World record on-stream time for SKW Piesteritz GmbH HP CO2 strippers with Sandvik 2RE69 tubes

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Contents

Summary

SKW Piesteritz has achieved a world record on-stream time for the strippers in their CO_2 stripping urea plants. The record currently stands at 35 years for a HP CO_2 stripper with Sandvik 2RE69 tubes, but is likely to be 36 years when the stripper is scheduled to be replaced in 2011. This outstanding performance can be attributed to many factors including high quality tubing and great care in the fabrication and operation of the plant.

1. Introduction SKW Piesteritz and Sandvik Materials Technology

SKW Piesteritz is the largest ammonia and urea producer in Germany and one of the most innovative fertilizer producers in Europe. The plant is located in Lutherstadt Wittenberg, in a largely agricultural region of Saxony-Anhalt in eastern Germany. The roots of the fertilizer production located there can be traced back to the year 1915. Today SKW Piesteritz is part of the Czech Agrofert Holding, a.s. Around 770 employees at sites in Piesteritz and Cunnersdorf produce a broad range of agrochemical and industrial chemical products, around three million tons of products every year. Around half of SKW Piesteritz' turnover is derived from products for industrial chemistry, such as ammonia, urea or nitric acid. SKW Piesteritz' agricultural products have been closely oriented to the changing requirements of both crop producers and the environment. The product portfolio ranges from traditional nitrogen based fertilizers to stabilized nitrogen fertilizers and different fertilizers with sulphur. These modern products for plant nutrition were developed in the company's own research and development centre near Leipzig. Therefore comprehensive application engineering studies are being carried out on more than 4,500 test plots. In 2005 also an Agrochemical Institute was founded by SKW Piesteritz and the University of Halle-Wittenberg where scientific Know-how and modern, technical equipment are being combined with industrial product management and the infrastructure of a chemical site. In order to expand the range of specialist products, numerous new facilities and additional modern logistics areas have recently been built. SKW Piesteritz' huge advantage is also the ideal geographic location of Lutherstadt Wittenberg at the interface of eastern and western Europe. Major national highways and the most important railway lines between eastern and central Germany intersect the city. Besides it is located right next to the river Elbe so that the own industrial port opens up the route to the German and European waterway network. Furthermore SKW Piesteritz is actively involved in the commercialization of the Agro-chemical Park Piesteritz as an attractive industrial location. The Agro-chemical Park is unique in Germany. 1.500 employees are already working here. On the spacious works grounds there are 30 hectares with a full industrial infrastructure available for future investors.

Sandvik Materials Technology, which headquarter is located in Sandviken in Sweden, is a world leading producer of high technology stainless steels, special alloy materials and advanced value-added products, developed in close cooperation with customers. Sandvik was founded in 1862 by Göran Fredrik Göransson, who was first in the world to succeed in using the Bessemer method for steel production on

an industrial scale. At an early stage, operations focused on high quality and added value, investments in R&D, close contact with customers, and exports. This is a strategy that has remained unchanged through the years. The Sandvik Group currently has 44,000 employees with operations in 130 countries.
Sandvik is a world leading producer of seamless stainless steel tubes. Sandvik has total control over the entire production process from steel melt to the finished product. Sandvik tubes are typically used within industries such as: chemical and petrochemical, oil and gas, power generation, fertilizer, pulp and paper and mechanical. Sandvik Materials Technology has supplied quality products for high pressure urea service for more than 30 years. The modern large scale urea plants are very efficient, in spite of the highly corrosive environments in the critical equipment. The high pressure and temperature in combination with toxic ammonia calls for best special stainless steel as Sandvik 3R60 Urea Grade, Sandvik 2RE69, Bimetallic tubes or Sandvik Safurex®. The high standstill cost is about USD 250.000 per day, which easily motivate the use of special material for longer and safer service. Sandvik manufactures and stocks tubes, pipes, fittings, bar, plates and welding consumables. The products conform to the specifications from leading licensees like Stamicarbon and Saipem (Snamprogetti).

