# CHEMERAL TECHNOLOGY

PROVISIONAL PATENT APPLICATION

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## The Periodic Table and the Big Bang theory

by Carl Schonborn, PrEng

Nuclear physicists focus on the structure of the elements and their position in the Periodic Table (PT) which allows for the harnessing of the immense power that the nuclei are able to produce.

The Periodic Table of the elements is just that: a table in which are arranged the elements in order of increasing number of protons in the nucleus of an atom or 'atomic number'. It was not until 1860 when an accurate list of the atomic mass of the elements became available, listing, like the modern periodic table, all the elements in order of increasing atomic number.

The symbol Z is the atomic number of the element, the atom consisting of a positively charged atomic nucleus, with protons and neutrons and a negatively charged atomic shell containing electrons. The number of electrons equals the number of protons which makes the atom neutral.

For example, the first element in the PT is hydrogen, H, where the atomic nucleus consists of one proton. Every element can also have isotopes which have the same number of protons but a different number of neutrons. Isotopes of an element do not differ in chemical properties. Hydrogen has three naturally occurring isotopes and a few more heavier unstable isotopes with half-lives measured in zeptoseconds.

The stable isotopes are proteum, deuterium and tritium. As there is an imbalance in the number of protons and neutrons, the atom is an unstable isotope and starts to decay. The particles emitted from this decay are radioactive and charged. Three types of radiation are emitted: Alpha, Beta and Gamma. A Geiger counter is used to measure the radiation, which in turn is the rate of decay. Paper or your skin can protect you from Alpha radiation, a wooden plank can protect you from Beta radiation, and a wall of lead is required for Gamma radiation protection.

But how did all these elements actually present themselves in various numbers and locations in our galaxy? The excellent book by RJP Williams and JJR Frausto da Silva, "The natural selection of the chemical elements", details the development of timed natural selection of elements from just after the Big Bang when a state of energy/matter that was homogeneous and at equilibrium began to expand and cool with time.

These processes involved immense changing pressures and temperatures and if measured in our current sense of time took no more than 10<sup>.41</sup> seconds. The beginnings of the formation of light elements H and He and their isotopes were also very rapid and possibly the reactions were so fast that these light nuclei formed in equilibrium with radiation and the base neutrons and protons well within one minute so that the universe remained homogeneous.

Some 105 to 106 years later the decoupling of matter and radiation (photons) broke up this homogeneity, and galaxies, nebulae and stars formed. Since that time local kinetic limitations have governed the formation and evolution of even small nuclei in the universe, for example, C, N and O. The reactions took place (and are taking place) in isolated giant stars as they formed (and form) due to further fluctuations in the initial gas.

In turn the explosion of these stars and further cooling allowed formation of larger nuclei and then in turn elements, gaseous compounds and finally co-operative condensed systems including the Earth and likewise the planets. The cooling temperatures allowed for the natural selection of the elements within chemistry and the only chemical changes of real sophistication occurred in the temperature range of 3 000 to 200 K where nuclear transformations no longer occur.

The Periodic Table, one of mankind's simplest tables, contains a wealth of information used by scientists in almost all disciplines. With nuclear energy looming large in South Africa, it is essential that our engineers and technologists understand nuclear technology, particularly that of the specific nuclear energy reactors South Africa is in the process of procuring.

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## Are South African patents going to be stronger in the future?

by Claudia Berndt, BEng, LLB, Patent Attorney, Hahn & Hahn, Pretoria, South Africa

The South African Patent Office recently announced, however, that it has plans to commence, in about two years' time, substantive examination of patent applications.



A sanyone who has filed a patent application in South Africa will know, the South African patent office does not examine patent applications for patentability of the invention. If all formalities are complied with, a patent will then be issued on every patent application. In terms of the Patents Act, it is the duty of the patentee to ensure that his or her patent is valid by taking all known prior art into account, but there is no check on this by the patent office.

The South African Patent Office recently announced, however, that it has plans to commence, in about two years' time, substantive examination of patent applications. Examiners are currently being trained and, if all goes according to plan, selective examination of South African complete patent applications will commence in or before mid-2017. The term 'selective' is used because patent examiners are highly qualified individuals with technical knowledge of the subject matter relating to the patent application.

#### How does the process work presently?

At the moment, the South African Patent Office only carries out a check on applications to confirm whether they comply with all the formal filing requirements, eg, have the correct fees been paid and all application forms submitted; have an Assignment of Invention (if applicable) and a Declaration and Power of Attorney been submitted, and so on.

Once all formal filing requirements have been complied with (and sometimes even if they have not), the application is accepted and advertised, on which date the patent is deemed to have been granted. As a result, many South African patents will have been granted which are not valid in terms of the criteria of novelty and inventive step prescribed by our Patents Act.

This so-called 'deposit system' has worked well in South Africa, having kept the Patent Office's official fees low. The validity of patents is only decided upon when it really matters, namely, in court, during either patent infringement or revocation proceedings, which typically go hand-in-hand.

Section 34 of our present Patents Act prescribes that the Registrar examines (in the prescribed manner) every application for a patent and every complete specification accompanying it (or lodged at the patent office in pursuance of such application) and, if it complies with the requirements of this Act, the Registrar will accept it.

In practice this 'examination' relates to only the formal requirements and, mainly due to a lack of qualified examiners to do so, the Registrar will not consider the sections of the Act dealing with the substantive validity of patents, eg, lack of novelty or lack of inventive step.

## What does substantive examination entail?

Substantive examination looks into the patentability of the subject matter described in the claims of a patent. Three core criteria need to be fulfilled in order for an invention to be patentable in terms of our law: novelty; inventive step/ obviousness; and industrial applicability.

The subject matter of a patent is 'novel' if it has not been part of the 'state of the art' prior to the date of that invention, ie, the invention may not have been disclosed to the public in written, printed, physical, or any other form anywhere in



the world before the first patent application disclosing the invention was filed.

In practice, this means that any single document which discloses the subject matter of one claim of the patent being examined is a bar to the patentability of the whole of the claimed invention.

The subject matter of a patent is deemed to involve an inventive step if it is not obvious to a person skilled in the art, regarding any matter which forms, immediately before the priority date of the invention, part of the 'state of the art'.

In practice, this allows an Examiner to cite several documents together against a patent application if he or she thinks that, (vis-à-vis the disclosure contained in all of these documents), a person with extensive knowledge of the said invention, would find the invention obvious. It is obvious then that an Examiner would have to be such a person! Typically, Examiners will cite existing patents or patent applications as well as articles from scientific journals against a patent application.

Based on the conducted search and a critical examination of the documents found, the Examiner will issue an examination report which details how the documents affect the patentability of the invention or patent application under examination.

In addition, there are certain inventions which are not patentable in terms of the South African Act, regardless of whether or not they are new and inventive. The applicant for a patent of any of the following types, must be informed accordingly: a discovery; a scientific theory; a mathematical method; a literary, dramatic, musical or artistic work or any other aesthetic creation; a scheme, rule or method for performing a mental act, playing a game or doing business; a program for a computer; or the presentation of information.

The applicant will have a chance to respond to the Examiner's report. Arguments in support of the patentability of an invention are also generally submitted in response to an examination report. A second report will then be issued informing the applicant whether his or her response has overcome the Examiner's objections. What happens after this, if the Examiner decides not to allow the application to proceed to grant, differs from country to country.

#### **Potential drawbacks**

The forthcoming changes in the local Act mean that the official fees payable to the South African Patent Office when filing a patent application will have to be dramatically increased. In addition, a patent attorney will need to be consulted to prepare a response to an examination report, adding further costs to those related to the filing of the application.

Substantive examination will prolong by a significant period, the time it takes for a South African patent application to proceed to grant, substantive examination naturally taking longer than merely a formal examination. Additionally, South African courts currently have no judges specifically trained to hear patent matters. Perhaps training an expert panel of judges to adjudicate upon patent matters would have been a more sensible way of testing the validity of South African patents.

If you need advice on patents, then think of us first, Hahn & Hahn, Hahn@hahn.co.za.

## Electric cars will save the planet **but destroy the grid**

by Gavin Chait

Sometime in the next few months we'll cross one of those made-up milestones: 1 million electric cars will be on roads around the world.

his is early-days for electric cars and they're still waiting on their mobile phone moment: when they stop being a glamourous luxury for the wealthy, and become something you see attached to every teenager (old enough to drive).

Elon Musk's Tesla is building major new battery production capacity in the US, and Porsche is looking to do the same in Europe. China is accelerating and producing the majority of battery capacity. As these new plants come online, coupled with lower-cost vehicle designs, we'll hit the starting blocks. Somewhere in the next ten years we can expect to see a critical velocity of electrics on our roads.

And we're not ready.

There are about 8,7 million vehicles on our roads, consuming about 11,2 billion litres of petrol and 11,9 billion litres of diesel annually.

My go-to for looking up energy consumption and production data is "Sustainable energy - without the hot air" by the inestimable David MacKay. He doesn't disappoint. He estimates that the average liquid-fuelled vehicle, travelling 50 km per day, is equivalent to about 40 kW of power.

If, at some point in the future, our entire rolling-stock is replaced by electric vehicles, charging them will require about 350 gigawatts of power.

By way of comparison, the current South African grid is only 43 gigawatts. And that includes the additional 2 % (795 MWe) that Medupi brings to the table.

Sure, a great deal of production goes to waste overnight, but not sufficient to power that fleet. Neither will everyone charge their cars from midnight. Many will want to recharge at the office (especially if they have hellish commutes) and many will simply plug in as soon as they get home.

We can do some estimates to figure out how many cars our grid could absorb. Being generous, perhaps we have



10 % capacity overnight. That's about 100 000 cars, or only 1 % of the current fleet.

Now think of how long it took (started in 2007 and, seven years later, still not complete), and how much it cost (a still-rising R154 billion), to add Medupi's 2 % (at some point, rising to 10 %) to the grid.

I figure we probably have about a decade till there are 100 000 electric cars on our roads. Even considering these issues will cause a certain amount of anxiety, we must persevere. We must take a long, hard look at the full extent of the risk facing the South African electricity grid. For that is only one of the problems.

Porsche's research and development chief, Wolfgang Hatz, is hoping that their approach to vehicle charging will become the de facto standard for electric vehicles. Their TurboCharging system can recharge their Mission E electric sports car to 80 % in 15 minutes. They're looking at charging stations delivering 800 V, twice the current standard, and capable of reassuring drivers that, even if they forget to charge, they can be on the road in minutes.

Making those chargers available across the EU would cost an estimated €100 to €200 million. "For Porsche this is big," he says, speaking in the UK 'Telegraph', "but if we [car makers] got together, it would be easy and maybe over the next 10 to 15 years it could be done. The business model is there."

