

Environmental Technology

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News

Jan Klok wins the public vote of the Prins Friso engineering award



With his innovative reactor design to remove hydrogen sulfide from natural gas, ETE researcher Jan Klok won the public vote of the Prins Friso engineering prize last March. The Prins Friso prize is yearly awarded by the Royal Institute of engineers (KIVI) to the 'engineer of the year' who's research has demonstrated expertise, innovation, impact on society and entrepreneurship. Besides this jury award, the public's favorite engineer is awarded by votes from the general public.

Cost reduction

Natural gas contains the highly toxic hydrogen sulfide (H_2S), and this has to be removed. 'The removal of this huge waste stream of H_2S accounts for about half of the total costs of the oil and gas industry', Klok states. Already in the early 1990's, ETE professor Cees Buisman developed the 'Thiopaq', a reactor where bacteria convert H_2S present in gas into pure sulfur. The efficiency is high: about 90 percent. The Thiopaq resulted in a substantial cost reduction, mainly due to a reduced need for chemicals. Based on a theoretical approach and experimental data obtained by himself and his predecessors of ETE, Klok predicted that by enhancing conditions for the sulfur-producing bacteria, the conversion efficiency of H_2S could be increased to over 98 percent! His idea is now being tested and optimized in a new pilot reactor by the company Paqell and ETE.

Column

Guest writer Joost Timmerman, Managing Director Paqell

Almost 50 years ago Gatze Lettinga invented a technology to purify wastewater by using bacteria. Just over 40 years ago, a PhD student of Prof. dr. Lettinga, Cees Buisman, started his research on purifying biogas with bacteria using a revolutionary technology. Exactly 25 years ago, this resulted in the first Thiopaq plant. It was taken into operation at Industriewater Eerbeek to remove hydrogen sulphide (H_2S) from biogas.

Twenty years ago, Paques started a partnership with Shell because natural gas often contains H_2S . This cooperation resulted in the formation of the joint venture Paqell seven years ago. Under the leadership of Paqell's R&D manager and Engineer of the Year 2018 Jan Klok, the Paqell engineers have made great progress in improving the desulfurization technology in recent years. This is done in close cooperation with the Department of ETE.

In the ETE lab Annemerel Mol studies the behavior of sulfur particles, while Rieks de Rink uses a large Thiopaq pilot installation for the research of H_2S removal from natural gas. The cooperation with ETE is of great added value for Paqell. Well done ETE!

New X-ray diffractometer to support a wide variety of scientific fields

A valuable and costly new addition to ETE's analytical laboratory is the X-ray diffractometer (XRD). The XRD was purchased by the Shared Research Facilities Group, initiated by Environmental Technology (ETE), Biobased Chemistry and Technology (BCT) and Biobased Products (BBP).



Important tool

Many materials form crystals, for example salts, minerals, metals, but also biological substances like proteins, nucleic acids and lipids. Therefore, X-ray diffraction is an important tool for many scientific fields. The precision machine can be used to determine the structure of a crystal by using X-rays. 'The machine sends a beam of X-rays under a continuously changing angle to a sample', technician Ilse Gerrits explains. 'The beam is subsequently reflected from the sample's surface in different directions'. All these reflected beams are detected by the machine and translated into a peak diffraction pattern. Since this pattern is unique for each crystalline substance, it can thus be used for identification. For example, ETE's research on sulphur formation from hydrogen sulphide in natural gas uses the XRD to confirm the composition of the produced sulphur particles (fig.1). But the machine may also reveal the atomic structure of new materials, follow the exact process of crystal formation over time and at different temperatures.

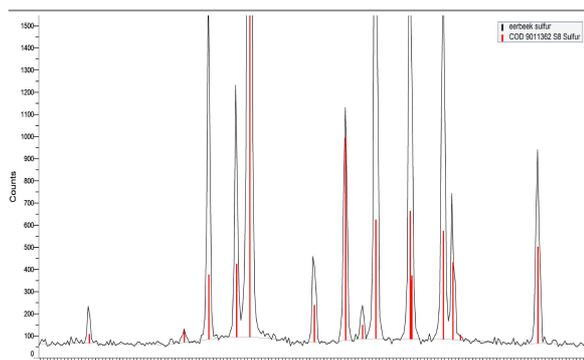


Fig. 1. Peak diffraction pattern of sulfur

The XRD has applications for many research fields. Not only ETE, BCT and BBP are using the new machine. 'Also other departments and interested companies may rent the machine to carry out their analyses', Gerrits says.

Analyzing particle size distribution using laser diffraction



Using a small pipet and a steady hand, ETE scientist Annemerel Mol puts a droplet of a whitish sulfur suspension in a liquid-filled Quartz cuvette. In slow motion, the sample fans out in a fantastic cloudy swirl; science can be amazingly beautiful. After mixing with a small metal device, Mol places the cuvette in her brand-new *laser diffraction particle size analyzer*. Within a minute, the particle size distribution of the sulfur suspension is analyzed and shown on the computer screen (fig.2).

