Providing the basis for success. Gas applications for the pulp and paper industry.

Linde Gas





# **Enhancing productivity and performance.**Gas applications and know-how from Linde Gas.

Linde Gas supports 1.5 million customers in 50 countries, providing industrial and medical gases, application know-how, extensive services, and equipment to help make their operations more profitable, more efficient, and more environmentally sustainable.

For the pulp and paper industry, technologies from Linde Gas provide modern, environmentally friendly manufacturing processes that enhance productivity and performance. Linde Gas has a wealth of knowledge and experience concerning gas-based solutions and unique technologies for paper production, pulp production, and chemical recovery. Experts from Linde Gas work closely together with customers in research and development as well as in production and operational management, in order to achieve tailor-made solutions that improve the overall mill economy while also reducing environmental impacts.

Each mill and each process calls for a special solution. When it comes to developing practical and profitable gas applications for the pulp and paper industry, nothing can replace local presence at mill sites and hands-on activity.





# Adjust your process to your demands – and keep it rolling. Using gases in paper mills.

Carbon dioxide ( $\mathrm{CO}_2$ ) is widely used in the paper industry today. It is used in paper machines to adjust and stabilize pH, to buffer the papermaking system, to decrease calcium levels, or to increase dewatering, for instance. Today, Linde Gas has installations at various stages between the stock preparation and the headbox for around 40 paper machines, running with chemical pulps, mechanical pulps, and recycled paper.  $\mathrm{CO}_2$ -based applications are useful where conditions in the stock preparation and short circulation processes need to be stable.

### Regulating and stabilizing pH

Over the last few years, more and more mills have started to use CO₂, or a combination of CO₂ and caustic soda (NaOH) known as ADALKA™ Process Stabilizer, to regulate and stabilize pH. ADALKA™ also enhances the alkalinity or buffering capacity of the process, as well as stabilizing the wetend chemistry and unit operations such as beating and mixing. The increased buffering capacity also facilitates the optimization of chemical additions. The resulting sodium bicarbonate-based solution (NaHCO₃) is made on site from carbon dioxide and caustic soda in an alkalinity control unit reactor (ACU) from Linde Gas. Alkalinity and pH can be adjusted independently according to the process requirements. The buffer solution can then be added to the process to control pH and increase alkalinity at critical points.

# Reducing CaCO<sub>3</sub> dissolution

Calcium carbonate (CaCO<sub>3</sub>) is present in many papermaking systems today. Conditions in paper machines are often such that CaCO<sub>3</sub> starts to dissolve, leading to runnability problems, problems with precipitation and deposits, and higher consumption of many chemicals. Carbon dioxide or bicarbonate can be added to the process to reduce the dissolution of CaCO<sub>3</sub>, cutting calcium levels in the papermaking system by as much as 50 %.

CaCO<sub>3</sub>-related problems are particularly common when CaCO<sub>3</sub> is introduced as a filler in the production of paper qualities containing mechanical pulp, such as newsprint and supercalendered paper. To solve such problems, Linde Gas has designed an application known as GRAFICO<sup>TM</sup> Calcium Carbonate Saver, which can be used to stabilize processes where local pH variations, bacteria or slightly acidic conditions would otherwise increase the dissolution of CaCO<sub>3</sub>. This application is already used in various ways in many mills around the world.

Recycled paper also contains CaCO₃. Our carbon dioxide application CODIP™ Process Improver has been developed primarily for newsprint production, where de-inked pulp is the main raw material. CODIP™ is presently in use at a number of large paper mills. Benefits include lower calcium levels, increased paper machine runnability, and stabilized pH profiles.





# Environmentally friendly, economically beneficial. Using gases in the fiber line.

The driving force behind the introduction of gas applications to the fiber line has been the urgent need to reduce environmental impacts. New gas applications also aim to reduce pulp production costs and improve quality, while low capital investment solutions are also clearly desirable. Linde Gas is one of the main gas suppliers for the following applications:

## Oxygen delignification

Oxygen delignification is an integral part of any modern fiber line producing bleached kraft pulp. Environmental considerations were originally the main factor behind the introduction of this process, as effluent loads from bleaching plants could be cut by 50 %.

Other advantages of oxygen delignification include decreased contents of shives and extractives as well as a reduced need for bleaching chemicals. Yields of cellulose and hemicelluloses are increased, as oxygen delignification is more selective than kraft cooking in terms of lignin removal. Capacity also increases in the digester and recovery boiler, two common bottlenecks in a mill. With the recent development of a two-stage process, oxygen delignification can take care of an even larger share of the delignification work in a pulp mill.