Tesla, similarly, has a fast charging station that delivers 120 kW of power, offering 20 minutes to 50 % charge. This sounds wonderful if you're one of those people who would buy an electric car (if they were price-competitive with other high-end sedans) but are worried about range limits. Think, however, of what would happen to the grid if – come five o'clock and everyone heads home – 100 000 cars are plugged into their superchargers at 6 pm.



GENEVA - The Renault Zoe Fully electric concept car on display at the 81<sup>st</sup> International Motor Show Palexpo-Geneva on March 8, 2011 in Geneva, Switzerland.

The Tesla Model X is a singularly beautiful motorcar. Introduced in 2012, it only reached its first customers in October 2015. Even so, 30 000 people have preordered their cars. Compare that to the 75 000 of the Model S sold worldwide. The S has been 'Car of the year' just about everywhere with an accumulated 1 billion electric miles having been travelled in June 2015. Nissan Leaf and GM Volt vehicles are only slightly behind that.

They're beautiful cars. They're fun to drive. They're torquey and exciting. And a planning nightmare.

Right now it's only a small number of wealthy people who can afford them, but Elon Musk intends to chase costs down and pursue the mainstream. The Model 3 will have a starting price of US\$30 000 (by the time you read this, just north of R20 million) and Tesla needs to sell 500 000 of them a year to reach breakeven.

I stress: they're beautiful cars. They'll be more sophisticated than petrol cars and more fun to drive. Carmakers from Toyota to BMW are paying attention. They're all working on their own versions. Importantly, governments want them too. They want zero emissions cars. Europe and the US are in the lead here and where they go, the rest of us have no choice but to follow.

For here is the last thing that concerns South Africa. Of the 500 000 or so vehicles manufactured every year, over 340 000 are exported. The huge subsidies and tax benefits manufacturers receive is predicated on those exports. Factories are designed around the requirements of those export markets. And those export markets are European. As Europeans begin to buy more electric cars, South Africa's factories will either need to be upgraded, or they will be closed down. The local market is too small to support the existing capacity.

This leads to the similar quandary which has faced our

liquid fuels refining industry. As European rules required lower vehicle sulphur emissions, and our manufacturers upgraded their processes to meet those rules, an upgrade to our existing refineries was required. Then the government announced they were building a new refinery – at the EU standard – equivalent to the entire refining capacity of the country.

The rest of Africa, though, still drives mostly elderly vehicles. So our refiners took the decision to keep going with their existing systems and sell their extra into the rest of the continent. That decision may still be possible for our vehicle manufacturers when the time comes to decide on upgrading. However, we then lose our access to western markets.

At least, however, that would reduce the pressure for South Africans to adopt electric cars faster than the grid can accommodate them. That's not really a high note.

South Africa is certainly not alone in having to deal with a dramatic change as we move from driving around our own liquid-fuels-to-energy generators, to driving around vehicles that simply store energy manufactured elsewhere.

The thing is, petrol and diesel really are astonishingly energy-dense. Every country is going to have to cope with adding in about ten times their existing capacity as we replace it. In places like China, this will be unremarkable. But European nations hate new power stations even though they have the functional capacity to pay for them.

South Africa, along with other nations, stands on the brink of a precipice to which we seem blind.

It's all well and good to demand zero emissions and electric cars. But we also need to build the capacity to keep those vehicles going.

Now is the time to start planning.

## How an engineering firm **buys a valve**

by Ron Merrick, Fluor Daniel, USA and Susumu Mizuguchi, JGC, Japan

Engineering contractors need a lot of things from manufacturers, and they need to feel confident that they really get what they ask for. The specific data, knowledge and confidence in the manufacturer that are important at each stage are discussed in this article.



When a new process or power plant is built today, chances are an engineering contractor is involved. Early construction projects, such as the Great Wall or the Grand Canal, were built with labour that was essentially conscripted just the same way an army was raised. Eventually, with the evolution of political systems and the market economy, it was no longer possible to simply order something to be done. Now, even if you were a king, you had to pay for it. That led to the rise of contractors, as well as financiers and the banking system. But the role of engineering contractors, which began with the serious development of engineering as a discipline during the nineteenth century, greatly influences the course of construction and the success or failure of a project.

A number of the major engineering contractors in the world today actually began as construction contractors. At least two of the major engineering companies began as shipbuilders, one began by manufacturing trams and expanded into building track for them to run on and power plants to run them, and quite a few started as general contractors doing civil construction, roads and dams. Many have roots at least as far back as 1900 and quite a few are older than that.

Engineering contractors need a lot of things from manufacturers, and we need to feel confident that we really get what we asked for. The specific data, knowledge and confidence in the manufacturer that are important at each stage will be listed.

#### The role of engineering contractors

Depending on the requirements and preferences of the

owner, the responsibility of the engineering contractor can vary widely. At its greatest, the engineering contractor's scope is what is known as 'turn-key', or delivering a complete, ready-to-operate plant to the owner, or it can be as small as doing upgrades to the owner's specifications in preparation for the next capital project. However, regardless of the breadth of scope, the engineering contractor's role with valves can vary from complete to almost nil depending on the owner's preference.

Here, we're defining the engineering contract as anything that includes engineering, whether or not there is also any construction or construction management. The subject of this article assumes that there is material acquisition and/or material management, but the engineering contractor can also influence valves even if someone else actually buys them.

In the old days, the role of engineering contractor was often referred to as 'consulting engineer', when the owner had significant numbers of staff who played an active role in designing a new project and was also the administrator of other contracts such as construction, or perhaps performed some of the construction with the owner's own personnel. Today, although that mode of operation still occurs, it is somewhat unusual and is on the decline, since most owners consider it more cost-effective to hire out the engineering work rather than doing it themselves. The unfortunate part about this change is the loss of continuity.

Our main interest here will be the two-part function of, first, specifying the required valves, and second, managing the actual acquisition of these valves. The owner plays a more or less active role in these two functions, but as a general



rule, the activities are the responsibility of the engineering contractor.

#### **Determining the requirements**

In the typical design process for a new unit, after the feasibility studies as to the economics of the unit and the conceptual engineering has been done, the first set of drawings to be produced are the metallurgical flow diagrams. These drawings show most of the equipment and the major lines connecting them, and are used to work out heat and material balances and as aids in sizing the major equipment. The only valves that are shown are the principal control valves, and those are primarily shown to diagram the logic used to control the process (flow into a particular column being dependent on the temperature in the column, for instance).

After these drawings are approved, engineering proceeds on the next set of drawings, where the majority of the valves are displayed for the first time. These are known as the piping and instrument diagrams (P&IDs), also known as process flow diagrams and utility flow diagrams, depending on the system they portray.

The flowsheets are used to help write piping line classes. The line class groups related services together, to organise the requirements for specific services as to corrosivity, wall thickness and so on. This information, along with design conditions, determines what material is required for valve body and trim, and pressure rating and size range.

What a contractor needs from manufacturers at the design and selection stage is:

· Catalogue data (published on paper or online) showing

what is available, and what the product size ranges are, including dimension tables;

- Drawings or descriptions showing how the valve operates (for unusual or proprietary designs);
- Confidence that these valves really exist, and have been built before.

#### **Describing the valve**

There are two types of valves used in plants, namely 'tagged items' and 'bulk items'.

Any valve that is sized specifically for the flow conditions that exist in one location is assigned a tag number. One example of this is a control valve, whose functioning depends on process data taken from points nearby and whose output is a process variable for the next piece of equipment in line. This valve is a unique item whose tag number is assigned based on a structured format which is easily identifiable by process control systems (DCS or PLC, for example).

Other tagged items may include specially-sized valves such as boiler blowdown, which are not connected to any control system and thus may be numbered as specialty items or minor equipment items. There are also automated on-off valves, which are not control valves but are connected to a control system and thus have an 'address' for the control system to interface with.

These valves are described on a data sheet, one for each valve, with its process data, actuation data, power source data, and a brief description of the valve type and material. These forms are now often automated, wherein the data can be input and maintained in an electronic format, often with automatic links to other data that keeps the data sheet updated during the course of design engineering.

By contrast, the bulk items are generally identified by a code number. The purpose of this code number is to identify a type of valve by its characteristics rather than identifying a specific valve. For any particular valve description, the plant might need one, or might need thousands, of them because they do not need to be designated to a specific location and service.

The descriptions can be written in many ways, from a set of narrative sentences in a freeform manner, to a template that requires specific information to be filled in for each type of valve somewhat like a data sheet. Good description-writing practice has the various different types of valve with different terminology arranged in ways that provide consistency from one type to the next, and from one individual description to another.

Engineering firms who do business for a variety of end users maintain a catalogue of valve descriptions of their own. Some owners, especially the larger ones, also have their own valve catalogues. At this point, a couple of things happen. While it's generally fastest and cheapest to allow the engineering firm to use its own catalogue, many end users want to see their valve numbers used. One way of solving this dilemma consists of using the owner's numbering system for valves, while attaching to them the descriptions that the engineering firm already has. Appropriate editing is required, of course. Now that most data is electronic, this is definitely the easiest way.

Another way involves bringing in the complete text of the owner's description, but systems are rarely compatible enough for that to do too much good. Yet another way is to use a paper copy of the owner's descriptions and reference them from within the engineering firm's material system. Many end users are surprised to find that this is the hardest and least efficient way, but this is true since most electronic material systems are designed to present all the data together and, if you can't extract data from within the system, things get very cumbersome.

Another part of the engineering business that is quite different from an end user's practice, with regard to managing valve description data, is that an engineering firm lives on data. Efficient, effective managing of data is vital to an engineering firm. In a plant, if need be, you can go out and look at a valve and say in effect, "I want one just like this one". An engineering firm has no such luxury and must be equipped to correctly and completely specify a product the first time around. Failure to do so jeopardises the construction schedule and budget, even more so since the lost profit of bringing a unit on line later than planned is vastly higher than a typical construction budget.

What a contractor needs from manufacturers at the specification stage is:

- Clear catalogue data (on paper or on-line) that shows the product line;
- Description of figure numbering system, or otherwise a method of calling out the correct valve with no confusion;
- Drawings of valves showing outline and cross-section (on request);
- Confidence that the submitted information won't change if an order is placed.

#### Determining appropriate manufacturers

The subject that arouses the most fear and trepidation among sales personnel, other than whether or not they will get an order, is the question of whether their products are on the 'approved list'. Approved lists are not as simple as they seem. On the highest level, an approved list consists of products that the owner has reviewed, perhaps visiting the manufacturer first, auditing the quality process, reviewing certifications, perhaps even requesting changes in the product, before the product is deemed acceptable. In many cases, the products made for that user are slightly different than products made for any other customer. At all events, the items that are subjected to such scrutiny are truly 'approved'. Owners who have such well- maintained lists are typically the leaders in their industry.