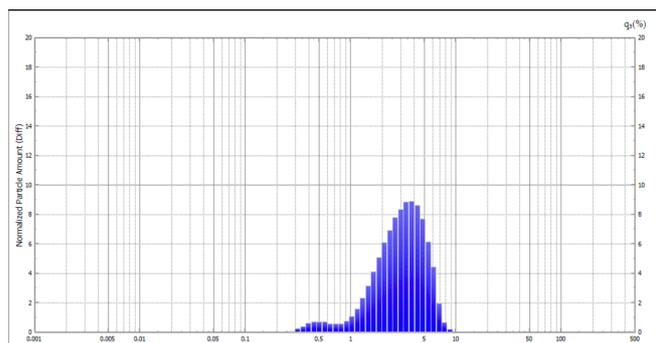


Fig. 2. Particle size distribution of a sulphur suspension

Mol: 'As the bar diagram shows, this sample contains sulfur particles ranging from 0,02 to 10 micrometers in size. Particles between two and six micrometers take up the biggest volume.'

Irreplaceable

The new machine is an irreplaceable tool for Mol. Her research is closely linked to the Thiopaq O&G Ultra, where bacteria convert hydrogen sulfide (H₂S), present in natural gas, into pure sulfur particles. 'The industry wants these particles to be as large as possible, so they can be harvested more easily', she says. 'My research focuses on the conditions that may increase the size of these sulfur particles.' Some of these factors may be linked to reactor conditions, like the ratio H₂S – oxygen. But also, the composition of the bacterial population may influence sulfur particle size.

The particle analyzer gives Mol reliable and hard data on the sulfur particle size in different samples from the Thiopaq O&G Ultra. Mol: 'I'm extremely happy with this machine, I couldn't do my research without it!'

Book published by Cees Buisman

In January 2018, ETE professor Cees Buisman published his book 'De mens is geen plaag' (Man is not a plague). In the book, Buisman analyses some of the most serious problems of the world, like CO₂ emissions, overpopulation and shortage of resources. He argues that the lack of fresh water is one of the biggest issues. Science and technology simply can't solve this problem.

Despite potential fresh water shortage, he claims overpopulation is not the problem: according to Buisman the earth may provide for 10 billion people. But only if there will be a mentality change: the western world must be willing to share resources and work with nature and not against it. He argues that humanity needs to reach a higher level of 'consciousness' instead of immorality and luxury which are our present objectives. This eventually would lead to a better society and a higher sustainable welfare for everybody.

From September 15th 2018 the English translation is available.



Cees Buisman
De mens is geen plaag
Over het gevaar van een onttoverde wereld

Science: Sustainable water use by smart modelling

ETE scientist Joeri Willet is developing a model to better match water supply and demand of the industry. Within two years, he aims to have built a model that is capable of matching water supply and demand by finding alternative local water sources. In addition, the model calculates how to utilize supply sources in a sustainable way. Willet: 'We want to enable water users to match their water consumption with the availability in the local environment, as well as with the water availability at any particular moment.'

Climate warming is expected to change future water supply, while alterations in society will change demand. Increased population size as well as intrusion of salt water due to sea level rise, make water supply for consumers and industry more uncertain and unpredictable. 'Smart use of available water sources and finding alternative sources are essential to prevent



future problems related to water availability', says Willet. With more water users and an increased overall water consumption, it will be necessary to better match water supply and demand. Sustainable use of available water sources, with minimal impact on

ecosystems, is an important criterion.' The size of reservoirs of available water depends on a variety of factors and is best illustrated in the water cycle (fig. 3). It describes how water moves between the different reservoirs like lakes, rivers, ground water, salt water (oceans, salty groundwater) and atmospheric water (clouds). Depending on local climatic conditions, water moves between different reservoirs due to precipitation, surface runoff (rivers and streams), evaporation from oceans, transpiration by plants, and condensation. Use of these available water sources needs to be smart, efficient and sustainable in the near future.

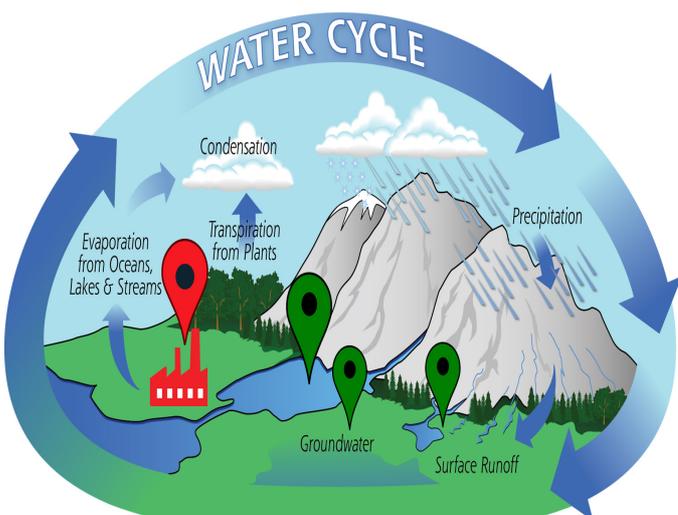


Fig. 3. The water cycle.

