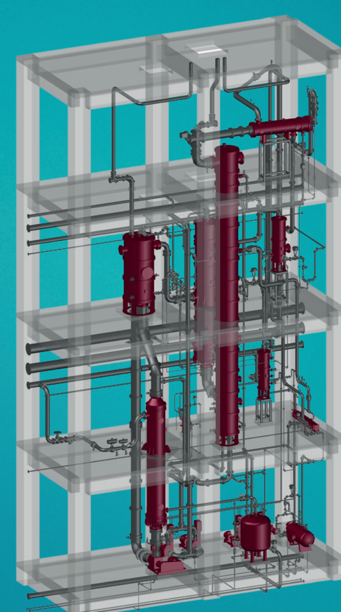
sgl carbon

HCl recovery using azeotrope shifters

Process Technology – White paper

Tailor-made extractive distillation unit applying $MgCl_2$ as entrainer with patented heat integration for achieving minimal energy demand for the recovery of HCl from azeotropic hydrochloric acid.



↑ $MgCl_2$ extractive distillation

Hydrochloric acid is involved in many chemical processes and is often processed in a closed loop in which HCl (hydrogen chloride) gas is taken out as needed and fed in as an acid by product.

For hydrochloric acid loops in which the water balance cannot be closed by conventional methods such as absorption-desorption, azeotrope shifters are often applied to generate HCl gas and remove water.

Different concepts for azeotrope shifters are available, each of which has distinctive advantages and disadvantages. As a manufacturer of corrosion-resistant impervious graphite and PTFE-lined pressure vessel equipment, SGL Carbon not only builds equipment that meets the process requirements for azeotrope shifters but also designs processes for your individual needs. Such processes are optimized for product quality, reliability, energy demand or other specific requests as required by your case.

Many processes in chemical industry produce diluted hydrochloric acid as a by-product. For economic and environmental reasons, such acids often need to be recovered to generate concentrated acids or hydrogen chloride gas (HCl).

Other applications require HCl gas from available concentrated hydrochloric acid but need to manage the weak acid by product generated during the distillation process.

For such applications, azeotrope shifters are common solutions for splitting hydrochloric acid into its compounds, water and HCl. SGL Carbon provides various process solutions for azeotrope shifters that are typically tailor-made for specific process requirements.

Azeotropic barrier

When distilling strong hydrochloric acid under atmospheric conditions, the composition of the gas phase does not differ from the composition in the liquid phase at a concentration of ~20wt.% [HCl], making it impossible to separate the compounds water and HCl by distillation. Therefore, azeotropic acid is generated as by-product. To overcome this azeotropic barrier for hydrochloric acid, two common concepts are typically applied.
Pressure swing distillation, which takes advantage of the pressure sensitivity of the azeotropic concentration and extractive distillation, which applies an entrainer with low volatility to shift the azeotropic concentration to a minimum level.

Pressure-swing concept

In the pressure swing concept, HCl is desorbed in a pressurized column. This allows the production of clean HCl gas at elevated pressure, which is beneficial for applications that otherwise would require a compressor.
The sump product of the pressure column is fed to a vacuum column from which water is distilled. Depending on the selected reflux ratio in the vacuum column, minimal HCl concentration can be achieved in the wastewater. This results in in high HCl recovery rates and additionally minimizes the chloride load sent to the wastewater treatment.

Since the distillation does not involve highly corrosive entrainer or extractive agents that may crystallize or react with impurities, the process is highly reliable with minimal down times. Avoiding an entrainer also minimize the risk of contamination of the HCl gas, which is often of special importance for high purity HCl applications.
The narrow vapor-liquid equilibrium between the two distillation units results in a higher energy demand. Applying heat integration to minimize the energy demand is crucial to provide an economic process.

Extractive distillation

The extractive distillation concept involves an entrainer for separating the acid. The entrainer should be selected with care. Using calcium chloride as extractive agent effectively splits the azeotrope at elevated concentration. Yet, care must be taken to prevent the risk of crystallization.
Additionally, reactions with impurities in the feed acid may have severe impact on the performance of the system. Sulfuric acid entrainers are highly corrosive and may impact the lifetime of graphite equipment when operated under severe conditions. Entrainers in general increase the boiling point in the distillation column and limit the HCl gas pressure accordingly.

The key advantage for extractive distillation units is the lower energy demand compared to the standard pressure swing concepts. Nevertheless, extractive distillation systems are still considered energy intense processes in which sophisticated heat integration measures should be considered.

Our patented heat integration concept between the brine regeneration and the HCl distillation sections, when applying magnesium chloride as entrainer, sets a benchmark for low energy demand in extractive distillation units*. The need of less sophisticated heat integration methods and a simpler brine regeneration section generally leads to lower investment costs. Extractive distillation is also an interesting process route when entrainer compounds are already included in the feed or downstream process and can be used to manipulate the azeotrope.

Your benefit

Reliable and efficient HCl recovery units require process know-how and material & equipment expertise. Our long-term experience with azeotrope shifters, appropriate design tools and ideally suited graphite DIABON®, PTFE lined POLYFLURON® equipment, as well as carbon fiber SIGRABOND® internals allow us to tailor make your optimum process.

*) SGL Carbon patent CN104755417

Comparison of pressure swing and extractive distillation systems

Design criteria	Pressure swing system	Extractive distillation system
Product quality	Highest purity, pressure up to 6 barg	Pressure up to 3 barg depending on entrainer
Energy demand	Elevated energy demand w.o. heat integration	Minimum energy demand
Reliability	Highest reliability	Potential risk of crystallization, fouling and corrosion
HCl recovery rate	99 %	96-98 %

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