2. Stamicarbon urea process and the role of HP CO_2 stripper

Stamicarbon
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Stamicarbon was founded in the coal mining area of Limburg, the most southern province of the Netherlands, in 1947. Stamicarbon set itself the goal of ‘obtaining and exploiting inventions, patents and working methods in general, and in particular in the field of the purification of pit coal’.
Stamicarbon commissioned its first urea plant as early as the 1950s but it was in September 1956, that its flagship urea plant was commissioned in Geleen, the Netherlands (in an empty soda plant). Production capacity was 150 metric tons per day (mtpd). The following year, Stamicarbon sold its first urea license to the Société Carbochimique in Tertre, Belgium. As the demand for coal decreased, Stamicarbon’s focus on urea and related chemicals increased. The first license was granted in Russia in 1964. In the 1990s new breakthrough innovations in the urea synthesis section were made with the development of the Urea 2000*Plus*™ PoolCondenser and PoolReactor technology, simplifying the design and construction and consequently lowering the investment cost. During this decade also the Safurex® material and Stamicarbon fluid-bed Granulation technology were developed. Economy of scale is getting more and more important leading to the development of the Mega Plant technology for production capacities up to 5000 mtpd. Stamicarbon’s most recent development is the Avancore® Process, which combines the advantages of Urea 2000*Plus*™, Safurex®, low plant height and results in the lowest cost of ownership. Since last year Stamicarbon new owner is Maire Tecnimont, Italy, where Stamicarbon has become the Licensing and Intellectual Property Group Center of Maire Tecnimont.

In 1967 Stamicarbon revolutionized the urea process by the invention of the HP CO_2 Stripper by Mr. Petrus JC Kaasenbrood. US patent 3,356,723 describes the invention of the HP CO_2 stripper.

