

# Vinyl chloride and polyvinyl chloride

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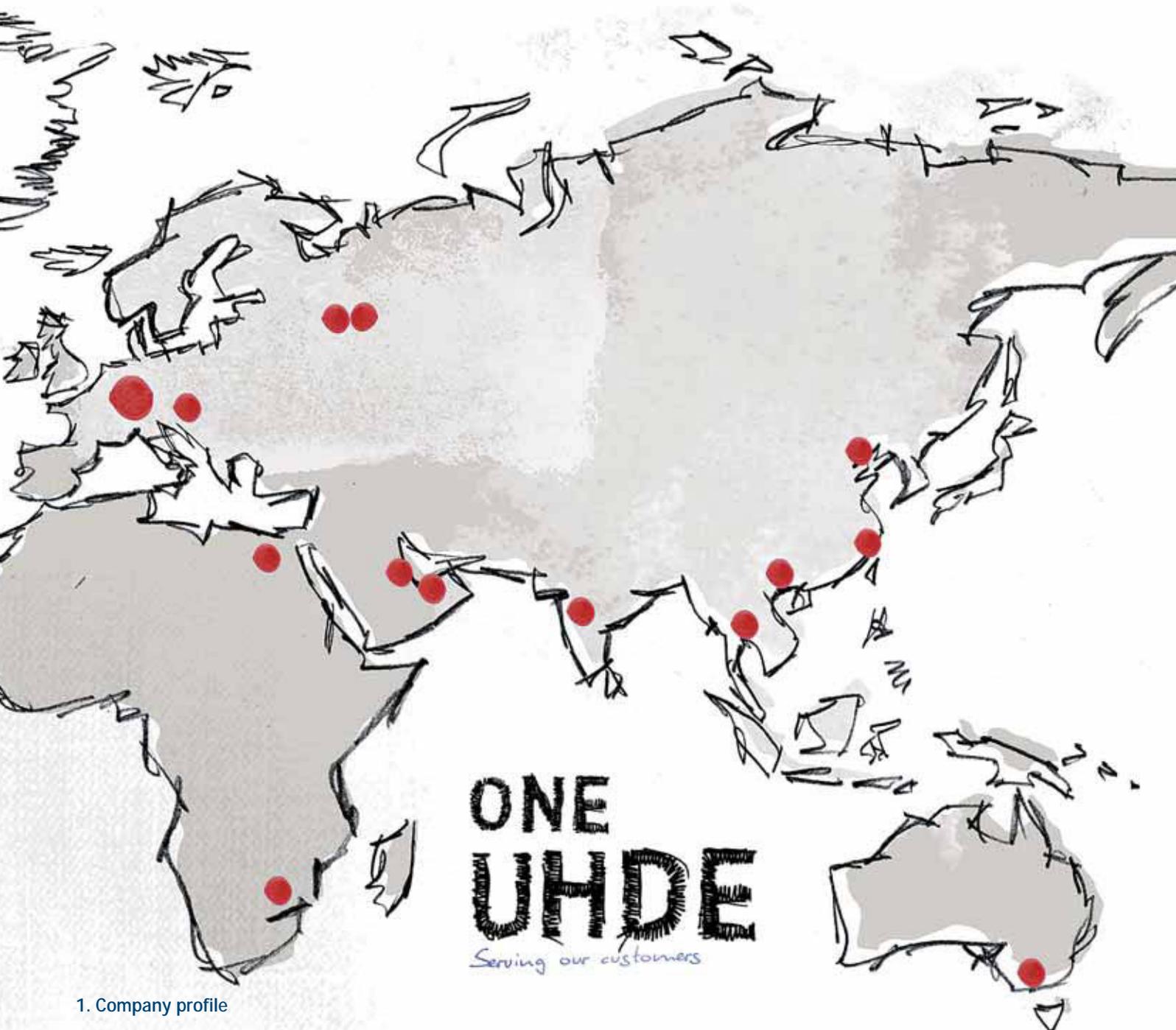


**ThyssenKrupp**

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## 1. Company profile

With its highly specialised workforce of more than 5,600 employees and its international network of subsidiaries and branch offices, Uhde, a Dortmund-based engineering contractor, has to date successfully completed over 2,000 projects throughout the world.

Uhde's international reputation has been built on the successful application of its motto **Engineering with ideas** to yield cost-effective high-tech solutions for its customers. The ever-increasing demands placed upon process and application technology in the fields of chemical processing, energy and environmental protection are met through a combination of specialist know-how, comprehensive service packages, top-quality engineering and impeccable punctuality.

### Uhde and Vinnolit – Partners for vinyl chloride and polyvinyl chloride

Our licensor for the Ethylene Dichloride (EDC), Vinyl Chloride Monomer (VCM) and for the Polyvinyl Chloride (PVC) process is Vinnolit GmbH & Co. KG.

Vinnolit is one of Europe's leading EDC, VCM and PVC producers with a capacity of 780,000 t/year of PVC, 665,000 t/year of VCM and upstream chlorine plants. They enhance and optimise their process technology on a permanent basis. Vinnolit was founded in 1993 as a 50/50 joint venture between Hoechst AG and Wacker Chemie GmbH. The new company drew on the experience of its two founders, both active in the vinyl sector for almost 60 years. In 2000 Advent International acquired Vinnolit. Advent is one of the world's largest and most experienced private equity investment firms.

Since 1964 the licensor has granted licences for a capacity of more than 14 million tonnes of EDC, approx. 6.5 million tonnes of VCM and about 2.9 million tonnes of S-PVC.

The cooperation between the licensor and Uhde has been successful for some 40 years. Uhde is the sole basic engineering partner for Vinnolit's EDC, VCM and PVC processes.

## 2. The Vinnolit VCM process



Qatar Vinyl Company (QVC),  
Mesaieed, Qatar

Capacities of the complex:  
360,000 t/year of DC-EDC  
175,000 t/year of Oxy-EDC  
230,000 t/year of VCM

Vinyl chloride (VCM), which is made from ethylene and chlorine, is used as feedstock in the production of the standard plastic material PVC.

The market for PVC and hence VCM has continued to grow, thus dispelling the forecasts made in the 80s, according to which PVC would be substituted by other plastics.

The reasons for this were not only the manifold applications and properties of PVC, but also the progress made in limiting emissions and by-products during production. PVC production capacity attained growth rates of approx. 6% per year, accounting for approx. 47 million tonnes worldwide in 2010. For the next few years, growth rates in the order of 4% per year are again expected.

As a chemical engineering contractor, Uhde added VCM to its range of processes some 40 years ago and has to date designed and constructed plants with a total nominal capacity of approx. 6 million tonnes.

The VCM process applied by Uhde is licensed by Vinnolit. The current high technological standard was reached through intensive development work on the part of Vinnolit in collaboration with Uhde. The process has been successfully applied at Vinnolit's existing plants at Gendorf (Bavaria) and at

Knapsack (Cologne), which have a combined capacity of 665,000 t/year, as well as at many other plants worldwide.

The modern Vinnolit process for the production of VCM has the following major distinctive features:

### High operational reliability:

- Reliable reaction control
- Time-proven materials and equipment
- State-of-the-art process control system

### High economic efficiency:

- Low energy consumption due to the utilisation of reaction and waste gas heat and integration with PVC or caustic soda plants
- High yields
- Optimised reaction conditions and reaction control
- Utilisation of by-products containing  $\text{Cl}_2$  along with the recycling of HCl gas
- High on-stream factor
- Low personnel requirement
- Low maintenance costs
- High flexible, wide range of load

### Extremely low pollution levels:

- $\leq 0.01$  ppm VCM (annual average) in working areas
- Extremely low VCM emissions
- Small waste water quantities with EDC/VCM contents  $\leq 1$  ppm
- In-plant disposal of low-boiling and high-boiling constituents in conjunction with HCl gas recycling and steam generation
- Special facilities for preventing emissions when the plant is shut down
- Thermal waste gas treatment

### Expected consumption figures for raw materials and utilities per 1,000 kg VCM product

|          |         |                     |
|----------|---------|---------------------|
| Ethylene | (100 %) | 459 kg              |
| Chlorine | (100 %) | 575 kg              |
| Oxygen   | (100 %) | 139 kg              |
| Steam    |         | 250 kg <sup>1</sup> |
| Fuel gas |         | 2.7 GJ              |

<sup>1</sup>Combined figure for VCM/PVC plant: 435 kg

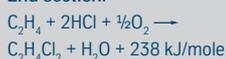
## 2.1 General process description

Biggest VCM plant in China  
SINOPEC Qilu Petrochemical Corp.  
Linzi, Zibo, Shandong Prov., China  
400,000 t/year of VCM (balanced)

### 1st section:



### 2nd section:



### 3rd section:



The process for the production of vinyl chloride monomer (VCM) from ethylene proceeds in several process sections.