Part of the approval process is the review of manufacturing procedures, including the source of components, and the types of machinery and the skill of the work force. Changing any of these conditions, as happens when factories move or when new foundries are used or when the manufacturer changes manufacturing procedures, really means that the product changes. Owners don't like finding out that they are buying something different from that they originally approved, because there is a chance that the product is not as good as their original understanding. This is why suppliers are put on hold or taken off approved lists.

What does an engineering firm do if an owner's approved list needs to be improved? This can happen if, for instance, the engineering company is building a plant of a type the owner has never had before. Often, new valve types are required that are not covered by the existing list. Or, more often, the list is out-of-date and does not contain enough viable manufacturers who make the desired product.

The engineering firm, while having a responsibility to perform work the way the owner wants it, is also obligated to help the owner with improvement. The approach of "this item's not on the approved list, so don't offer it" is usually too easy. The engineer should at least take the responsibility of verifying the contents of a list in terms of whether there are enough different manufacturers on it, and of all the proper categories, to build the desired plant.

However, if there is any reasonable concern that the product being offered is equal or superior to the products already on the list, and if. in addition. there is any engineering requirement to add to the list, then some effort should be expended. This last point is very important. No rational person needs 20 or 30 different manufacturers in a category of valves, yet there could be that many offered in a year's time. In any given time period, perhaps one out of three or four of the items presented as 'new' has any merit as an item worthy of addition to a typical project's list. This one out of three or four that attracts your attention would be because of being lower cost for a similar quality, or an improved quality, or easier to obtain, than products on the list already, to a significant degree, to make it worth considering.

Often, there will be a specific approved list for a specific project. In the real world, it should be expected that this list would expand as the project evolves. This is a significant point, because engineering moves too fast today for an 'approved list' to be created at the beginning of the project, and

"Owners don't like finding out that they are buying something different from that they originally approved" stand unchanged throughout the design and procurement phases. It is a real necessity for project personnel to be able to add manufacturers to the list, as requirements evolve, and as more suitable manufacturers become available.

It's too short-sighted to ignore such developments with the dismissive "you're not on the list". Of course, this flexibility assumes that there is a reason for the addition, as discussed above. It should be expected that some requests to add manufacturers to a list would be turned down after evaluation of their merits or lack thereof.

What a contractor needs from manufacturers at the bidder selection stage is:

- · List of customers, showing what was furnished;
- Statement of where the manufacturer is, their size and experience, and identity and location of suppliers for castings and other major components;
- References of which end users or certifying bodies have performed successful audits;
- Procedures for ordering castings and components including reference to industry standards, manufacturing procedures and inspection procedures with acceptance limits (on request);
- Confidence that all submitted procedures will be followed to the letter and that any deviations will be requested in writing before being performed;
- Confidence that none of the above will change during the course of the manufacturing process, if an order is placed.

#### The procurement process

Valves, like everything else bought for a project, go through a procurement process that is governed tightly both the company's and the owner's internal rules and the national laws. We won't dwell on these, except that there are some particular problems that valves present.

Valves are different from other engineered equipment, in that there are large numbers of items that vary from lowvalue threaded bronze to exotic, heavy wall, high alloy items that can cost more than a small pressure vessel. At the low end, valves are essentially commodity items, but regardless of their value, all valves pretty much travel the same path.

Sometimes in the bidding process, the valves are tossed in with other piping material for stockists to quote on; in other cases there is a single package containing all the valves and nothing else; and the third common method is to break out valves into packages by type, roughly corresponding to the breakdown in manufacturers who could build each type of valve. An advantage of this last method is that the buyer can separate special valves and commodity valves into different packages, or separate valves to be bought locally from valves that only a few companies in the world can make. As long as each of these three methods results in the quotation package being addressed to a sufficient number of bidders who can assemble a serious response, any one will work.

Quotes are also evaluated in different ways. In some parts of the world, bidders are instructed to prepare two distinct packages, one technical and one commercial. The technical package normally contains no pricing or other commercial information, while the commercial package normally contains less in the way of detailed information such as drawings. That's a fine theory, the separation of data, and in environments where the possibility of collusion or under-the-table dealings are common, it might have an advantage.

However, this method requires more work overall to evaluate, and in some opinions, it is quite a bit less efficient because the principles of engineering economics are neglected. In other words, the pricing information is often very relevant to the engineering evaluation. If the same items are quoted with wildly different prices from different sources, maybe the quotes aren't really equivalent. If one quote is markedly lower in price from the others, maybe something has been left out. Information like this is very difficult to uncover by looking at a quote package that is technical-only.

The best arrangement for the separation of powers between engineering and procurement is if the two look at the same quote package, and each group strike out the quotes that do not meet requirements, whether technical or commercial. A few items such as delivery time could be argued as belonging to either group. Regardless, the surviving quotes can then be tabulated, and the best offer selected.

Here is another difference between an engineering company and an end user. An end user who is ordering valves for a specific location may have latitude to call out one specific manufacturer, or to arbitrarily select one from the bid tab. In other words, this is the power to be able to overtly select the offer desired. In an engineering environment, however, there is a mandate to select the offer that is the best price (or the best delivery, if that is the criterion), after having thrown out the quotes that are not both technically and commercially acceptable. Whichever manufacturer has the best offer gets the order, if all of the criteria are met. End users may believe, especially in fixed price contracts, that an engineering company will select the cheapest item that can be possibly obtained and leave the end user to replace the valves with ones that actually work. While that is theoretically possible, in the authors' experience, most contractor engineers understand the principle of delivering a good and usable product, and work valiantly to keep out the unknown, the uncertain and the unsuitable valves from the finished plant. Unquestionably, it is the engineering company's charter to do so.

"In an engineering environment, however, there is a mandate to select the offer that is the best price or the best delivery"

What a contractor needs from manufacturers at the order entry and manufacturing stage is:

- Complete schedule data, listing each activity and when it will occur;
- Plan for what to do if a milestone is missed (not required if original schedule is maintained throughout);
- Full and complete transparency about manufacturing processes;
- Notification, in a timely manner, of inspection witness points and hold points, especially pressure testing and material identification testing;
- Confidence that each procedure in manufacturing and testing was followed completely.

The items listed above are by no means a complete list, but these are the most important items and the ones most frequently requested.

#### **Farewell to a stalwart**

Since his tenure as managing director of KSB Pumps and Valves, Wolfgang Demmler has steered the company through more than a decade of sustained growth, while simultaneously playing a significant part in the development of the local pump and valve industry. With his promotion to head up the group's iconic GIW slurry pump company in the USA, he is able to look back proudly at the leadership role that KSB has taken within the local industry, having steered the industry towards more efficient technologically enhanced pumps, as well as promoting adherence to international quality standards.

Through booms and busts in recent years the company has maintained an enviable year-on-year growth rate to enable continued investment in products and infrastructure to further develop and grow its influence locally. The company has even played a part in keeping the country's lights on during the power crisis when its pumps service division was able to maintain and refurbish the ageing, hard-pressed boiler circulating and feed pumps at the country's base-load power stations.

Looking back at his achievements, Wolfgang attributes much of his success to the people he has worked with during his 11 years at the helm. "I came to SA in November 2004 and officially took over at the start of 2005. Having spent 14 years in headquarters in Germany it was quite an adjustment to get used to a new culture.

"Fortunately, the company I was taking over already had a 45 year history in the market and was substantially committed to manufacturing in SA. This gave me space to make plans for the company and focus on our customers' requirements. With a good team in place I also had room to seek opportunities for the company and seize opportunities to improve our offering and grow the business.

"Some of the most significant changes included the development of our service division and the manufacturing plants in line with international standards. Simultaneously we split the plant into three separate divisions to handle standard pumps, engineered pumps and a self-sufficient parts distribution centre to ensure the best possible support of our pumps throughout the continent.

"Then we opened service divisions to refurbish and maintain large pumps such as Eskom's power station pumps and later a valve service division to look after KSB's range of valves out in the marketplace."

He concludes that the company is poised for the next phase of growth under succes-



Wolfgang Demmler of KSB Pumps and Valves South Africa

sor, Dr Sven Baumgarten. "Our strength is in our strong management team and our broad exposure to different markets including agriculture, water, chemical and mining. Sub-Saharan Africa is the only big market worldwide that still needs to be developed and KSB Pumps and Valves South Africa is perfectly positioned to assist with its development.

For more information contact Annett Kriel, on tel: +27 11 876 5600, email: Annett.Kriel@ksb.com, or go to www.ksbpumps.co.za

#### WPIL acquires another pump company, Aturia

Customers in mining, industry and petrochemicals are likely to benefit from increased competition in the South African pump market resulting from the acquisition in June this year by WPIL of Italian pump company Gruppo Aturia. WPIL is the holding company of local manufacturers APE Pumps and Mather+Platt, both well known in the South African and southern African pump markets.

The group consists of the following companies: Aturia, established in 1927, patenting their electric submersible motor in 1946. Rotos was acquired by Aturia in 1990. 2005 saw the manufacture of magnetic drive centrifugal pumps. Marelli, founded in 1891, joined the Aturia family in 1990 which allowed the Gruppo Aturia Company to extend their product range. Audoli & Bertola were acquired by Gruppo in 2003. Aris Chiappa originally a steel plant, but began production of vertical pumps began in 1940 and over the next 40 years partnered with the world's top turbine manufactures developing pumps for special lubrication applications.

Some of the products now available from the group include the following, to name a few:

• Multistage pumps TK-TKR-VTK-TKK series The pumps are all high pressure multistage centrifugal. Design concept features ring section sealed with 'O' rings. Pumps are available from 65 mm to 100 mm. The axial thrust is accommodated by the hydraulic and dynamic balancing of each impeller on the rotating assembly.

- Horizontal split case pumps PD & PDV The range consists of single stage double entry horizontal centrifugal pumps. The pumps, which are split along the axis, allow for ease of maintenance or inspection of the rotating assembly. The pumps are fitted with closed double suction impellers which will provide stable operation with high value efficiencies.
- Vertical electric submersible turbine pumps The present range is manufactured to suit wells from 150 mm to 640 mm. The hydraulic design has been focused on obtaining the maximum efficiencies and a stable performance.
- Submersible motors All motors are asynchronous, Three Phase. The rotor is dynamically balanced thus guarantying operation without vibration. The thrust bearing pad is self-aligned and water lubricated. Drive bearing is in graphite or rubber and is water lubricated.

- Centrifugal pumps PCM /PCM-SP series The PCM pumps are single stage end suction centrifugal pumps with magnetic drive. Volute casing and all wetted parts are machined from solid blocks of PP and PVDF material.
- Turbine pumps PTM / PTM-SP series This range consists of pumps manufactured with regenerative, turbine or peripheral type impellers also incorporating mag drive technology. PTM non-metallic pumps are suitable for various chemical compounds and offer excellent resistance, and low wearing rates.
- Turbine pumps NDM series ISO2858 Centrifugal end suction mag drive pumps manufactured to the ISO2858 specification. Pumps are volute foot mounted with single volute and flanged connections. All pumps have been designed to a modular concept so that inventory of components are reduced.

