Desmet Ballestra Italy
Chemical Plants

Phosphoric Acid and Fertilizers Plants

Science behind Technology
www.desmetballestra.com
Desmet Ballestra is an International Group with solid know-how in plant design and supply for Oils&Fats, Oleochemicals, Chemical, Detergents, Surfactants and Soap businesses.

Desmet Ballestra Group, headquartered in Paris, includes some of the best companies on the specific markets, each with a long track record of successful experiences:

- **De Smet** (Belgium), founded in 1946, the world specialist in oilseed preparation&extraction and edible oils&fats refining and modification plants, housing also the headquarters of the Desmet Ballestra oleochemical&biodiesel activities that have met an outstanding success thanks to their reliability, versatility and performances.

- **Ballestra** (Italy), founded in 1960, the world leader in process plants for detergents and surfactants industries since its establishment. Since the 90’s it has become a reputable and well-known player within the inorganic chemicals (sulphuric acid, phosphoric acid) and fertilizers industry (potassium sulphate, NPK, ammonium sulphate, SSP/TSP and others). Ballestra merged into Desmet in 2007.

- **Rosedowns** (UK), the world leader in the field of oilseeds pressing, acquired in 1988.

- **Stolz** (France), specialized in animal feed & agro food plants with wide expertise in storage and handling equipment. Joined the Group in 2007.

- **Mazzoni LB** (Italy), the world leader in soap&glycerine processing plants and finishing lines. Joined the Group in 2017.

Our core value is having an advanced understanding of our customers and their needs, developing and supplying sustainable technologies of superior quality.

Our mission is to achieve this goal through an organisation that attracts the finest people and maintains our historic principles of integrity and long term relationships.

By the successful pursuit of our commitment, we expect to maintain our leadership in the industry.
DBI is focused on Chemical Plants and active in a wide range of inorganic chemicals.

**Phosphoric Acid - Merchant Grade (PA MG)**
DBI is a long-term licensee of Prayon Technologies (Belgium) for PA MG processes. Available technologies are based on Hemi-Hydrate, Di-Hydrate process or a combination of the two. The most appropriate solution is selected and tailored on Customer technical, economic and environmental requirements.

**Purified Phosphoric Acid (PPA)**
DBI provides the best technologies to refine merchant grade phosphoric acid to get a purified grade. The selection of purification steps depends on rock quality and required final product purity (up to food grade).
DBI, being familiar with both PA-MG production and PA purification, is able to integrate the two units maximizing P₂O₅ recovery and minimizing effluents.

**Sulphuric Acid**
DBI entered years ago in the sulfuric acid business in relation to its proprietary processes and know-how for SO₃ gas sulphonation that has been implemented since the ‘60s. DBI gained deep experience in the fundamentals of modern H₂SO₄ production technology and related processes (e.g. SO₂ and SO₃ production) executing several projects within the fertilizers, mining and chemicals industries.

**Fertilizers**
**SSP/TSP/NPK**
DBI can supply SSP/TSP/NPK plants based on in-house know-how.
The production processes are based on the reaction between sulphuric or phosphoric acid with phosphate rock to obtain SSP or TSP, respectively.

**Potassium Sulphate**
DBI offers plants with in-house technology based on Mannheim process, developed in cooperation with Marchi Industriale for the furnace section and in-house know-how for the balance (e.g. HCl recovery).

**Other**
DBI has in place cooperation schemes with world leader partners (e.g. GEA, INCR0) to integrate its portfolio with further technologies:
- Ammonium Sulfate
- Water Soluble MAP/DAP
- Granular MAP/DAP/NPK

**Integrated Fertilizers Complexes**
DBI capabilities include almost the full range of derivatives from Sulphur, Phosphorus and Nitrogen. Having available a wide range of technologies, DBI can support Clients in the definition, design and implementation of Fertilizers complexes making available its experiences on both process design (important for proper overall energy/water/steam balances) and budget definition (based on in-house cost database coming from the projects DBI executed or estimated).