In the first process section, ethylene dichloride (EDC; 1,2 dichloroethane) is produced by direct chlorination, in the second section by oxychlorination. Both reactions are exothermal.

The EDC produced by direct chlorination is fed straight into the cracking section without any further purification.

The heat of this exothermic reaction can be used for PVC drying in the PVC plant or for heating of columns in the EDC distillation unit depending on the individual plant configuration.

The EDC formed by oxychlorination passes through a purification stage (EDC distillation).



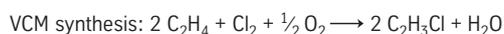
In the third process section, the EDC is cracked, and the VCM formed there, as well as the hydrogen chloride and unconverted EDC, are separated in a VCM distillation unit. The VCM is temporarily stored in a tank, while the HCl is returned to the oxychlorination unit and the unconverted EDC to the cracking section.

Any process water obtained undergoes treatment. Waste gases containing pollutants as

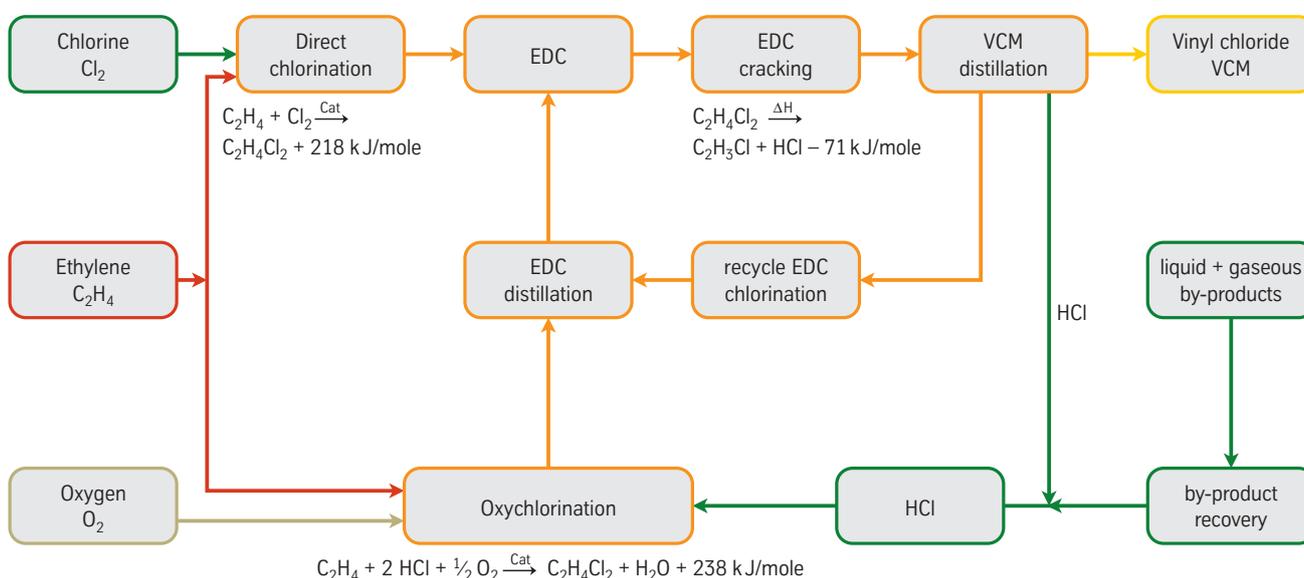
well as liquid by-products are fed to the HCl recovery unit and converted to HCl, CO<sub>2</sub> and water.

The recovered HCl is reused in the oxychlorination process, which leads to a complete conversion of the input chlorine.

The diagram shows the individual sections of the overall process which are described on the following pages.



Schematic diagram of a VCM plant



## 2.2 Direct chlorination

In the direct chlorination process, EDC is produced by means of a highly exothermal reaction of ethylene and chlorine.

The main feature of the Vinnolit direct chlorination process is an innovative boiling reactor with natural convection flow. Recently, as a result of a joint development project of Uhde and Vinnolit, the compact natural circulation (CNC) reactor was developed and now is ready for introduction on the market. In the CNC reactor, the natural circulation is established in an internal loop consisting of a riser section and a downcomer section, leading to a more compact and cost-saving reactor design.

The Vinnolit Direct Chlorination process operates at boiling conditions with a temperature of 120°C. The heat of reaction is removed by boiling off EDC from the boiling reactor. A big portion of this heat can be recovered by several heat recovery options, e.g. heating of distillation columns in the EDC distillation unit or heating of a fluidised bed PVC drier in the PVC plant yielding a reduction of steam consumption of up to 700 kg/tonne of EDC.

The reaction is carried out in the riser section of the CNC reactor. In contrast to other processes, gaseous ethylene is first completely pre-dissolved in the lower part of the riser section of the CNC reactor.

Gaseous chlorine is added via an injector nozzle to a relatively small circulating EDC side stream withdrawn in the downcomer section of the CNC reactor and cooled to allow the chlorine to be better pre-dissolved. This cooling provides another opportunity to recover the heat of reaction.

The ethylene solution and the completely predissolved chlorine are mixed in the reaction zone of the riser and react to EDC in a fast liquid-phase reaction which significantly lowers by-product formation.

Due to the reduced static pressure head in the top section of the riser, the EDC starts boiling. The product amount and some excess EDC are withdrawn from the upper part of the CNC reactor and passed on to the product vessel and a stripping column to achieve 'Sales EDC' quality, if required. The excess EDC is recycled to the main reactor loop.

In contrast to competitive direct chlorination processes, the Vinnolit Direct Chlorination process does not use  $\text{FeCl}_3$ , but a complex compound as catalyst. The catalyst suppresses the formation of by-products and ensures higher selectivity to EDC.

Thus the Vinnolit Direct Chlorination process combines the energy efficiency of a high-temperature chlorination (HTC) process with the EDC purity of a low-temperature chlorination (LTC) process. The catalyst is fed to the reactor loop before start-up and does not have to be topped up in normal operation.

The process is particularly environment-friendly, because:

- The energy recovery options lead to a significant reduction of  $\text{CO}_2$ -emissions
- The formation of high-boiling constituents is significantly reduced
- Extremely small quantities of low-boiling constituents are formed (only a few ppm)
- No scrubbing water is required and
- No catalyst is discharged with the product.

The catalyst has no corrosive properties because of its complex structure, and therefore the process equipment can be made mainly of ordinary carbon steel. Existing plants can be converted without any difficulty.

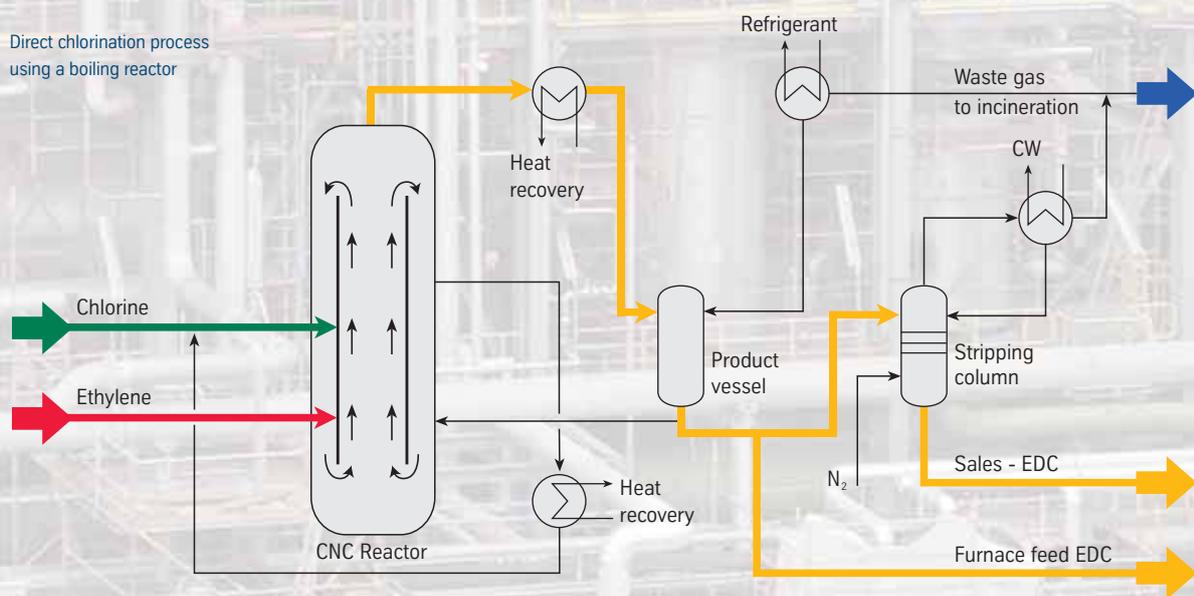
The advantages of the process can be summarised as follows:

- Nearly no consumption of catalyst
- High raw material yields
- High EDC purity: 99.9%
- Utilisation of reaction heat, e.g. for heating of distillation columns or drying of PVC, leading to a reduction in steam consumption of up to 700 kg/tonne of EDC.
- Low investment costs
- Complete reaction in only one reactor
- Proven materials and reliable and simple equipment
- High active and selective catalyst

Utilising the reaction heat saves energy and reduces emissions of  $\text{CO}_2$  by an amount equivalent to the energy savings. Thus, carbon certificate trading has a positive effect on production costs.