For more information please contact Dave Johnson,Marketing & Business Development Manager, Mather+Platt - APE PUMPS on tel: +27 11 824 4810, email dave@matherandplatt.com.



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### Verder Pumps South Africa introduces a new double-acting high-pressure AODD pump

Industrial pump manufacturer and distributor Verder Pumps South Africa now offers a new, FDA-approved high-pressure, double-acting diaphragm pump, suitable for filter-press applications where the discharge pressure is higher than the available compressed air pressure.

The new VA25-HD (DA) high-pressure diaphragm pump features the traditional advantages associated with high-pressure pumps, including

- stalling against closed discharge, which means that no safety pressure valve is required;
- boosting pressure double the compressed air pressure;
- no need for ancillary equipment to regulate flow at raising discharge pressures.
   Some features that are unique to this pump include:
- The new model has the same maximal flow rate as a standard Verderair VA25 diaphragm pump
- It is double acting, therefore produces stable and efficient flow;
- It has a low to high-pressure switch that allows for it to be more efficient.

The VA25-HP (DA) is, therefore, the ideal pump for filter-press applications.



Example of a filter press application with Verderair VA25-HP (DA)

The existing range of high-pressure diaphragm pumps, which are single-acting pumps, can deliver fluid pressures of up to double the supplied compressed air pressure. This results in a pulsating flow, high compressed air consumption and a 50 % reduction of the flow rate.

In addition, the VA25-HP (DA) pump has a switch to change the pump operation from low pressure to high pressure. At the low-pressure setting the pump operates in normal, low-pressure mode with optimum use of the compressed air. When operating in high-pressure mode, the pump boosts the liquid pressure to double the compressed air pressure; with flow rates double that of a single-acting, high-pressure pump.

**For more information:** Verder Pumps South Africa, email info@verder.co.za.

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# Contaminants of emerging concern in drinking water in South Africa

#### An LC-MS/MS-based survey

by Christiaan Odendaal and Maitland T Seaman of the Centre for Environmental Management, University of the Free State, Bloemfontein, South Africa, and Gabre Kemp, Huibreght E Patterton, and Hugh-George Patterton of the Department of Microbial, Biochemical and Food Biotechnology, University of the Free State, Bloemfontein, South Africa

> Advances in many analytical techniques allow the detection of compounds in water at very low concentrations which has facilitated the identification of many compounds in drinking water that went previously undetected. The range of CECs detected in drinking water, and seasonal and geographic variability in CECs levels, warrant a more frequent screening programme.



dvances in analytic technologies allow the identification of chemical compounds at exceedingly low concentrations (10-9 g/L) in drinking water. [1] This permits the identification of compounds which, until recently, were undetectable in water. These compounds fall into broad categories, including pesticides, pharmaceuticals and personal care products. Because we are only now becoming aware of the presence of these chemicals in drinking water, most of these compounds are not included in routine monitoring programmes. Although these compounds are generally present at concentrations several orders of magnitude below established acute toxicity levels, the effect of long-term exposure to very low concentrations of these compounds on human health and development is not known. This is particularly relevant to pharmaceutical contaminants, which are designed to be physiologically active at very low concentrations. Furthermore, some of these compounds interfere with the human endocrine system (endocrine disruptors), which may result in severe developmental defects with exposure of foetuses or infants during critical developmental windows. There is therefore a pressing need to investigate the potential health impacts of these compounds in drinking water, collectively known as contaminants of emerging concern (CECs).[2,3]

The US Geological Survey undertook several national reconnaissance studies, including a 1999/2000 programme, in which samples were analysed from 139 streams across 30 states in the USA.[4] A wide range of chemicals present in residential, industrial, and agricultural wastewaters was found to occur at low concentrations in streams in the United States. The chemicals detected included human and veterinary drugs, natural and synthetic hormones, detergent metabolites, plasticisers, insecticides and fire retardants. One or more of these chemicals was found in 80 % of the streams sampled. In a national groundwater study by the US Geological Survey, samples from 47 wells in 18 states were analysed for 65 chemicals.[5] A profile of chemical pollutants similar to that observed in streams was found, although the contaminants were generally present at much lower levels. In another US Geological Survey study of untreated drinking water from 25 groundwater and 49 surface water sites in 25 states, pharmaceuticals, plasticisers and fire retardants were detected.[6] Taken together, these studies provided valuable baseline information on the presence of CECs and other compounds in the US water system, and provides a valuable frame for further toxicity and public health impact studies.

The list of CECs is extensive, and includes sucralose, antimony, siloxanes, musks, nanomaterials, perfluorooctanoic acid, perfluorooctane sulphonate and other perfluorinated compounds, pharmaceuticals, hormones and hormone- active compounds, collectively known as endocrine disrupting compounds, drinking water disinfection by-products, sunscreens/UV filters, brominated flame retardants, benzotriazoles, naphthenic acids, cyanobacterial toxins, perchlorate, dioxane, pesticides and pesticide degradation products, and microorganisms, including viruses.[7]

Generally, organisations involved in water health and safety monitor CECs based on available technologies, known occurrence and health impacts.[8,9] A technique that is currently widely used to monitor CECs is high performance liquid chromatography coupled with tandem mass spectrometry (LC-MS/MS). [7] <image>

Here we report the first national survey of CECs in the drinking water of major South African cities. The survey includes a qualitative screen for approximately 700 compounds, as well as the quantitation of three critical compounds identified in the qualitative screen, atrazine, terbuthylazine and carbamazepine. Atrazine is a herbicide used for the control of broadleaf weeds in the maize, sorghum and sugar cane agricultural industries. Epidemiological studies showed a correspondence between elevated atrazine levels in drinking water and low sperm volume and motility[10], foetal growth defects, including restriction[11], small-forgestational-age[12] and intrauterine growth retardation[13], foetal gastroschisis[14] and increases in limb reductions (upper and lower), hypospadias and epispadias, cryptorchidism, and spina bifida[15]. Terbuthylazine is a general, broad-spectrum pre- or post-emergence herbicide used in agriculture. Terbuthylazine was shown to cause an increase in DNA damage in cultured mammalian cells at concentrations equivalent to the occupational exposure limits.[16] Carbamazepine is a therapeutic used as an anticonvulsant and a mood-stabilising drug. While it was reported that epilepsy patients who receive carbamazepine therapy during pregnancy delivered babies with an increased rate of congenital anomalies such as neural tube defects, and cardiovascular and urinary tract anomalies[17], no epidemiological studies on the presence of carbamazepine at low concentrations in drinking water have been published to date.

#### Materials and methods Reagents and materials

High purity (>98 %) chemical standards for atrazine and

carbamazepine were purchased from Sigma Aldrich (St Louis, MO, USA), while terbuthylazine and deuteratedatrazine were purchased from Dr Ehrenstorfer (Augsburg, Germany). Stock solutions for each standard were prepared in methanol (1  $\mu$ g/L). High-performance liquid chromatography (HPLC) grade methanol (MeOH), acetonitrile (ACN), formic acid and ammonium hydroxide were purchased from Sigma Aldrich.

Ultra-pure water (18 m $\Omega$ ) was prepared with a Milli-Q purification device (Millipore, Billerica, MA, USA) and used in all experiments.

#### Method development and validation

The quantitative method was developed according to the Food and Drug Agency guidelines for method validation. [18]

#### Sampling

Samples (1 L) were collected in amber glass bottles from water treatment plants (WTPs) in Cape Town, Port Elizabeth, Durban, Pietermaritzburg, Johannesburg, Pretoria and Bloemfontein during months in each of the four seasons (February, [3] April, July and October 2012), as well as from residential taps in Bloemfontein south and Bloemfontein north, supplied by two different reservoirs. Confidentiality agreements were entered into with the WTPs to not disclose the identity of the individual plants. Samples were collected and stored at 4 °C until analysis, usually within 24–48 h.

#### Solid phase extraction

Sample preparation involved compound extraction and reconstitution in 1 mL of  $H_20$  / 0,1 % formic acid. Solid phase

Table 1: Precursor and fragment m/z values						
	Precursor <i>m/z</i>	Fragment 1 <i>m/z</i>	Fragment 2 <i>m/z</i>			
Atrazine	216.0	174.1	104.0			
Terbuthylazine	230.0	174.1	104.0			
Carbamazepine	237.1	194.2	192.1			

Analyte	Bloemfontein						Johannesburg		93
	Jan 2010	Oct 2010	Jan 2011	May 2011	Jul 2011	Jul 2011	Dec 2010	Jun 2011	Occurrence (%)
Amphetamine	•	•		•	•			•	63
Atrazine		•	•			•	•	•	63
Carbamazepine	•	•	•		•		•		63
Diphenylamine								•	13
Imidacloprid								•	13
Metolachlor			•	•	•	•	•	•	75
Oxadixyl		•							13
Simazine			1					•	13
Tebuthiuron				•	•	•	•	•	63
Telmisartan		•				1			13
Terbuthylazine	•	•	•	•	•	•	•	•	100

Note: A solid circle indicates that the stipulated compound was identified in the water sample.

extraction is still the preferred approach of extraction, because it produces higher yields than liquid/liquid extraction, can be automated and significantly reduces preparation time.[7,19] Milli-Q water fortified with CEC standards was used to optimise solid phase extraction parameters. Different solid phase extraction cartridges with varying sorbent characteristics were analysed to identify the cartridge with the best recovery.

Before extraction, cartridges were equilibrated with 6 mL pure MeOH. After equilibration, samples were loaded at a flow rate of approximately 6 mL/min. After samples were loaded, cartridges were washed with 6 mL of ultrapure water. Extracts were eluted into 6 mL tubes using 2 mL of MeOH and 2 mL of acetonitrile. Eluates were evaporated using a Savant SC 210A Speedvac concentrator with a Thermo RVT 4104 refrigerated vapour trap. Extracts were reconstituted in 1 mL of H<sub>2</sub>O / 0,1 % formic acid and suspended using a vortex (Velp Scientifica, Italy) as well as by sonication (Branson, USA).

#### LC-MS/MS analysis

The analysis was performed on an HPLC (Agilent 1200) linked to a 3200 QTRAP hybrid triple quadrupole mass spectrometer (AB SciEx, Framingham, MA, USA). The HPLC was fitted with a 3- $\mu$ m Gemini- NX-C18 110-Å (150 x 2 mm) column (Phenomenex, CA, Torrance, USA). Formic acid (0,1 % v/v) in water (solvent A) and formic acid (0,1 % v/v) in MeOH (solvent B) were used as elution solvents for positively charged analytes. Negatively charged analytes were separated in NH<sub>3</sub>OH (0,1 % v/v) in water (solvent B).

