Advanced Tube Technology for Urea Plants

SALZGITTER MANNESMANN STAINLESS TUBES

A Member of the Salzgitter Group

Table of contents

Seamless stainless steel and nickel-based alloy tubes and pipes are our everyday passion and our history at Salzgitter Mannesmann Stainless Tubes. As early as 1885 Reinhard and Max Mannesmann invented a rolling process for the production of seamless steel tubes in Remscheid, Germany. In the 1890's they developed it futher until it reached marketability: the production method they invented was the pilger process, which still is widely in use today.

Our group integrates the tradition of three seamless stainless steel worlds (Mannesmann, Dalmine and Vallourec). Resulting in "DMV Stainless" from this international merger in 1994, DMV became a part of Salzgitter group in 2003 and adjusted its name to Salzgitter Mannesmann Stainless Tubes in 2008.

With an international network of plants and offices, we are a global top player in our markets and a consistently reliable business partner, ensuring quick and customer focused answers to changing market requirements.

Our customers profit from one of the most comprehensive product ranges in our business:

- from small instrumentation tubing to large pipe sizes with outside diameters from 6 to 250 mm (from 0.24 up to 9.84 inches) and with wall thicknesses from 0.5 up to 50 mm (from 0.02 up to 1.97 inches)
- in materials from standard austenitic stainless, duplex and super-duplex steels to highly sophisticated nickel-based alloys – this variety offers highest corrosion resistance, heat resistance and/or high-temperature, high-strength materials.

We combine high quality products for critical environments with efficient and reliable services: our customers thus enjoy a supportive personal account management.

Ongoing cycles of investment ensure that we work according to the latest technical standards. This gives us the trustworthiness to equip the so called "critical spots" of customers´ plants, products and processes with the special qualities of our tubes and pipes.

Typically, these "critical" service conditions are defined e.g. by

- high temperatures
- high pressure
- aggressive media (acids or basic)

Materials used for urea plants

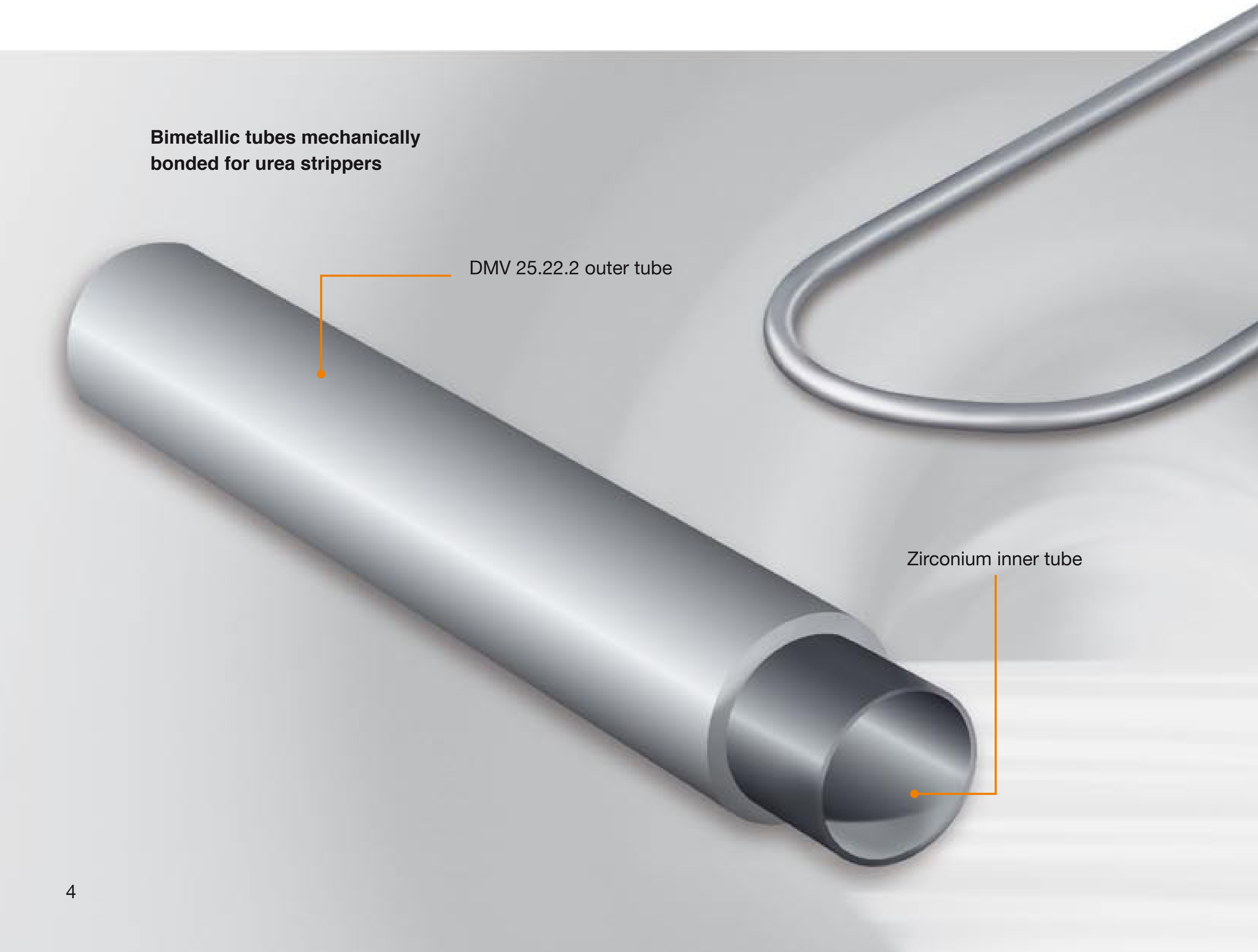
Urea's share in the world-wide production of nitrogen-based fertilizers is around 40 %.

