up worldwide. Still, it is imperative to further improve the CO<sub>2</sub> balance in solar module production itself. Linde engineers have now found a way to replace the extremely harmful greenhouse gas nitrogen trifluoride – and thereby to significantly improve the economic balance of modern thin-film solar modules.

Photovoltaic is one of the most charming energy forms. Rising efficiency and sinking manufacturing costs make the modules profitable even where the sun seldom shines. Thin-film technology, a material-saving and thus cost-effective alternative to classical photovoltaic systems, should now sink to even lower prices. The heart of the conventional modules is made of the semiconducting material silicon, which is also used to make computer chips. But in factories the silicon is usually laboriously sawed from massive blocks into 150 micrometre-thick slabs, or wafers. The module is ultimately composed of multiple wafers. But silicon is expensive, and therefore: who saves silicon, saves money.

That is exactly the goal in mind with thin-film technology. In this process, silicon and other semiconducting materials are evaporated in a vacuum chamber and deposited as an extremely thin layer on a glass sheet. In full, this highly sensitive silicon skin is one to two micrometres thick – 100 times thinner than classical wafers. In the past years, more than 30 companies worldwide have nurtured the silicon thin-film process to maturity, bringing more and more modules to the market. The plant technology is still young, the output low and

accordingly the price for a module not much less than that of a classical wafer module. But the potential is enormous: in an optimistic study, the European Photovoltaic Industry Association (EPIA) in Brussels predicts that photovoltaic can deliver 12 percent of electricity demand Europe-wide by 2020. As it now stands, thin-film technology should contribute a third of that.

## THIN-FILM TECHNOLOGY FOR COST-EFFECTIVE SOLAR CELLS.

As a regenerative energy source, photovoltaic also naturally contributes to reducing emissions of the greenhouse gas carbon dioxide. But there is something which spoils the young thin-film technology's lustre: for its production, one frequently needs nitrogen trifluoride (NF<sub>3</sub>) – an especially climate-threatening

greenhouse gas, whose 'Global Warming Potential' is about 17,000 times greater than that of carbon dioxide. Nobody had anticipated this when in the mid-1990s it became a component in the manufacturing of computer chips, later in the production of TFT flat-panel displays and finally in thin-film photovoltaic. Today we know that about 16 percent of the 6,000 tonnes of NF<sub>3</sub> produced yearly accumulates in the atmosphere – and the trend is rising. Where and how NF<sub>3</sub> leaks from the industrial plants is still largely unsolved. The Ame-





rican Environmental Protection Agency (EPA) has sounded the alarm and added the substance to its list of particularly problematic greenhouse gases, and meanwhile in Germany the Federal Environmental Agency is examining in detail the dangers of NF<sub>3</sub> in an ongoing study.

### Environmentally friendly cleaning process

The trepidation about the dangerous greenhouse gas is great, although it actually only plays a minor role in photovoltaic production, since NF<sub>3</sub> is a common cleaning agent used to clean the vacuum chamber of a thin-film plant. During coating, the silicon and other semiconducting materials don't merely sediment on the glass sheets, but also on the walls of the chamber. These impurities disturb the finely tuned coating process and must therefore be permanently removed. Once a glass sheet has been coated, the next step is to clean. The nitrogen trifluoride is compressed into the chamber. In a matter of seconds the highly reactive fluorine atoms tear the silicon from the walls of the chamber. It creates silicon tetrafluoride gas, which is simply pumped back out. The next coating procedure can begin.

"Until recently, there was no environmentally friendly alternative in thin-film technology," says Andreas Weisheit from Linde Electronics, a venture of Linde AG. But in the last year, the engineer and his team, along with the German thin-film photovoltaic firms Malibu and Masdar PV, have made a breakthrough. The cooperation partners have put two pilot plants in operation, which use the entirely climate-neutral fluorine (F<sub>2</sub>) in place of NF<sub>3</sub>. Normally the conversion of a plant to environmentally friendly processes costs money – but not in this case. "We could show that the production process has become not only more eco-friendly, but even cheaper

and faster," explains Weisheit. The firm Malibu, a joint venture of the energy supplier E.ON and the building material producer Schüco, has its own research laboratory where new technologies are developed. A new pilot line has been installed here. Linde delivered the core component: a fluorine generator which produces pure fluorine for vacuum chamber cleaning on-site.

"The technology is established. For about ten years Linde has delivered such devices for cleaning processes to the computer chip industry," says Weisheit. For five years, manufacturers of TFT flat-panel displays have furthermore had quite large fluorine generators at their disposal, which deliver up to 100 tonnes of fluorine gas per year for vacuum chamber cleaning. Naturally the requirements of a thin-film photovoltaic plant are different in detail. "One of our tasks was adapting the fluorine generator to the new requirements, so that it could be easily integrated into the production line," says Weisheit. The results are quite impressive: under realistic production conditions, the production line (including coating and cleaning) delivers thin-film elements of the usual high quality. And there's more: thanks to the fluorine generator, the plant works considerably faster than before. The reason? Pure fluorine is more chemically reactive. The individual fluorine atoms are much more loosely bound to one another in the gaseous F<sub>2</sub> molecule, which contains two atoms, than in the NF<sub>3</sub> molecule. With just minimal energy input, the atoms in the F<sub>2</sub> molecule separate into individual charged fluorine ions, which then react with the silicon deposits on the vacuum chamber walls. "The speed of thin-film production is governed by its most integral components, the coating process and the downstream cleaning," says Weisheit. "Since F<sub>2</sub> works more efficiently, the entire

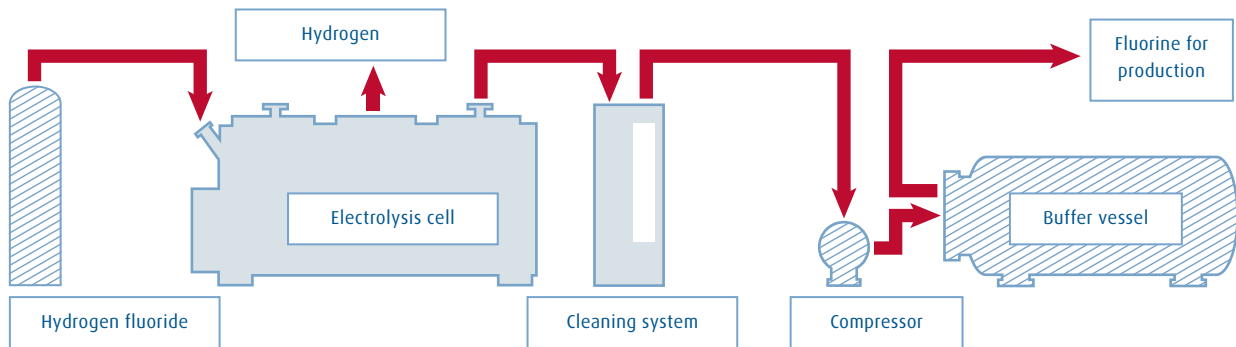
## CLIMATE-NEUTRAL FLUORINE REPLACES FUTURE GREENHOUSE GASES IN PRODUCTION.



*High tech for solar electricity: in Spain's first factory for thin-film solar cells, 2.2 x 2.6-metre large solar modules are manufactured from nitrogen, hydrogen and climate-neutral fluorine.*

## THE WAY TO A PROPER CLEANING AGENT

With the F<sub>2</sub> generator, fluorine (F<sub>2</sub>) for the cleaning process can be generated directly on-site: hydrogen fluoride (HF) serves as a fluorine source, which is separated into its components in an electrolysis cell. The F<sub>2</sub> gas streams into a cleaning system which is filled with sodium fluoride salt. This is how potential HF residue is filtered out. Then the F<sub>2</sub> moves to a compressor which compresses the gas to a moderate working pressure (ca. 1.5 bar). A buffer vessel ensures that enough F<sub>2</sub> is available at short notice even on high demand.



production process becomes faster. Our tests show that the cleaning time has been halved and can thus accelerate the entire production by around ten percent.” The experiments at the pilot plant show that the ionisation of pure fluorine requires nearly 60 percent less energy than nitrogen trifluoride.

### Milestone in environmental protection

Masdar PV of Ichtterhausen has also already built a pilot plant with an F<sub>2</sub> generator. „We’re not only attaining the best cost-benefit ratio with this plant, with this new approach, we are also setting a milestone in the field of environmental protection,” says Rainer Gegenwart, CEO of Masdar PV. For fluorine is a very chemically reactive and corrosive element which reacts with many different substances. The security demands for plants in which fluorine is used are high. Adding to the difficulties, fluorine in its gaseous form is as a rule always stored under a relatively high pressure of around 30 bar. At the site of operation, it is relaxed to a working pressure of about 1.5 bar by pressure regulators. “Such a system requires many valves and pressure regulators,” notes Weisheit. “Those are sensitive points where leaks can occur.”