LEGENDA: Ammonium nitrate (AN), Ammonium Sulfate (AS), Single superphosphate (SSP), Triple superphosphate (TSP), Monoammonium phosphates (MAP), Diammonium phosphate (DAP), Sulphate of Potash (SOP), Potassium nitrate (KN)

(*) The use of any leagentic compound is related to the NPK formulation. Other compounds not indicated in the table may be used for NPK production.
Source: Desmet Ballestra, A.T. Kearney

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DBI is since 2009 a permanent licensee of Prayon Technologies (Belgium) and executed several projects based on different configurations. Prayon Technologies has available a wider range of solutions based on Di-Hydrate (DH) or Hemi-Hydrate (HH) gypsum formation with a relevant combination along the various process stages (reaction, filtration). The table below summarizes the specific advantages of the most common configurations:

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<thead>
<tr>
<th></th>
<th>Mark4 (DH)</th>
<th>CPP (HH)</th>
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<tbody>
<tr>
<td>Efficiency</td>
<td>(+)</td>
<td>(+++)</td>
</tr>
<tr>
<td>Investment cost</td>
<td>(lower)</td>
<td>(+)</td>
</tr>
<tr>
<td>Plot area</td>
<td>(smaller)</td>
<td>(-)</td>
</tr>
<tr>
<td>Weak PA (%P₂O₅)</td>
<td>(+)</td>
<td>(+++)</td>
</tr>
<tr>
<td>Product PA (%SO₃)</td>
<td>(-)</td>
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DBI will support in defining with Customer the most appropriate configuration, based on specific throughput need and phosphate rock available. Laboratory testing and pilot plant validation campaign are available on request.

Common features for each process configuration are:

- **Air pollution control**, by means of a dedicated scrubber, to contain the plant emissions to the minimum level required by the most stringent laws and standards.
- **High-quality construction materials** and well-proven know-how in material selection assuring the best resistance against acid corrosion and erosion.
- **High efficiency converting P₂O₅** included in the phosphate rocks and phosphate losses controls, granted by the best available technology together with Prayon process design, allowing for unlikely plant clogging risk and an extended plant availability.
- **Tailor-made configuration.** DBI Phosphoric Acid plants are highly customizable. It is possible to process several types of phosphate rocks and maximize the plant efficiency.

The **Mark 4 Di-Hydrate Prayon Process© (DPP)** has been widely applied in most of the phosphoric acid projects, becoming the leading process in the market.

- Well-proven process
- Ability to efficiently convert different types of phosphate rock (sedimentary and igneous)
- Low maintenance cost and high operating factors
- Single-stage filtration
- Ease of operation/shut-down, flexibility and easy transport of gypsum
- Lower grades of construction materials required
- Easier control of water balance
Phosphoric Acid Plants
Merchant Grade (PA MG)

DPP technology incorporates the most updated Prayon technological solutions:

- **Multi-compartment** reactor design, allowing flexibility and easy control of the sulphate in the attack section, reducing P$_2$O$_5$ losses in calcium sulphate.

- **Sulphate gradient** in attack tank slurries, which minimizes the insoluble losses.
  The sulphate level from one zone to the other can be adjusted based on process parameters and the origin of phosphate rock.

- **Low-Level Flash Cooler (LLFC)**, which is more accurately controllable than air cooling, especially when the cooling rate must exceed nominal capacity.

- **Prayon Proprietary Agitators**, having high efficiency and low power consumption, which is a critical parameter for the economic sustainability of the phosphoric acid production.

- **Prayon Tilting Pan Filter**, incorporating the latest development (“fast drain” cells, central valve, the inverting track design), which is the best-known filter in the phosphoric acid industry, having the highest washing efficiency.

The **Central-Prayon Process (CPP)** was developed to produce a calcium sulphate which could replace the natural gypsum in different applications.

This process is Di-Hydrate (DH) Hemi-Hydrate (HH). During the first stage, a slurry containing dihydrate crystals is produced. From that flow, the quantity corresponding to the product acid is sent to storage, the remaining quantity being sent with the solids to the conversion tank.

In this reactor, sulphuric acid and steam are added to transform the dihydrate into hemihydrate solids liberating most insoluble losses. Solids are filtered and washed.

This process, compared to DPP, makes available:

- a **higher acid strength**, with much higher P$_2$O$_5$ content, thus allowing for lower steam consumption for concentration

- **gypsum with fewer impurities** (that thus can be considered for use in the cement or plaster industry)

It can process both types of phosphates, igneous and sedimentary.

