SPECIAL ONLINE ANALYSIS OF NH₄ required by new method for nitrogen elimination

By Dr. Volker Koschay and Hans-Peter Mascha

Conventional methods of waste water treatment at municipal plants include the treatment of process waste water from the sludge processing in the main flow of the clarification plant. Supernatants and mud liquids lead to a significant increase in nitrogen contamination. The waste water from sludge processing often shows an NH₄-N concentration of 1000 mg/l and more. This increases the total N discharge values in a waste water treatment plant (WWTP).

As regards the German WWTP Landshut, the combined treatment of both the municipal waste water and the discontinuously accumulating process water from sludge processing in the plant would have required the enlargement of the nitrification volume due to high NH_4 peak loads. In order to fullfill the legal requirements of 13 ppm total Nitrogen at the outlet of the plant, this would have involved building costs in the order of 30 million Euros for WWTP Landshut, which was built for 270.000 inhabitants.

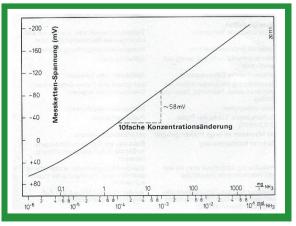
Therefore, the operators tested a new method with regard to the treatment of partial flows of process water from sludge processing which, in the meantime, has been patented as "Terra-N – method".

"Terra-N-method" for the treatment of partial flows

The "Terra-N-method" includes the conventional treatment of municipal waste water supplied to the WWTP: Preclarification, activation, final clarification. At first, however, the highly contaminated waste water from the sludge processing goes through the process stages described in Illustration 2, before being supplied to the denitrification stage of the WWTP. This procedure enables the degradation of more than 90% of the ammonium in the process



Figure 1: AMMONO-FIX online analyser at the WWTP Landshut



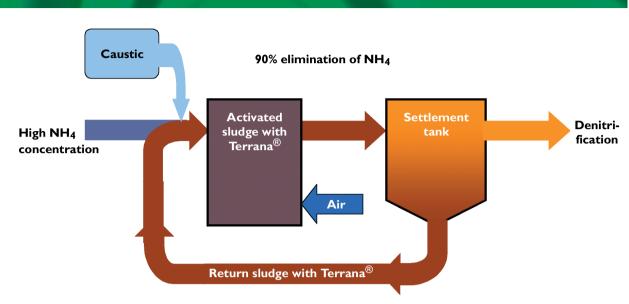


Figure 2: Process description of the "Terra-N-method" for the partial flow treatment of process waste water from the sludge treatment

water. As regards the "Terra-N-method", a loading rate may be obtained which achieves 5 -10 times normal activation, due to the specific carrier material for the nitric bacteria.

In order to optimise nitrogen elimination in the biological stage of the "Terra-N-method", it is imperative to monitor the purification process by means of continuous measurement. As for this application, the online measurement of the parameter ammonium in both the inlet and outlet of the partial flow treatment has proven successful. The ammonium analyser to be employed had to meet particular requirements.

Selection of the suitable measuring principle

With respect to the measuring range of above 1000 mg/l NH_4 -N, which was unusual in the field of waste water technology until now, the attention must focus on the selection of an online analyser with a suitable measuring principle, as this determines the maximum possible measuring range. Basically, two different measuring methods are applied in the field of waste water technology for the determination of the NH_4 concentration:

- Gas-sensitive NH₃ electrodes (potentiometric measuring method)
- Photometric measuring method

Photometric measurement

During photometric ammonium determination, the NH_4^+ ions are converted into a colour complex. Absorption of the blue-coloured solution in a photometer is a measure for the NH_4 concentration of the sample. As for the photometric measuring principle, measuring ranges of up to a max. of 100 mg/l NH_4 -N for the undiluted sample may only be covered. The measuring ranges of established brands of online analysers are even lower. Ammonium values above 1000 mg/l NH₄-N may not, therefore be measured directly by means of photometrically working analysers. As regards photometric analysis systems, this high measuring range could only be covered by dilution of the sample to be measured. However, the dilution factor would be 10:1 at least. As dilutions of this degree lead to significant distortions in the measurement values, and dilution devices are very costly, photometrically working analysers may not be employed for the high-load biology at issue at the WWTP Landshut.

Measurement using gas-sensitive electrodes

An analyser which measures NH₄ using gassensitive electrodes is AMMONO-FIX of GIMAT Umweltmesstechnik from Polling, Germany. For the potentiometric measurement of NH_4 , the pHdependant equilibrium between $\mathsf{NH}_4^{\scriptscriptstyle+}$ ions and gaseous NH_3 is used. At pH values above 9, the NH_4^+ ions dissolved in the sample convert into gaseous ammonia (NH₃). NH₃ diffuses through a specific gas-sensitive membrane and evokes a change in the pH value inside the electrode. As the electrolyte is sensitive to NH3, this change in the pH value is proportional to the NH₄-N concentration in the sample. Therefore, the potentiometric measurement of NH_4 is, in the end, a measurement of the pH value. By analogy with that, the logarithmic-linear characteristic curve of NH₃ electrodes (Illustration 3) enables the measurement of ammonium concentrations in the range of I to 2000 mg/I NH_4 -N using one and the same electrode. For this reason, measurement with gas-sensitive electrodes represents the sole applicable measuring principle for high-load biology in plants working "Terra-N-method". After extensive tests, the operators of the WWTP Landshut decided to employ the AMMONO-FIX. With this analyser it is even able to cover a maximum measuring range of 2000 mg/l NH₄-N. After almost three years of operation, it turned out that, besides measuring accuracy, the online analyser also meets all further-reaching requirements such as reliability, maintainability and low operating costs. Thus, the GIMAT analyser decisively contributes to process reliability as well as to the process-related optimised operating mode of the "Terra-N-method".

Figure 3: Logarithmic-linear correlation between NH₃ concentration and electrode voltage of the gas-sensitive GIMAT electrode

IET March/April 2004

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