ON THE BEAM

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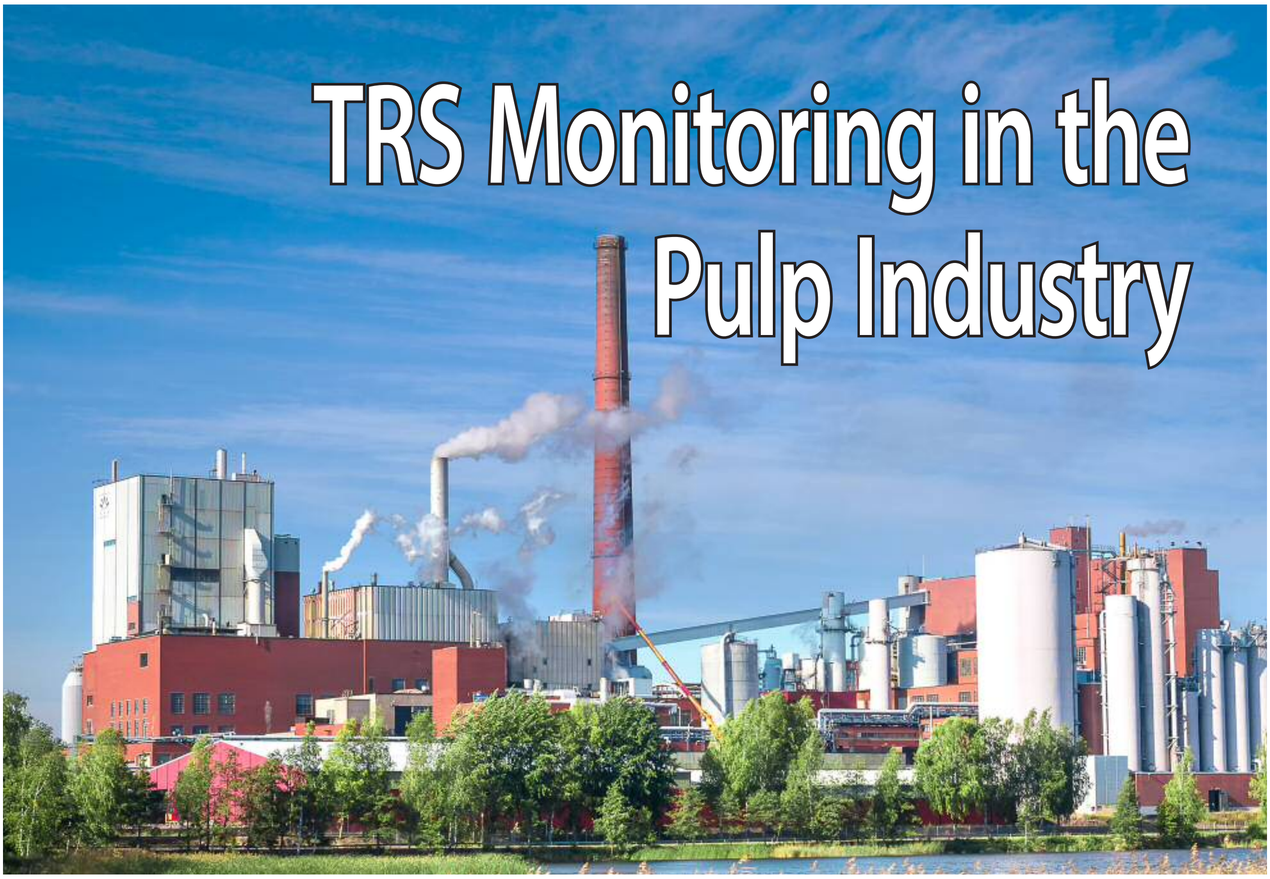

"The smell of money" is something you may hear close to a pulp production facility, but to be honest, the odour is not pleasant. However, modern technology and modern emissions monitoring mean that the smell and the emissions in general are becoming less of a problem for the industry.

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TRS Monitoring in the

The regulations on emissions from a pulp production facility are similar to those of a power plant. However, special attention is also given to some odour-generating compounds.