Potential mismatches

By modelling water use of chemical company DowDuPont in Terneuzen, Willet aims to get a better understanding of potential mismatches between water use and water availability. At the moment, DowDuPont extracts part of their water from National Park De Biesbosch, while they also utilize and recycle water from the wastewater treatment plant in Terneuzen. The aim of the model is to reduce the company's dependency on Biesbosch water, and suggest alternative water sources for water extraction that are more sustainable. 'The problem for companies like DowDuPont is that it is hard to predict if their water demand matches with the current and future supply', Willet explains. 'If supply appears to be insufficient, the company has several options: transport water from far away, desalinate salt water, or include an extra cleaning step for their cooling water, so it can be recycled. But these options all result in increased costs.' Therefore, a model to better balance the

regional water availability, by taking into account the local renewable availability of water, is essential to ensure continued operation with minimal environmental impact.

Local ecosystems

Based on the locations and sizes of regional water sources (ground as well as surface water), precipitation, evaporation, and the maximum water amount that can be extracted without impacting local ecosystems, the model calculates how water demand can be matched in the most efficient way. In addition, costs to transport water from source to user are included. This may result in a complicated maze of possibilities to acquire water from different sources, resulting in different costs (fig. 4).

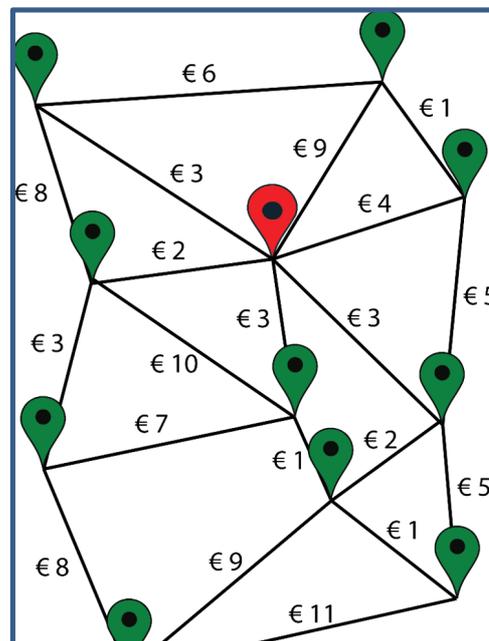


Fig. 4. Schematic overview of possible costs of water transport from source (green balloons) to user (red balloon).

Based in these factors, the model calculates where water may be sustainably extracted with a maximum efficiency, i.e. minimal costs, while maximizing logistical efficiency and sustainability.

Willet: 'Within two years the model should be able to help companies to find the best and most sustainable water sources for their water supply by smart use of all possible local water sources.'

Spin-off: Highly efficient sulfur removal from natural gas

In the early 1990-ies, ETE professor Cees Buisman developed the Thiopaq, an efficient method to remove H₂S from gas streams using bacteria. The company Paqell, a joint venture of Paques and Shell, adapted the system to de-sulfurize natural gas at industrial scale. Recently, ETE scientist Jan Klok suggested to add a second bioreactor to the traditional system to improve its efficiency. Operation of a pilot-plant to test the process at ETE showed over 99% efficiency. Ph.D. researcher Rieks de Rink further optimizes the process and reactor design.

While balancing on a ladder about 3 meters above the floor, ETE guest scientist Rieks de Rink takes a white-greyish liquid sample from a four meters high, complex looking device.



Hoses connected to large glass containers, bright stainless steel screws and an impressive looking control panel make up a newly designed bioreactor system for de-sulfurizing natural gas: the Thiopaq O&G Ultra. Inside the pilot reactor, billions of microorganisms convert the toxic hydrogen sulphide (H₂S), present in natural gas, into pure sulfur. After the sample has been stored, de Rink adjusts some screws and bolts to fine tune the reactor. 'We will analyze the amount of dissolved H₂S in the sample. This will tell us how much of this chemical is taken up by the bacteria', de Rink explains. 'With the information we know if this first step of the de-sulfurization process is working correctly.' The second step of the gas purification, the formation of pure sulfur, takes place in a lower placed reaction vessel. Also from this vessel De Rink takes some liquid: 'Samples from this aerobic bioreactor gives us information about the process efficiency of sulfur formation, the final step in the process.'