The best known production processes include those developed by Snamprogetti, Stamicarbon, Toyo Engineering and Urea Casale. In the process, liquid ammonia and gaseous carbon dioxide are converted in a reactor under pressure (150 - 200 bar) at high temperature (180 - 190°C) to ammonium carbamate, urea and water.

$$CO_2 + 2NH_3 \longrightarrow NH_2COONH_4$$
$$NH_2COONH_4 \longrightarrow (NH_2)_2CO + H_2O$$

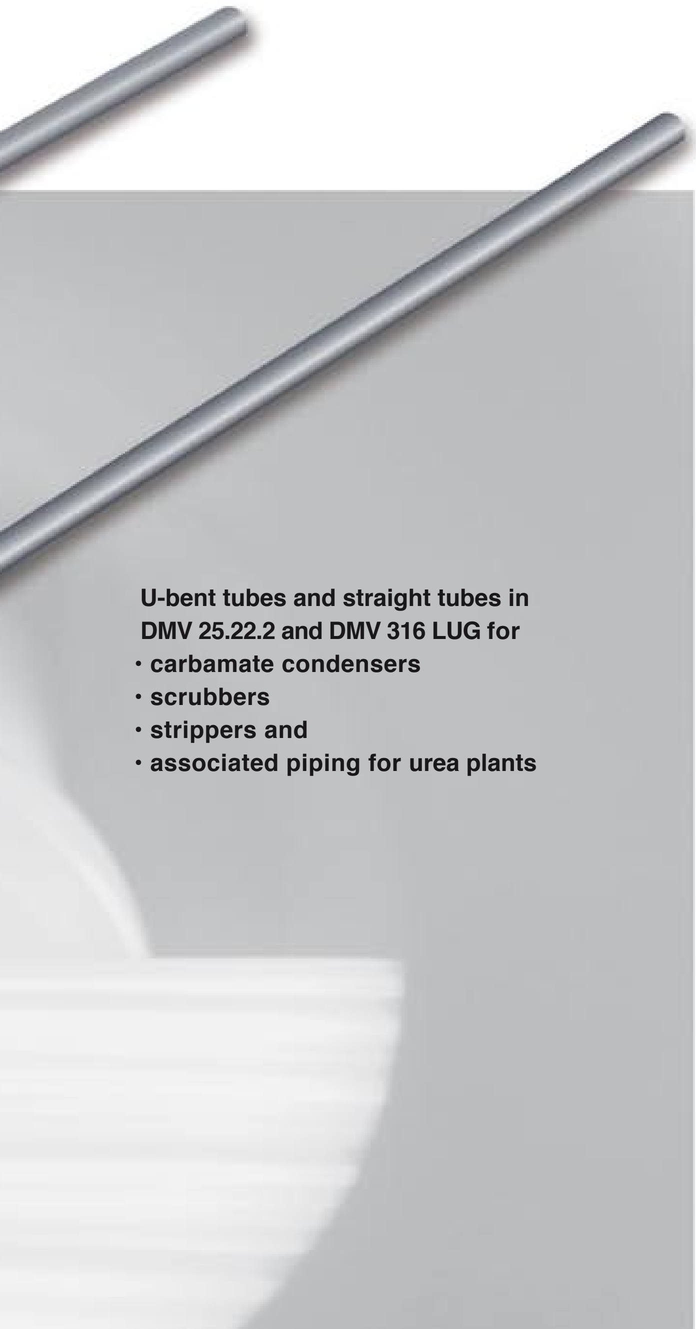
Modern energy-efficient processes foresee the extraction of the carbamate, not transformed into urea, in a stripping column working at the same pressure as the reactor while the off-gas from the stripper is condensed in the carbamate condenser also working at the pressure of the reactor and the stripper. Condensation heat is recovered as steam. Ammonium carbamate at approximately 180 - 250°C and 150 bar is extremely aggressive to materials. The customary steels of 304 L / 316 L type cannot withstand such conditions. For this reason, special "urea" steels have been developed: DMV 316 L Urea Grade (UNS S 31603). Its increased nickel content (more than 13 %) gives it improved resistance to corrosion and, in conjunction with a small addition of nitrogen secures austenitic stability. The DMV 25.22.2 (25.22.2 Cr Ni Mo) stainless steel has even better resistance to austenitic decomposition and corrosive attack, and is the preferred material for the highly susceptible parts of equipment. In order to provide high operating flexibility limiting at the same time the contents of oxygen necessary for passivation, Snamprogetti has employed titanium for the stripper and subsequently has patented and now is routinely using special bimetallic tubes lined with zirconium.

Bimetallic tubes mechanically bonded for urea strippers



Bimetallic tubes