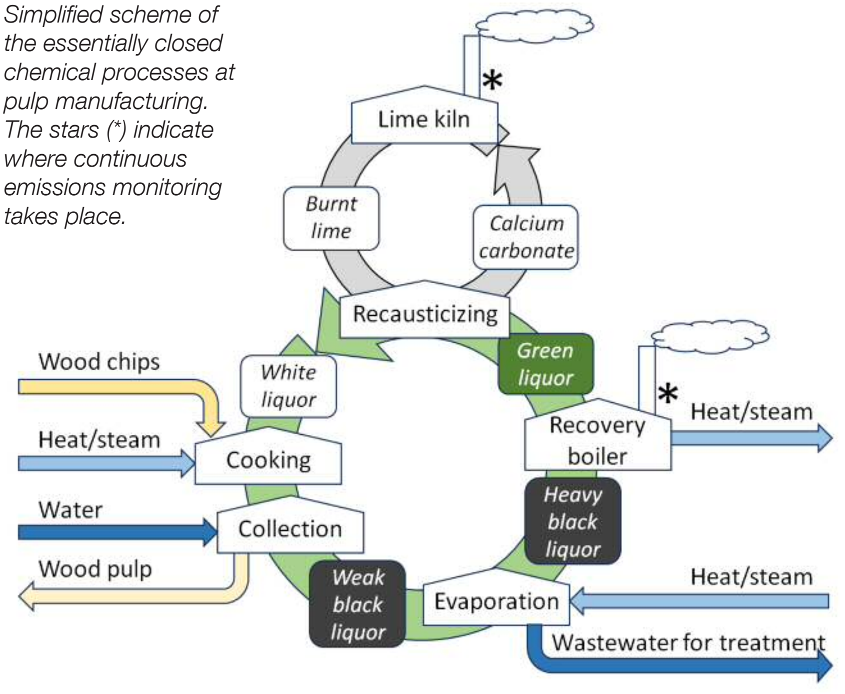
The smell associated with pulp production originates from different sulfur compounds. The most well-known is probably hydrogen sulfide, H_2S (H-S-H) but there are also compounds like methyl mercaptan (CH_3-S-H), dimethyl sulfide (CH_3-S-CH_3), and dimethyl disulfide (CH_3-S-S-CH_3). These four substances are collectively referred to as "total reduced sulfur", TRS. Emissions of TRS together with the usual combustion gases SO_2 and NO_X (NO and NO_2) are regulated and often monitored continuously at pulp production facilities. TRS emissions are regulated not the least to prevent odours from reaching the surroundings.

Paper Production

Paper might be through of as a consumable, but the production requires large, complicated, and resource intensive industrial processes and a certain respect for the product is commendable.

The production process starts with pulp wood. This is turned into wood chips, mixed with chemicals, and boiled. This separates the cellulose fibres from the lignin and other materials. The cellulose is caught and aggregated to pulp. The pulp is then forwarded to the actual paper production where it can be further treated to give the paper the desired properties. Subsequent pressing and drying forms the final paper products.

Simplified scheme of the essentially closed chemical processes at pulp manufacturing. The stars (*) indicate where continuous emissions monitoring takes place.



Quite often, the pulp and paper production facilities are co-located but there are also pulp industries without paper production and paper producers receiving pulp or other raw material from sub-suppliers. This article focusses on the pulp production since that is where most of the emissions to air occur.

Pulp Beyond Fiction

Let's turn back to the process stage where the cellulose is extracted. Nowadays, the dominating method for this is the sulfate process, also known as the kraft process after the German word for "strong" (the inventor of the process was German) and the fact that it produces strong fibres. The active chemicals are essentially a mixture of sodium sulfide (Na_2S) and sodium hydroxide (NaOH), known as white liquor. The chemicals are consumed in high volumes, several cubic metres of white liquor are required to produce one tonne of dry pulp, and it's not unusual to find production rates in the range of a thousand tonnes of pulp per day. The chemicals must therefore be recycled both for cost and environmental reasons, and several of the process steps at a pulp mill is about this recycling.

What remains after extraction of the cellulose is a mixture of water, sodium compounds, and other chemicals known as black liquor. Most of the sulfur from the sodium sulfide has been oxidised to sodium sulfate (Na_2SO_4) and the remaining sodium mostly appear as sodium carbonate (Na_2CO_3) in the black liquor. The first step in the recovery process is evaporation where water is separated from the black liquor in a series of heat exchangers. The solids content goes from about 20 % to some 70-80 % solids. The remaining heavy black liquor and specifically its organic content is then used

Pulp Industry

By: Bengt Löfstedt

as fuel in a so-called recovery boiler which sits at the heart of the mill's large heat and power plant. An output power of several hundred megawatts is not unusual. Other than the supply of wood, a pulp mill can be self-sufficient when it comes to heat (steam) and electricity, and there can be excess power to provide to for example district heating networks in surrounding cities.