Giant leap

H₂S is a toxic, corrosive gas present in biogas as well as natural gas. It causes acid rain and smog. Usually, these gas streams are purified using chemical processes. These methods use a number of chemicals, that are harmful for the environment. For example, to purify small amounts of biogas, sodium hydroxide (NaOH) is used. The H₂S present dissolves in the alkaline NaOH solution, and is subsequently converted into sodium phosphate. This salt contaminates the environment: it causes eutrophication as well as salinization. In addition, this method is expensive due to use of chemicals. In 1993, ETE Professor Cees Buisman developed a more environmentally friendly biotechnological method to remove H₂S from biogas streams produced during wastewater treatment: the Thiopaq. Together with ETE Professor Albert Janssen, the invention was successfully put in the market. It was a giant leap towards sustainable and



Sulfur formation in the second reactor vessel of the Thiopaq O&G Ultra pilot plant at ETE.

cost-effective gas desulfurization. Instead of chemicals, bacteria were the main players to remove H₂S. De Rink: 'In one single step, the original Thiopaq converts more than 90 percent of H₂S into pure sulfur.

Completely new process

The performance and efficiency of the Thiopaq was impressive. But based on a recent critical evaluation of this revolutionary system, ETE scientist Jan Klok, currently employed at Paqell, hypothesized that the performance could be improved. According to him, the sulfur-forming bacteria had to compete with bacteria

of another type: the sulfuric acid (H_2SO_4)-forming bacteria. This competition, eventually reduced sulfur production, due to H_2SO_4 formation. In addition, the H_2SO_4 formed needed to be balanced using NaOH to prevent acidification of the process. To minimize the use of chemicals and improve the sulfur production efficiency of the Thiopaq, these bacteria should be suppressed, so the sulfur-forming bacteria would get an advantage. Based on this theory, the scientists added an extra reactor to the process.



Bottom part of the Thiopaq O&G Ultra pilot plant. Sulfur formation, the final step, occurs in the glass reactor vessel on the right-hand side.

De Rink explains: 'Based on the suggestions of Klok, the whole process was optimized by adding an extra step to the original Thiopaq design. In this process, the H_2SO_4 -forming bacteria were inhibited in a separate reaction vessel.' To achieve this, the scientist focused on blocking the bacteria's enzyme systems, responsible for synthesizing H_2SO_4 , by creating anaerobic conditions and subsequently adding elevated levels of H_2S . This compound binds to the enzymes, and effectively blocks their activity, knocking out the H_2SO_4 synthesis. In a second reaction vessel, with oxygen, the sulfur-forming bacteria now have less competition from the H_2SO_4 -forming bacteria, resulting in a higher conversion of H_2S into sulfur and a lower yield of H_2SO_4 . The new process also reduces chemical consumption by about 80-90%, which makes the process more sustainable and attractive for use in the oil and gas industry.

Self-regulative system

The first test results were spectacular. Sulfur production increased from about 90 percent in the original Thiopaq, to over 99 percent in the upgraded Thiopaq O&G Ultra. After filing a patent to protect the new design, de Rink is now optimizing the process even further and aims for a fully self-regulative system: 'Due to a lot of experience, I am pretty confident in running the system at a high efficiency', de Rink says. 'The challenge is to improve the design



The Thiopaq O&G Ultra pilot plant at ETE's laboratory. The upper part is the newly added extra step of the bioreactor. Here, the H_2SO_4 -forming bacteria are inhibited. It improves the overall reactor efficiency to over 99 percent.

in such a way that also other operators can maximize the sulfur production.' To achieve this, de Rink wants to include automatic measurements of hard-core parameters, such as bacterial activity, H_2S concentrations, and sulfur production. Based on the results, the future system should respond automatically by adjusting parameters like nutrient concentrations and gas flow. Then, the Thiopaq O&G Ultra will be a fully self-operational gas cleaning system.



Agenda

PhD defences (Aula, Wageningen):

Jouke Dykstra June 15th 2018 16.00 h. 'Studies on Capacitive Deionization.'

Abiodun Jegede October 15th 2018 11.00 h. 'Optimization of domestic biogas plant.'

Yvonne Mos October 19th 2018 13.30h. 'Biocrystallisation of Magnetite from groundwater.'

Indra Firmansyah October 22nd 2018 11.00 h. 'Development of a planning approach for resource recovery and reuse on small islands.'

Sam Molenaar November 7th 2018 13:30h. 'Microbial rechargeable battery: energy storage through acetate.'

Mark Roghair November 16th 2018 16.00h. 'Control strategies for ethanol-based chain elongation processes.'

Jorge Ricardo Cunha November 30th 2018 **in Leeuwarden**. 'Recovery of calcium phosphate granules form anaerobic treatment of black water.'

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