The **PH1/PH2/PH3 processes** all produce hemihydrate crystals and high-strength acid; they differ in plant configuration and products throughput. Selection to be made according to rock quality, gypsum disposal mode and energy cost.

The **DA-HF process** is a modern process leading to high P$_2$O$_5$ yield and a by-product, hemihydrate gypsum. DH gypsum is produced in the attack section where the phosphate is reacted with sulphuric acid. Then, the gypsum slurry recrystallizes into hemihydrate in the conversion section, before being filtered to collect the acid. This process has been developed to produce phosphoric acid with a high P$_2$O$_5$ concentration with one filtration step, only.

The configuration of this process route makes it also eligible, to debottleneck existing PAP plants based on the DH process, aiming to increase the production capacity with a limited investment cost.
Fluorine Scrubber and Recovery Section

Fluorine Recovery Section includes a fluorine scrubber that reduces the fluorine content in the process gas upstream the gas cooling section. The scrubber installation avoids cooling water contamination. The fluorine recovered in the fluorine scrubber is discharged in the form of Fluosilicic Acid (H$_2$SiF$_6$). This acid can be either sold as a product, transformed in different marketable products (e.g. HF) or neutralized and delivered to disposal.

Phosphoric Acid Plants Customization

DBI phosphoric acid plants have a high degree of customization according to process/site conditions: raw water availability, phosphoric rock feedstock quality, effluents treatment/disposal philosophy.

- The PAP plant can be designed with two possible configurations for the cooling medium:
  - open cooling water circuit with cooling water discharge OSBL
  - closed loop circuit equipped with evaporative cooling towers to avoid the cooling water effluents
- In case of phosphoric rock low quality (high concentration of Fe, Al and Mg compounds), an additional filtration step by Press Filter is foreseen if required to avoid the build-up of Fe/Al/Mg. This filter is installed downstream the Concentrated Acid Settling and is used to separate and dispose of the unrecoverable solids from the sludges of the Settling Section.
- Vacuum filtration: Tilting pan filter is widely adopted but Horizontal Belt Filter (HBF) technology is also available in case of specific Client needs. Fast filtration cycles and efficient cake washing (up to three counter-current washing) provide a high P$_2$O$_5$/m$^2$ ratio.
- The gypsum cake from Filter Section and optional Press Filter Section can be discharged in different ways depending on the preferred cake transport method:
  - The dry cake can be delivered to a permanent gypsum stack at Battery Limits using a belt conveyor.
  - If temporary, the subsequent transport to permanent disposal can be performed by truck.
  - Alternatively, the filter cake can be re-suspended and pumped to a stock area at Battery Limits through pipe.
Purified Phosphoric Acid (PPA)

DBI has Phosphoric Acid Purification in its Chemicals technology portfolio since 2015, when it has been awarded the contract for a large Phosphoric Acid project, including both Phosphoric Acid MG production and purification.

Phosphoric Acid purification process is the result of several impurities removal steps put in sequence and with recycles to achieve the target quality and recovery yield starting from the specific PAMG (that is the result of the upstream Phosphate Rock and PAMG production route that has been selected) used as feedstock in the most efficient way.

Please find below the purification steps typically considered:
- Pretreatment Unit to reduce Sulphates, As, Organics, Ca
- Mixer Settler Units for Extraction, Washing and Stripping to remove metals and impurities
- Concentration Unit to increase P₂O₅ %
- Final Stripping to reduce Chlorides and Fluorides
- Final washing and filtration to remove any residual organic

The Main Features of a Phosphoric Acid Purification that DBI proposes are:
- Yield: 80-85% P₂O₅ recovery (maximized by the integration with the Phosphoric Acid Merchant grade plant)
- Modularity: purification is done by addition of modular stages (mixer settlers)
- Solvent for extraction: TBP + Kerosene

PPA technology advantages:
- Solid Technology background through License or Cooperation Agreements in place with world-class reputed technology providers.
- Western standards technology and high yield recovery in the PA TG unit compared to the Eastern solution.