Analytes were detected and quantified using multiple reaction monitoring using precursor and two fragment transitions for each of the analytes.[20,21] The m/z values used are shown in Table 1. Multiple reaction monitoring provides increased selectivity and reduces the likelihood of spectral interferences.

#### Results and discussion Initial screening

We performed an initial LC-MS/MS analysis of drinking water from Bloemfontein and Johannesburg to obtain an insight into the range of CECs present in drinking water in

South African cities. We made use of a MS/MS fragmentation library of approximately 700 compounds (see Supplementary Table 1 online at http://www.sajs.co.za). The result of this initial screen is shown in Table 2.

A review of the frequency of occurrence, coupled with toxicity data and community health impact from epidemiological studies,[22] where available, suggested that atrazine, terbuthylazine and carbamazepine posed the highest public health risk to the South African water consumer. For this reason it was decided, apart from the general screening of drinking water for CECs, to also quantitate atrazine, terbuthylazine and carbamazepine in all collected water samples. In the absence of an established method, we needed to develop a robust protocol for the quantitation of these three CECs by LC-MS/MS. Method selectivity, accuracy and precision, as well as analyte recovery and stability are generally essential parameters to consider in method development and validation.[18]

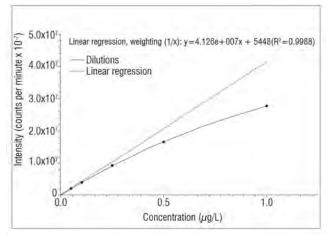
#### Method validation

#### **Calibration curve**

A calibration curve was determined by measuring the MS ion count over a concentration range of  $5 \times 10^{-5}$ ,  $1 \times 10^{-4}$ ,  $5 \times 10^{-4}$ ,  $1 \times 10^{-3}$ ,  $5 \times 10^{-3}$ ,  $1 \times 10^{-2}$ ,  $5 \times 10^{-2}$ , and  $1 \times 10^{-1} \mu g/L$  for each of atrazine, terbuthylazine and carbamazepine. The representative calibration curve of atrazine is shown in Figure 1. Comparable results were obtained for terbuthylazine and carbamazepine (data not shown).

The limit of detection, lower limit of quantification and upper limit of quantification were determined for each of the three CECs using the MS spectra in the concentration range  $5 \times 10^{-5} - 1 \times 10^{-1} \mu g/L$ . The limit of detection and lower limit of quantification were determined at signal-to-noise ratios of 3 and 10, respectively.[23,25]

The upper limits of quantification were defined as the highest concentration of analyte detectable with reasonable precision and accuracy.[18,24,26] The lower limit of quantification, upper limit of quantification, recoveries, coefficient of variance and maximum contaminant levels are shown in Table 3. An internal standard, deuterated atrazine, was added at  $1 \times 10^{-1} \mu g/L$  before solid phase extraction. The same concentration of internal standard was injected into



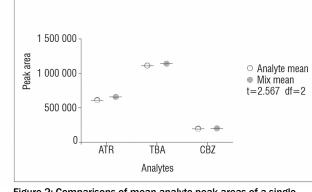


Figure 2: Comparisons of mean analyte peak areas of a single analyte and in a mixture revealed no significant differences

Figure 1: Calibration curve for atrazine

Table 3: Measures of optimised measurement method								
Analyte	Linearity ( <i>R</i> ²-value)	Lower limit of quantifica- tion (µg/L)	Upper limit of quantification ( <i>µ</i> g/L)	Recovery <sup>†</sup>	Precision <sup>†</sup> (% coefficient of variance)	Accuracy <sup>†</sup> (% bias)		
Atrazine	0.99880	0.00010	0.10000	103 %	2 %	3 %		
Terbuthylazine	0.99860	0.00005	0.10000	103 %	3 %	3 %		
Carbamazepine	0.99000	0.00005	0.10000	120 %	1 %	20 %		

†Measured at 5×10-2 μg/L

each of the vials  $(5 \times 10^{-5} - 1 \times 10 \,\mu g/L)$ , and was used during quantification of atrazine and terbuthylazine.

#### Selectivity and crosstalk

The selectivity of a method can be verified by establishing the absence of analyte peaks in a blank sample at the determined elution time for that analyte.[18] The absence of crosstalk is shown by detecting comparable concentration for an analyte in a sample containing the single analyte compared to a sample containing a mixture of different, possibly interfering, analytes. To establish the selectivity and absence of crosstalk in our quantitation protocol, three vials were filled with 50 ng/L atrazine, terbuthylazine or carbamazepine, and a fourth vial was filled with a mixture that contained 50 ng/L of each of atrazine, terbuthylazine and carbamazepine. It was particularly important to demonstrate the absence of crosstalk for atrazine and terbuthylazine, because the m/z values of the two major fragments were identical (Table 1). The single analytes showed no significant difference compared to that of the mixture of three analytes in three independent repetitions of the experiment (paired t-test, confidence interval = 99 %). Similarly, no analyte could be detected in sample blanks. The results are shown in Figure 2. Comparisons of mean analyte peak areas of a single analyte and in a mixture revealed no significant difference.

#### Accuracy and precision

The precision and accuracy of the quantitation protocol was demonstrated by determining the concentration of each of the three analytes in standard samples of  $5 \times 10^2 \,\mu$ g/L, a concentration in the intermediate range between the lower limit of quantification and upper limit of quantification. In all cases, the coefficient of variance was less than 15 % and the bias less than 20 % (see Table 3), within the prescribed limits.[18]

## Presence and seasonal variation of CECs in drinking water

Drinking water samples were taken at seven WTPs in major cities in South Africa at a point before the water entered the reticulation system. The samples were extracted on a solid phase cartridge, eluted, and analysed by LC-MS/MS. The precursor m/z as well as the m/z values of two major fragments were compared to a library of compounds (see Supplementary table 1 online). Compounds were identified where the precursor and well as both fragment m/z values could be matched to a library entry. The combined results of the screening of the seven drinking water samples are shown in Table 4. Atrazine, terbuthylzine and carbamazepine were detected in more than 60 % of the drinking water samples. The seasonal distribution of atrazine fitted with its agricultural use as herbicide for summer crops. Carbamazepine, an anticonvulsant that is also prescribed for treatment of bipolar disorder, was present at a steady level in more than 70 % of the samples. Cinchonidine, which is used in the chemical synthesis industries, was detected in almost 90 % of the samples. Diphenylamine, which was present in about 40 % of the samples, has wide application, including as an anti-scalding agent for fruit. The antifungal fluconazole and herbicides hexazinone and metolachlor were present in approximately 16 % of the samples, with the latter present exclusively in the summer, most likely as a result of its agricultural application. Phenytoin, an anticonvulsant drug prescribed under the trademark 'Epanutin' in South Africa, was present in drinking water throughout the year. The antibacterial agent, sulphisomidine, was present in 18 % of the samples. The herbicides, terbuthiuron and terbuthylazine, were consistently present in drinking water throughout the year. Interestingly, ephedrine, used as a decongestant and bronchodilator, was observed only in the winter, consistent with its expected increased medical use. Enilconazole, an antifungal agent widely used in the growing of citrus fruit, was observed only in autumn. Interestingly, we never detected any cyanobacterial microcystins, but had no information on the occurrence of upstream algal blooms.

Having established the frequency of occurrence of a range of pesticides and therapeutic compounds in metropolitan drinking water, it was decided to quantitate the levels of atrazine, terbuthylazine and carbamazepine, as these three compounds were present at very high frequency and were also associated with significant public health risks.

## Quantitation of three critical CECs in drinking water

The drinking water samples, treated as before, were separated by reverse phase HPLC and quantitated by multiple reaction monitoring on a hybrid triple quadrupole mass spectrometer using the developed method described above. This procedure involved the integration of the ion count during elution of a compound from the HPLC column, with concomitant confirmation of the identity of the compound by the presence of peaks at the correct precursor and major transition fragment m/z values. The peak area was used to deduce the concentration from the standard curve of each of the three compounds of interest. The concentrations are tabulated in Supplementary Table 2 online.

The guideline value proposed by

the World Health Organization (WHO) for atrazine is 100 mg/L[27], whilst the maximum contaminant level stipulated by the US Environmental Protection Agency (EPA) is 3 mg/L[8]. Figure 3 indicates that the highest level of atrazine recorded during the one year survey was more than an order of magnitude below the maximum contaminant level set by the EPA. The level of atrazine was consistently high throughout the year in Johannesburg, compared to the average value recorded for all the samples. Interestingly, high atrazine values were also recorded in tap water in Bloemfontein in the autumn and spring, even though low levels were recorded at the WTP at the same times. This suggested that the concentration of atrazine may vary very sharply, and that a much higher sampling frequency is required to accurately determine its variation over time.

The guideline value proposed for terbuthylazine by the WHO is 7 mg/L.[27] The EPA has no set maximum contaminant level for terbuthylazine.[8] Referring to Figure 3, it is seen that the highest recorded concentration for terbuthylazine in drinking water (Pretoria, autumn) is at least an order of magnitude less that the WHO guideline value. Johannesburg, again, showed a consistently high level of terbuthylazine throughout the year, compared to the other WTPs.

The maximum contaminant level for the pharmaceutical

Analytes	Summer (%)	Autumn (%)	Winter (%)	Spring (%)	Average annual occurrence (%)	
2-deoxyguanosine	0 %	0 %	14 %	0 %	4 %	
Atrazine+	86 %	71 %	29 %	57 %	61 %	
Benzocaine	0 %	0 %	0 %	14 %	4 %	
Carbamazepine+	71 %	71 %	57 %	86 %	71 %	
Cinchonidine	86 %	86 %	100 %	71 %	86 %	
Cinchonine	0 %	0 %	0 %	14 %	4 %	
Diphenylamine	14 %	43 %	0 %	100 %	39 %	
Enilconazole	0 %	14 %	0 %	0 %	4 %	
Ephedrin	0 %	14 %	14 %	0 %	7 %	
Flecainide	0 %	14 %	0 %	0 %	4 %	
Fluconazole	14 %	29 %	14 %	14 %	18 %	
Hexazinone	14 %	14 %	14 %	14 %	14 %	
Imidacloprid	0 %	0 %	0 %	14 %	4 %	
Metazachlor	0 %	14 %	0 %	0 %	4 %	
Metolachlor	71 %	0 %	0 %	0 %	18 %	
Minoxidil	0 %	14 %	0 %	0 %	4 %	
Nalidixicacid	0 %	0 %	14 %	0 %	4 %	
Paracetamol	0 %	14 %	0 %	0 %	4 %	
Phenytoin	29 %	57 %	29 %	43 %	39 %	
Sebuthylazine-desethyl	14 %	0 %	0 %	0 %	4 %	
Simazine	0 %	14 %	0 %	0 %	4 %	
Sulphisomidine	29 %	29 %	0%	14 %	18 %	
Tebuthiuron	71 %	57 %	57 %	43 %	57 %	
Telmisartan	14 %	71 %	0 %	29 %	29 %	
Temazepam	0 %	14 %	0 %	0 %	4 %	
Terbumeton	0 %	14 %	0 %	0 %	4 %	
Terbuthylazine+	86 %	86 %	86 %	100 %	89 %	
Thiabendazole	0 %	14 %	0 %	0 %	4 %	

Table 4: Seasonal screening and analyte occurrence (%) at all sampling sites: Cape Town, Port Elizabeth, Durban, Pietermaritzburg, Johannesburg, Pretoria and Bloemfontein

+Contaminants of emerging concern that were quantitated in this study.

carbamazepine was set at 12 mg/L.[28] The highest level of carbamazepine detected in drinking water (see Figure 3) was significantly less than this level. Interestingly, the level of this anti-epileptic and mood-stabilising drug was consistently high throughout the year in Bloemfontein, compared to the average national level. Particularly high levels were recorded in the summer (Figure 3). We again observed a discordance between the carbamazepine concentrations recorded at the WTP and in tap water in Bloemfontein in the autumn. This result also suggests significant concentration spikes, indicating a need for a high sampling frequently to obtain a reliable insight into the level of this CEC in drinking water.