The bimetallic tubes for urea strippers have been developed and patented by Snamprogetti. These consist of two concentric tubes: an external tube in DMV 25.22.2 having a minimum thickness of 2 mm, and an internal tube in zirconium Gr. 702 having a minimum thickness of 0.7 mm. The two tubes are fabricated separately according to Snamprogetti specifications, then they are assembled and drawn. During the drawing operation, proper bonding according to Snamprogetti specification is obtained.



The first bimetallic tube for a Snamprogetti urea stripper has been manufactured in our German factory in the 80's.
In 1990 Snamprogetti put into operation, in the USA, the first urea stripper with the bimetallic tubes made by SMST-Tubes. Our Italian factory has supplied all the bimetallic tubes for the urea stripper of the largest single stream urea plant of the world in Argentina (Profertil Baja Blanca), and for some further considerable projects in China and India.

Only approved suppliers can produce bimetallic tubes. No more than two other companies in the world are qualified besides SMST-Tubes.

U-bent tubes and straight tubes in DMV 25.22.2 and DMV 316 LUG for
- **carbamate condensers**
- **scrubbers**
- **strippers and**
- **associated piping for urea plants**

Corrosion in the urea process

Ever since the early development of industrial processes based on direct reaction between ammonia and carbon dioxide, urea plant designers and owners have been faced with the problem of corrosion. Silver and lead have been widely used as lining materials to protect the surface of some apparatus. This was a serious shortcoming for many years since it not only endangered the good performance of urea plants but it was also an obstacle to the efficiency improvements of the process itself. The situation has now considerably changed, but the process conditions, temperature, pressure and particular fluid composition at the various operating stages of the process and the presence of intermediate compounds still require not only a careful selection of construction materials but also an adequate design.