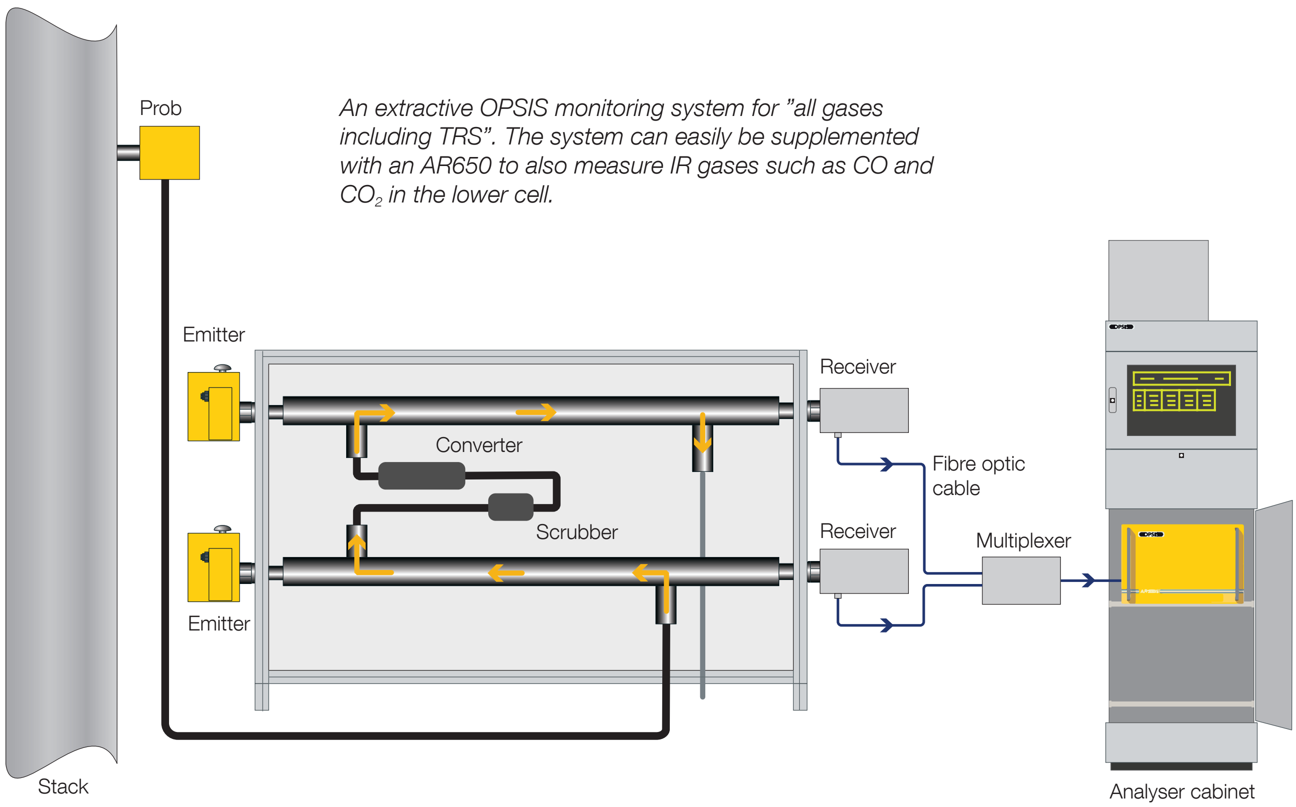
Chemical Recovery

The recovery boiler takes care of the residuals from the wood chips and produces energy for the processes, but it also plays a central role in the recovery of the chemicals. In the boiler, there is a reaction between sodium sulfate (Na_2SO_4) and coal which restores the original sodium sulfide (Na_2S). The resulting mixture of sodium sulfide and sodium carbonate is called green liquor. By adding calcium hydroxide ($Ca(OH)_2$, slaked lime) the sodium carbonate is converted back to sodium hydroxide (NaOH) in a process called recausticizing, also resulting in calcium carbonate. The white liquor is thereby restored and can again be used to extract the cellulose from the wood chips.

What now remains is to figure out how to source the slaked lime and what to do with the resulting calcium carbonate ($CaCO_3$). The answer is perhaps a bit surprisingly "cement production". The calcium carbonate is fed into a rotating lime kiln of the same type used at cement plants. This generates burnt lime, CaO, which then is converted to slaked lime by reaction with the water in the green liquor. This closes the process steps involving calcium too.

Water is also circulated in the processes as condensate is fed back into the production, but there is also a need to add fresh water to the process, primarily to wash the fibres before collection. Pulp industries are therefore located close to rivers or other water streams. Before the excess wastewater can be returned to the stream, it goes through an extensive treatment process. A pulp production plant therefore not only hosts a power plant and a cement kiln but also a wastewater treatment facility. You must be versatile if you want to produce pulp!

TRS can occur as a side product in several process steps, but as far as possible, the gases are normally collected and led into the recovery boiler where they are dissociated by incineration. The



An extractive OPSIS monitoring system for "all gases including TRS". The system can easily be supplemented with an AR650 to also measure IR gases such as CO and CO_2 in the lower cell.

odours from TRS can thereby be prevented or at least notably reduced. A separate TRS burner can be standby to take care of the TRS gases if the recovery boiler temporarily goes off-line.