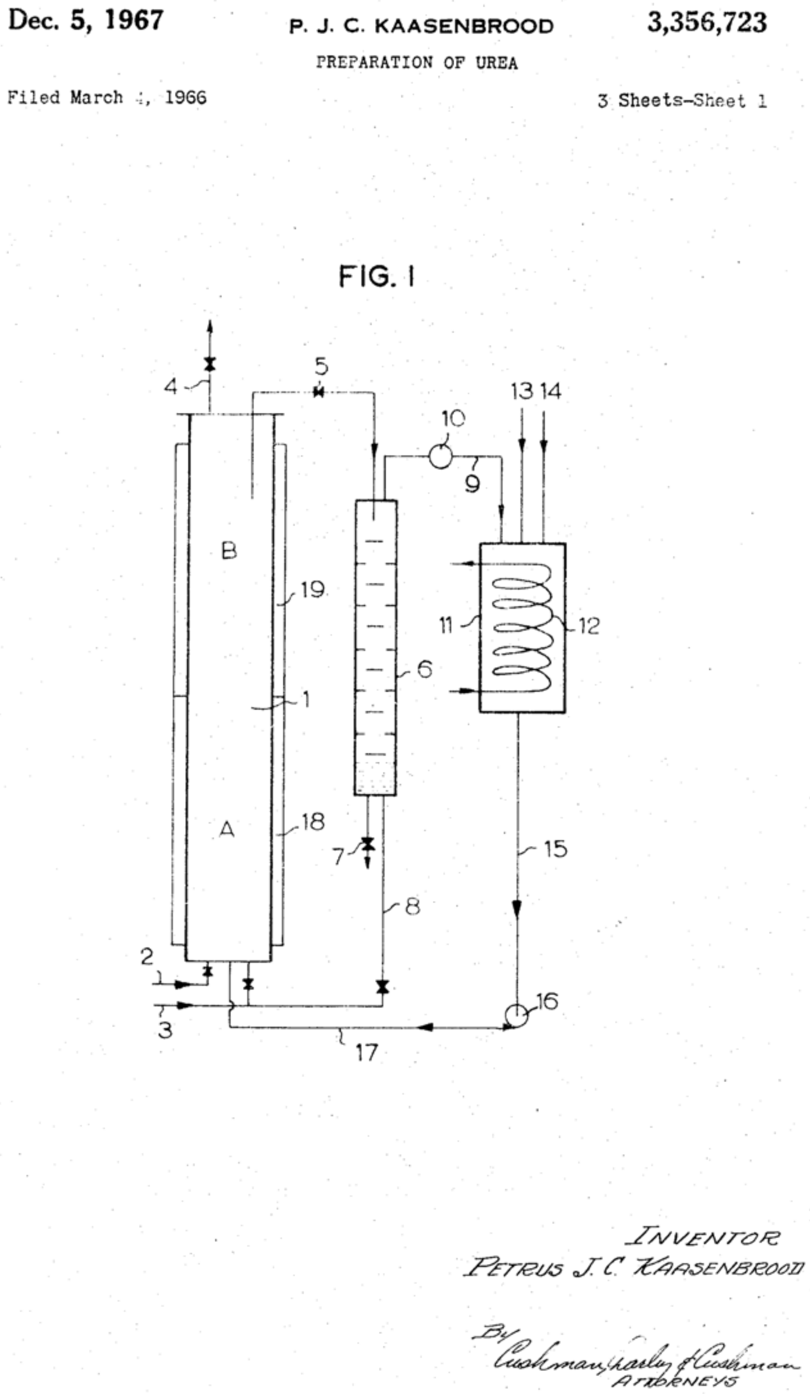

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Figure 1: US patent 3,356,723: HP CO_2 Stripper by Mr. Petrus JC Kaasenbrood

The first claim in this patent states:

"In a continuous process for the preparation of urea wherein NH_3 and CO_2 are reacted at elevated temperature and pressure to continuously provide an ammonium carbamate melt, thereafter in an autoclave, said melt being converted into a urea solution containing ammonium carbamate and the carbamate being stripped from said solution by decomposing said carbamate into NH_3 and CO_2 by heat and expelling NH_3, CO_2 and H_2O from said solution, the improvement which comprises continuously stripping the urea solution with CO_2 in a stripping zone outside said autoclave and at a pressure of at least 50 atmospheres up to urea synthesis pressure wherein the urea solution flows downwardly along the inside of externally steam heated tubes in the stripping zone and CO_2 stripping gas passes upwardly in said tubes in contact with said urea solution, the pressure of the heating steam being in the range of 15-30 atm., whereby NH_3 and CO_2 are expelled from said solution, condensing the resulting mixture of CO_2 gas and gases expelled from said urea solution after addition of further NH_3 and at a pressure of at least 50 atmospheres up to urea synthesis pressure to form a carbamate solution and returning the thus formed carbamate solution to said autoclave for further urea synthesis."

In the HP CO_2 stripper urea reactor effluent is thus treated counter currently with carbon dioxide in a stripper at high pressure in order to dissociate carbamate and at the same time enable easy condensation of the carbamate gasses without the addition of water. Preferably this is done at the same pressure as the reactor is operating. The condensation of strip gasses will produce steam leading to significant reduction in steam consumption to produce urea.
This patent from 1967 has revolutionized urea technology and nowadays all modern urea processes operate a HP stripper.

A HP CO_2 stripper did lead to three main benefits:

1. the carbamate could be recycled at synthesis pressure so now extra water needed to be added to recycle the carbamate;
2. no medium pressure recirculation section was needed anymore and
3. with the condensation of strip gasses in the high pressure carbamate condenser low pressure steam could be produced, which could be used in the downstream sections leading to a reduction of the steam consumption of a urea plant of about a factor two.

The figure below shows the flow scheme of the Stamicarbon AVANCORE® urea process, which is one of the most modern urea technologies nowadays and where still the HP CO_2 stripper plays a vital role.