- Lower TIC compared to pulsed column solution.
- Full knowledge of process integration with MG PA plant for yield maximization.
- World-class demonstrated capabilities for pilot tests in well-equipped laboratories, which are fundamental to develop the correct plant configuration: a wrong plant configuration definition cannot be recovered during project execution.
- The PPA plant can be in large extent modularized, with the core of the plant being shipped in pre-assembled containerized skids, with most of the piping and cabling connections pre-installed, ready for installation on the foundations. This would greatly reduce project execution time and erection works/site supervision time and cost. Additionally, a modularized plant keeps a much higher terminal value after amortization, which is a good point when looking for bank financing.
**Sulphuric Acid Plants**

Most of the reactions leading to fertilizers include sulphuric acid as a starting material. Over more, sulfuric acid production plants are based on exothermic reactions that lead to MP and LP steam production that can be integrated with the requirements of the other units of the fertilizer complex in terms of steam and electric power demand.

DBI capabilities are integrated with:
- DuPont MECS® leading technology for large integrated H₂SO₄ plants
- Proprietary know-how for small size plants (up to about 200 TPD)

The processes that DBI makes available can produce sulphuric acid from several sources:
- Elemental sulphur, based on dry air combustion (conventional process)
- Exhaust SO₂ gas, coming from roasting/smelting of pyrites, copper, zinc, lead, nickel ores and similar
- Spent acid or sludge obtained from alkylation processes
- H₂S and SO₂ off-gas from various other chemical processes

Possibility to produce high-quality H₂SO₄ for special applications like battery grade, analytical grade and similar.

**Wide range of production capacities**, from the small size of 50÷100 TPD for local or very specific applications to large industrial production units up to more than 2,000÷3,000 TPD. Option for production of Oleum as well as liquid SO₂ and liquid SO₃.

**Compact plant layout**, for investment cost optimization (e.g. piping and duct routing), taking into account safety/maintenance/operation principles and according to customer site requirements.

**Waste heat recovery** by steam production, with steam turbine power generation systems to increase the overall plant efficiency and boost the return on investment.

DuPont MECS® HRS technology to maximize the heat recovery from the plant.

**Air pollution control system**, to contain the plant emissions to the minimum level required by the most stringent laws and standards.

**High-quality** construction materials and the use of acid resistant special alloys.

**High yield** of conversion, granted by the best available technology together with DuPont MECS® catalysts allowing for an extended lifetime, low pressure drop and low screening losses.

**SO₂ emissions control**
100 ppm by five conversion stages combined with other specific solutions (catalyst selection, double absorption)
< 100 ppm by tail gas scrubbing including the possibility to minimize effluents and increase steam production by Dupont MECS® proprietary regenerative absorption system (SolvR™ and Max3™).
DCP Production
(Low Grade Phosphate Rock Enhancement)

The Prayon DCP route has been studied to process low grade or with high level of impurities phosphate rocks. A simple, low in equipment number plant can convert untreated ore to valuable products. The process consists of two main steps:
- Attack of the rock (in blue)
- Precipitation of dicalcium phosphate (in red)

Phosphate rock and sulphuric acid are reacted in diluted conditions: impurities will stay in solid phase, whereas $P_2O_5$ is transferred to liquid phase.

The two phases are separated by filtration and the liquid phase neutralized with a Ca basic salt, thus converting the $P_2O_5$ in dicalcium phosphate. The newly formed solids are separated, and the liquid recycled to attack section.

The process allows the use of low-grade rocks (< 15% $P_2O_5$), so no beneficiation plant is required.

Sulphuric acid can be of any grade, even spent acid.

DCP quality can be selected from feed to industrial grade.

Feed grade is obtained by a simple chemical purification step; the product can be directly used for animal feeding.

Industrial grade can be used for fertilizer production or phosphoric acid production.

Produced phosphoric acid will be of high quality.

Gypsum by-product will be of high purity, too, suitable to be marketed as a blender in cement or plaster production.
Potassium Sulphate Plants Technology

DBI has developed $\text{K}_2\text{SO}_4$ production technology based on Mannheim process in cooperation with Marchi Industriale (a European fertilizer producer based nearby Venice – Italy) for the furnace section and taking benefit of in house know-how for the balance of the sections.

The process is based on the endothermic reaction between $\text{H}_2\text{SO}_4$ and $\text{KCl}$ that takes place under temperature control in the Mannheim furnace. $\text{K}_2\text{SO}_4$ production releases gaseous hydrochloric acid ($\text{HCl}$) that is quenched and absorbed in multi-stage absorption towers.