## Extraction and bleaching processes

Alkaline extraction stages are conventionally reinforced with an oxidative chemical – which may be oxygen alone or oxygen in combination with hydrogen peroxide. The idea here is to take advantage of the pulp retention time during the hot alkaline stage, in order to achieve further lignin breakdown while the lignin – which has already been fragmentized in the previous bleaching stage – is being removed from the fiber.

Pressurized peroxide bleaching stages conducted at high temperatures can also benefit from the addition of oxygen, as the properties of the two oxidative chemicals are not identical.

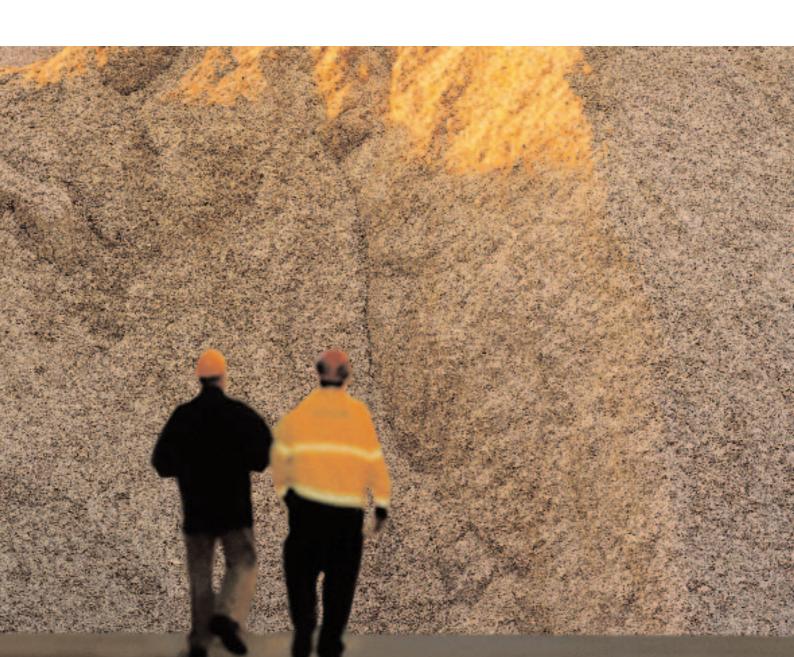
### Ozone bleaching

Ozone bleaching was also originally introduced for environmental reasons, as an alternative to chlorine-based bleach-

ing processes. Ozone is a powerful oxidant, which reacts rapidly even at low temperatures. Its use in the production of bleached kraft pulp has been growing rapidly in recent years, and today ozone is widely used for delignification and bleaching in both chlorine-free and chlorine-containing bleaching sequences. Ozone processes are highly cost-efficient, especially where new fiber lines are being set up.

## CO<sub>2</sub> pulp-washing

Our  $\mathrm{CO_2}$  pulp-washing technology is in use in more than 30 fiber lines, including both bleached and unbleached lines. It is typically applied in mills' existing washing systems, with benefits including better runnability, reduced steam consumption, lower wash water volumes, reduced usage of defoamer agents and pitch dispergents, and savings on maintenance.





# Boost your capacity – with minimum investment costs. Using gases in the recovery area.

Linde Gas creates and implements process solutions for the recovery area, aiming to improve the overall mill economy while also reducing environmental impacts.

## Oxygen applications

In white liquor oxidation, oxygen may be used alone or as a complement to air. Oxygen from Linde Gas is already being used at several mills together with the air added in existing oxidation equipment, leading to increased capacity without any major investment. Using additional oxygen in this way increases the production of oxidized white liquor at low cost, with no need to replace existing equipment.

Adding oxygen to lime kilns can increase their capacity by up to 30 %. Fuel savings of as much as 30 % per ton of lime additionally contribute to the high profitability of oxygen addition. Linde Gas has extensive experience of these types of furnaces and combustion processes in many countries. Our technical solutions for increasing the capacity of lime kilns using oxygen can be installed at very low investment costs.

### TOMLOX™ superstaged gasification technology

The TOMLOX™ method from Linde Gas can increase the capacity of recovery boilers where capacity is limited on the flue gas side. Reducing the amounts of cold nitrogen supplied with the combustion air by replacing air with oxygen will considerably improve the combustion characteristics in the lower furnace. This reduces "carry-over", due to the lower upward gas velocities, allowing more black liquor to be processed.