With the F<sub>2</sub> generators a different path has been taken. The fluorine is not delivered as a compressed gas under high pressure. Instead, the plant produces its own F<sub>2</sub>. Liquid hydrofluoric acid (HF) is stored in a barrel. According to need, an amount of the acid is channelled to a connected electrolysis chamber where it is separated into its components hydrogen (H<sub>2</sub>) and fluorine. In a cleaning module the existing fluorine gas is cleaned, then condensed to a working pressure of 1.5 bar with a compressor and finally conducted to the coating plant. The plant commands a buffer tank, so that sufficient F<sub>2</sub> is always available. All components are built into a large system cabinet and can easily be integrated into existing processes. “Natu-

rally, installation still demands a certain amount of effort, just like the adaptation of coating plant software,” Weisheit says. But that is straightforward. All the more so since Linde Electronics, as the operator of the F<sub>2</sub> generators, undertakes the necessary installation work. Nonetheless, other thin-film manufacturers hesitate to apply the technology. “The branch is young. Most productive plants have only been running for a few years,” according to Weisheit. To some, an alteration in procedure is just a disruption. But Weisheit and his colleagues have already taken up contact with other manufacturers. For instance the US firm Applied Materials, one of the world’s largest manufacturers of semiconducting materials, participated in some of the experiments with the pilot plants. But one still wants to wait for the fluorine generators to prove themselves. “Presently the challenge lies in qualifying the technology in order to convince others,” says Weisheit.

Winged by their success so far, Linde in collaboration with Malibu and Masdar PV has already established new production lines for both ventures. These should now produce thin-film solar cells in routine operation. It is already becoming apparent that the large plants also work remarkably more efficiently than their predecessors. Weisheit: “Whoever wants a climate-friendly production of environmentally friendly thin-film solar cells will sooner or later have to part with NF<sub>3</sub>.”

**LINKS:**

[www.recyclingportal.eu](http://www.recyclingportal.eu)

<http://linde-electronics.com>



*Only CO<sub>2</sub> can make water into a tingly drink*

## *NO PLEASURE WITHOUT CARBONIC ACID*

Without carbonic acid, we would have to swear off all sparkling drinks. The business of carbon dioxide is stable, but its seasonal fluctuation is considerable. To optimally supply clients in the beverage industry particularly in summer, Linde has built a sophisticated CO<sub>2</sub> supply system.

It's the number one climate killer, but without any CO<sub>2</sub>, life would lose its freshness: cola would taste flat, freshly-tapped pilsner would have no pep and the tingly refreshment of mineral water after sports – that would be gone too. For carbon dioxide reacts with water to make carbonic acid, and so brings the raw materials for bubbles and fizz. But so-called beverage carbonisation has other advantages too: "The procedure also stabilises plastic bottles and beverage cans and prevents oxidation. It thus ensures longer storage life for bottled liquids," explains Klaus Brandl from the Linde Gases Division. The principle applies: the higher the CO<sub>2</sub> content in cola or water, the more it fizzes and the longer the beverage lasts. The carbon dioxide content is also subject to geographic differences: "Asians and Americans prefer more carbonic acid than Europeans," says Brandl.

### **Loan from the chemical industry**

How much CO<sub>2</sub> is contained in individual beverages depends on the producers' recipe. Most of the carbon dioxide used comes from the chemical industry. There, the gas accumulates as a by-product of synthesis processes: for instance in ammonia synthesis, that is, in the generation of nitrogen fertilisers and in the production of ethylene oxide and hydrogen. While the CO<sub>2</sub> generated from brown coal power plants is poorly suited for further economic use on account of its composition and pollution, raw carbon dioxide from the above-named applications and processes is purified and compressed in special plants. "We don't produce supplementary carbon dioxide, but we borrow the process gas and use that," Brandl explains the advantages of recycling, "thus delaying the CO<sub>2</sub> emissions." A small portion of the





**CARBONIC ACID STABILISES PET BOTTLES, ENSURES TANGINESS AND LONGER STORAGE LIFE.**



*Gas for healthy beverages: the predominate part of the carbon dioxide that Linde delivers to the beverage and food industry stems from chemical processes and is purified and liquefied in special plants – ensuring that mineral water bubbles.*

the hot season sales and logistics often have to allocate 200,000 to 400,000 more tonnes for sparkling drinks in Europe within a few days.

“Right at the start of summer we begin pre-filling the tanks and optimising the filling routes for clients, so that the vehicle fleets arrive punctually at the beverage producers – and that without costly detours which would release supplementary and unnecessary CO<sub>2</sub> in transport,” informs the 44-year old industrial engineer. The entire supply chain management – from production, to client tank management with data transmission, up to individual bottles for restaurants – runs at top speed during summer.

**Secure CO<sub>2</sub> supply even during summer peak**

To adapt capacities to the needs of the beverage industry, heighten the company’s flexibility and guarantee supply security for customers even during summer peaks, Linde is presently synchronising and networking its 19 European recycling sites. Besides that Linde is currently building three more CO<sub>2</sub> purification and liquefaction plants: in the southern German town Gendorf, in Rouen (France) and in Jurong Island (Singapore). The plant in Rouen should be finished by mid-year 2010. “With this location we are improving and securing our West-European client supply network in particular. Thereby the gain will be up to 70,000 tonnes more per year,” explains Brandl. In Rouen, crude gas from fertiliser production will be processed. In Gendorf, ethylene oxide production will serve as the initial process for secure and stable CO<sub>2</sub> recycling; the plant is planned to go into operation in the latter half of 2010. “With Rouen and Gendorf, we will reach a capacity in Europe in excess of one million tonnes. Only thus can we optimally safeguard against possible resource shortages or the summer peak for our clients,” elaborates Brandl. With the plant in Jurong Island, Linde will also further cement its position in Asia. In Singapore the first carbon dioxide tanks will be filled at the start of 2011.

Brandl: “To guarantee an optimal CO<sub>2</sub> delivery service for our clients without getting into delivery problems during the summer peak, it is essential to invest in recycling plants for CO<sub>2</sub> near our clients, to optimally connect the logistical CO<sub>2</sub> network and to secure the highest CO<sub>2</sub> quality criteria, especially for use in the food industry.” A combination for a fresh beverage future: so that soda may evermore fizz in abundance, and that beer flow freely from the tap of every bar.

gases delivered by Linde comes from natural sources, while the predominate part comes from process carbonic acid.

Under the brand name Biogon®, Linde alone supplies German beverage producers with over 160,000 tonnes of the highest food-grade liquid carbon dioxide yearly. The yearly per capita consumption of beverages in Germany stands relatively constant, at around 750 litres. About 90 percent of that is produced and bottled in Germany. About 50 percent of all beverages consumed in Germany contain carbonic acid. Of that, beer makes up almost ten billion litres, carbonated water a good eleven billion litres and around 9.5 billion litres are comprised of other carbonated refreshment drinks.

**Constant business trend for beverage producers**

The business of beverage producers has run steadily for years. Linde clients from this segment have even observed a continual course of growth. “In contrast to the semiconductor or steel industry,” reports Brandl. The beverage industry battles with a completely different problem – the seasons. People drink considerably more soda, beer and mineral water in summer than in the winter months. Brandl: “There is a summer peak in this cyclical business.” In the cold months, customers consume about 800,000 tonnes of liquid carbon dioxide; in

Author: Heidi Wahl  
Image source: Linde AG

**LINKS:**

[www.waterquality.de/hydrobio.hw/2CHEM.HTM](http://www.waterquality.de/hydrobio.hw/2CHEM.HTM)  
[www.linde-gas.com](http://www.linde-gas.com)

[www.food.wi.tum.de/downloads/BWLDGetr.pdf](http://www.food.wi.tum.de/downloads/BWLDGetr.pdf)



*Better eco-balance through Linde cleaning process*

## *CLEAN THROUGH CO<sub>2</sub> SNOW*

Carbon dioxide has by now become an indispensable agent for special processes in industry: in the form of cryogenic snow particles, CO<sub>2</sub> is especially effective at cleaning plastic or metal surfaces prior to lacquering. The innovative new Linde process 'CRYOCLEAN® snow' is additionally more climate-friendly and economical than conventional methods.

Sometimes it even snows in factory buildings: almost at the speed of sound, streams of miniscule snow crystals blast out of two nozzles on a robot's arm, which move over a plastic component. From this jet of air and frozen carbon dioxide, only a bluish-white shimmer is visible which quickly dissolves into nothing. The tiny CO<sub>2</sub> snow particles tear dust and dirt from the surface of the plastic component, on its way to the paint-spray line and later to become a radiator grill. There, any impurities on the surface could prevent the lacquer from adhering correctly and possibly lead to unsightly bubbles. Therefore the radiator grill must be cleaned beforehand – a task which the robot accomplishes perfectly in a few seconds with the help of the CO<sub>2</sub> snow jet.

### **Cleaning 5,000 radiator grills per day**

The cleaning plant, which processes around 5,000 radiator grills a day, is located inside a production hall of Bolta Werke GmbH, about 20 kilometres away from Nuremberg, Germany. The process is called CRYOCLEAN® snow, developed with the help of Linde engineers. The plant requires several hundred tons of CO<sub>2</sub> per year. But the carbon dioxide used is not generated anew. "It accrues as a valuable by-product in industrial processes, and would normally make its way into the atmosphere unused," explains Rolf Heninger, Leader of the 'Plastics & Cryo' segment of Linde Gas. An example of such a process, wherein CO<sub>2</sub> builds up unavoidably, is the production of ammonia. Countless products rely on this basic material from the chemical industry: from fertilisers, to textile fibres and lacquers, up to antibacterial medications.