Advantages of DBI-Marchi Industriale design compared to Mannheim standard design

The solutions that DBI proposes includes several improvements in the combustion chamber design, granting a better heat transfer from combustion to reaction chambers, preferable temperature distribution and more efficient insulation.

Moreover, the material selection for combustion/reaction chambers has been improved, leading to longer lifecycle for wear parts.

The overall advantages of DBI-Marchi design are:
- lower fuel consumption
- wear parts longer life, reducing operational costs
- shorter shut-down time for the wear parts substitution
- higher plant productivity and profitability

Products characteristics

Potassium sulphate produced by DBI plants is soluble in water, with $\text{K}_2\text{O} \geq 50\%$ and with $\text{Cl}^-$ content as low as 0.5%. Within the same SOP production plant, the $\text{Cl}^-$ content in the product can be adjusted influencing the production capacity (higher production rates can be achieved allowing a higher $\text{Cl}^-$ content in the product).

Potassium sulphate is mainly used as fertilizer. However, it can also be used as:
- hardener in the production of cements and plasters
- detergent additive
- raw material for chemical synthesis

Hydrochloric acid is produced in commercial concentration (30÷33%) and has profitable and widely varied uses as:
- raw material in several industrial chemical processes
- production of organic compounds (e.g. PVC, Bisphenol A)
- ion-exchange resin regeneration
- urban and industrial waste water treatment
- production of $\text{Cl}_2\text{O}$
- production of pesticides
- production of starch derivative in the food industry
- production of printed circuits for electronics
Ammonium Sulphate

Ammonium Sulphate Plants Technology

Ammonium sulfate (AS) is especially valuable where both Nitrogen and Sulfur are required, as its high solubility provides versatility for a number of agricultural applications.

It has a low pH that makes it suitable for alkaline soils and sulphur has been recognized to support the synthesis of amino acids, proteins, enzymes and chlorophyll.

DBI collaborates with GEA - Germany (with offices worldwide, including one in Milan) and its proven technology to produce coarse and uniform AS crystals.

Three different crystallizer configurations are available:
- (A) Forced circulation (FC)
- (B) Draft-tube-baffle (DTB)
- (C) Fluid bed (OSLO)

Each can be arranged in several ways:
- single or multiple stages
- single or multiple effects (if evaporative)
- with recompression of produced vapours (thermal or mechanical)

In reactive crystallization, the creation and growth of crystals occur within the crystallizer, due to the supersaturation of the solute.

The dissolution/reaction heat is sufficient to operate the process without any external thermal source to provide the necessary evaporation.

In evaporative crystallization, the feedstock is usually an aqueous solution, so heat is necessary to create the supersaturation necessary for the crystallization process (water evaporation).

Reactive crystallizers are more and more used due to the much lower OPEX.

According to feedstock quality and required results in terms of crystals size, the crystallizer configuration and mode of operation will be selected.

Average achievable Particle Sizes are reported below:

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<th>Range of D50 (mm)</th>
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<tr>
<td></td>
<td>FC</td>
</tr>
<tr>
<td>Evaporative Crystallization</td>
<td>0,6 - 1,0</td>
</tr>
<tr>
<td>Reactive Crystallization</td>
<td>0,4 - 0,6</td>
</tr>
</tbody>
</table>
DBI has developed Single Super Phosphates (SSP) and Triple Super Phosphates (TSP) production technology in cooperation with Industrie Chimiche Puccioni (a European fertilizer producer based nearby Vasto – Italy) and in-house know-how.

The P-SSP/P-TSP production starts from Phosphate Rock and Sulphuric Acid (for SSP) and Phosphoric Acid (for TSP) feedstocks.

The reaction is carried out in a proprietary design reactor. Depending on the size of the plant, two reactor types are available:
- Kuhlman-Den type
- Broadfield-Den type

These reactors design grants several advantages:
- Product leaving the reaction phase is in powder form, with no granules or lumps
- The reaction section can be fully emptied at the end of a shift or production run
- High retention time of the product in the reaction section, granting easy operation on downstream SSP/TSP handling devices
- Possibility to have an in-line inspection of the reaction section by means of manholes installed on the fixed hoods
- Low mechanical complexity
- Easy construction and maintenance of the reactions fumes/gases sealing systems
- No presence of internal anti-fouling devices.