Direct chlorination process using a boiling reactor



## 2.3 Oxychlorination

In the oxychlorination process, EDC is formed by a highly exothermal catalytic reaction of ethylene with hydrogen chloride and oxygen.

The reaction takes place in a fluidised-bed reactor, and the reaction heat is used for steam generation. In the downstream quench column, a major portion of the reaction water is removed by condensation. To remove small quantities of chlorinated hydrocarbons from the reaction water, it is transferred to the effluent treatment facilities.

By cooling the reaction gases further by means of cooling water (CW) and refrigerant (R), the raw EDC is removed by condensation and fed to the EDC distillation unit, where it is purified to obtain "feed EDC quality".

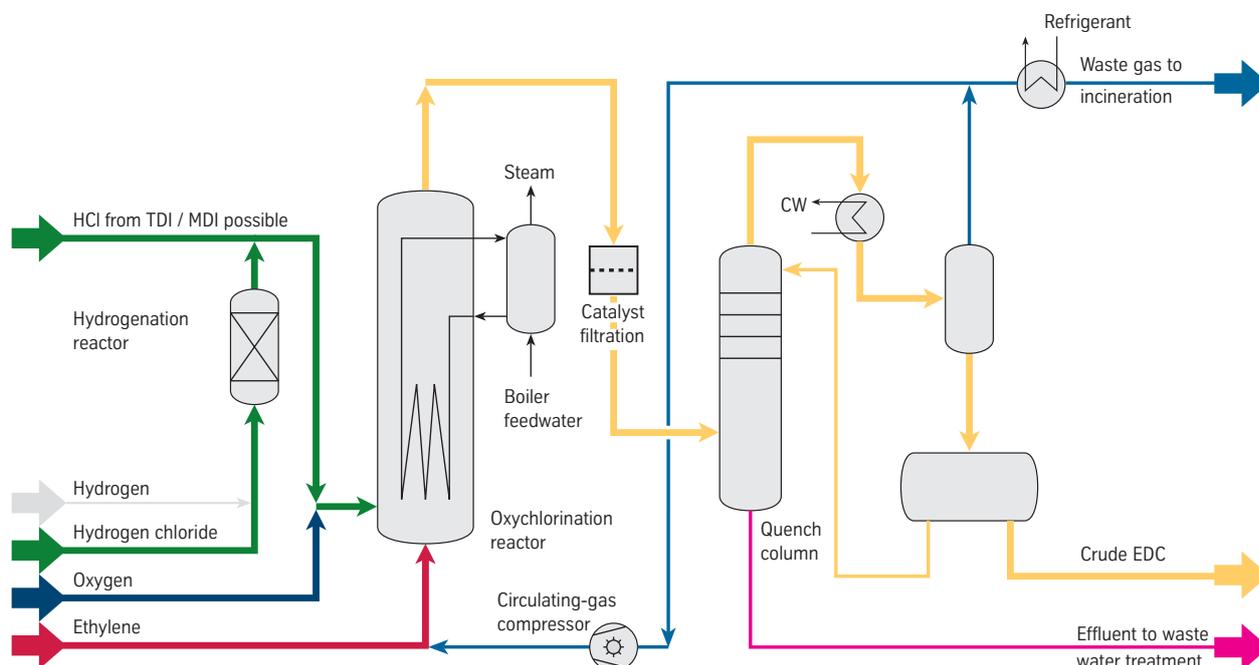
The Vinnolit oxychlorination process can use oxygen from air separation units as well as oxygen from pressure swing adsorption units (PSA oxygen). In the reactor the catalyst is fluidised with circulation gas. Just enough oxygen is added to the reactor to keep the concentration of the circulation gas outside the flammable range (oxygen lean operation). The very small off-gas stream of inerts and carbon oxides which is formed in the process is fed to the HCl recycle unit without further treatment. The reaction

mixture, consisting of  $C_2H_4$ , HCl and  $O_2$ , is catalytically converted in the fluidised-bed reactor to EDC in a highly exothermal reaction at a temperature of  $> 200^\circ C$ . The heat is dissipated via internal cooling coils and recovered to generate steam. Independent of load the generated steam has a constant pressure level.

The excellent distribution in the fluidised-bed makes it possible to maintain a constant temperature, to ensure low by-product formation and to achieve optimum process control.

The reaction gas passes a filter unit in which the catalyst fines are separated from the gas. Depending on customer's requirements, also a waste water treatment section comprising a precipitation and sludge filtration step can be implemented. To remove the reaction water, the hot reaction gases are quenched and the EDC is condensed with the aid of chilled water in a multi-stage condensation unit. The crude EDC is purified in an EDC distillation unit to obtain "feed EDC quality".

The reaction water obtained is passed to the waste water treatment facilities to remove the small quantities of chlorinated hydrocarbons it contains.





Oxychlorination reactor



Erection of oxychlorination reactor BorsodChem Rt., Hungary

The modern oxychlorination process of Vinnolit has the following distinctive features:

- Fluidised-bed reactor with good reaction heat distribution: no hot spots, no catalyst stickiness
- Proven materials and reliable and simple equipment
- Reactor and cooling coils made of carbon steel
- Crude EDC purity: 99.6 %
- High conversion of  $C_2H_4$  to EDC: 99.0 %
- Low catalyst consumption
- Removal of catalyst fines either by simple waste water treatment or by catalyst filtration
- High flexibility of the plant, wide range of load
- Production of 10 bar steam for distillation units possible
- High safety standard,  $O_2$  content < 1 %

## 2.4 EDC distillation



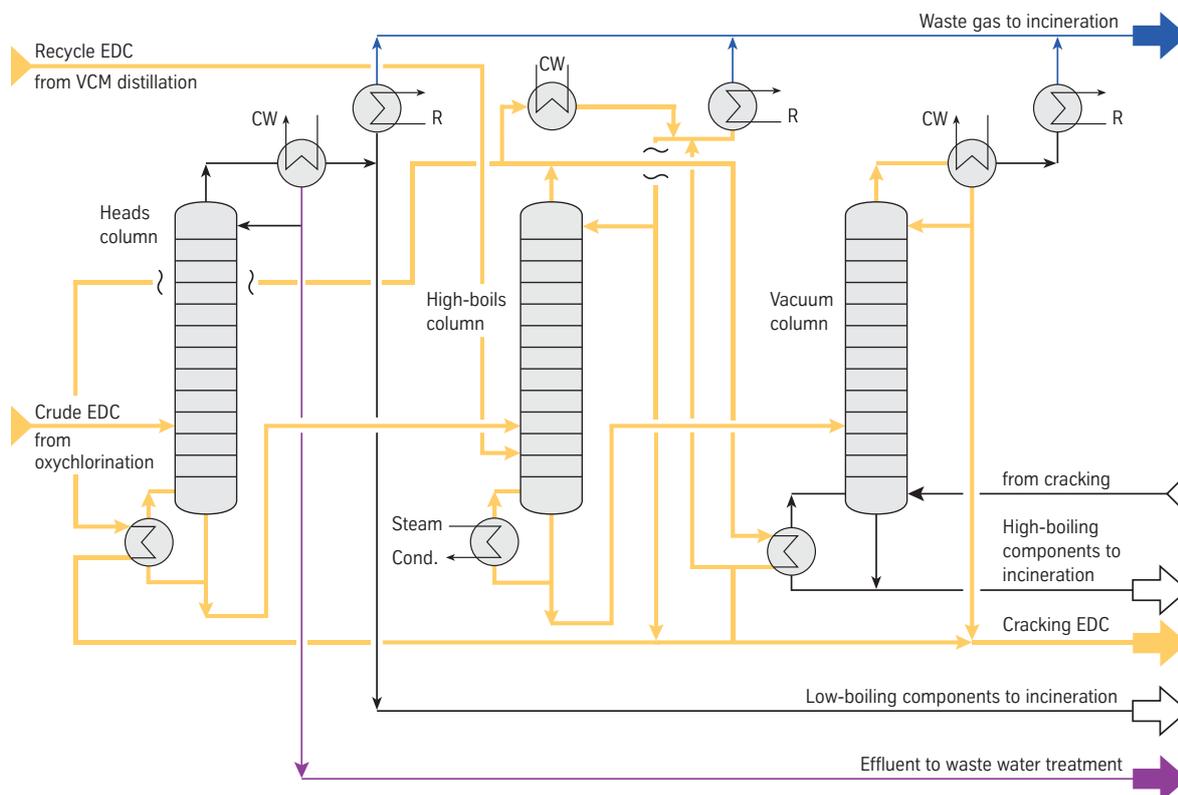
EDC evaporator and cracking furnace

To produce pure feed EDC, both the EDC obtained in the oxychlorination process and the EDC not converted in the cracking process (recycle EDC) are treated in the EDC distillation unit in order to remove water as well as low-boiling and high-boiling components.