This new, low-capital technology has been implemented and tested for a year at a mill in Sweden – with the following benefits:

- Increased liquor-burning capacity
- Increased production of high-margin incremental pulp
- Extended run-time between water washes in spite of higher capacity
- Short delivery time
- Usable whenever needed
- Higher reactivity and controllability resulting in improved air emissions
- Higher thermal efficiency

### CO<sub>2</sub> for soap acidulation

Using carbon dioxide for soap acidulation in the production of crude tall oil (CTO) can reduce sulfuric acid consumption by 30 to 50 %, while also allowing the pulp mill to control the sulfur/sodium-balance. Dissolving carbon dioxide in water forms carbonic acid, which reacts with the crude tall oil soap, bringing the solution's pH down from about 12 to below 8. At this pH level, two phases separate: a creamy soap oil, and a bicarbonate brine in which the black liquor components are dissolved. The two phases are separated and the creamy soap oil phase is acidulated into CTO. This pretreatment process can be designed for batches or continuous mode, and may be operated through the regular control system.



# **Increase your cleaning power.** Using gases in wastewater treatment.

Wastewater treatment can be improved significantly by using oxygen and carbon dioxide. Activated sludge treatments purify wastewater by ensuring that organic matter is degraded by aerobic bacteria in the presence of dissolved oxygen. At many treatment plants, the growing stringency of standards set by the authorities is putting increasing pressure on existing treatment capacity. The oxygen levels required for aerobic bacteria are typically ensured by means of surface aerators, various bottom aerators or blower-fed membrane units. Adding pure oxygen to wastewater instead of air (which is only 21% oxygen) increases its oxygen content by a factor of 4.8. Additional pure oxygen is widely used to improve the capacity of biological wastewater treatment plants and to facilitate shaving of incoming seasonal and daily peak loads.

## Preventing H<sub>2</sub>S formation with oxygen

Hydrogen sulfide (H<sub>2</sub>S) smells unpleasant and is toxic even in low concentrations. It begins to form when dissolved oxygen and nitrates in the water have been used up, and the remaining sulfates begin to be reduced by bacteria. H<sub>2</sub>S only forms where there is a serious lack of oxygen. The cheapest option is to prevent its formation in the first place. Injecting pure oxygen into the water in sewers and pipelines can maintain oxygen concentrations at a sufficient level without additional odor problems. Water may need to be constantly treated with oxygen in order to maintain suitable oxygen concentrations.

## Neutralizing alkaline wastewater with CO<sub>2</sub>

Carbon dioxide is a weak acid, which (unlike mineral acids) occurs naturally in water. This means that carbon dioxide can be safely applied as a substitute for mineral acids to neutralize alkaline wastewater. Whereas the use of strong acids can lead to sudden changes in pH values, the neutralization curve is considerably smoother with carbon dioxide, meaning that pH values can be more easily set and better controlled. Using carbon dioxide also increases the buffering capacity of the treated effluent.

Linde Gas also supplies a wide range of equipment for the effective injection and dissolution of varying quantities of oxygen and carbon dioxide, under the brand names  $SOLVOX^{TM}$  (purification of industrial sewage with  $O_2$ ) and  $SOLVOCARB^{TM}$  (neutralization of alkaline sewage with  $CO_2$ ).

### More information

Would you like to know more about SOLVOX™, SOLVOCARB™, or other cutting-edge gas applications from Linde Gas? No problem: just contact your local Linde Gas representative or go to www.linde-gas.com.



 $\mathsf{SOLVOX^{TM}}$  and  $\mathsf{SOLVOCARB^{TM}}$  are trademarks of the Linde Group.

# Vorsprung durch Innovation.

Linde ist mehr. Linde übernimmt mit zukunftsweisenden Produkt- und Gasversorgungskonzepten eine Vorreiterrolle im globalen Markt. Als Technologieführer ist es unsere Aufgabe, immer wieder neue Maßstäbe zu setzen. Angetrieben durch unseren Unternehmergeist arbeiten wir konsequent an neuen hochqualitativen Produkten und innovativen Verfahren.

Linde bietet mehr – wir bieten Mehrwert, spürbare Wettbewerbsvorteile und erhöhte Profitabilität. Jedes Konzept wird exakt auf die Bedürfnisse unserer Kunden abgestimmt. Individuell und maßgeschneidert. Das gilt für alle Branchen und für jede Unternehmensgröße.

Wer heute mit der Konkurrenz von morgen mithalten will, braucht einen Partner an seiner Seite, für den höchste Qualität, Prozessoptimierungen und Produktivitätssteigerungen tägliche Werkzeuge für optimale Kundenlösungen sind. Partnerschaft bedeutet für uns jedoch nicht nur wir für Sie – sondern vor allem wir mit Ihnen. Denn in der Kooperation liegt die Kraft wirtschaftlichen Erfolgs.

Linde - ideas become solutions.