The dominant alternative to the new CO<sub>2</sub> snow shower up until now – washing plastic parts off with water, at most mixed with cleaning liquids – only seems more climate-friendly upon first glance. One such automated process whereby plastic parts are cleaned before lacquering is called 'Powerwash'. "When it comes to climate and environmental protection, CRYOCLEAN® snow has the advantage over the Powerwash process," says Heninger. Because with Powerwash, a component can pass through up to four different showers: the first cleans with 60 degrees Celsius warm water which contains an organic cleaning agent. Passages with conventional and demineralised water then follow. Leftover dampness and cleaning agent residue are finally blown away. Thereafter, the component usually has to dry off for half an hour at 80 degrees Celsius before lacquering. "The heating of the water and the furnace, the cooling, cleaning and recirculation of the water – that all requires a lot of energy, which today comes for the most part from natural gas and coal, which in turn release CO<sub>2</sub> when burnt," Heninger elaborates. Add to that the consumption of water, ion-exchange resins for demineralisation and cleaning chemicals. Summing it all up in the eco-balance, 'washing off' doesn't look nearly so 'green' after all.

*USING CO<sub>2</sub> FROM  
THE CHEMICAL  
INDUSTRY  
AND CLEANING  
AUTOMOBILE  
PARTS – ENTIRELY  
WITHOUT  
ORGANIC SOLVENTS.*

It would also be false to assume from the use of recycled carbon dioxide in the CRYOCLEAN® snow process that this cleaning method is absolutely carbon-neutral. "Clearly, energy is required to separate CO<sub>2</sub> from industrial sources, to liquefy and finally bring it to its site of operation," explains Heninger. The level of CO<sub>2</sub> emission

Author: Frank Frick  
Image source: Getty Images





*Clean without solvents: using CRYOCLEAN® snow, automobile parts can be cleaned efficiently and very economically. The dry ice process cleans the component surfaces in a single operation and makes organic solvents superfluous. It can reduce costs by up to 39 percent in comparison with conventional cleaning processes.*

depends on, among other things, the length of the transport route and whether the electricity used comes predominantly from coal-fired power plants as in Germany, or whether many atomic power plants are in operation as in France. For Germany, the extra emissions for each kilogram of carbon dioxide used are below 300 grams. "We now have to relate this result to the cleaned surfaces and then compare it with the value of the Powerwash process," argues Heninger. From this comparison, the Linde process comes out on top as the winner for the climate. And irrespective of climate relevance, CRYOCLEAN® snow still avoids the use of organic solvents as in the washing liquids.

### Economical and space-saving

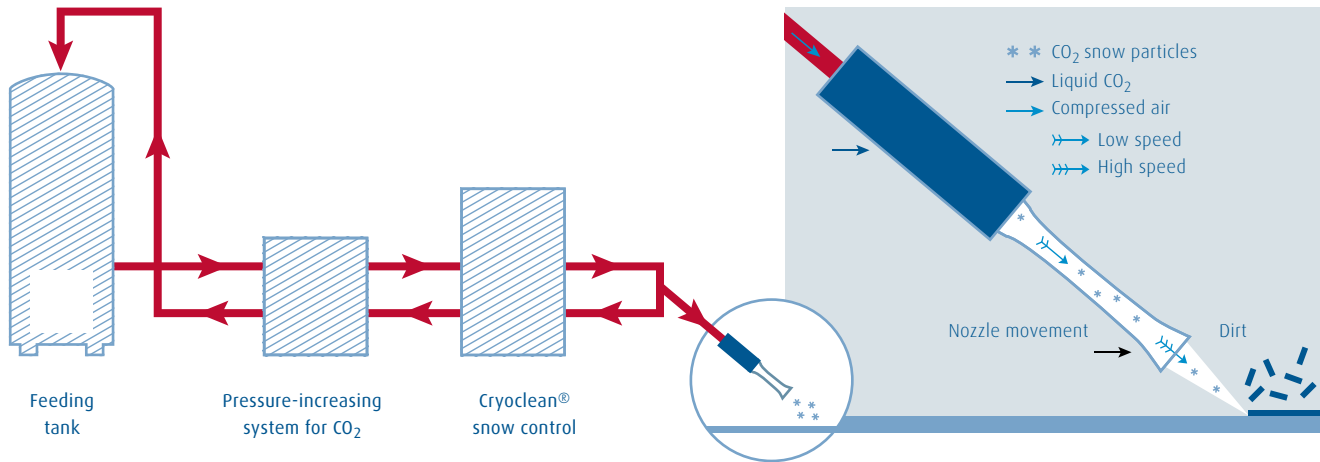
Another advantage is that "the cleaning is performed in one step and claims little space," says CRYOCLEAN® Project Leader Martin Blanke.

In contrast, the many showering and drying zones of the Powerwash plant require much space. Above all, though, CRYOCLEAN® snow is more economical. The Fraunhofer Institute for Production Systems and Design Technology (IPK), Berlin, can also confirm this. During the two-year joint project 'SnowLacquer', supported by the German Federal Ministry of Economics and Technology, both processes were directly compared to one another. The result: "The determined costs per component for the Powerwash process were found to be up to 39 percent higher than for the CO<sub>2</sub> snow jet cleaning," report Martin Bilz and Simon Motschmann from IPK in a trade journal. Heninger and his team at Linde appraise the investment costs with CRYOCLEAN® snow at around 75 percent lower than with Powerwash plants. "Moreover, in terms of operation costs, our process is normally cheaper," says Heninger. Blanke adds: "It also dispenses with the great effort of



## CLEAN WITH DRY ICE

The CRYOCLEAN® snow system has one basically new functional principle: the dry ice particles for cleaning are produced directly for momentary demand. By feeding liquid CO<sub>2</sub> into a specially designed snow chamber, exceptionally solid dry ice particles are generated and immediately blasted with pressurised air onto the surfaces to be cleaned: the dirt embrittles, and the adhesion diminishes.



water conditioning and handling cleaning agents.” For the CO<sub>2</sub> snow shower, liquid carbon dioxide is fed from a tank or cylinder into a special streaming apparatus wherein the liquid expands and cools accordingly. In split seconds solid, minus 79 degrees Celsius cold snow particles develop with a diameter of one to 10 micrometres. Besides that pressurised air is conducted into the streaming apparatus. This accelerates the CO<sub>2</sub> snow with the help of a nozzle, whereby the speed attained determines its cleaning efficiency.

### Dirt becomes brittle – adhesion diminishes

Two of the effects on which the cleaning depends are of mechanical nature: the CO<sub>2</sub> particles transfer their speed-dependent momentum to the surface of the substrate and thereby remove impurities. The force of the air jet supports this process. A temperature effect certainly also plays an important role: the coldness of the solid carbon dioxide embrittles the dirt, which hence can be easier destroyed mechanically. Beyond that, the dirt cools off more than the substrate, thus shrinking more. The resulting tensions eliminate the surface adhesion.

When the solid snow particles come in contact with the component surface, they change directly into gaseous CO<sub>2</sub>. In this process, also called sublimation, the volume of the carbon dioxide suddenly expands and creates a small shock wave. This also helps to detach dirt from the surface.

### Opening further areas of application

In the meantime, countless plastics processors have chosen CRYOCLEAN® snow: besides radiator grills, other products such as

automobile bumpers, high-value plant containers and vacuum cleaner housings are being cleaned. The industry is also using the process for metallic components, for instance to remove the smoke traces resulting from the welding of shock absorbers. Finally, the CO<sub>2</sub> snow also frees the moulds with which aluminium components are manufactured from release agent residues and other impurities. “Despite its countless pre-existing applications, the possibilities of the CO<sub>2</sub> jet cleaning are far from exhausted,” says Heninger. He is convinced that the cleaning process is also suited to more materials and for the preparation of components for gluing or welding. At present he and his team are working to increase the cleaning effectivity of CRYOCLEAN® snow and thus to open other areas of application.

LINK:  
[www.linde-gas.com](http://www.linde-gas.com)

*CO<sub>2</sub> for greenhouses and gas fields*

# NEW PIPELINES TO AID CLIMATE PROTECTION

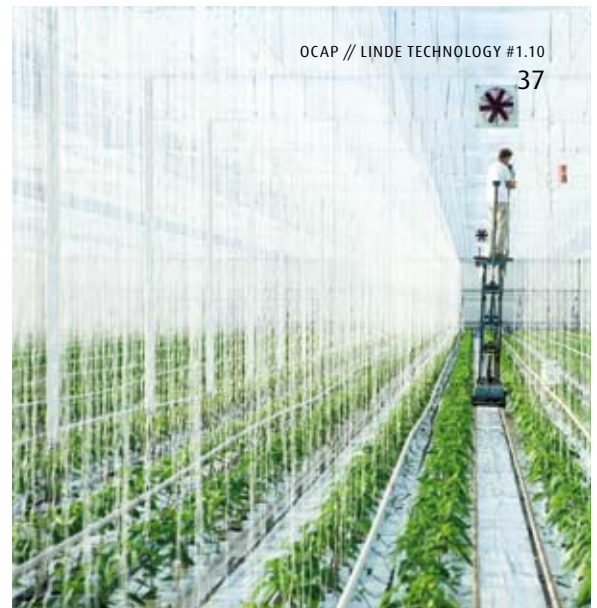
Half of the CO<sub>2</sub> emissions of an oil refinery are used to promote plant growth in Dutch greenhouses. Now there are plans to pipe the CO<sub>2</sub> into empty natural gas fields as well.