Austenitic tubes for urea applications are also available in the U-bent version. The high deformability of material allows cold bending down to a very small bending radius. Annealing after cold bending is an optional treatment offered by SMST-Tubes.

Corrosion mechanism and testing methods

The two types of mechanism found are active corrosion and intergranular corrosion:

Active corrosion can be prevented by injecting oxygen and using metals which are easily passivated.
Intergranular corrosion of passive steel selectively attacks the grain boundaries of metals. It is caused by the highly oxidizing action of oxygen-containing urea-carbamate solution, a low NH_3/CO_2 ratio and the segregation of impurities in steel. The resistance to the intergranular corrosion can be improved by optimizing the amount of passivation oxygen injected to protect materials by operating at a higher NH_3/CO_2 ratio, and by improving the corrosion resistance of the grain boundary through the use of austenite/ferrite control or by using materials with a lower carbon/high chromium content.

The most common test for evaluating stainless steel grades in nitric acid and in the high-pressure synthesis loop of a urea plant is the Huey test according to ASTM A 262 practice C.

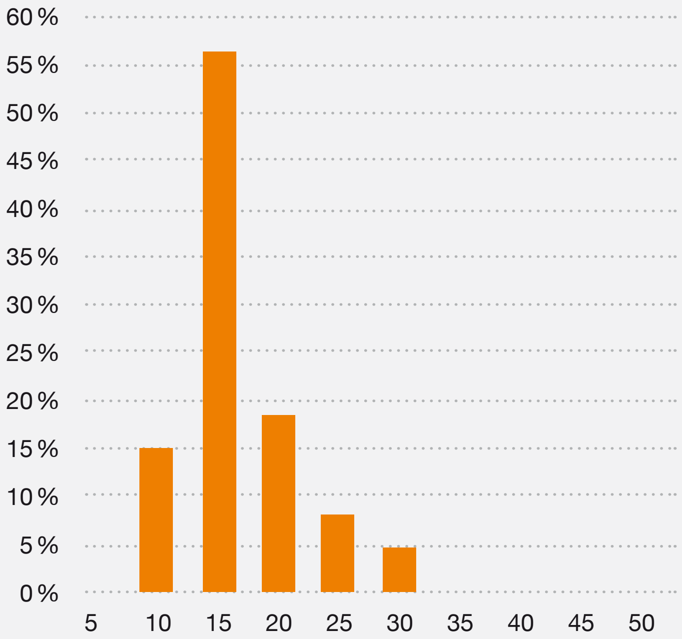
The Huey test defines the degree of homogeneity of the austenitic structure as precipitated phases lead to intercrystalline attack and thus to an increased weight loss in the transpassive range. Increased corrosion rates in the Huey test clearly indicate a poor process during tube production, heat treatment and welding.

For the metallurgy of the stainless steel grade it is a must:

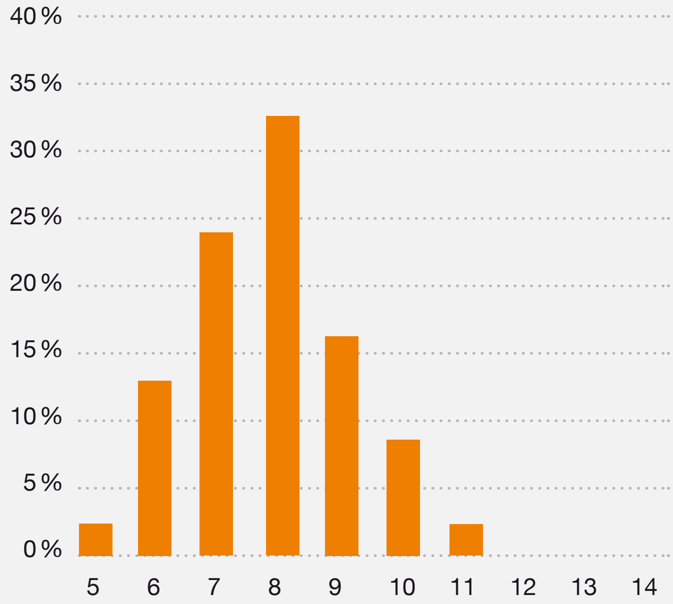
- to secure optimal homogeneity of structure by choice of suitable combinations of hot/cold working and heat treatment
- to avoid sensitizing and precipitation
- to avoid coarse grain structures

For urea production plants, the corrosiveness of the chemicals involved in the process shall be taken into special account. This applies not only to material selection, but also to the metallurgical processes and the fabrication of alloy steels. Only a limited content of impurities and some special measures taken during heat treatment can ensure corrosion-resistance during operation for the special steel types selected.