The wet raw EDC from the oxychlorination unit is fed to the heads column in order to remove the water and low-boiling substances by distillation. The water phase of the head product containing small quantities of chlorinated hydrocarbons and sodium chloride is transferred to the waste water treatment unit. The organic phase and the off-gas are fed to the incineration unit.

The dry bottom product from the heads column together with the unconverted EDC from the cracking process are separated from the high-boiling compounds in the high-boil and vacuum columns. These high-boiling compounds are withdrawn from the bottom of the vacuum column and sent to the incineration unit.

By default, the high-boil column is operated at elevated pressure and the overhead vapours of this column are used to heat the heads column and the vacuum column. Depending on customer's requirements also other heat recovery options can be realized.



## 2.5 EDC cracking

The cracking of 1,2 dichloroethane takes place in a cracking furnace heated by fuel. VCM and HCl are formed at temperatures of 480°C, the reaction being endothermic and incomplete.

In addition to VCM and HCl, by-products of various chemical structures and coke are formed.

The external EDC pre-evaporation facility reduces the formation of coke in the cracking furnace considerably. The operating periods between two decoking intervals are very long (up to 2 years).

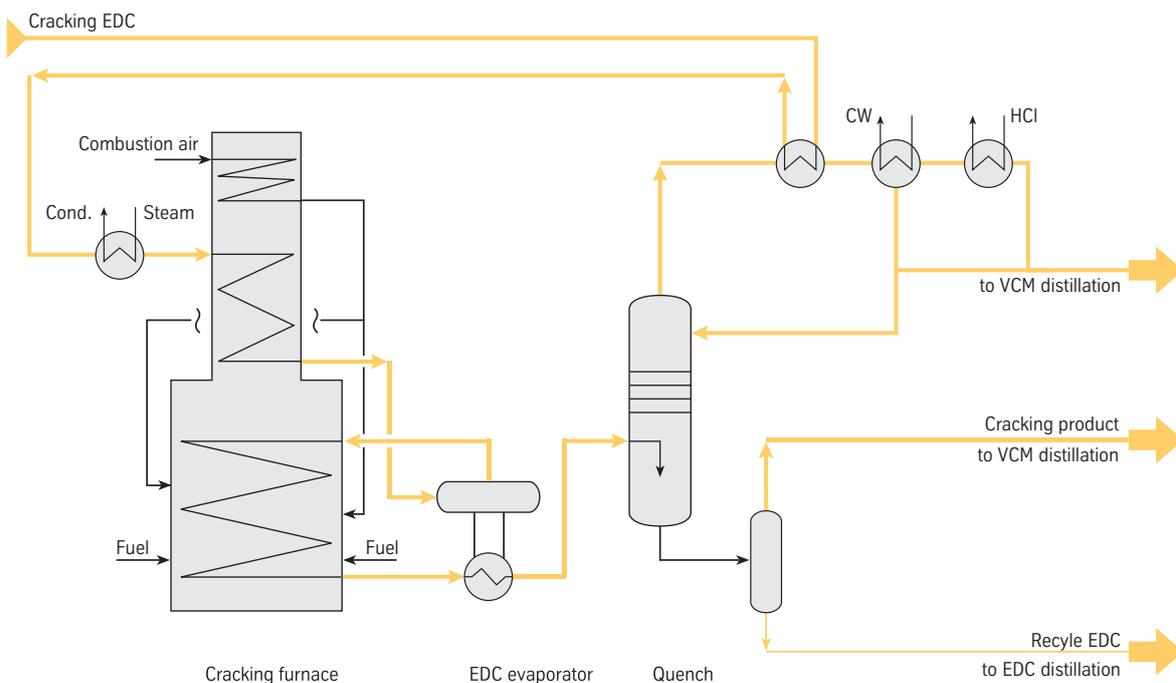
The advantages of Vinnolit's modern EDC cracking process can be summarised as follows:

- High reliability due to low coke formation
- High savings in primary and secondary energy, due to:
  - External EDC pre-evaporation using cracking gas heat
  - Utilisation of flue gas and cracking gas heat to preheat combustion air, to generate steam or to preheat EDC
- Low maintenance costs
- Proven materials and reliable equipment



3D model of one of the world's largest PVC complexes ARVAND Petrochemical Co., Bandar Imam, Iran  
On the left: The EDC cracking furnaces

Capacities of the complex:  
570,000 t/year of chlorine  
329,000 t/year of sales EDC  
343,000 t/year of VCM  
340,000 t/year of PVCa



## 2.6 VCM distillation

The product from the cracking unit consists of VCM, HCl, unconverted EDC and by-products of various chemical structures.

Hydrogen chloride is recovered in the HCl column and fed to the oxychlorination unit. Vinyl chloride is obtained at the top of the VCM column.

Any traces of HCl are removed from the VCM in the HCl stripper. The overhead product of the HCl stripper is recycled to the HCl column via a H<sub>2</sub>O removal unit which removes moisture from the distillation process and protects against moisture build-up.

The bottom product of the VCM column, i.e. un-converted EDC, is returned to the EDC distillation process after the low-boiling compounds have been converted by chlorination to high-boiling compounds. Thus the difficult and energy-consuming separation of recycle EDC from other low-boiling components is avoided.

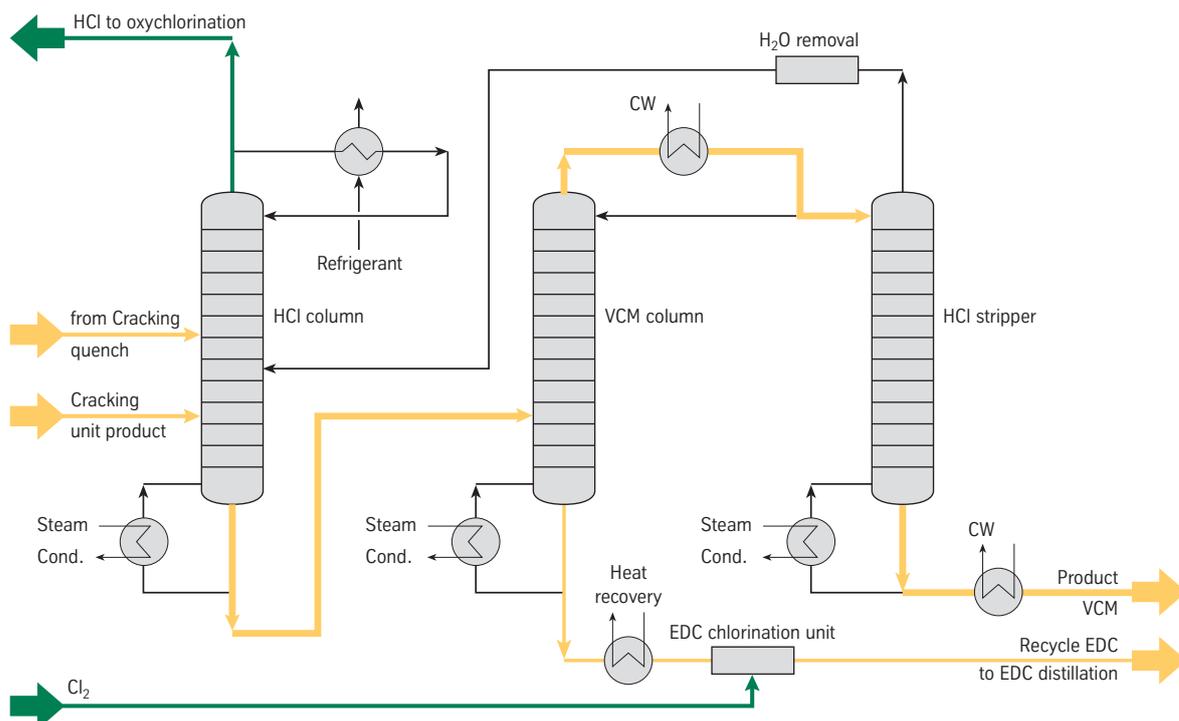
The Vinnolit EDC distillation unit can do without a low-boil column for recycle EDC with all its related problems.

Advantages of the VCM column:

- HCl content in VCM < 1 ppm without using caustic
- Long on-stream time of VCM distillation unit, because of no coke carry over from hot quench system
- Vapor feed of HCl stripper overhead product to the HCl column, no condensation system necessary
- Lower power consumption for HCl condensation compared to low pressure HCl column

Advantages of the recycle EDC chlorination:

- No separation of low-boiling compounds necessary
- Low investment cost in comparison to a low-boil column
- Easy operation
- No steam consumption
- Low maintenance cost



## 2.7 Measures to recover by-products and to protect the environment



HCl recovery unit

The treated waste gas complies with all applicable German statutory regulations in force since 3.5.2000, including those concerning the concentration of dioxins and furanes ( $< 0.1 \text{ ng TE/m}^3$ ).