The greenhouse gas carbon dioxide has already come into high demand – at least in the area around Rotterdam: the CO<sub>2</sub> emissions from a Shell refinery located there are completely sold-out during the summer months. “We have been distributing the gas to greenhouse owners for five years now to accelerate and improve the growth of their plants,” says Hendrik de Wit, Director of OCAP and Linde employee. The gas is streamed from the refinery into hundreds of greenhouses through a pipeline network of around 300 kilometres. Each year more than 350,000 tonnes of carbon dioxide are re-used in this manner. “That yields a CO<sub>2</sub> emission reduction equivalent to emissions of a West European town with 150,000 inhabitants because the greenhouses stopped burning natural gas for CO<sub>2</sub> production,” reports de Wit. An additional and considerably smaller amount of the carbon dioxide is liquefied all-year-round by Linde and mainly sold to the food industry.

However, the demand for fertilising gas abates drastically when winter draws in. “During the colder months, the firms heat their greenhouses using gas ovens and thus produce their own carbon dioxide,” states de Wit. The carbon dioxide emissions from the refinery are then almost entirely expelled into the atmosphere. The OCAP partners now want to change this by making transport and compression possible so as to store the excess carbon dioxide in empty natural gas fields to the southeast of Rotterdam. An idea that very much stands to reason – in more ways than one: “The fields are not even 20 kilometres away from the refinery,” explains de Wit. Each year, they could accommodate around 280,000 tonnes and even 400,000 tonnes of carbon dioxide after three years, and this for up to almost 30 years of storage. OCAP’s role? Channeling the carbon dioxide through new pipelines to the former natural gas fields and compressing it to injection pressure.

But it’s not only the technical and construction details of their plans that the responsible parties are currently working on. They also

Author: Andrea Hoferichler  
Image source: Linde AG



**Greenhouse gas:** CO<sub>2</sub> from an oil refinery is to be stored in empty natural gas fields via a pipeline off the Dutch coast. So far, a pre-existing pipe network already serves hundreds of greenhouses, helping the plants there thrive.

**STORING  
280,000 TONNES  
OF CO<sub>2</sub> PER YEAR.**

have to gain acceptance for their idea. “The idea of underground carbon dioxide storage is simply unnerving for many people,” grants de Wit. This fear is to be dissolved by informational events. After all, carbon dioxide is neither poisonous, nor as flammable as the methane that was once stored in the fields. De Wit assumes that the first streams of carbon dioxide will enter the fields by 2013 at the latest. He already has new storage facilities in sight: “In the long term,” he says, “our pipeline network could also be expanded for offshore reserves of carbon dioxide.”

As there will definitely be more than one carbon dioxide supplier, more storage capacity will be required soon. “In the future, we want to be able to supply the greenhouse operators who until now missed out in summer,” explains de Wit. For this reason, OCAP wants to integrate a bioethanol production plant in 2011 into the grid which could supply around 200,000 tonnes of carbon dioxide emissions – and thus additional fertiliser for the plants – each year. “However, we are still waiting for Dutch funding which has to be approved by Brussels,” says de Wit. As soon as they are awarded this, they will install the facilities. Then a further 20 kilometres of pipeline will be laid near Rotterdam to aid climate protection.

LINK:  
[www.turf.msu.edu](http://www.turf.msu.edu)

*Bartering gases below sea level*

# AN ICY ENERGY SOURCE

Warmer oceans aren't just making the polar ice caps melt. Methane ice – found in large amounts in the seabed – is also melting, threatening the climate. Linde is working together with partners to develop technology designed to safely recover the greenhouse gas from its submarine sources for use as energy, while simultaneously storing the CO<sub>2</sub> produced by power plants.

There is a time bomb ticking under the seabed: methane hydrate. Captured at present within a cage of ice, the gas is stable. This is due to high pressures and low temperatures on the ocean floor. But climate change is warming the ocean. If the methane, currently frozen in porous sediments, were to bubble out of the ocean it could speed up climate change enormously. This is because methane is approximately 23 times more dangerous than the greenhouse gas carbon dioxide. Methane is also produced by cows' stomachs and rubbish tips, however by far the largest deposits of the gas can be found stored in flat seabeds close to the coast, on the continental shelf regions, and in permafrost.

## Giant methane deposits worldwide

Methane, however, has more than just a dark side: the gas is as useful as an energy source as it is damaging to the atmosphere. Natural gas is comprised largely from colourless, odourless methane. It produces far fewer CO<sub>2</sub> emissions than coal or crude oil when burnt. Geoscientists and oceanographers predict large deposits of methane ice around the globe, which could be used to provide energy. However, mud containing methane hydrate and large methane ice boulders cannot simply be removed from the water. Above the surface, the pressure is too low and the temperature too high: the methane crackles and pops when it is released from its icy cage. It escapes into the atmosphere in the blink of an eye.

But it's not just the instability of the hydrate which makes using methane difficult. Sediments also react sensitively when the gas volatilises. "As the methane transforms from a solid to a gas, there is an explosive increase in volume to almost 170 times the ori-

ginal size," says Dr Christoph Windmeier, process engineer in the Research and Development Department at Linde. If this occurs on a large scale, formidable amounts of earth can be displaced. This happened 8,000 years ago during the 'Storegga Slide' off the coast of Norway. The 20 metre high tidal wave reached all the way to Scotland - the destructive power of a similar tsunami would have dramatic consequences in this day and age.

Scientific and economic researchers are working on a way to make methane hydrate a usable energy source without destabilising the sediments. The German Federal Ministry of Economics and Technology and the Federal Ministry for Education and Research have allocated 13 million euros to assist the development

*METHANE FROM  
UNDER THE  
SEABED WILL  
BE REPLACED  
WITH CO<sub>2</sub>.*

of technology for harvesting the hydrate, under the project name SUGAR (SUBmarine GAS hydrate Resources). Thirty industrial and scientific partners are involved. Their goal: to develop the technology required to extract methane from maritime hydrates. In return, carbon dioxide from power plants and other industrial factories is to be stored under the seabed. "We have been working with our project partners under the general management of the Leibniz Institute of Marine Sciences in Kiel, Germany, since mid-2008," explains Dr Robert Eckl, project manager for process engineering development at Linde. "Our part of the research project is to develop technology for the production, pelletising, and transport of the methane hydrate from the offshore platform," says Eckl.

The ultimate goal is to exchange one gas for the other: instead of methane, CO<sub>2</sub> molecules will be captured in the ice cages. The benefit: the carbon dioxide counterpart is significantly more stable. The gas exchange won't just preserve the sediment, it will also

Author: Caroline Zörlein  
Image source: Marc Steinmetz / Visum








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METHANE HYDRATE: CAGED ENERGY

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The actual amount of energy-rich methane ice clumps can only be guessed at. Scientists assume that the global methane hydrate reservoir represents a larger energy source than all known deposits of coal, oil, and natural gas combined.

The energy-rich ice contains methane and water – in a one to six ratio.

The water molecules surround the methane just like a crystalline cage – called a clathrate. The gas hydrates are only created under high pressure – starting at approximately 50 bar – and low temperatures, between two and four degrees Celsius. If the pressure eases, or the temperature warms up, the methane can vaporise out of the icy cage. The gas can be ignited, and the ‘ice’ appears to be burning.

safely store CO<sub>2</sub> as a hydrate-complex. But the ‘simple’ barter of gases is an incredibly complicated undertaking. The project partners have to retrieve detailed information on where worthwhile hydrate deposits can be found, and then characterise the structure of the stone and sediment.

### Dependent on mass: transport via pipeline or ship

Not every methane hydrate deposit is suitable. “In order to avoid destabilising the geological formation, we can only use strata containing methane ice located under appropriately thick sediment,” says Eckl. The largest methane hydrate deposits are found at continental margins. “Continental shelf regions have high enough pressure on the one hand, and on the other low enough temperatures due to the geothermic activity of the earth,” Windmeier explains.

The SUGAR project intends to compress CO<sub>2</sub> into the seabed and use a second drilling to bring gaseous methane up to an offshore platform. Once this has taken place, the Linde experts come into play. “For example, the distance from the coast will determine whether it is better to use a pipeline or to liquefy the methane,” says Eckl. But the capacity of the deposit, or the possible gas flow rate, plays a large role in the decision. “Particularly for small and medium amounts per drilling, it is useful to use – as opposed to a pipeline or liquefaction – the ‘pellet transport’ method,” explains Eckl. This involves immediately transforming the unearthed gas back into methane ice. Like encapsulated snow balls, the gas hydrate is then easy to ship via container.

The advantage of this approach: the amount of cooling required for the pellets is, at minus 20 degrees Celsius, significantly less than, for example, that of the liquid methane. Methane requires a temperature of approximately minus 160 degrees Celsius to remain in a liquid state. Pellet production saves up to a third on energy. “At the same time,” cautions Windmeier, “you are transporting an awful lot of water with the methane. Six water molecules are attached to each methane molecule. We have to take this additional work load into account when considering the most effective method.” This is why the experts at Linde test suitable technologies and develop concepts which can be applied at an industrial scale – like those envisioned by the SUGAR project.