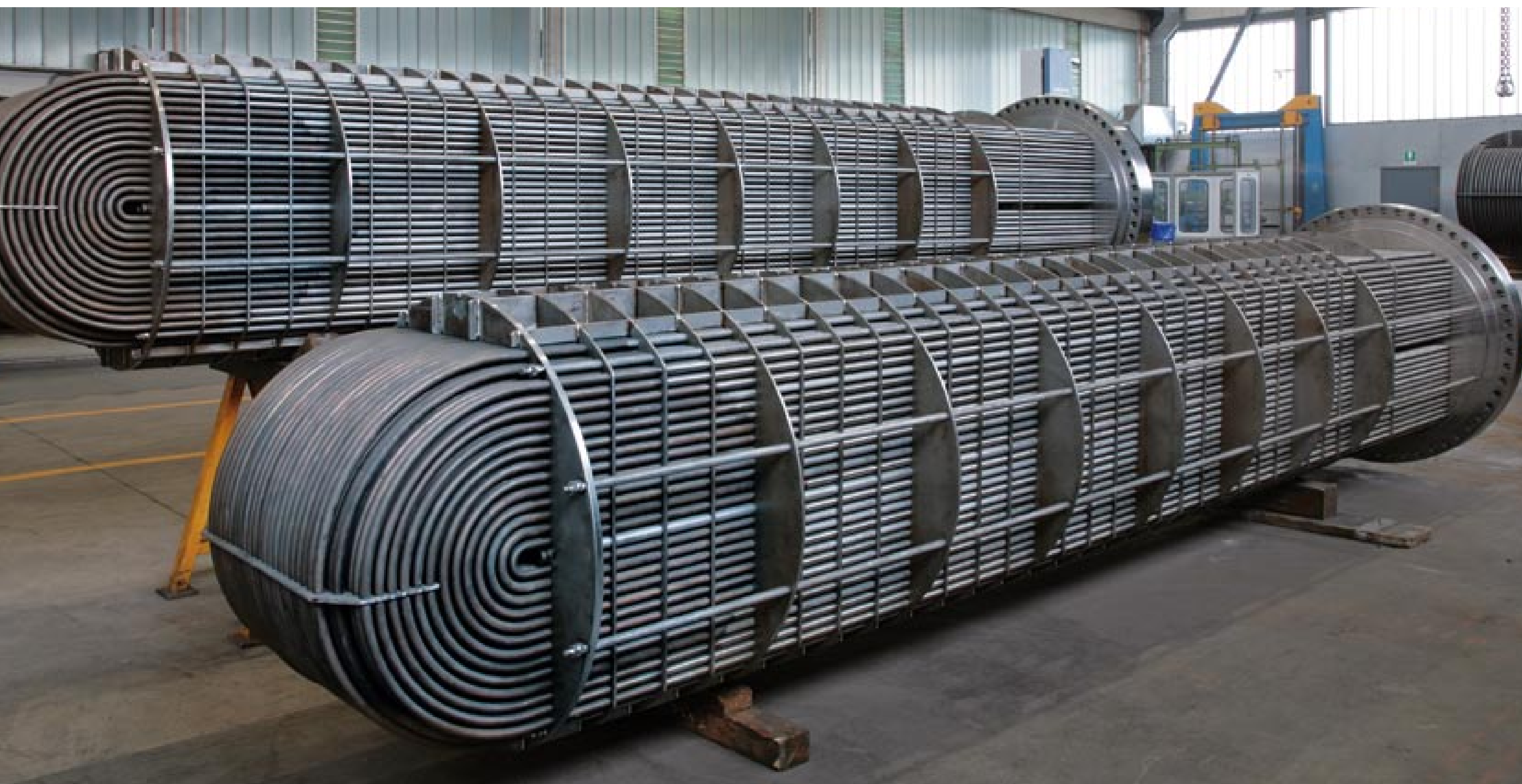
Selective attack (micron)