#### Conclusion

During this analysis, a method was developed to determine atrazine, terbuthylazine and carbamazepine quantities in drinking water. A qualitative analysis identified 29 potential CECs (Table 4). Importantly, the critical CECs identified during preliminary analyses were also part of the subsequent qualitative list of CECs. Quantification of atrazine, terbuthylazine and carbamazepine revealed no immediate health risks, since all concentrations were below the published thresholds.

Although the concentration levels were below published

0.35 а 0.3 BFN North tap BFN South tap 0.25 Concentration (µg/L) Johannesburg BFN South tap 0.2 Pretoria Iohannesburg hannesburg Johannesburg 0.15 etermaritzbur 0.1 **3FN North tal** South t **BFN North** ort Flizahe Town ipe Towr 0.05 retoria SEN 0 Winter Summer Autumn Spring Season 0.35 b 0.3 0.25 Pretoria Concentration (µg/L) Johannesburg Johannesburg 0.2 annesburg 0.15 etermaritzburg **3FN North tag** BFN North tap Pretoria Bloemfontei 0.1 North BFN South North tag South tar Durban Flizaheth BFN 0.05 SEN 0 Winter Summer Autumn Spring Season Bloemfontein BFN North tap С 0.35 0.3 0.25 Concentration (µg/L) **BFN North tap** BFN North tap Bloemfonteir 0.2 Pretoria 0.15 BFN South tap 0.1 ap N North South tap anneshiird South t South 0.05 0 Summer Autumn Winter Spring

Season

WATER TREATMENT

Figure 3: Concentration of (a) atrazine, (b) terbuthylazine and (c) carbamazepine – three major contaminants of emerging concern – in the drinking water of major South African cities.

This article was originally published in the South African Journal of Science, Volume 111, Number 9/10, Sept/Oct 2015 and is supplemented with online only material. Available at http://www.sajs.co.za.

maximum contaminant level thresholds, the range of CECs routinely detected in drinking water, and the large geographical and seasonal variability that we observed, suggest that a qualitative survey and quantitation of select CECs should be performed more frequently to have a current view of the presence of levels of CECs in drinking water that may impact on human health. Also, with an increase in the pressure on water health as this resource is increasingly being utilised, the introduction of such a CEC monitoring programme becomes essential to ensure the production of healthy and safe drinking water for the consumer.

#### Acknowledgements

We thank the Water Management in Water-scarce Areas and the Advanced Biomolecular Research clusters at the University of the Free State for their contributions to this project. This study was supported by a grant from the Water Research Commission (to HGP).

#### References

References for this article are available from the editor at chemtech@crown.co.za

## **CHEMICAL TECHNOLOGY:** FOCUSING ON WATER PROBLEMS AND SOLUTIONS IN SOUTH AFRICA

As we enter the new year of 2016, it is imperative that our magazine, 'Chemical Technology' (ChemTech) focuses on those matters of greatest urgency for the future, not only of our country, but of the world. The magazine will therefore be concentrating on providing a platform for investigation into the problems facing South Africa at this time, which, indeed, are very much the same as those faced in the rest of the world.

he World Wildlife Fund-SA states in its 2014 Report, 'Understanding South Africa's most urgent sustainability challenge': "We live in an interconnected, interdependent world. This idea, of intersected systems that underpin our natural world and couple resources has gained currency in recent years . . . WWF encountered exactly this 'nexus' phenomenon when [it] prioritised the need to understand and build awareness of the confluence of food, energy and water resources and the implications for development and planning in South Africa." The Food, Energy, Water (FEW) Nexus Report demonstrates the state of the resources at the centre of which is Water.

The challenges presented by the state of both the availability and the quality of water in South Africa constitute serious constraints on the country's development. Pertinent in the extreme for ChemTech is the matter of ongoing deterioration of water quality.

We shall be publishing topical articles on water's role, highlighting solutions to the problems facing us, which are unfortunately becoming ever more critical with the ongoing effects of climate change.

Allied to the water-energy synergy are the subjects of renewable energy production, and the achieving of sustainable energy provision in the country. A report by the Energy Research Centre of the University of Cape Town in 2013 stresses the inextricable link between water use and energy supply.

#### **Future features**

Thus our feature articles will hone in on the efforts to find workable solutions for the following challenges, to name but a few:

- A better understanding of the role of energy in the water value chain – pumping, transportation, treatment, desalination, irrigation,
- Ion technology electrochemical desalination for brackish water
- Water resource toxicity bacteria (Mission 2017)
- Decentralised water distribution systems: wells, pumps, rainwater collection tanks
- Public-Private Partnerships (PPP)
- Acid Minewater Drainage (AMD)
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## Design guidelines for the chemical treatment of distillation columns – Part 2

by Karl Kolmetz, KLM Technology Group, Johor Bahru, Malaysia

Proper chemical treatment in distillation systems involves understanding distillation principles such as the chemistry of the process. Successful application must also include reviews of fouling, corrosion and economic and environmental constraints. Part 1 of this article appeared in the September 2015 issue.



## Increased high temperature naphthenic acid corrosion activity

Processing crude oil blends high in TAN can increase the potential for naphthenic acid corrosion in crude oil distillation units. This phenomenon has been well documented in industry literature. If not controlled, high temperature naphthenic acid corrosion can result in higher equipment replacement costs, lower unit reliability and availability, and increased severity of downstream unit fouling due to elevated levels of iron naphthenates in crude unit distillates. Colour stability may also be affected by the presence of iron naphthenates in crude unit distillates.

Naphthenic acid corrosion activity is dependent upon a number of key variables. The most important variables include:

- The naphthenic acid content of the hydrocarbon streams, typically measured by TAN (mg KOH/gram sample). Naphthenic Acid based corrosion is either reduced or augmented depending on:
- 1. Wt % sulphur
- 2. Whether TAN is high or low
- 3. Whether fluid phase is liquid or vapour
- The temperature of the metal surfaces being contacted by the corrosive hydrocarbons
- 1. Naphthenic acids concentrate above 260 °C boiling range
- 2. Highest concentration in 316-427 °C boiling range
- 3. Lowest temperature where attack occurs ~200 °C
- 4. Above 450 °C disintegrates into lower molecular weight acids

- 5. Naphthenic acids corrosion activity is often high in location where acids condense out of the vapour phase.
- The shear stress of the hydrocarbon moving across the metal surface (a function of velocity and turbulence of the flowing stream)
- At low velocity, acid concentration caused by boiling and condensing causes attack. Small erosion effect on corrosion if velocity is between 0,36 -2,0 m/sec.
- 2. At high velocity, multiphase stream rapid corrosion can occur due to erosion-corrosion. Naphthenic acid corrosion is accelerated in furnaces and transfer lines where the velocity of the liquid/vapour phase is increased. High turbulence areas have severe corrosion.
- 3. Turbulence and cavitation in pumps may result in rapid attack
- The type of alloy in use where hydrocarbon TAN, surface temperature and shear stresses make the system susceptible to naphthenic acid corrosion attack
- Metallurgy 316SS, 317SS and materials with higher alloys (more molybdenum) are more resistant to naphthenic acid corrosion.

Many areas of the crude distillation unit can be susceptible to high temperature naphthenic acid corrosion. These areas can most simply be identified as those which:

- Are exposed to hydrocarbon fluids that contain corrosive levels of naphthenic acids (Generally considered to be any stream with TAN > 0, 5 mg KOH/g, though lower thresholds apply in some cases).
- 2. Operate at temperatures of 220 400°C, and;



 Are constructed with metallurgy not generally considered to be resistant to naphthenic acid corrosion attack. 316, 316L, 317 or 317 L stainless steels are generally considered to be resistant materials.

Areas of the crude unit that are susceptible to naphthenic acid corrosion according to the above parameters typically include:

- Hot crude preheat exchanger network
- Atmospheric heater tubes
- Atmospheric tower transfer line
- Lower section of atmospheric tower (lining, trays) and associated atmospheric gas oil (AGO) pump around/ product draw system
- Atmospheric tower bottoms line and any bottoms heat exchangers (if not integrated with vacuum unit)
- · Vacuum heater tubes
- Vacuum tower transfer line
- Vacuum tower (lining, trays, packing) and associated LVGO, and HVGO pump around/product draw systems
- Vacuum tower over flash draw and 'pump back' lines and associated equipment
- Vacuum tower bottoms line and heat exchangers.

Other areas of the unit may also be susceptible depending on crude blend properties, unit design, operating conditions and actual materials of construction.

One of the greatest concerns refiners face when processing high TAN crudes is the potential for high temperature naphthenic acid corrosion attack. However, years of experience in this area have yielded several strategies that can be implemented to identify susceptible areas of the unit, to successfully mitigate naphthenic acid corrosion, and to effectively monitor this type of corrosion activity.

The first phase of an engineered solution is to perform a comprehensive high TAN impact assessment of a crude unit processing a target high TAN blend under defined operating conditions. An important part of the any solution system is the design and implementation of a comprehensive corrosion monitoring program. Effective corrosion monitoring helps confirm which areas of the unit require a corrosion mitigation strategy, and provides essential feedback on the impact of any mitigation steps taken.

With a complete understanding of the unit operating conditions, crude oil and distillate properties, unit metallurgies and equipment performance history, a probability of failure analysis can be performed for those areas which would be susceptible to naphthenic acid corrosion. Each process circuit is assigned a relative failure probability rating based on the survey data and industry experience.