Efficient transport of methane hydrate pellets is also of great interest for transporting other natural resources. “If classic natural gas fields have only small production rates left, it’s usually not worth it to build a pipeline. This is where an all-purpose technology could be a very practical solution,” says Eckl.

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**LINK:**

[www.sugar-projekt.de](http://www.sugar-projekt.de)

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Essay

# ENERGY IN THE EARTH SYSTEM – THE PATH TO SUSTAINABILITY

Our energy system must be sustainably restructured to cover the energy demand of a growing world population. Transitional technologies such as the geological storage of carbon dioxide could help us gain time, says Professor Dr. Dr. h.c. Reinhard Hüttl, CEO GFZ German Research Centre for Geosciences.

*Geological researcher: Professor Dr. Dr. h.c. Reinhard Hüttl leads the GFZ German Research Centre for Geosciences and is the scientific advisor of High-tech Climate Protection Strategy of the German Federal Ministry of Education and Research (BMBF).*



The challenge for research is formidable. With the likely growth of the human species to nine billion by 2050, we must deal rationally with our planet. The problem of raw materials and space for coming generations can only be acceptably solved if we understand our own inevitable and contingent interferences in the earth system – if only in a rudimentary way.

And therefore the topic 'Energy' must concern us all. For it is apparent that our present-day unrestricted consumption of raw materials and energy will not be possible for much longer. The geological sciences have a key role to play here, since the energy available to us – conventional or regenerative – stems from the earth system. A glance at the energy balances of industrial countries shows what little energy efficiency we have attained so far. More efficient use of energy is the best chance to save it.

The research on the subject of energy at the GFZ German Research Centre for Geosciences comprises a wide range. How are deposits of energetic raw materials created, where are they found, which tectonic processes are they based on? What is geothermal energy? Are methane hydrates or shale gas possible energy sources

of the future? What should be done about CO<sub>2</sub>? Newer estimates assert that 'burning ice', or gas hydrates, could be a future energy source quantitatively much greater than the entire supply of natural gas. These methane hydrates are created under high pressure and low temperature, above all in the marine sediments on the continental slopes. But such slopes are potentially instable. The possibility of undersea landslides is a certain risk of extraction. 8,000 years ago the Storegga Slide on the continental shelf of Norway created a violent tsunami, triggered by natural processes. The geological sciences are now looking into these connections in order to be able to make risk assessments.

This much is clear: according to all serious calculations, fossil fuels will continue to represent an integral part of the world energy supply for the foreseeable future. To this must be added inevitably rising CO<sub>2</sub> emissions, which contribute to the climate dynamic. From a globally unique research location in Ketzin in Brandenburg, the GFZ is examining whether carbon dioxide can be stored in the pores of a saltwater-bearing sandstone at a depth of about 650 metres. With the most comprehensive surveillance system for such a research project worldwide, the carbon dioxide's underground behaviour is directly

## INCREASING EFFICIENCY: THE BEST WAY TO SAVE ENERGY.



observed at the site of the injection. Further possible deposits for the geological storage of CO<sub>2</sub> are largely mined crude oil or natural gas fields. In the CLEAN Project in the Altmark region of north-eastern Germany, GFZ scientists are exploring this process. Storing CO<sub>2</sub> in such formations simultaneously has the advantage that the gas pressure, heightened by the CO<sub>2</sub> injection, can better drive out residual hydrocarbons.

In any case it is still not a matter of industrially applicable processes for geological CO<sub>2</sub> storage. There are still many questions to be answered: do we understand the physical, chemical, and biological processes involved in the storage? Can we monitor the migration and behaviour of the carbon dioxide underground? Can we model the processes quantitatively? How pure must the injected CO<sub>2</sub> be? What happens to the displaced fluids in the depth? Can we assess and value the storage capacities? And with what certainty can we exclude leakages?

At least for major point sources like power plants, the cement, steel, sugar and paper industry and petrochemicals, the separation and geological storage of CO<sub>2</sub> would be a path towards reducing CO<sub>2</sub>

atmosphere contamination. If this path is proven to be feasible, a reservoir would then be found where considerable amounts of this greenhouse gas could be stored, and worldwide at that. Thus from this technology an option could open for the developing economies of Asia and Africa, since these societies will still be using their domestic coal reserve for some time to come.

Energy is the key variable for the development of modern societies and their respective economic structures. A sustainable energy supply, dependent only on regenerative sources, cannot be built globally in a few years. At present about 80 percent of the world energy supply is based on fossil sources of energy. Transitional technologies like the geo-

logical storage of carbon dioxide can help us gain time to set the necessary conversion of the energy system in motion.

*TRANSITIONAL TECHNOLOGIES HELP GAIN TIME FOR SYSTEM RESTRUCTURING.*

LINKS:

[www.gfz-potsdam.de](http://www.gfz-potsdam.de)

[www.clean-altmark.org](http://www.clean-altmark.org)



*Medical gas mixture facilitates respiration*

# REACHING THE PATIENT'S BED BY PIPELINE

In St. Peter's Hospital in Chertsey, Great Britain, a pipeline system delivers the gas mixture Heliox directly to the intensive care unit. Heliox is used to facilitate respiration for patients with severe airway obstructions.

When gases or gas mixtures are to be sold for use in medicinal therapy, they must have an authorisation as pharmaceuticals. This process requires that the company can prove that the product is safe and effective and that the company follows drug law in the manufacture, handling, patient delivery and promotion of these gases. Documented, randomised, controlled clinical trials, where the gas is tested on volunteers, are also needed to complete the licence process. The gas mixture Heliox 21 (79 percent helium, 21 percent oxygen) from Linde Healthcare has a pharmaceutical licence in the UK and Australia.

Today, Heliox is not licenced in the rest of the world. This is either because no authorisation has been applied for or because the country authority has not seen enough evidence to give the approval. In countries with no authorisation, it is the treating physician who decides if they should use Heliox and it is then done under their responsibility.

Pharmaceutical law does not allow Linde or any of its employees, to promote the use of Heliox outside of the UK and Australia. It is possible, however, to explain how it is used by physicians in the UK. Dr Ian White, an Intensive Care Specialist at St.

Peter's Hospital in Chertsey, UK, is convinced by Heliox. For him, treatment using Heliox has become routine. Out of approximately 500 patients who enter intensive care each year, one or two a week will be treated using Heliox. Some are administered the gas mixture for only a few hours, others up to ten days – depending on how well they recover and how long they rely on it to aid relieved breathing.

## Saving on cylinder changeover

Recently, Dr White and his assistants have also been able to take a breather. Up until now they have had to exchange the ten-litre cylinder, in which the gas mixture is transported to the patients in their beds, by hand. Some patients require 24 bottles a day. However, as of mid-2009 continuous manual change has no longer been necessary: a pipeline has been installed that channels the gas mixture directly to the patient.

The pipeline leads directly to the intensive care ward, exactly where the gas is needed to treat for example, a patient admitted for status asthmaticus, a prolonged attack of asthma that does not respond to treatment to the patient's usual medication. In an asthma attack, the muscles inside the bronchial tubes start to contract, meaning used-up air that is still in the lungs can hardly escape. The mucous membranes in the respiratory canal become inflamed and swell, producing a thick phlegm that makes it very difficult to breathe. Asthma attacks do not stop on their own without treatment and when their routine medicines don't work, patients naturally become very anxious.

## Spasms make breathing difficult

"This is a frightening experience for the patient," says the intensive care doctor, Timothy Gould, from the Bristol Royal Infirmary in Bristol, UK. "If the bronchospasm gets worse, then even asthma sprays and oxygen therapy are barely of any help. This is because, if they are to work, the medication first has to reach the lungs. However, the

**HELIOX 21:  
A GAS MIXTURE  
MADE OF 79  
PERCENT HELIUM  
AND 21 PERCENT  
OXYGEN.**



*Intensive care: patients suffering from shortness of breath need immediate help. At the intensive care unit of St. Peter's Hospital in Great Britain, the gas mixture Heliox helps give relief.*





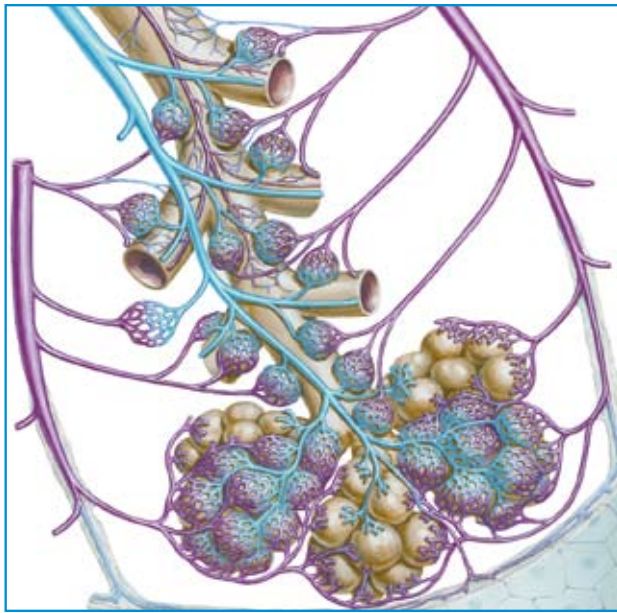
bronchospasm during the asthma attack increases the work of breathing and the patients become tired very quickly before the drugs have chance to work," continues Gould.