Corrosion rate (micron/month)



Statistical data on SMST-Tubes production for grade DMV 25.22.2



Welding working practices

The aggressive process fluids in high pressure equipment of urea plants sets high demands on all welds. Some good working practices for stainless steel material welds recommend:

In general during all the equipment fabrication phases including welding, it is necessary to follow proper prescriptions for electrodes, preheating and post weld heat treatment.

In the case of welding of stainless steel materials in contact with the high temperature process solution there are specific rules for urea which are obtained from experience.

The most important ones are the following:

- **Type of filler material**
  The type of filler material (electrodes, flow rods, flux, etc.) shall be exclusively the one indicated by the licensor.

- **Welding operators**
  Welding operators, especially for manual and semi-automatic welds, shall be highly qualified as the welds have to be made with the greatest care.

- **Cleaning**
  Weld edges and the adjacent zones shall be absolutely clean. In the high pressure loop equipment of urea plants, pollution by foreign materials is very harmful.

- **Weld craters**
  Weld craters must absolutely be avoided.

- **Roughness**
  Weld shall be smooth and free from roughness since roughness does not facilitate passivation.

- **Weld splatter**
  Weld splatter has to be avoided.

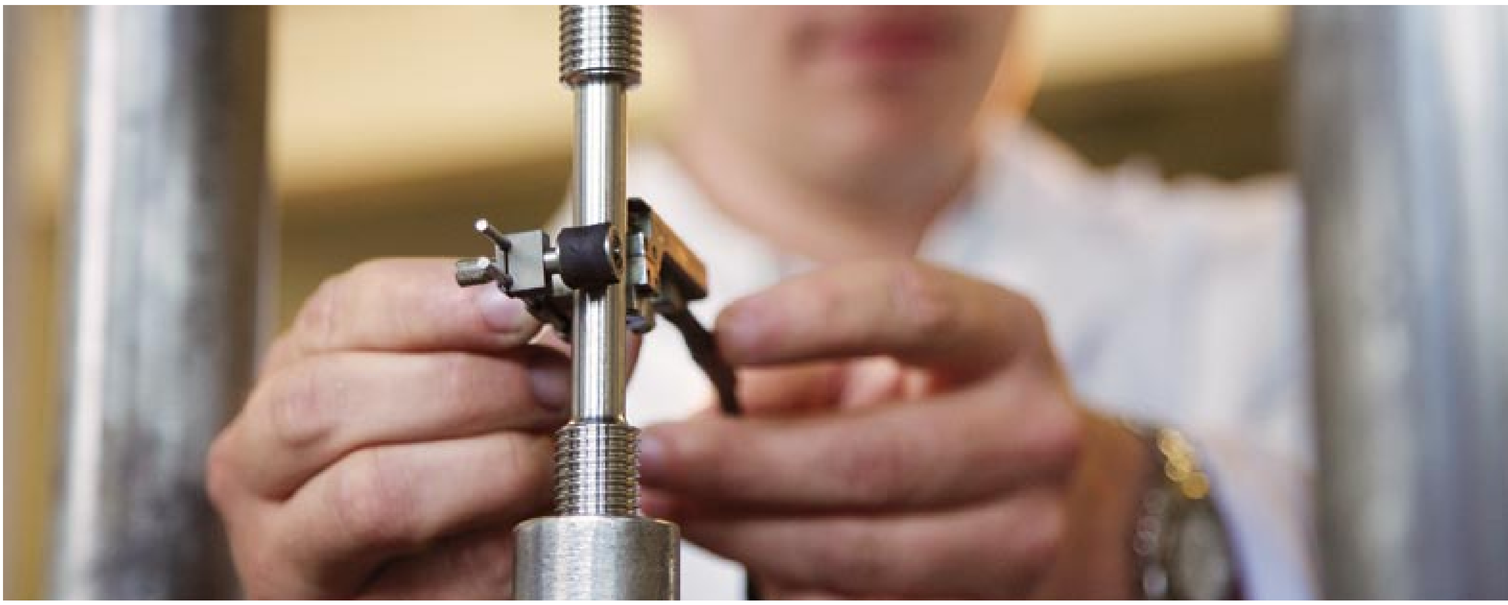
- **Grinding**
  Weld grinding should be avoided (if possible).