The advantages of the HCl recycling process are:

- Recovery of hydrogen chloride from the by-products
- Optimum utilisation of the input chlorine to produce VCM
- Utilisation of the energy content of the by-products in the form of steam
- Use of proven technology and materials
- Environment-friendly process

### 2.7.2 Waste water treatment

The process effluent from the VCM plant and any splash water are sent to a waste water treatment unit. Chlorinated hydrocarbons are removed by distillation, hydrogen chloride by neutralisation with caustic soda solution. A copper content of less than 1 ppm is ensured either by dry catalyst filtration in the oxychlorination or by treatment of the waste water using flocculation, sedimentation and filtration.

The treated effluent, which meets the statutory purity requirements, is subsequently fed to a biological treatment unit.

The sludge obtained as a waste product is dumped or incinerated.

### 2.7.3 Liquid and waste gas collection systems

Liquid EDC and VCM from drains, cleaning of filters, reboilers etc. are collected in closed systems and returned to the process loop to protect the environment.

Sources of continuous waste gas streams are connected to waste gas headers and the gas is sent to the HCl recovery unit.

#### 2.7.1 HCl recycling with waste gas heat recovery

In the production of VCM, not only 1,2 dichloro-ethane is produced as a desirable intermediate product, but also further by-products, consisting of a mixture of high-boiling and low-boiling compounds, are obtained in liquid or gaseous form.

In a new modified Vinnolit process, these by-products are completely converted in an

oxidation process to form  $\text{CO}_2$ , water and hydrogen chloride. This process operates with an excess of air at approx.  $1,150^\circ\text{C}$ .

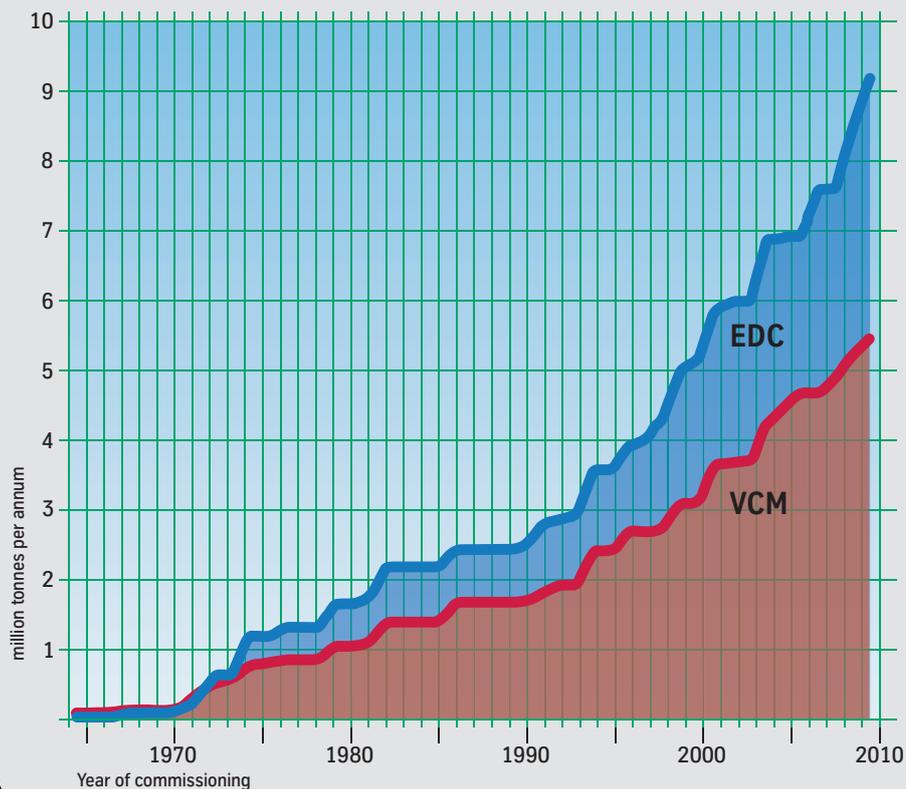
The heat of the hot combustion gases is exploited to generate steam, and the hydrogen chloride is recovered as a valuable feed-stock which is returned in gaseous form to the oxychlorination process.

Alternatively, aqueous HCl of 25 to 30% can be produced.

## 2.8 Cumulated capacity of reference plants

Uhde is one of the world's leading engineering companies in the fields of EDC and VCM, having built plants with a total capacity of more than 8 million tonnes per year of EDC and approx. 5 million tonnes per year of VCM (see diagram).

**Cumulated Capacity of EDC & VCM Plants Designed by Uhde**



An aerial photograph of a large industrial facility, identified as a VCM plant. The image shows a complex network of pipes, walkways, and structural steel. Two prominent, tall, grey cylindrical chimneys stand out against the sky. The ground is a mix of industrial structures, including buildings and storage tanks, and some greenery. In the background, a railway line with several trains is visible. The overall scene is one of a large-scale, modern industrial operation.

The view of Europe's biggest and most modern VCM plant at Vinnolit in Knapsack near Cologne.

Capacity: 190,000 t/year of EDC  
370,000 t/year of VCM

### 3. The Vinnolit S-PVC process



3D model of one of the world's largest PVC complexes  
ARVAND Petrochemical Co.,  
Bandar Imam, Iran

Capacities of the complex:  
570,000 t/year of chlorine  
329,000 t/year of sales EDC  
343,000 t/year of VCM  
340,000 t/year of PVC

The suspension polymerisation process for manufacturing polyvinyl chloride is the most important way to produce a variety of general-purpose and highly sophisticated grades of PVC. This process was invented in 1935 and first patented by Wacker Chemie GmbH, one of the former parent companies of Vinnolit. Continuous developments had been made in recipes, product quality and technology. Due to this long experience and continuous improvements, Vinnolit can offer a modern and highly economic process for the production of S-PVC worldwide. A Vinnolit team of specialists is available to tailor plant design according to licensee's requirements.

Vinnolit technology is characterised by:

- Vinnolit's proprietary technology for all units
- Clean and closed reactor technology
- High productivity
- Low raw materials consumption
- Low waste water amount (waste water recovery)
- Low energy consumption
- Low investment cost
- Low maintenance cost
- High safety level
- Leading in environmental protection – DIN ISO 14001 certified
- High product quality – DIN ISO 9001 certified

## 3.1 Description of the S-PVC process

Vinyl chloride and hot water are fed to the Vinnolit High-Performance Reactor by means of a special charging program.

Once the polymerisation has been completed the content of the reactor is discharged into a blowdown vessel and from here continuously fed to the Intensive Degassing System.

The nonconverted monomer is stripped out, condensed and fed back into the process.

After degassing and recovery of the latent heat, the water is separated by centrifuge and the wet PVC leaving the centrifuge is fed into the drying section. A big part of the water from the centrifuge is recovered in a waste water recovery unit (for pipe grade) and sent back to the high performance reactors.

The wet PVC is dried by means of heated air in a fluidized bed drier or the Vinnolit MST Cyclone drier

After drying, the PVC powder is conveyed pneumatically to the silo and bagging unit.

### Consumption figures for raw materials and energy

Low consumption of monomers, demin. water, chemicals and auxiliary materials, low energy consumption due to heat recovery, results in low production cost.

Especially, the utilization of hot water generated in the VCM plant for heating of the PVC drier yields very low energy consumption in the PVC plant.