He and a number of other doctors have now found that instead of using additional air or oxygen, they can use Heliox. "The effect is really amazing," says Dr Gould. "The patients are visibly better even after the first couple of breaths. Despite the bronchospasm the Heliox allows oxygen and medication to flow in and out of the lung more effectively. The patient suddenly is less frightened as they actually find they can breathe again with less effort. This is now such routine therapy in our hospital that we ventilate many fewer asthmatics in our intensive care unit than before we used Heliox. After several hours, most patients have recovered to such a point that they can breathe normally again. If they are still bad enough to need ventilation then Heliox is used via a ventilator until the bronchospasm responds to conventional therapies."

After hydrogen, helium is the chemical element with the lowest density. If, as with Heliox, it is mixed with 21 percent oxygen, the gas takes on a four times lower density than normal air. This physical characteristic of the gas means that it can stream through an obstruction in the airway with relatively low resistance and can be inhaled and exhaled four times more easily. "It is exactly these characteristics that are decisive for the asthma sufferers," explains Dr Gould. "Their lungs are actually very capable of receiving oxygen, but one problem is rather, that they don't have the strength to breathe in. They also have difficulties exhaling because the bronchial tubes contract so much during a serious asthma attack, they become so narrow that the used-up air can hardly escape. The body attempts to expel the carbon dioxide by-product, produced during metabolism, but to no avail. Heliox, however, allows the used up air to leave the lungs more easily, thus leaving more room for fresh oxygen."



*HELIOX CAN HELP TO STABILISE THE  
CONDITION OF PATIENTS WITH  
SHORTNESS OF BREATH, AND THEREBY  
TO GAIN TIME FOR OTHER THERAPIES.*



***Central supply:** through a pipeline system – the first of its kind in Great Britain – the gas mixture Heliox arrives directly at the intensive care unit from its storage location in another part of the hospital. This saves the wards precious space. Thanks to the new pipeline the gas mixture is now available at any time, and no more cylinders need replacing at the wards. Heliox is a ready-to-use gas mixture made of 79 percent helium and 21 percent oxygen. It facilitates respiration for patients with severe airway obstructions.*

### Gaining time for other therapies

The body reacts in a very similar manner to implanted stents – finger-nail-sized tubes that are inserted into the lungs in order to alleviate the patient’s breathing. These stents are used for patients where their respiratory tubes are damaged by a chronic inflammation and parts of the lungs are cut off from gas exchange. After such an implantation the bronchial tubes are often so extremely narrow that the patient can hardly take in air, similar as to after a tumour operation. “If that is the case, we ventilate the patients for several hours with Heliox,” says Gould, making one thing clear: “The gas does not cure the sickness. It does help us, however, to stabilise the patient’s condition. We gain valuable time during which other therapies can start to take effect.”

Gould already experienced the value of this ‘additional time’ a few years ago when treating a 17-year old patient. Due to a condition known as ‘Wegener’s granulomatosis’, her lung tissue had

been very badly damaged. Doctors had already inserted a stent in her lungs, but within one year, the tissue around the small tube had grown so much that the tube itself was almost completely shut off.

“The shock came when we had to attach her to a normal ventilator,” Gould remembers. “It still didn’t help. Her body just couldn’t expel the gas anymore.” Using Heliox was the first turning point. From this moment on, the young patient was again able to breathe. The doctors were then able to operate on the tissue surrounding the stent to allow the opening of the tube to be large enough again. For seven days, the girl breathed in the gas mixture exclusively.

**LINK:**

[www.ashfordstpeters.nhs.uk](http://www.ashfordstpeters.nhs.uk)

## Lead-free soldering in the electronics industry

# WAVE BATH IN A NITROGEN ATMOSPHERE

Electronics are made up of more than just microchips. Circuit boards in flat-panel displays or MP3 players are also equipped with resistors, capacitors, and coils. Linde Technology provides the optimal soldering joint for these devices – lead-free, cost-effective, and durable.

63/37 – this is what experts call the metal alloy with which humanity has been soldering for 5,000 years. It is a mix of 63 percent tin and 37 percent lead. Despite intense efforts to find a suitable substitute, no alternative mix of materials came to the fore until 2003. One thing, however, was clear: lead's era as a soldering agent was going to end – whether or not a perfect alternative could be found. The European Union had published the 'Directive on the Restriction of the Use of Certain Hazardous Substances in Electrical and Electronic Equipment'. An increasing number of electronic devices were becoming part of our daily lives, finally ending up in the rubbish dump. The lead in these devices, not to mention any other heavy metals and flame retardants, was becoming an increasing danger for the environment and health.

### Satellite malfunction

The mandatory abandonment of lead presented new challenges for the electronics industry:

some lead-free soldering agents with high tin content are in danger of developing a hair-like branching crystalline effect in the soldering joint. These 'tin whiskers,' as they are called by experts, were apparently responsible, for example, for the malfunction of the "Galaxy 4" satellite in 1998. Suddenly 40 million North American pagers – small devices used for radio-paging services – were no longer operational.

In addition, lead-free solder has a significantly higher melting point compared to the traditional 63/37 mixture. However, this heat can cause serious problems for sensitive electronic components. Due to problems such as these, there are exceptions to the general ban on lead in electronic devices to this day, for example for aeronautics or medicine technology. On top of that, fused and lead-free solder has, under normal processing conditions, a different surface tension from that of leaded solder and coats surfaces less efficiently. But its properties are significantly improved with help from a

nitrogen atmosphere. "This is why the conversion to lead-free solder has made nitrogen extremely important for the soldering process," explains Werner Reiss, an expert at Linde Gas for the industry sector 'Heat Treatment and Electronic Packaging'. This is because you can only securely manufacture a reliable connection between the electronic component and the circuit board if the melted solder is properly dispersed and ready for contact.

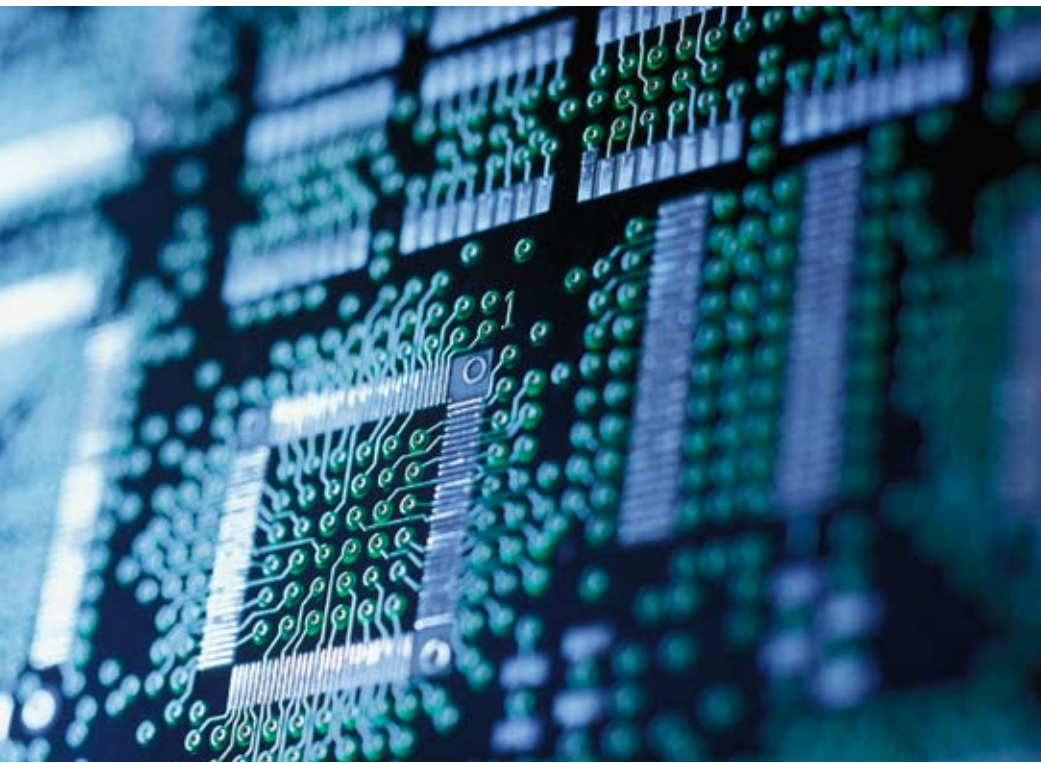
During the so-called reflow solder, with which surface mounted devices, or SMD's, are automatically soldered, nitrogen can to a large extent hinder the 'tombstone' effect. This effect is caused by local differences in the surface tension of liquid solder. The electronic component, along with its two connections, lifts itself away from the circuit board on one side, while the other side of the component sinks into the solder. This causes the capacitor or electronic resistor to look like a tombstone, and leaves behind defective soldering joints, with only one section of the component attached to the board. "Practical investigations have shown that a nitrogen atmosphere can reduce the number of defective soldering joints during wave soldering by more than half, another important procedure," says Linde's expert, Reiss.