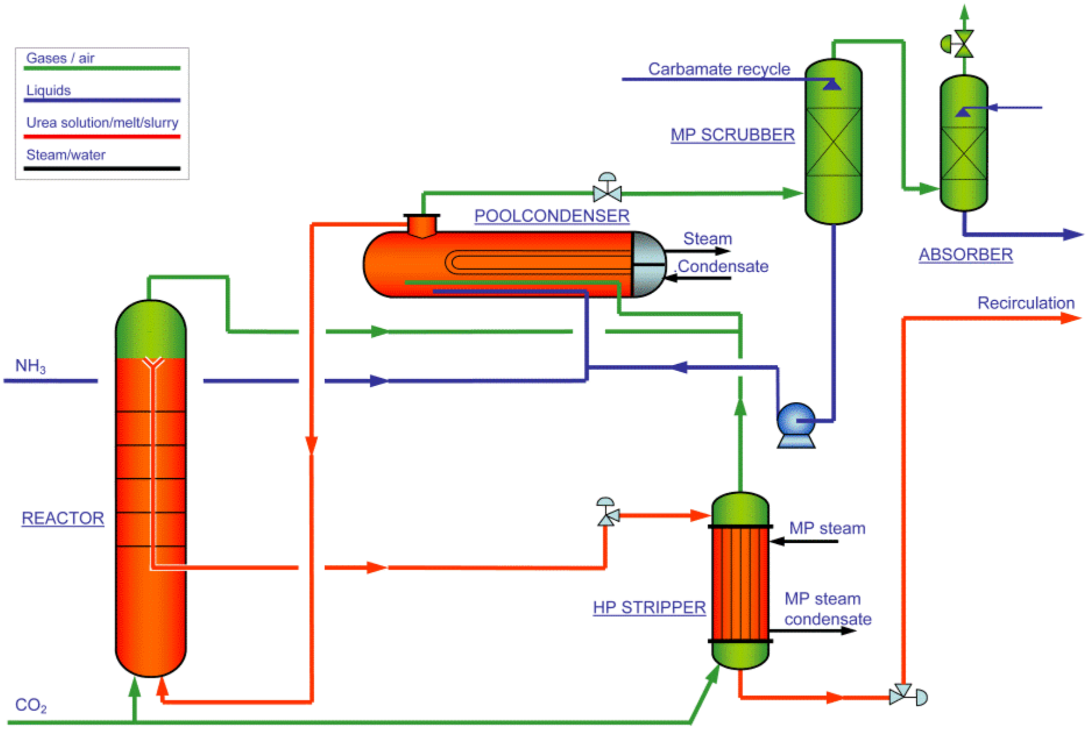


Figure 2: Stamicarbon AVANCORE® urea process

The process conditions in a HP stripper are quite severe when looking at corrosion sensitivity: high temperatures and low partial pressures of oxygen are the main causes for these severe conditions. Although the CO_2 contributes significantly to the stripper efficiency, still relatively high temperatures are needed to dissociate the carbamate. And as carbamate dissociates CO_2 and NH_3 gasses leave the urea solution leading to a relatively low partial pressure of oxygen in the gas phase. The presence of sufficient oxygen assures a passive lay of chromium oxides on the austenitic stainless steels, which limits the corrosion rates on these stainless steels to acceptable levels.
At that time it became obvious that the application of X2 CrNiMoN 25-22-2 austenitic stainless steel as the material of construction for the HP stripper heat exchanger tubes was a pre-condition to realize an acceptable corrosion rate and economical acceptable solution. This paper will elaborate how it has been possible to realize the world record on-stream production time of any HP stripper of 35 years.

3. Operational and maintenance experiences SKW Piesteritz HP CO_2 strippers

SKW operates three Stamicarbon CO_2 stripping urea plants with an original design capacity of 1050 mtpd each. Plant #1 started production in 1974 while Plant #2 and #3 started production in 1975.
The plants were constructed by Stamicarbon Licensed Contractor Chemoprojekt from Czech Republic.