Corrosion inhibitors are often the most economical choice for mitigation of naphthenic acid corrosion. Effective inhibition programs can allow refiners to defer or avoid capital intensive alloy upgrades, especially where high TAN crudes are not processed on a full time basis.

The use of Best Practices for high temperature inhibitor applications ensures that the correct amount of inhibitor is delivered safely and effectively to all of the susceptible areas of the unit.

Crude blending is the most common solution to high TAN

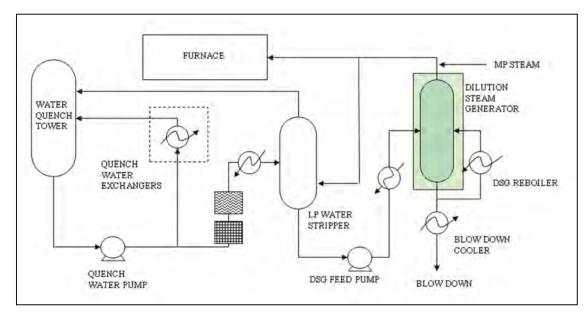


Figure 5 A: Olefin and diene polymerisation in ethylene units

crude processing. Blending can be effective if proper care is taken to control crude oil and distillate acid numbers to proper threshold levels.

#### **Fouling control**

Several general factors influence the distillation fouling potential of a process. These include feedstock, chemistry, temperatures, reboiler heat fluxes, and hydrocarbon residence time. The type of feedstock for a distillation column has a large influence on the fouling potential. Feeds that have olefin or diene concentration will have increase foaming and fouling potentials. The column operating temperature affects fouling rates. In a refinery the crude unit and hydrotreater units might have towers that run under a vacuum to reduce the bottoms operating temperature to reduce fouling and product degradation.

In an ethylene unit a DePropanizer tower might have the overhead cooling be refrigeration to reduce the tower bottom temperature. The goal would be to operate the column below the fouling initiation temperature of the contained fouling species.

For highly fouling services, restrict the reboiler heat flux. A typical reboiler might have as much as 3 % vapourisation and high heat fluxes. Reducing the percent vapourisation and using a lower heating medium will reduce fouling potential. The hydrocarbon residence time will affect the fouling rate. Design columns to have lower residence times in fouling services. At lower charge rates residence time is increased, minimise low charge rates when possible.

#### Olefin and diene polymerisation in ethylene units

The pyrolysis cracking in olefin furnaces will produce olefin and diene compounds. The first cracking furnace was designed to produce crude butadiene for synthetic rubber applications, and the ethylene and propylene were flared as an unwanted co-product. The styrene and the butadiene produced in the pyrolysis reactions can create issues in the downstream distillation columns. If the styrene is allowed to form an organics and hydrocarbons emulsion in the

can polymerise

Figure 5 B: Heated styrene

quench water tower, the styrene can travel with the normal water streams and, when heated, polymerise as shown in Figure 5 A and Figure 5 B. It is important to keep an emulsion from forming in the bottom of the quench water tower for this reason. The proper pH control in the tower will reduce the chance of emulsions.

#### **Olefin unit distillation**

Olefin unit distillation is a series of towers separating the species. Each olefin vendor has a preferred flow sequence. Some will have the DeMethanizer first and some will have the DePropanizer first.

#### DeMethanizers

Each flow sequence will have similar issues with the olefins and di-olefins. Typically the DeMethanizer has only minor fouling potential. This is because the operating temperatures are below the polymer initiation temperature and the concentrations of the reactive monomers are low at this point in the process.

#### DeEthanizers

DeEthanizers can have very high fouling potentials depending on their operating conditions. One of the author's first assignments when he joined an ethylene gas cracker in 1995 was to troubleshoot a DeEthanizer polymerisation issue. The margins were excellent and the unit was run at high capacity and severity – producing many olefins and di-olefins. The reboiler run lengths were about 20 days. The chemical vendors were given multiple opportunities to experiment. One vendor decided to try a dispersant and inhibitor at same time. The run lengths were successfully extended to 8 months. Later, plant modifications were made to extend the run lengths.

#### DePropanizers

DePropanizers are one of the most challenging fouling potentials in an olefins unit due to the tower bottoms' temperature being close to the polymerisation initiation



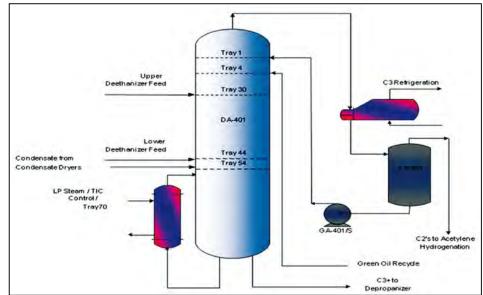


Figure 6: Stream flow and compositions in a DeProponizer

Table 1: Stream flows and compositions							
Stream	Flow	Composition	Temperature				
Feed	45 t/hr	Butadiene 14%	56 C				
Reflux+Recycle	56 t/hr	Butadiene 1 %	43 C				
Distillate	67 t/hr	Butadiene 1%	43 C				
Internal flow above the feed	57 t/h						
Internal flow below the feed	102 t/hr						
Reboiler circulation	172 t/hr	Butadiene 23 %	85 C				
Tower bottoms	34 t/hr	Butadiene 23 %	85 C				

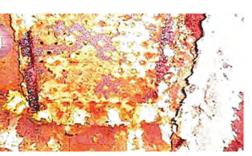


Figure 7: Example of butadiene fouling

temperatures and the high concentration of the monomers (butadiene, styrene and isoprene). Some designs utilise a dual DePropanizer design with low and high pressure towers to reduce the polymerisation potential. Some designs utilize a single DePropanizer that has refrigeration in the overhead to reduce the polymerisation potential.

Even with the dual towers and refrigeration, fouling does occur because the butadiene species is reboiled. In one application the producer decided to reduce the chemical treatment to save cost. The reboiler fouled to the extent that the bundle could not be pulled. The shell and tubes were sent to an external vendor for cleaning.

It is important to monitor the heat transfer coefficient, the tower pressure drop and consider the amount of residual chemical in the DePropanizer. A cross check of the monitoring of the heat transfer coefficient is the steam chest pressure.

A key point for chemical treatments is to remember the liquid flows and compositions inside the column. We tend to measure the external flows and compositions – feed, reflux and tower bottoms.

For example, Figure 6 shows how in the DePropanizer the stream flows and compositions may be reviewed. In the reflux there is an added recycle stream so the mass balance has to take this into account.

Figure 7 shows an example of butadiene fouling in the bottoms of a DePropanizer column.

#### DeButanizers

In theory, Debutanizers in olefin plants should be a con-

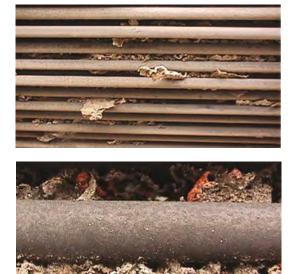


Figure 8: Butadiene fouling in an overhead condenser

trollable application, but they seem to have many challenges. Most of the butadiene fouling species should enter with the feed and be distilled overhead. The styrene and isoprene would normally be in py the gas from the quench system, but small concentrations will be in the DeButanizer. From the feed point to the overhead condenser will need some inhibitor as the di-olefins will be concentrated in the distillate. Some plants only add inhibitor to the overhead condenser.

The reboiler, even though it has high temperatures, should have low fouling potential. If the tower is not controlled properly and the fouling species, the di-olefins, are allowed to be present in the reboiler, fouling will occur. This can happen by under loading the tower and reducing tray efficiency.

For a tray operation to be efficient there needs to be 70 % of the design vapour and liquid loading. What often happens on the Debutanizer is that feed rate might be 60 % of the design rate. The operations personnel tend to match the reflux rate to the feed rate, not understating that a low feed rate needs increased reflux needs to meet this 70 % efficiency requirement.

As the tray efficiency decreases, the fouling species travels down the column and fouls the trays and reboiler. The tray efficiency guideline is important to review during start up and low feed rate scenarios.

Monitor the tower bottoms' chemical treatment during startup and other non-routine scenarios to insure the higher temperature of the tower bottoms is protected from fouling during these events.

#### Styrene applications

Styrene monomer (SM) is the fourth largest chemical produced on an industrial scale and most ethylbenzene is utilised in styrene monomer production. The largest chemical produced on an industrial scale is ammonia for fertiliser production, followed by crude oil refining, and then ethylene by furnace pyrolysis. Styrene monomer has been manufactured commercially for more than 50 years with advances in the key unit operation areas of reactor design and distillation.

Styrene monomer (SM) is an important petrochemical used in the production of polystyrene and other styrenic resins such as acrylonitrile butadiene styrene (ABS) and styrene acrylonitrile (SAN). Ethylbenzene (EB) is produced primarily by alkylation of benzene with ethylene. EB is then converted to SM by dehydrogenation.

#### Radial bed reactor overview

The feedstock, ethylbenzene, is catalytically dehydrogenated to styrene in the presence of steam in a fixed bed, radial flow reactor system. The dehydrogenation reaction is favoured by low pressures and is generally conducted under deep vacuum. Toluene, benzene, and some light compounds are formed as by-products. The overall reaction is endothermic with heat supplied by steam in the adiabatic reactors. Reactor effluent waste heat is recovered through heat exchange with combined feed and by generating steam which is utilised in the process.

The off gas stream is compressed, processed through the off gas recovery section, and used as fuel in the steam super heater. The condensates from the condenser and off gas recovery section flow into the separator where hydrocarbon and water phases separate. The dehydrogenated mixture is fractionated to recover the styrene monomer product and recycle ethylbenzene, as well as benzene and toluene by-products. Inhibitors are added to prevent styrene polymerisation in the process equipment. The energy needed for the reaction is supplied by superheated steam (at about 720 °C) that is injected into a vertically mounted fixed bed catalytic reactor with vapourised ethylbenzene. The catalyst is iron oxide-based and contains  $Cr_2O_3$  and a potassium compound (KOH or  $K_2CO_3$ ) which act as reaction promoters. Typically, 2,5-3 kg steam is required for each kilogram of ethylbenzene to ensure sufficiently high temperatures throughout the reactor. The superheated steam supplies the necessary reaction temperature of 550-620 °C throughout the reactor. The ethylbenzene conversion is typically 60-65 %. Styrene selectivity is greater than 90 %. The three significant byproducts are toluene, benzene, and hydrogen.

#### Styrene distillation overview

After the reaction, the products are cooled rapidly (perhaps even quenched) to prevent polymerisation. The product stream (containing styrene, toluene, benzene, and unreacted ethylbenzene) is fractionally condensed after the hydrogen is flashed from the stream. The hydrogen from the reaction is used as fuel to heat the steam (boiler fuel).