### Soldering mobile telephones and MP3 players

The industry prefers to use reflow soldering for devices such as mobile telephones, MP3 players, etc. In comparison, wave soldering plays a particularly important role for mounting components via through hole technology in longer-lasting electronic devices, such as those in cars, industrial complexes, or washing machines. This procedure involves inserting the electronic component's wire terminations through the circuit board's contact holes. The assembly created with this method is then pre-heated and manoeuvred over a container full of liquid solder with a certain distance between the assembly and the contain-

**NITROGEN REDUCES DEFECTS CAUSED DURING LEAD-FREE SOLDERING BY HALF.**





*Defect-free electronics: defective soldering joints can cause electronic components on circuit boards inside mobile telephones or MP3 players to fail. A new soldering procedure developed by Linde prevents many of these defects. This reduces the number of bad parts rejected by quality control.*



er. A pump creates two waves in the solder bath, which is heated to around 270 degrees Celsius. These waves slosh high enough to reach into the contact holes on the circuit board. To finish the procedure, the assembly is then conveyed out over a ramp to cool in a controlled manner – the soldering joints are finished.

Linde has developed a system whereby wave soldering machines which previously worked with air can be modified to work with nitrogen: the Solderflex® LIS (which stands for local inerting system) consists of a dome which is immersed in the solder bath, a gas duct with three supply points and a gas control panel. "This simple installation and refined nitrogen supply significantly improve the quality of the solder," says Reiss. In addition, the system clearly re-

duces the amount of so-called dross – a mix of tin oxide, solder, and impurities which has to be regularly skimmed off the solder bath as waste. The reduced build up of dross also reduces the amount of tin used by at least 60 percent, while simultaneously cutting down on the work required to clean and maintain the equipment. "In terms of a single shift operation, you will typically make back the cost of the modification in savings within approximately five months of purchasing Solderflex® LIS and the nitrogen to go with it," says Reiss.

Linde was working closely together with SEHO Systems GmbH from Kreuzwertheim in Lower Franconia, Germany, from the moment they started marketing the Solderflex® LIS. Since then, this strategic partnership with the world's leading manufacturer of soldering machines for the electronics industry involves not only modifying existing systems, but also developing innovations for equipment that is to be operated using nitrogen. "This partnership gives us access to a client base with whom we, as a gas supplier, wish to work with more closely," says Reiss. Because good contacts are important for more than just electronic devices.

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**LINKS:**

[www.seho.de](http://www.seho.de)

<http://linde-electronics.com>

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*Banana boat: bananas ready for export are freighted in cargo ships refrigerated so as to halt the natural ripening process. But pests too make it into the freighters' cargo holds.*



Image source: Miquel Gonzalez / laif  
Author: Hubertus Breuer

*Specialty gas mixture protects foodstuffs from pest infestation*

# FRUIT ON A GRAND VOYAGE

Fruits and grains are transported halfway around the world. Their frequent fellow travellers: insects, who manage their way amongst the freight into the bellies of ships. These pests can now be combated with an environmentally friendly and highly effective speciality gas mixture.

Stowaways prefer to remain invisible – especially when they are feasting on the cargo. Bacteria, mites, cockroaches, moths, spiders, mice or rats can render entire shipments of bananas, soy beans or mangoes unusable. And since today exotic fruits, nuts or grain varieties are shipped halfway around the world, the problem is ever more acute. Global commerce in bananas alone should come to 14.3 million tonnes in 2010, according to the Food and Agriculture Organization of the United Nations.

Among the many ships that depart weekly from the Philippine harbour Davao on the island of Mindanao is a freighter headed for New Zealand. In its cooled cargo holds: freshly harvested Cavendish bananas, still slightly green. Before arriving at their destined harbour, the fruits have been warmed to 18 degrees Celsius and fumigated with hydrogen cyanide – thus treated against pests like spider mites or mealy bugs. But the necessary provision had a drawback: the active ingredient is highly toxic. And the warming of the bananas shortened their storage life by three days. Pests are a global problem for farmers and corporations who handle agricultural goods. Beet-

les in particular are often known by their food of preference: etymologists are for instance familiar with bread, tobacco, lentil, pea, bean and flour beetles. And for the longest time, man was powerless against these tiny, ravenous creatures. The Chinese used lime and wood ash against storage pests, and in the Talmud it is even recommended to blend salt and dust into one's grains. In the 20th century researchers and inventors finally set out to eliminate the scourge with a whole battery of combating agents: with hydrogen cyanide, with the poisonous salt 'Paris Green' used against potato beetles, with refrigeration processes that actually destroy the cell structure or even with radiation. The greatest success was the invention of methyl bromide in 1932. This gas was effective, cheap, easy to employ and quickly permeated the industry.

But scientists then discovered that methyl bromide is harmful to the ozone layer. In the so-called Montreal Protocol of 1987, the international community resolved to gradually reduce ozone-damaging chemicals and to ultimately discontinue their use. That made way for the great popularity of another gas for combating pests in

*THE VITAMIN-  
PACKED CARGO  
MUST ARRIVE  
AT ITS DESTINATION  
HARBOUR FRESH  
AND UNHARMED.*





*VAPORMATE™ IS IDEAL  
FOR USE WHEREVER  
FRESH GOODS ARE TRANS-  
PORTED, STORED OR  
PROCESSED – FROM  
GRAINS AND BANANAS TO  
TOBACCO AND COCOA.*

*Paradise for pests: bananas are harvested while still green and then shipped halfway around the world, but for pests like the spider mite (below) the unripe fruit is a delicacy – one in which they don't hesitate to indulge during their long overseas journey.*



grain silos and on freighters: phosphine. Still, this substance also has a catch: it is toxic and the treatment of fruits and grains lasts several days. In the meantime, insects in some parts of Australia and Asia had developed a resistance to the agent. Since the discontinuation of methyl bromide and the problems with phosphine, the need for effective pesticides is immense.

The Dole Food Company – the world's largest purveyor of fresh fruits, vegetables and cut flowers – began to look for alternatives in 2002. They decided to participate in a pilot experiment. Together with CSIRO, the Australian national science agency, then-BOC – now Linde – developed a pest-combatant gas: Vapormate™ – a mixture of carbon dioxide and ethyl formate. The organisation's initial laboratory tests on grains met with success. Following that, the New Zealand Institute for Plant and Food Research tested the gas on apples, calla lilies and onions against thunderbugs and aphids. Dole then ventured on the first commercial project – to their profit. The business group has since then put the treatment into effect.

#### **Protective gas coverings for pineapples and Co.**

"Vapormate™ acts rapidly and thoroughly and there are no known resistances," says Lex van Leeuwen, who is responsible for the worldwide commercialisation of new fumigation agents by Linde. The liquefied mixture is delivered in steel cylinders – the active ingredient is 17 percent ethyl formate, the rest is carbon dioxide. The substance is found in many plants and is even licensed as a foodstuffs additive. In its pure form, it is highly flammable, but not in the correct mixture with carbon dioxide. The carbon dioxide serves as a propellant, spreading the ethyl formate in a mist of micrometre-fine aerosol particles. As they vaporise, they evenly coat the grains, bananas or pineapples. The gas attacks the insects' respiratory system, which explains its quick effect. On grains the treatment takes only 24 hours, and just four hours for fruits and vegetables in confined spaces. There is no dangerous residue, since Vapormate™ decomposes into formic acid and ethanol, both substances occurring in nature.

Thus, Vapormate™ is ideal for pest control on fruits and other agricultural products. Even tobacco stands to profit by it, since before it enters the world market, it is processed and stored for extended periods. The leaves are then particularly vulnerable to pests like caterpillars, cacao moths and the larvae of tobacco beetles.

Vapormate™ can be implemented everywhere where fresh goods are transported, stored or processed: in farm silos, for the quarantine treatment of imported fruits in warehouses or even right after the harvest, just before shipping. So Willy Bayerl, responsible for specialty gases applications at Linde, developed a proportioning





*Stowaways in the pineapples: in most countries of origin, fruit is still packed for transport by hand. The pests are mostly invisible to the naked eye, and thus arrive in the transport container hidden amongst the fruit.*

system for Vapormate™ for the Dole Company. No meagre task, since adverse circumstances govern the banana plantations: high humidity, dust and heat. The efforts didn't remain unnoticed for long. In 2007, Vapormate™ reached the finale in a competition for the National Australia Bank's agriculture and business prize in the category 'Technology and Innovations'.

### Decomposition into natural components

Up to now, Linde's innovative pesticide has been licensed in Australia, New Zealand and Israel. Clearances are currently underway in Korea, Brazil, Kenya, the United States, in the Philippines and in South Africa. The process takes from two to three years in each country. Additionally, Linde is starting activities in other countries, too. Vapormate™ need not be registered in those countries receiving the exported products, as by the time of the fruit's arrival the gas has long since decomposed into its natural components.