- **Tube/tube sheet weld**
  For the tube/tube sheet weld it is suggested to use automatic computerized Tig welding in order to avoid lack of fusion and overheating of tubes.

Our manufacturing and quality control processes for urea grade stainless steel tubes and for bimetallic tubes:

Stainless steel tube	Bimetallic tube
Steelmaking and bar forgings	**Zirconium production*** Zirconium technology
Hot extrusion Water quenching Deglassing and pickling	NDT inspection* UT and EC
Hollows inspection	Visual and dimensional check*
Cold pilgering Degreasing	Material tests* Chemistry, mechanical properties
Heat treatment Bright or open air annealing	Tube cutting and cleaning*
NDT inspection UT and EC	Outer stainless steel pointing
Visual and dimensional check Grade check	Assembling and drawing of stainless steel tube and zirconium tube
Material tests Chemistry, mechanical properties Corrosion tests Micrographic examination	Point and end cutting
Tube cutting and cleaning	Cleaning
Marking and packing	Straightening by press
	NDT inspection EC, sound test
	Material tests Bonding test Corrosion tests Mechanical properties
	Visual and dimensional check grade check
	Marking and packing

*Qualified external supplier



SMST-Tubes supply

Straight and U-bent tubes can be delivered for use in

- carbamate condensers
- scrubbers
- strippers and
- associated piping

Tubes are delivered in cold or hot finished conditions, depending on size and specification, in the range of

- 6 to 250 mm (from 0.24 up to 9.84 inches) outside diameters and
- 0.5 up to 50 mm (from 0.02 up to 1.97 inches) wall thicknesses

Urea grades DMV 25.22.2 and DMV 316 LUG can be delivered in accordance with all commonly used international standards and the specifications of the main engineering and licensor companies.

For further technical information about urea grades, i.e. their chemical composition, mechanical, physical and corrosion properties etc., please refer to our specialised technical datasheets.

SMST-Tubes has delivered tubes and pipes to a wide range of worldwide customers in the urea industry. References are available upon request.

For any specific queries, please contact our sales offices.

Photo kindly provided by Officine Luigi Resta S.p.A

Urea stripper licensed by Snamprogetti

Salzgitter Mannesmann Stainless Tubes GmbH
Wiesenstraße 36
45473 Mülheim an der Ruhr
Germany
Tel.: +49 (0) 208 458 01
Fax: +49 (0) 208 458 2640

dmv@smst-tubes.com
www.smst-tubes.com

Salzgitter Mannesmann Stainless Tubes Deutschland GmbH
Sales:
Wiesenstraße 36
45473 Mülheim an der Ruhr
Germany
Tel.: +49 (0) 208 458 2611
Fax: +49 (0) 208 458 2641
salesgermany@smst-tubes.com
Production:
Bahnstraße 61
42859 Remscheid
Germany

Salzgitter Mannesmann Stainless Tubes France SAS
Route de Semur
21500 Montbard
France
Tel.: +33 (0) 3 80 89 52 00
Fax: +33 (0) 3 80 89 52 26
salesfrance@smst-tubes.com

Salzgitter Mannesmann Stainless Tubes Italia S.r.l.
Via Piò 30
24062 Costa Volpino (BG)
Italy
Tel.: +39 035 - 975 744
Fax: +39 035 - 975 803
salesitaly@smst-tubes.com

Salzgitter Mannesmann Stainless Tubes USA, Inc.
12050 West Little York
Houston Texas 77041
USA
Tel.: +1 713 - 466.7278
Fax: +1 713 - 466.3769
salesusa@smst-tubes.com

SMST-Tubes Urea Plants 02/2009
www.heselsvomberg.de

SALZGITTER
MANNESMANN
STAINLESS TUBES
A Member of the Salzgitter Group