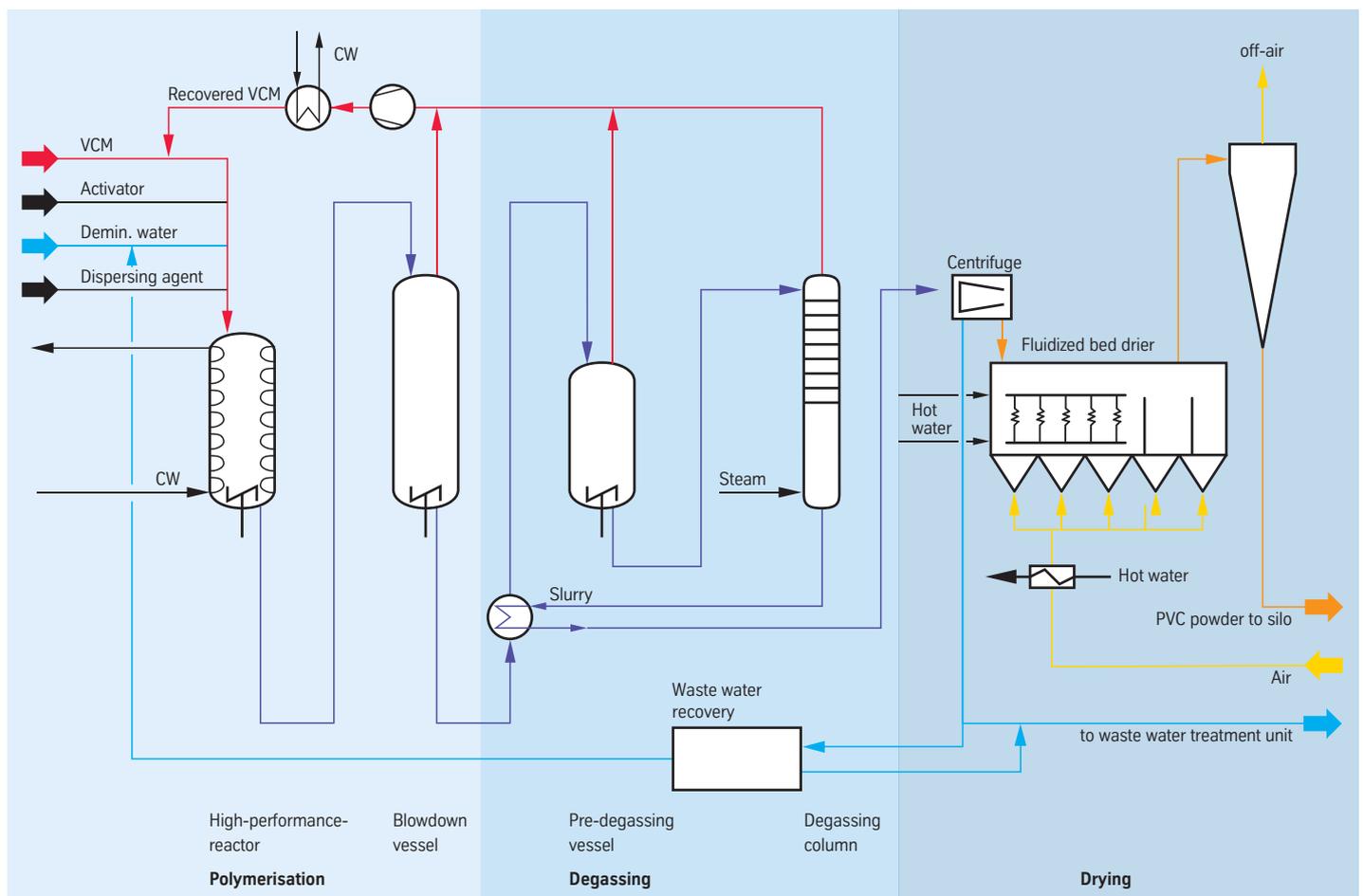
Consumption per 1,000kg of PVC powder at the production plant including VCM recovery:

|                     |                      |
|---------------------|----------------------|
| Vinyl chloride      | 1,001 kg             |
| Demineralised water | 1.4 m <sup>3</sup> ) |
| Chemicals           | 2.5 kg               |
| Steam               | 700 kg <sup>4)</sup> |

<sup>3)</sup> Without waste water recovery 2.3 m<sup>3</sup>

<sup>4)</sup> Combined figure for VCM and PVC plant: 435 kg

This data is based on average values. The consumption values depend on K values, on recipes and location.



## 3.2 Advantages of the S-PVC process

### Clean reactor technology

Scale-free operation is achieved through the use of reliable lining inhibitors, optimum operating conditions during polymerisation and a reactor designed to suit the requirements specified.

This means:

- High-Performance Reactor
- Clean and closed reactor technology
- Heat dissipation remains constant

It is therefore not necessary to frequently open the reactor for cleaning purposes.

### Process control system

The whole plant is controlled with the aid of a digital process control system.

This results in:

- Precise metering of the individual components during reactor charging
- High constancy of the present process parameters

- Excellent reproducibility of the process giving extremely consistent product quality
- High level of plant safety and reliability
- Low personnel requirement

### Intensive Degassing System

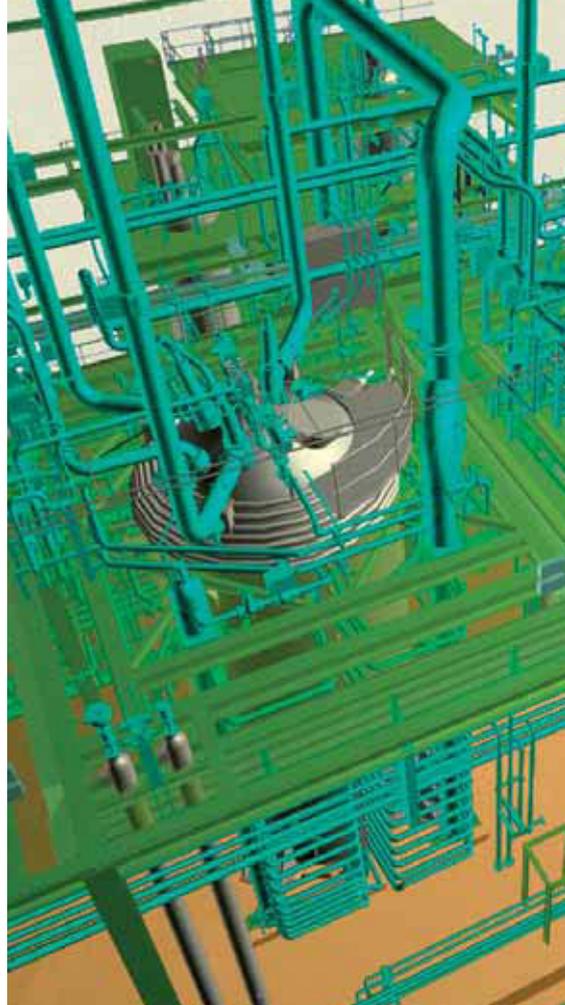
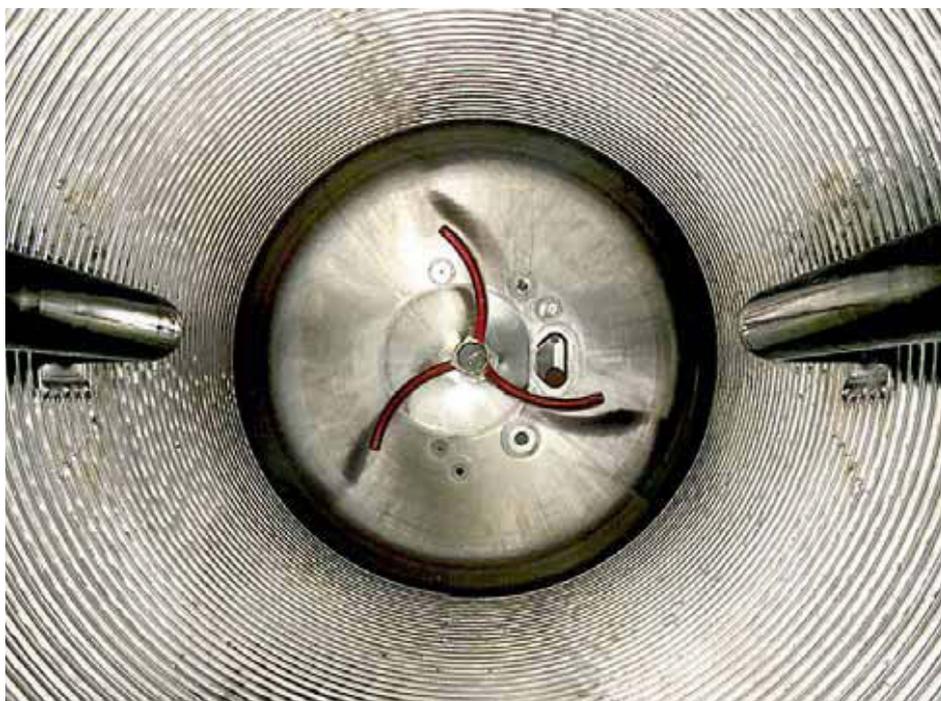
Our own work on the development of an intensive column degassing technology has resulted in perfect, continuously operating processes with the following conditions:

- Extremely low residual VCM content in the PVC slurry and in the PVC products
- Gentle degassing conditions
- Grade change without opening the column
- Extremely low VCM emissions

### Drying

In a fluidized bed drier, the PVC is dried to the required moisture content. This operation can be performed highly economic because of the possible heat integration with the VCM plant.

PVC High-Performance Reactor (inside view)



Polymerisation Reactors

### The safety concept

The whole safety concept, including its computer process control system, permits a particularly high level of operational safety.

In addition, the polymerisation system is completely safeguarded and can stop the reaction under extreme conditions e.g. simultaneous failure of coolant and power supply.