In case of SSP production, the Kuhlman-Den reactor can be fed directly with concentrated sulphuric acid, avoiding the acid dilution and almost all the whole waste liquor stream from the scrubbing system can be recycled to the reactor, therefore nearly eliminating the necessity of its disposal.
Environmental impact control
DBI SSP/TSP plants are equipped with a tail gas scrubbing section to contain the pollutant emissions. Depending on the emissions target, different solutions can be designed.

Starting from the basic solution, composed of a single-stage dry scrubbing section up to the most advanced 3-stages scrubber + oxidation that complies with the most stringent international standards and laws.

With the most performing scrubbing system, emissions can be as low as
- 10÷20 mg/Nm³ for dust
- 0.5÷5.0 mg/Nm³ (as HF) for fluorides

- 3 Venturi + Water Scrubbing Finishing + Oxidation (NaClO or H₂O₂)
- 3 Venturi + Water/Soda Scrubbing Finishing + Mist Eliminator
- 3 Venturi + Mist Eliminator
- 1 Venturi + Water/Soda Scrubbing Finishing + Mist Eliminator
- 1 Venturi + Cyclonic Scrubber + Mist Eliminator
Granulation Plants Technology
DBI offers plants based on a technology developed in-house or based on INCRO Pipe-Reactor Technology.

Granulation plants can produce SSP or TSP fertilizers as well as create N-P-K based fertilizers. The main feedstocks commonly used are:
- **N-based feedstocks:**
  - Ammonium Sulphate
  - Urea
- **P-based feedstocks:** TSP, SSP, MAP, DAP.
- **K-based feedstocks:**
  - Potassium Chloride
  - Potassium Sulphate

Additional feedstocks are added in minor quantities to improve the product characteristics.

Advantages of DBI design
- **Wide range of NPK products**
- **High operation Flexibility:** the same plant can produce SSP, TSP and NPK fertilizers
- **Compact plant layout,** based on specific criteria for the design of solid handling equipment, in compliance with safety and economic principles and according to customer site requirements
- **High automation degree,** reducing the personnel required for plant operation
- **Possible integration with DBI P-SSP and P-TSP plants** for a no-liquid emissions process design

Integrated process and synergies with DBI P-SSP and P-TSP plants.
Granulation plants can be installed downstream P-SSP or P-TSP plants to granulate the powder products of these plants.

This integrated plant has great advantages in terms of environmental impact since the whole water effluent rich in fluosilicic acid from P-SSP/P-TSP plants is used as water feedstock in the granulation plant.

INCRO pipe-reactor technology is available when specific formulations are required.

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Desmet Ballestra Capabilities

Wide Range of Expertise
Desmet Ballestra Italy (DBI) is based in Milan and, through its Chemicals Segment, is active in a wide range of inorganic chemicals plants including Sulphuric Acid, Phosphoric Acid and Fertilizers.

Process technologies are either proprietary or sourced from Licensors (DuPont MECS®, Prayon Technologies, UOP) and/or fertilizers and chemicals producers (ICP, Marchi Industriale, INCR0) with whom DBI has consolidated and well-proven cooperation schemes.

From initial design to plant start-up
DBI can support Clients during all the project phases:
- feasibility study
- definition of process design
- detailed engineering
- material supply
- project implementation
- management of the start-up phases based on agreed execution and contractual schemes for effective and cost-saving design and execution.

Site Assistance
DBI has experienced people that can provide support during construction and commissioning phases up to the start-up of the plant.

After Sales
DBI offers full assistance to Client after the plant start-up with technical support to study plant improvements or revamping and with a dedicated team for spare parts.

Worldwide Presence
DBI has several operational offices in different countries offering worldwide assistance to its Clients.

Commitment to Safety & Environment
DBI is ISO 9001 compliant and holds other specific certifications.
DBI designs and supplies Plants in full compliance with the most stringent:
- International safety and environmental regulations
- Clients specific requirements, local regulations providing the highest quality standards, plant/process reliability, flexibility and low operating cost.

A team of 300+ experienced people in Milan and other DBI Italian offices (Busto Arsizio, Rome) is available to achieve the project targets.

Full 3D design
Desmet Ballestra takes advantage of the most up-to-date engineering techniques, such as fully integrated 3D design to grant optimized plant layout and straightforward construction at site.