At the same time, Vapormate™ is not the only gas from Linde which will likely assume the place of pesticides like methyl bromide and phosphine. It belongs to a group of gases, named by Envirosol,

which should reach the market in the coming few years. Common to them all is that fluid carbon dioxide can serve as a propellant to the intermixture. One of these products is 'Sterigas', whose active agent ethandinitrile should combat pests in soil and wood above all. Another is 'Cosmic' with carbonyl sulphide, which is adapted to grains and also fights against insects. Both have so far only been tested in the laboratory, but Linde has already initiated the first pilot projects. They perfectly complement Vapormate™, which aims to resolutely ensure that kiwis, oranges and pineapples can make it crisp and fresh to supermarket shelves without pest infestation.

**LINK:**

[www.linde-gas.com](http://www.linde-gas.com)



*India's industry continues to be on the rise*

## *OXYGEN FOR THE STEEL INDUSTRY*

India's economy is still growing at a staggering rate. Steel, automotive and computer industries need gases like oxygen, nitrogen and argon. In order to cover increasing demand, Linde is building ultra-modern air separation plants on the subcontinent. The largest will be in Jamshedpur, in the north-eastern state of Jharkhand.

In the north-eastern state of Jharkhand, there lies a modern Indian city blessed with an abundance of minerals such as iron ore, coal, manganese, bauxite and lime. Its namesake, Mr. Jamshedi Tata, founded the city at the turn of the 20th century; now, Jamshedpur is an industrial metropolis of 1.6 million inhabitants. Situated almost in the centre of the city is India's oldest and largest iron and steel plant, operated by the Tata Iron and Steel Company, or TISCO. Indeed, owing to the company's dominant presence, Jamshedpur is commonly known as 'Tata Nagar', or 'Tata Town'.

The Tata Group is responsible for much of the public infrastructure and civil amenities in Jamshedpur, and plays a key role in local enterprises from road construction to school administration. Beyond the industrial zone, Jamshedpur is a green city full of avenues, parks and gardens, and its resident community enjoys a standard of living well above the national average.

Jamshedpur's diverse manufacturing activities also include truck manufacturing, tinplate production, and cement, but it owes most of its economic success to the progress made by the Indian steel industry in recent decades. When it comes to steel, Jamshedpur is India's undisputed leader.

***STEEL IS THE  
BACKBONE OF  
INDIA'S ECONOMY.***

When India became independent in 1947, its steel production amounted to about one million tonnes per year. Today, India produces 55 million tonnes per year, making it the fifth largest steel producer in the world – and experts are forecasting an as much as six percent yearly rise in growth. In fact,

the metal has become so integral to the Indian economy that a ministry of steel has been established. Now Tata Steel wants to expand its factory in Jamshedpur, doubling its steel production to ten million tonnes per year. This effort will both encourage growth within the Indian steel industry and foster local development in Jamshedpur.





*The engine of growth: the automotive industry contributes to the rising demand for steel in India. Small cars have especially good prospects in this huge market.*

## STEEL IN INDIA: ROSY PROSPECTS

At around 40 kg, India's yearly per capita consumption of steel products falls well below the international average of 200 kg. Depending on economic trends, it can be expected to rise between eight and 15 percent yearly according to an estimate by the Indian Stainless Steel Development Association (ISSDA). In order to satisfy the growing hunger for steel, Indian manufacturers must considerably expand their capacities. Today the steel plants are already working at 90 percent capacity, according to the business development corporation Germany Trade & Invest. According to the Indian Ministry of Steel, the yearly output should rise to nearly 300 million tonnes by 2020 – investment needs: around 180 billion euros.

### Extracting carbon from pig iron

Beside erecting several towering new blast furnaces, Tata Steel's expansion mission also involves a gigantic refrigeration unit, to be built together with Linde. By 2012, Linde plans to construct a progressive air separation facility on the grounds of the steel factory – the largest of its kind in all of India. In one day, the plant will liquefy a total of 2,550 tonnes of air, separating the primary components of nitrogen, oxygen and argon in giant tray columns. Oxygen is especially essential to steel production: blown into molten pig iron, it oxidises carbon to create carbon dioxide or carbon monoxide, which purify the molten iron as they escape it.

"Linde has cutting-edge technical expertise and experience in designing and operating air separation plants," says Hemant Nerurkar, the Managing Director of Tata Steel. "This, combined with their solid operational capabilities locally, makes Linde a strong partner for our world-class steel works in Jamshedpur." Tata and Linde have been partners in India for over 50 years. Linde already operates two older air separation facilities in Jamshedpur, and will assume operations in three air separation facilities previously managed by Tata. When the new plant reaches full capacity, it will provide Tata's steel factory with 3,400 tonnes of oxygen, 3,300 tonnes of nitrogen and 41 tonnes

of argon per day. "We are committed to continuously innovating and delivering the best technologies and solutions to better serve our customers' needs," says Mr. Srikumar Menon, the Managing Director of Linde's Indian operations. "2010 is a significant milestone for us as we are marking 75 years of successful partnership with industry in India, and we are delighted for this opportunity to further build upon our strong relationship with Tata in Jamshedpur."

### 285 million euros invested

In sight of growing demand, Linde is also involved in operations beyond Jamshedpur – just in the past three years, the technology group has invested 285 million euros in the subcontinent. For instance, another separation facility is under construction near the provincial capital of Dehradun in the north of India. In the western state of Maharashtra, Linde has invested in a facility that produces 500 tonnes of liquid gas per day. Thus Linde is securing its position as the leading supplier of liquid and bottled gases for the Indian industry. Dr Aldo Belloni, board member at Linde, affirms, "Our engineering solutions place us in good stead to fulfil the growing demands of India's steel manufacturers, refineries and petrochemical industry."

#### LINKS:

[www.tatasteel.com](http://www.tatasteel.com)

[www.steel.nic.in](http://www.steel.nic.in)

[www.gtai.de](http://www.gtai.de)



## CO<sub>2</sub> HELPS GRASS GROW

# WELLNESS CURE FOR THE TURF

Cold and shade are putting the grass in many European football stadiums under chronic stress. With artificial light and carbon dioxide from mobile greenhouses, Linde engineers are bringing the green back to the arena in top form – so fast that you can watch it grow.

An away game means a break: when the players of FC Groningen aren't playing in their own stadium, it begins to shine above the turf. The light comes from four living-room-sized polyhouses on wheels, in which plant lamps exude light and heat and administer an extra dose of carbon dioxide to the stadium's grass.

The new turf therapy is a guarantor of thick green with strong roots – and a patented development of Linde Gas Benelux. "Carbon dioxide and light accelerate photosynthesis and thereby, the turf's growth," says one of the inventors, Peter Krabbendam of Linde Gas Benelux. And the heat of the lamps creates temperatures about eight to ten degrees above the outside temperature. "Under these conditions, the turf can grow up to a centimetre a day, even in winter," reports the engineer. So fast, that you can literally watch it grow.

Therefore the Linde engineers have dubbed their system 'SeeGrow'. With the new greenhouses, stadium operators can not only defy frosty temperatures, but also outsmart the shade. "That is one of the major problems for modern arenas," Krabbendam adds. "There, the spectator stands are so high and steep that hardly any sunlight reaches the field." This applies especially for stadiums in northern and central European countries, where the sun tends to shine obliquely. The shaded turf withers away so rapidly that it must be replaced every three to four months. A wasteful and above all, expensive procedure. "Re-seeding can cost up to 125,000 euros," says the Linde engineer.

The method of stimulating plant growth with light and carbon dioxide is not new: "In Holland particularly we have a great deal of experience with this method," confirms Krabbendam.

Nonetheless the 'SeeGrow' greenhouses are unique, being tailored to the special demands of the football world. "They must be mobile and occupy minimum storage space," Krabbendam explains. Thus they run markedly smaller than greenhouses for tomato plantations, for instance. They are additionally on wheels, and the



Author: Andree Hoferichter  
Image source: Ursula Meissner / laif; Linde AG

houses' film-covered metal supports can be folded like the bellows of an accordion.

To cover the entire football field, the film tents are set in perpetual motion with an automated cable winch. "If you work with four greenhouses like FC Groningen, it takes a good week until the entire field is back in shape," informs Krabbendam.

Linde's greenhouses on wheels don't just create perfect football turf in the Netherlands, but also in Hampden Park Stadium in Glasgow, though currently only on a trial basis. But Krabbendam considers the chances of a 'red card' to be slim, and confidently expects a successful entry into one of Great Britain's leagues. He also has his sights firmly set on suitable stadiums in other countries, adding: "The list of interested football clubs grows longer and longer." For the World Cup in South Africa at least, there is no need to resort to the technique since: "There you actually have light and sun in excess," says Krabbendam.

LINK:

[www.turf.msu.edu](http://www.turf.msu.edu)

# Innovation is key for a successful global player.



This alpha-olefin plant was built on the strength of Linde's know-how. It uses a state-of-the-art process to generate hydrocarbons, which can be used to improve the tensile strength and elasticity of modern plastics. A perfect example for us as a world-leading gases and engineering company with almost 48,000 employees working in more than 100 countries worldwide to prove our innovative power. We are constantly developing new ideas that challenge the boundaries of technology. Outstanding operational excellence, best-in-class reliability and the ambition to set new standards help us to develop innovative ideas that play a key role in creating a future worth living.

LeadIng.



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