### Emissions

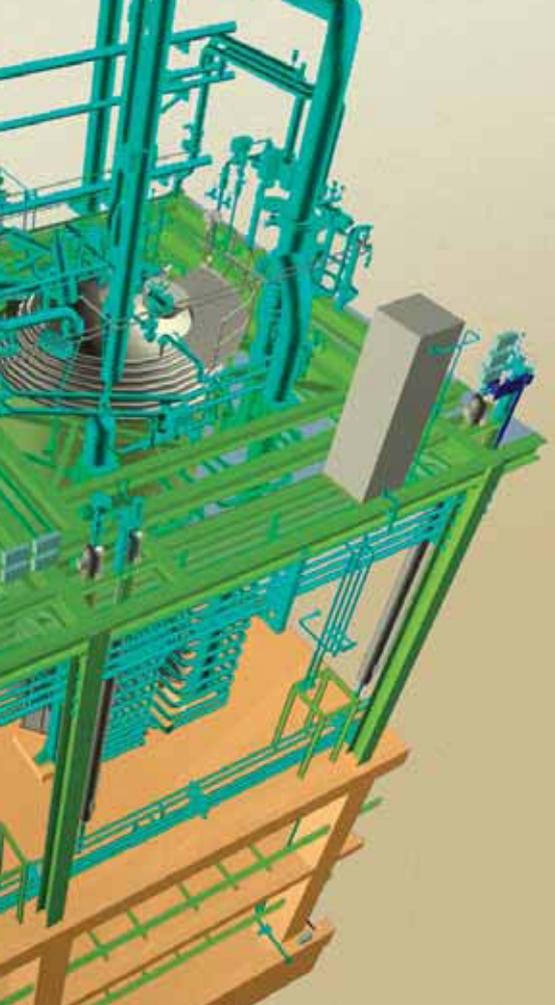
According to Vinnolit's commitment with regard to environmental protection, the offered S-PVC process sets a new standard.

Clean and closed reactor technology, process automation and effective degassing of product means that VCM emissions are kept at an extremely low level and under normal operating conditions are far lower than the figures required at present:

- Less than 1 mg/m<sup>3</sup> in drier off-air
- Less than 1 mg/m<sup>3</sup> in waste water
- Less than 2 vol. ppm (shift average value in the air at the workplace).

Effective measures keep PVC emissions in the drier off-air to less than 10 mg/m<sup>3</sup>.

### 3.3 The Vinnolit High-Performance Reactor for suspension PVC



Step by step Vinnolit has realised all requirements for a high-performance polymerisation reactor. The inner cooler reactor was developed as a last link in the optimisation. This completely new reactor design has been created and improved by Vinnolit engineers. The inner cooler reactor has demonstrated its outstanding suitability for the production of suspension PVC on an industrial scale for many years and is therefore a proven design.

In view of Vinnolit's inner cooler reactor, the choice was made for a combination of:

- Increased heat transfer area due to the half-pipe coil on the inner reactor wall
- Improved heat-transition coefficient due to the reduced thickness of the half-pipe coil
- Increased heat transfer due to higher turbulences at the wall.

This design combines high heat transfer rate with safe operation in a closed mode. Of course the other internal components of the inner cooler reactor like the agitator, baffles and nozzles are optimised as well to apply the reactor technology in the same way as in Vinnolit's conventional reactors.

The essential advantages of the Vinnolit High-Performance Reactor are:

- High output of up to 600 mt/m<sup>3</sup>/year
  - Very short non-reaction time
  - Very short reaction time
- High quality of product grades
  - Use of the Vinnolit recipes
  - Wide range of licensed grades
  - Heat dissipation only in the liquid phase as in a conventional reactor
- Large reactor Volumes of up to 160 m<sup>3</sup> ensuring
  - Low investment costs
  - Low maintenance costs
- Large heat transfer area and high heat-transition coefficient, providing a cooling capacity twice that of a conventional reactor; therefore no additional cooling area (such as a reflux condenser) is required
- Very simple and safe operation
  - Closed and clean reactor technology: using the Vinnolit anti-fouling technology dispenses with high-pressure cleaning or reactor opening
  - Automatic catalyst charging
  - Simultaneous charging of hot water and VCM
  - No heating up by means of a heating jacket
- Low operating costs because of
  - Adapted recipes
  - Use of cooling water instead of chilled water

The requirements of a modern high-performance polymerisation reactor with a high productivity:

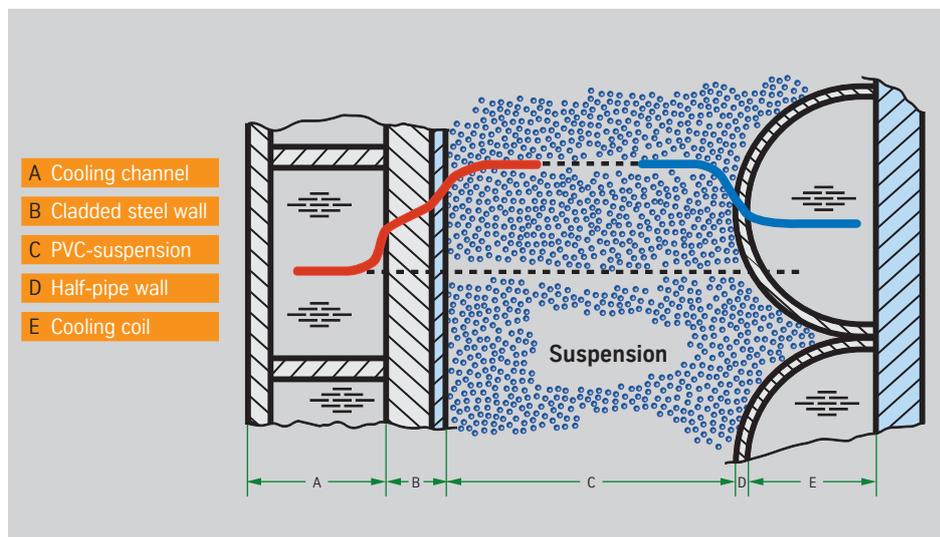
- Short non-reaction time to be reached by:
  - Closed and clean reactor technology
  - Efficient anti-fouling technology
  - No reactor opening
  - No high-pressure cleaning
  - No heating up of the batch
  - Optimised charging procedure, i.e. simultaneous hot water/VCM charging
  - Automatic catalyst charging
- Minimal reaction time to be reached by:
  - Fast reaction-heat dissipation
  - Large reactor technology
  - Volumes up to 160 m<sup>3</sup>
  - Adapted recipes

To achieve a minimal reaction time, the reaction heat has to be dissipated out of the reactor quickly.

- by increasing the heat transfer area by arrangement of half pipe coils inside
- by increasing the differential temperature between inside reactor and jacket, e.g. using chilled water
- by improving the heat-transition coefficient, e.g. using a thinner wall between inside reactor and cooling water
- by adding an external condenser

Heat transfer graph (typical) of conventional reactor cooling

Heat transfer graph (typical) of Vinnolit's High-Performance Reactor



## 3.4 Waste Water Recycling



Ultrafiltration unit for waste water in an S-PVC plant

### Description

Suspension PVC is produced in an aqueous process. Approx.  $2.3 \text{ m}^3$  of precious water are used in a conventional process per ton of PVC. Up to now this water could only be used for flushing purposes, but the demand for flush water in the downstream units is small compared with the water demand for polymerisation. So the water is usually after treatment in a biological waste water treatment discharged to a recipient.

Re-use of the waste water in the polymerisation was so far inhibited by quality problems caused by the residual PVC solid

content. But today the required purity can be achieved by a tailor-made special filtration process.

### Ultrafiltration

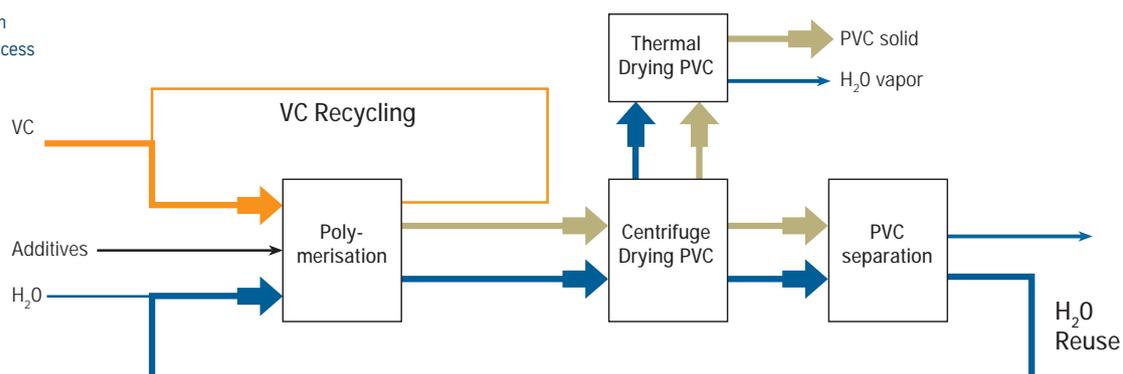
Ultrafiltration is employed to remove any solids from the decantation waste water. Ceramic membranes compatible with the other ingredients in the waste water are used in that process. The PVC contaminated waste water from the decantation centrifuge is treated in the special filtration unit. The treated water is free of PVC solids

and is recycled into the polymerization process in order to reduce the consumption of fresh de-mineralized water and at the same time the amount of waste water. The flux through the membranes can be preserved on an acceptable level by regular cleaning operations for at least 1 year.