Regulations on Emissions Monitoring

Within the European Union, the emissions from most industries are controlled by the Industrial Emissions Directive, the IED. This applies also to the pulp and paper industry. Here, the specific requirements on monitoring and emission limits are found in the "PP-BATC", which reads out as "best available technique conclusions for the production of pulp, paper, and board".

When it comes to the recovery boiler, there are requirements on continuous emissions monitoring (CEM) of at least NO_X, SO_2, and TRS, and in some cases also of dust. This may also apply to the lime kiln and to any separate TRS burner.

TRS can still be emitted despite incineration efforts, primarily through diffuse leaks. In addition to generating unpleasant odours, TRS is also harmful and in worst case lethal in high concentrations. Monitoring of TRS (primarily H_2S) may therefore also be done in the ambient air, as a matter of occupational health and safety.

Service technician Anders Hinders from OPSIS takes a closer look at the probe mounted on the flue gas duct.

The EX060-DTRS (see article in On the Beam No. 3, 2023), the central part of a TRS monitoring system with dual cells.

The OPSIS TRS Monitor

OPSIS has supplied the industry with CEM systems for many years. OPSIS nowadays also offers a specific CEM system for TRS. In combination with knowledge from system installations at both power plants and cement industries, OPSIS is therefore a natural choice of system supplier also to the pulp production industry.

As already noted, TRS is the name of a group of molecules whereof some are relatively complex. TRS can therefore not be measured directly ("in situ") using the proven OPSIS open-path DOAS technique (DOAS = differential optical absorption spectroscopy). Instead, the OPSIS TRS monitoring system is based on extraction of a relatively small flow of flue gas from the duct. In a first step, all SO_2 is removed from the gas mixture using a selective scrubber. In a second step, all remaining sulfur compounds, effectively TRS, are transformed into new SO_2 by means of a high-temperature converter. By monitoring the resulting SO_2 concentration, which is straight-forward using the DOAS technique, the TRS concentration expressed as sulfur can be established.

In the basic configuration, a TRS monitoring system from OPSIS has a single measurement cell and an AR600 gas analyser to measure the SO_2 concentration. However, in many cases, also other types of pollutants should be monitored. The basic system is then supplemented with a second measurement cell, resulting in a cost-efficient monitoring solution with low maintenance needs. The extracted flue gas is first lead into a measurement cell where the concentrations of typically NO, NO_2, and "true" SO_2 are measured using the AR600 analyser. The gas mixture then passes the scrubber and converter and is lead into a second measurement cell where the TRS concentration is measured as already described.

OPSIS also offers CEM systems monitoring H_2S only. H_2S is a molecule not very suitable to be monitored using the DOAS technique. It can be done in the IR part of the spectrum, but then only in high concentrations. However, by converting the H_2S molecules into another compound with the help of a patented technology, it is possible to also measure very low levels of H_2S concentrations with high precision. Measurements of both TRS, H_2S, and other gas concentrations can be achieved by applying a combination of measurement cells, converters, and scrubbers in a single monitoring system.

TRS Calibration

A gas calibration of a system monitoring the concentrations of both TRS and other gases is primarily made as usual, that is by feeding the first measurement cell with gas mixtures containing known levels of for example NO, NO_2, and SO_2, and then checking what the analyser reports. When SO_2 is supplied, it is also possible to check the efficiency of the SO_2 scrubber by measuring TRS (effectively SO_2) in the second cell. The reported TRS concentration should be zero since all SO_2 should be caught by the scrubber.

The SO_2 scrubber and the TRS converter between the two measurement cells. Note the red glow from the hot converter!

TRS is calibrated by feeding a known concentration of H_2S mixed with oxygen to the cells. The oxygen is required for the TRS converter to work. During measurements on the regular flue gas, the oxygen present in that gas is more than sufficient for the conversion. However, when calibrating with pure H_2S, the oxygen must be added deliberately. The H_2S molecules pass the first cell and the SO_2 converter unaffected but are oxidized to SO_2 in the TRS converter thanks to the oxygen. The reported TRS concentration (as sulfur in SO_2) in the second measurement cell should match the sulfur content in the H_2S gas mixture.

Sales manager Robert Törnblom from OPSIS checks the measurement results.

Experiences from Operation

The TRS systems OPSIS has delivered so far have in all cases been of the type also monitoring other gases and therefore having dual measurement cells. The systems have not yet been in practical operation for any extensive time, but they have so far worked just as expected. We look forward to new orders and deliveries with confidence.