After adding a polymerisation inhibitor, the styrene is vacuum-distilled in a series of four or five columns (often times packed columns) to reach the required 99,8 % purity. The separation is difficult due to the similar boiling points of styrene and ethylbenzene. Typical capacity per plant ranges from 70 000 to 100 000 metric tonnes per year in each reactor and most plants contain multiple reactors or units.

#### EB / SM splitter column

The purpose of an ethyl benzene (EB)/styrene splitter is to separate ethyl benzene from styrene. The distillate EB is recycled to styrene reactors and the bottom product Styrene Monomer (SM) is sent to the styrene Finishing Column for heavy key removal. The EB impurity in the SM should be in the range of  $100 \sim 500$  ppm.

EB/SM Splitters are operated under vacuum due to the polymerisation potential of styrene at elevated temperature. Polymers are undesirable in the monomer distillation column and can lead to plugging of distributors or packing and unit outages.

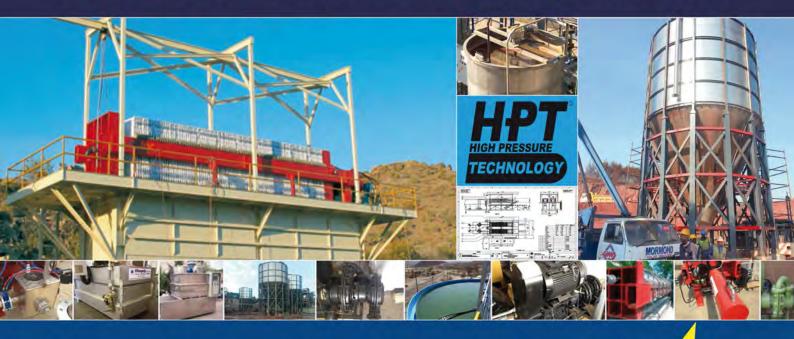
The rate of polymerisation is directly proportional to time and increases exponentially with temperature. Both residence time and temperate must be minimised to reduce polymerisation deposits. The current guideline is to keep the tower bottoms temperature below 120 °C.

Generally steam ejector systems are used to maintain vacuum at the top of the tower. The typical column top pressure is 100 to 400 mbar and the internals are carefully designed to reduce the tower overall pressure drop, minimise liquid hold up, reduce the bottom temperature and residence time. Some producers are increasing the tower pressure due to improvements in inhibitor formulations. This can increase capacity and improve heat recovery.

Many trayed towers have been upgraded to structured packing due to the polymer formation.

For Styrene Monomer (SM) distillation there are at least three types of chemical treatments that are utilised normally together with synergy. The first is a commodity chemical which is base-loaded into the distillation towers and can be

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60 month Capital lease finance available on all plant and equipment as well as Maintain & Operate Agreements recycled to reduce cost. Along with the commodity chemical are specialty chemicals which are anti-polymers and retarders. The three components will need to be balanced to attain synergy, maximum styrene production while maintaining the lowest treatment cost.

The challenge of commodity chemicals is the environmental and safety concerns. One of the first and still widely utilised low temperature commodity chemical inhibitors is TBC (tertiary-butyl catechol). TBC may cause permanent tissue damage. It is a low temperature inhibitor that is added to the overhead of the column, in styrene storage tanks and during shipment.

Several high temperature commodity chemicals exist and function as retarders such as dinitrophenols, phenylenediamine, and hydroxylamines. They include DNP (Di-Nitrophenolic), DNBP (2-Sec-butyl- 4,6-dinnitrophenol), DNPC, and dinitrocresol (DNC) compounds, which again have environmental and safety concerns, but they are less than TBC. A challenge of the nitrogen-based inhibitors is that the tar residual is sometimes burned as fuel. These nitrogenbased inhibitors can produce Nox as they are combusted.

DNBP may be one of the preferred commodity chemicals. In one application with DNPC the pH in the overhead of the column was lowered and some polymer was found cross linked in the tower bottoms.

The retarder acts as a safety net for an extended tower outage. Retarders have slower reaction rates to inhibit the polymerisation. They react at 10<sup>3</sup> to 10<sup>5</sup> ranges providing extended protection during power failures. The retarder can be recycled for extended usage. A normal retarder dosage

might be to maintain 400 to 600 ppm in the recycle stream.

True inhibitors have very fast reaction rates to inhibit the polymerisation rates. An example would be nitroxyl stable free radical. A true inhibitor tends to react in the 10<sup>7</sup> to 10<sup>8</sup> ranges and typically only provides a few hours of protection.

The polymer concentrations are monitored in each of the last three fouling towers. The EB Recycle Column might be targeted to be at 1 500 ppm polymer, while the SM Column might be targeted at 2,5 % polymer, and the Finishing Column might be targeted at 10 % polymer.

#### Conclusions

Proper chemical treatment in distillation systems involves understanding distillation principles such as residence time, internal vapour and liquid flows, reboiler design and the chemistry of the process.

Economics of chemical treatments and other engineering projects are very important and should be calculated for each application and project. Sometimes the actual calculation will surprise you by being not what you expect.

A successful application of chemical treatment must include how the chemical is added to the process and potentially removed. Chemical treatments need to be reviewed on several levels including corrosion or fouling abatement within economic and environmental constraints.

#### References

References for this article are available from the editor at chemtech@crown.co.za.

#### Filcon Filters introduces new line of gas coalescer elements

Filcon Filters, one of the leading liquid filtration companies in South Africa and the sole agent/ distributor of the products from FTC (Filtration Technology Corporation of Houston, USA) has announced the introduction of a new line of gas coalescence elements which have been especially engineered to provide the most costeffective high efficiency liquid coalescence of gas streams on the market.

The introduction of proprietary interception, coalescence and drainage layers pleated in conjunction with high efficiency micro-fibre media, ensures highest efficiency separation of sub-micron liquid aerosols from gas streams while minimising fluid carry-over.

These elements, available in 0,1 and 0,3 micron in both 99,0 % and 99,98 % efficiencies in four different sizes are the answer for removal of unwanted liquid contaminants such as amines, glycols, solvents, compressor lubrication oils, water, hydrocarbon condensates and other liquid phase contaminants.

Filcon Filters was established in June 2000 and has offices in both Johannesburg and Cape Town. In addition to representing a number of international filtration product manufacturers, Filcon Filters has a wide range of



filtration products manufactured to its design in Johannesburg. This range includes the Dirt Gobbla (a centrifugal separator), back flushing automatic strainers, in-line basket strainers, purge strainers, and bag and cartridge housings. Filcon Filters prides itself on the number of years of filtration experience that the technical members have which enables the company to provide the clearest solutions to filtration needs and problems.

If you would like more information about the topic, or to schedule an interview with Vernon Clarke (Technical Director), please call Tony Henfrey on tel: +27 21 702 0979 or email tony@ filconfilters.co.za.



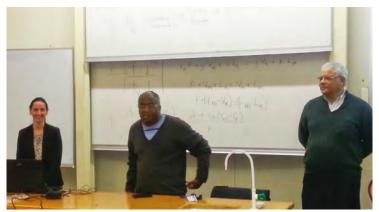
Written by Hamied on behalf of the Western Cape Branch



Lisa presenting Hamied Mazema (Western Cape Chairman) with his new membership certificate and membership card.

#### SAIChE IChemE Western Cape Branch News IChemE visit to Cape Town

Lisa Mc Donald (IChemE) recently gave a presentation to students from universities in the Western Cape region which teach chemical engineering. Her presentation outlined the roadmap from student to the highest professional grade. She also outlined everything SAIChE-IChemE has to offer its members. The presentation received an overwhelming enthusiastic response as a student chapter had already been established and launched on October 1, 2015.



Lisa presenting to students in the presence of Prof Daniel Ikhu -Omoregbe (Head of Chemical Engineering at Cape Peninsula University of Technology) and Hamied Mazema (Western Cape Chairman).



Students attending the presentation



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#### A big bioreactor breakthrough

When Trelleborg Sealing Solutions wanted to break into the highly innovative life sciences industry, the company sought ways to position itself as a provider of engineered solutions. Peter Krass, Key Account Manager at Trelleborg Sealing Solutions explains: "We were looking for demanding projects where we could show that by partnering with us, customers could get a wide range of products and tailor-made solutions from a single source, tapping into our global network." A lucky break came in 2009 when Sartorius Stedim Biotech, a leading international supplier to the biopharmaceutical industry, was scaling up its portfolio of disposable bags for single-use bioreactors to meet market demand. The project required developing a 2 000-litre bag - a huge challenge that dramatically increased the component requirements. There was massive torque applied to the stirrer inside the bag, and the drive coupling had to withstand very high forces. There were also very strict cleanliness demands. Sartorius already had some basic ideas and was more or less looking for sealing support when it became clear that their ideas would not suffice. "At the time, we only supplied some standard parts and did not have a very strong partnership," Krass says. "When we learned about their needs, we arranged a demonstration to show what we could offer." It had all started with a seal, but the Trelleborg concept encompassed an entire assembly, featuring a radial magnetic coupling, designed specifically according to client specifications. Based on the Trelleborg concept, a project team was put to-

gether that pooled expertise from the two companies and spanned three countries. The magnetic coupling was developed by Trelleborg Sealing Solutions in Colorado while engineering was undertaken in Trelleborg Sealing Solutions in Stuttgart, Germany, and the bag was produced at the Sartorius site in Aubagne, France. The resulting coupling design, the Biostat STR 2000L, was launched in May 2014 and the bags in January 2015. The bioreactor bag project has opened the door to more collaboration, and new projects have already started within the bioreactor segment as well as with other



Trelleborg concept encompasses an entire assembly, featuring a radial magnetic coupling, designed specifically according to client specifications.

Sartorius business units. Sartorius Stedim Biotech's 2 000 litre disposable bioreactor bag features a radial magnetic coupling using an assembly of special Durobal® and a housing of Zurcon® polyethylene welded to the bag. Durobal bearings are ideal in rotating applications, preventing metal-to-metal contact and offering low friction. They are self-lubricating for cleaner operating environments. Zurcon engineered plastic-based materials provide low friction, making them ideal for reciprocating, very slow rotating and oscillating applications that require high wear resistance.

For more information go to news@trelleborg.com.



Sartorius Stedim Biotech is a leading international supplier of integrated solutions for the biopharmaceutical industry, including fermentation, cell cultivation, filtration and purification.

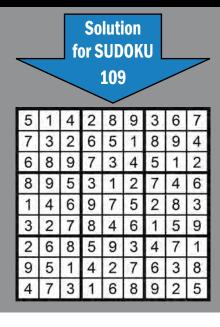
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SUDOKU NO. 110

Complete the grid so that every row across, every column down and every 3x3 box is filled with the numbers 1 to 9. That's all there is to it! No mathematics are involved. The grid has numbers, but nothing has to add up to anything else. You solve the puzzle with reasoning and logic. For an introduction to Sudoku see http:// en.wikipedia.org/ wiki/Sudoku

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