### Features

- Reduction of fresh water consumption to approx.  $1.4 \text{ m}^3/\text{t PVC}$  (pipe grade)
- Reduction of waste water
- Proven in production scale for pipe grade

Re-use of waste water in the suspension PVC process



## 3.5 Products and applications



Probably no other plastic can match the wide variety of possible uses offered by PVC.

S-PVC, in particular, can be produced in both a crystal clear, hard and a very soft flexible finished form, with good electrical properties. Only the major applications of the different basic types are listed as follows:

- Coarse-grained, porous, free-flowing S-types with a high bulk density for rigid and semi-rigid extrusion (pipes, sections, plates), bubble extrusion (hollow items) and injection moulding, low-fish-eye S-types for the calendering of rigid and semi-rigid film, the production of PVC bristles and deep-drawable rigid film.
- Coarse-grained, highly porous, free-flowing plasticiser S-types for dry blend production, free-flowing plasticised PVC mix for low-fish-eye extrudates and film, for cable sheaths and hoses.

| Application   | K value    | Viscosity number | Bulk density g/l | Screen analysis |          |          | Plasticiser absorption |
|---|------------|------------------|------------------|-----------------|----------|----------|------------------------|
|   |            |                  |                  | < 63 µm         | > 250 µm | > 315 µm |                        |
| Test method   | ISO 1628/2 | ISO 1628/2       | DIN 53468        | DIN 53734       |          |          | DIN 53417              |
| Injection-moulded articles, rigid film, hollow articles       | 57         | 80               | 600              | 2 %             | < 1 %    | < 0.1 %  | low                    |
| Rigid film, injection-moulded articles, plates, bristles      | 60         | 89               | 570              | 2 %             | < 1 %    | < 0.1 %  | medium                 |
| Rigid and semi-rigid sections                                 | 65         | 105              | 580              | 1 %             | < 5 %    | < 0.1 %  | medium                 |
| Rigid pipes and sections                                      | 67         | 112              | 570              | 1 %             | < 5 %    | < 0.1 %  | medium                 |
| Rigid pipes and sections                                      | 68         | 116              | 570              | 1 %             | < 5 %    | < 0.1 %  | medium                 |
| Plasticised film, sections and flexible tubing                | 65         | 124              | 510              | 5 %             | < 1 %    |          | high                   |
| Plasticised film, sections, injection-moulded articles, cable | 70         | 124              | 480              | 5 %             | < 1 %    |          | high                   |
| Plasticised film and profiles, medical articles               | 75         | 145              | 470              | 5 %             | < 1 %    | < 0.1 %  | high                   |

For further product information please refer to Vinnolit's internet homepage: [www.vinnolit.com](http://www.vinnolit.com)

## 4. References

| Completion                              | Customer                                       | Plant Site              | Product Plant  | Capacity mtpy                                |
|---|--|-------------------------|--|--|
| Recent references of EDC and VCM plants |  |                         |  |  |
| 2015                                    | Sayanskchimplast                               | Sayansk, Russia         | VCM  | 350,000                                      |
| 2014                                    | Qatar Vinyl Co. (QVC)                          | Mesaieed, Qatar         | EDC (Expansion)  | 470,000                                      |
| 2014                                    | Mexichem SA de CV                              | Coatzacoalcos, Mexico   | EDC, Direct Chlorination<br>EDC, Oxychlorination<br>VCM, EDC Cracking                | 460,000<br>480,000<br>600,000                |
| 2013                                    | Petroquímica de Venezuela                      | Maracaibo, Venezuela    | EDC (Expansion)<br>VCM (Expansion)   | 155,000                                      |
| 2010                                    | S.N.E.P.                                       | Morocco                 | EDC Direct chlorination,<br>EDC, Oxychlorination                                     | 115,000<br>112,000                           |
| 2010                                    | Sayanskchimplast                               | Russia                  | VCM, EDC Cracking  | 200,000                                      |
| 2009                                    | ARVAND Petrochemical Co.                       | Bandar Imam, Iran       | EDC, Direct chlorination<br>EDC, Oxychlorination<br>(Sales EDC)<br>VCM, EDC Cracking | 551,000<br>332,000<br>329,000<br>343,000     |
| 2008                                    | Formosa Plastics Corp.                         | USA                     | EDC Cracking   | 240,000                                      |
| 2007                                    | Sahara Petrochemical Co.                       | KSA                     | EDC Direct chlorination<br>(Basic engineering<br>implementation pending)             | 300,000                                      |
| 2009                                    | Vinnolit GmbH & Co.                            | Middle East             | EDC Direct chlorination<br>EDC, Oxychlorination<br>Sales EDC<br>VCM                  | 660,000<br>1,300,000<br>100,000<br>1,020,000 |
| 2008                                    | Tokuyama Corp.                                 | Japan                   | EDC, Direct chlorination<br>(Basic engineering for feasibility study)                | 200,000                                      |
| 2007                                    | Liwa Petrochemical Company LLC                 | Sohar, Oman             | EDC, Direct chlorination   | 307,000                                      |
| 2006                                    | Limburgse Vinyl Maatschappij (LVM)             | Tessenderlo, Belgium    | EDC, Direct chlorination   | 250,000                                      |
| 2005                                    | Sasol Polymers                                 | Sasolburg, South Africa | EDC, Direct chlorination<br>EDC, Oxychlorination<br>VCM, EDC Cracking<br>(Expansion) | 168,000<br>160,000<br>205,000                |
| 2005                                    | VESTOLIT GmbH                                  | Marl Germany            | VCM, EDC Cracking<br>(Revamp)  | 190,000                                      |
| 2004                                    | Sinopec International / Qilu Petrochemical Co. | Zibo, Shandong, China   | EDC, Direct chlorination<br>EDC, Oxychlorination<br>VCM, EDC Cracking                | 330,000<br>315,000<br>400,000                |
| 2004                                    | BorsodChem Rt.                                 | Kazincbarcika, Hungary  | EDC, Oxychlorination<br>(Expansion)  | 225,000                                      |
| 2004                                    | Shanghai Chlor Alkali Chemical Co.             | Shanghai, China         | VCM, EDC Cracking<br>(Expansion)   | 130,000                                      |
| 2003                                    | Petkim Petrokimya Holding                      | Aliaga/Izmir, Turkey    | EDC, Direct chlorination<br>VCM, EDC Cracking  | 136,000<br>152,000                           |
| 2002                                    | Vinnolit GmbH & Co. KG                         | Knapsack, Germany       | EDC, Oxychlorination<br>VCM, EDC Cracking  | 170,000<br>330,000                           |

| Completion                      | Customer  | Plant Site           | Product Plant  | Capacity mtpy     |
|---------------------------------|---|----------------------|--|-------------------|
| Recent references of PVC plants |   |                      |  |                   |
| 2013                            | Petroquímica de Venezuela                                 | Maracaibo, Venezuela | S-PVC (Expansion)  | 48,000            |
| 2010                            | Lukoil Neftochim JSC                                      | Kalush, Ukraine      | S-PVC, Polymerisation<br>S-PVC, Degasing<br>S-PVC, Cyclone drier | 300,000           |
| 2009                            | S.N.E.P.  | Morocco              | S-PVC, Cyclone drier   | 85,000            |
| 2009                            | Ercros  | Spain                | S-PVC, Polymerisation  | 120,000           |
| 2008                            | Spolana A.S.  | Czech Republic       | S-PVC, Cyclone drier   | 2 x 100,000       |
| 2007                            | Braskem   | Brasil               | S-PVC, Polymerisation  | 130,000           |
| 2007                            | Undisclosed   | USA                  | S-PVC, Polymerisation  | 250,000           |
| 2006                            | ARVAND Petrochemical Co.                                  | Bandar Imam, Iran    | S-PVC<br>PVC-E   | 300,000<br>40,000 |
| 2002                            | Zakłady Azotowe w Tarnowie-Moscicach                      | Tarnow, Poland       | S-PVC  | 100,000           |
| 2001                            | Royal Polymer Ltd.  | Sarnia, Canada       | S-PVC, Cyclone drier   | 80,000            |
| 1997                            | S.N.E.P.  | Morocco              | S-PVC, Cyclone drier   | 52,000            |
| 1996                            | Hydro Polymers Ltd.                                       | Newton Aycliffe, UK  | S-PVC, Cyclone drier   | 92,000            |
| 1996                            | Georgia Gulf Corp.<br>(former Vista Chemical Corporation) | Aberdeen, MS, USA    | S-PVC, Cyclone drier   | 110,000           |

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