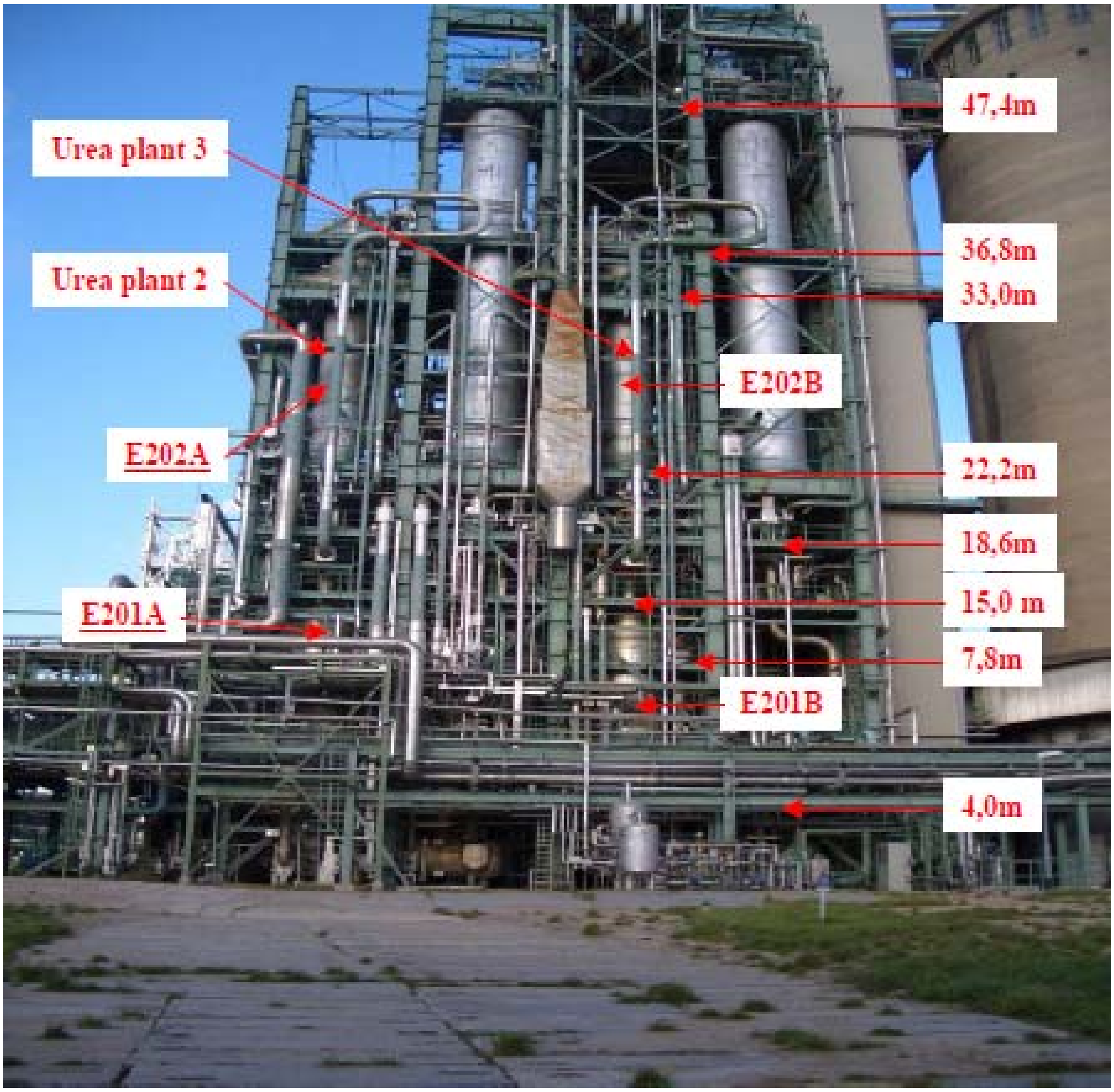
During its complete lifetime the urea plants have been operating on a continuous basis close or above its design capacities. In the past maintenance turnarounds have been performed every year, nowadays every two years. The name-plate capacity is 1.050 mtpd per plant. By installing Stamicarbon's Syphon Jet Pumps in the reactors and the Medium Pressure Add On technology in Plant

#1 ((Licensor: Stamicarbon, Engineering: Chemoprojekt) plus improvements by SKW engineers the capacity of all plants together could be increased upto 4000 mtpd.

Urea plant #1:
In Plant #1 the material of construction used for the heat exchanger tubes of the original HP stripper from 1974 was 316L Urea Grade, at that time in accordance with Stamicarbon specification 18005 Section 1 (now a daystype BC.01). In 1984 a new HP Stripper was installed in Plant #1 with X2 CrNiMoN 25-22-2 (A405) heat exchanger tubes from the VEW tube mill and also the the HP stripper was fabricated by VEW in -Kapfenberg in Austria. Over the years the average corrosion rate amounts up to some 0,06 mm a year. The HP stripper will be replaced in 2011 after 27 years on stream time.

Urea plant #2 and #3:
The HP Strippers in both plants #2 and #3 from 1975 were one of the first HP strippers in the world which used X2 CrNiMoN 25-22-2 (Stamicarbon specification BC.05) as the material of construction for the heat exchanger tubes. The fabricator of these HP strippers was Machinefabriek Breda in The Netherlands and for the heat exchanger Sandvik type 2RE69 tubes were applied.

The picture below shows Urea Plant #2 and #3; one can recognize that it is an identical double line urea plant.



Picture 1: SKW Urea Plant #2 and #3

One of the two strippers (E201B) has been replaced in August 2009, so after 34 years of operation. The second HP stripper (E201A) is still in operation at this moment and thus has a realized on-stream time of 35 years, which means a world record on-stream time of any HP stripper in a urea plant. This stripper is scheduled to be replaced mid 2011, so after 36 years of operation.

Together with this HP CO_2 stripper also the High Pressure Carbamate Condensers have been replaced. The whole replacement project has been carefully prepared and was executed successfully in only twenty two days. This was possible by making use of a temporary small steel structure in which the new HP stripper and new High Pressure Carbamate Condensers were temporarily parked. This created the opportunity to install the liquid distributors, leak detection system and insulation already before the turnaround.

All new high pressure equipment items used Safurex® as alloy protection were designed by Stamicarbon and were fabricated and supplied by Schoeller Bleckmann Nitec in Austria. Safurex® a material special developed for the urea industry has been developed in a close co-operation between Sandvik Materials Technology and Stamicarbon and has proven to be a very successful successor of 2RE69. Safurex® is stronger, has a higher corrosion resistance, also at low or even no oxygen levels and is not sensitive for chloride stress corrosion cracking.

Picture 2: Replacement project at SKW

But now let's go back to the world record HP strippers E201A and E201B of SKW Piesteritz, which used the Sandvik 2RE69 material for the heat exchanger tubes. These two HP strippers went into operation in 1975 and were fabricated in 1973.

Please find in the table below some construction details of these strippers.

Table 1: Construction details of the strippers

Manufacturer	Maschinenfabrik Breda (NL)
Year of fabrication	1973
Tube dimensions	32 x 3,5
Commissioning date	1975
Number of tubes	1.760
Tube length	7.000mm
Tube material	X2 CrNiMoN 25-22-2 (BC.05) of Sandvik, Sweden (2RE69)
Overlay welding material	X2CrNiMo17-13-2 (BC.01)
Liner material	X2CrNiMo17-13-2 (BC.01)

What means a world record on stream time of a HP stripper from process point of view ?
First of all the actual total plant capacity of 4000 mtpd should be secured. Based on this Stamicarbon has specified that max 10% of the tubes (=176) could be plugged, without a risk that the actual plant capacity could not be reached.
The already replaced HP stripper (E201B) had only 84 tubes plugged, while the other HP stripper has 80 tubes plugged. The minimum allowable tube wall thickness to ensure reliable operations was considered to be 1.55 mm taking into account the inaccuracy of the wall thickness measurements.

The first wall thickness measurements of the stripper tubes was performed by NDT-Specialists of SKW already in the 1980's. From mid 1990's Stamicarbon has been measuring the wall thickness every four years and from 2005 every two years. The average wall thickness reduction of both HP strippers has been 0,04 mm a year. The realized on-stream time of currently 35 years and at its replacement next year 36 years is an exceptional performance.

After thirty two on-stream years the Stamicarbon inspectors concluded that the weld overlay in the top cover of the both HP strippers showed severe corrosion and even to such an extent that restarting the plants with the overlay in such condition in these strippers was not advisable. As a consequence of that advice it was decided to cover the bad overlay with a loose liner. In only one week time, Schoeller Bleckmann–Nitec in Austria was able to install a new Safurex® liner in both strippers and to install a state in the art leak detection system. The specification came from Stamicarbon.

SKW did operate the urea plants at or above its design plant capacities and applied an oxygen supply as recommended by Stamicarbon (in the past 0,8 vol% and since 1990's 0,6 vol%).

During the first years after start up there were problems with (oil) fouling of the liquid holes in the liquid divider tubes of the HP strippers. SKW has modified the liquid distribution system by adding a special liquid distribution system above the hold down plate. The principles of this modification were developed by Stamicarbon. This modification was executed by Schoeller Bleckmann Nitec in 1980 and after that all problems were solved.

Early 21th century, after about 26 years on-stream time, the stripper efficiency of both strippers reduced as a result of scaling (oxides layer) build up in the heat exchanger tubes. Based on Stamicarbon's specifications, SKW has chemically cleaned all strippers.

4. Sandvik 2RE69 and quality control

The Sandvik 2RE69 was developed in the early 1970s and this material meant a revolution to the urea industry as this material was considerable better than the 316L Urea Grade. The Sandvik 2RE69 was not only stronger but also had better corrosion resistance properties and was able to withstand the harsh conditions in a HP stripper.
It is even more amazing to realize that such a young new material could realize a world record on stream time.
In the late 60s when the search for better material than 316 Urea Grade (BC.01) started, the situation was quite different from today with respect to the alloys available and the possibility to reduce the carbon content in the high alloy steels. There were not so many higher alloyed materials to choose from. Tests with the fully ferritic material with about 26% Cr had showed that higher chromium content could improve the corrosion resistance compared with 316L. The problematic welding properties of ferritic grades made it impossible to use the material in welded constructions in the urea process, in which a large number of welds are required to protect the carbon steel pressure bearing part from carbamate corrosion.

Compared with 316L Urea Grade the new Sandvik 2RE69 had a substantial increase in chromium content from 17 to 25%. The higher Cr content helps the material to form a dense and more stable passive chromium oxide layer. Since the ferrite content had to be low in the material to ensure good corrosion resistance the nickel content had also to be increased. That created another problem since the risk for hot cracking increased in the welded parts and more particularly in overlay welds. This problem was solved by increasing the manganese content in the welding consumables. Sandvik also strongly believes that low levels of carbon, sulphur and phosphorous are required to obtain the best possible corrosion resistance. On the other hand one should also understand that a higher chromium content increases the risk for formation of inter-metallic phases during heat treatment and welding. That must also be taken in account when redeveloping procedures for manufacturing and welding.

The tubes need to be clean from oil and other foreign particles prior to heat treatment as that can also result in reduced corrosion resistance. The large number of orders supplied over the years has definitely help to fine tune the manufacturing route. Each manufacturing lot must pass the corrosion test according Stamicarbon specification 53961 (based on ASTM A 262 Practice A, Huey test)..

The stripper tubes are heated with steam, which means the tube material will be exposed for the highest temperature in the process and thus the highest corrosion risk but, for a long service life not only high quality tubing is needed but also great care in fabrication of the equipment and operation of the plant. The outstanding service life of the tubes in the HP stripper at SKW and many other urea plants around the world proves the Sandvik 2RE69 concept has been outstanding.

5. Conclusions

SKW Piesteritz has realized an on-stream time for a HP CO_2 stripper of 35 years and likely 36 years when the stripper will be replaced next year, which is an exceptional achievement and means a world record on-stream time of a HP stripper. One other HP CO_2 strippers of SKW Piesteritz realized an on-stream time of 34 years.

<u>How it has been possible to realize such an exceptional achievement ?</u>

- ✓ Excellent process, equipment and material specifications by the licensor
- ✓ Adopting high quality standards during fabrication
- ✓ Installing properly the HP strippers to assure an equal liquid film inside the tubes
- ✓ Using high quality base materials for the tubes (Sandvik 2RE69)
- ✓ Respecting the details of the operating and maintenance instructions of the licensor
- ✓ Checking the diameters (pressure drop) of the liquid holes of the liquid divider tubes
- ✓ Doing a leak test after the installation of the liquid divider tubes
- ✓ Controlling the steam pressures and temperatures
- ✓ Controlling the required oxygen content in the CO_2 feed
- ✓ Controlling the steam quality
- ✓ Doing regular inspections by SKW and Stamicarbon experts, especially wall thickness measurements of the tubes anticipating the operating period until then next turnaround to avoid a tube rupture
- ✓ Doing repairs by reputable companies with qualified personnel
- ✓ Installing a modern process control system and training the personnel

Mark Brouwer was born on July 6, 1966 in Groningen, The Netherlands. He graduated in 1988 at the Technical University of Eindhoven at the faculty of Chemical Engineering. His thesis was about the production of ethylene by partial oxidation of natural gas.
After University Mark joined Military Services, Dutch Royal Navy where he was working at the Prins Maurits Laboratory of TNO in Rijswijk. In this period he was involved in Process simulation studies on the absorption of poisonous gasses on active carbon.

In 1990 he joined DSM, working for the Ethylene Plant No.4 as a Process Engineer. In these seven years he was involved in the Basic Engineering of a debottlenecking project of the ethylene plant at Stone & Webster in London and in the implementation of the first of its kind styrene extraction process (from conceptual engineering up to the successful start up).

Early 1997 he joined Stamicarbon as Licensing Manager Urea Revamps active in several countries like China, Russia, Iran, India and the Arab countries. Later he became Manager Stamicarbon Services responsible for all Stamicarbon's activities in existing urea plants, such as After Sales Services, Plant Inspections, Debottlenecking Projects, Reselling projects etc. In these nearly twelve years he did visit more than one hundred urea plants worldwide and was involved in numerous revamp, relocation, debottlenecking and grass root projects.

Since January 1, 2009, Mark Brouwer left Stamicarbon and started up UreaKnowHow.com.
UreaKnowHow.com is an independent group of urea specialists with an impressive number of years experience in designing, maintaining and operating urea plants. UreaKnowHow.com's mission is to support, facilitate and promote the exchange of technical information in the urea industry with the target to improve the performance and safety of urea plants.

Please feel welcome at UreaKnowHow.com, the website where the urea industry meets.

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