

AZV Breisgauer Bucht (Breisgau Bay wastewater association): Optimisation of CaCO₃ dosing with continuous alkalinity measurement

Background

Very soft water as well as heavy rainfall events occurring as a result of elevated topography in the plant's catchment area lead to a low acid capacity of the influent. Limit-related dosing of large amounts of acid precipitant, as well as a low availability of carbon for de-nitrification, further impair the acid capacity.

Solution

A Hach® EZ4000 series titrimetric online alkalinity analyser was installed first in the primary sedimentation effluent after pre-precipitation and then in the activated sludge stage effluent. The tests have shown that the measurement of alkalinity in the activated sludge effluent, taking into account the influent volume, is ideal as a control variable for the CaCO₃ dosage.

Benefits

Implementing the alkalinity analyser and dosing of Omya Optical based on the alkalinity deficit makes wastewater treatment plant operations less vulnerable to the fluctuating hydraulic loads and allows for a more targeted CaCO₃ consumption with savings of up to 30%.



Fig. 1: Aerial view of AZV Breisgauer Bucht from the AZV Annual Report 2019

Annual key figures

Parameter	Unit
TOC	6.3 mg/L
NH ₄ -N	0.09 mg/L
N _{inorg}	9.7 mg/L
P _{total}	0.21 mg/L
Performance when breaking down substances	
TOC	96.0%
N _{total} (N _{inorg} + N _{org})	79.4%
P _{total}	94.4%

Tab. 1: Performance 2020-figures for AZV Breisgauer Bucht acc. to the German Association for Water, Wastewater and Waste.

Introduction

Due to the catchment area and the diverse and large number of indirect dischargers, the sewage treatment plant's influent has a high nitrogen content. The annual average for the total nitrogen concentration here is 55 mg/L. Nevertheless, strict limits are imposed on the plant, as it discharges into an ecologically sensitive body of water. The annual values achieved by the treatment plant can be found in Tab. 1. Due to the very soft water, as well as heavy rainfall events in the catchment area of the wastewater treatment plant, monitoring of the acid capacity parameter was an essential component in optimising nitrification. The wastewater here does not have a sufficiently high acid capacity, which can lead to a drop in the pH value

below 7.0, as the nitrifying bacteria produced acid. In this pH range, however, both the nitrification and oxygen utilisation rates and flocculation are impaired. The high amounts of acidic precipitant added to maintain the very low P_{total} limit in the wastewater treatment plant effluent also have a negative influence on the acid capacity. The following application report discusses the tests carried out on-site to define a strategy for dosing CaCO₃ based on an acid capacity measurement.

Acid capacity as a measure of buffer capacity

The acid capacity is a measure of the buffer capacity, i.e. the pH value stability of the water compared to acids introduced or formed in the water. The acid formation associated with nitrification in the activation tank (release of H⁺ ions, see equation 1) leads to a reduction in the pH value. The decomposition of 1 mg NH₄-N consumes 0.14 mmol of acid capacity.

Equation 1: $2 \text{NH}_4^+ + 4 \text{O}_2 \rightarrow 2 \text{NO}_3^- + 4 \text{H}^+ + 2 \text{H}_2\text{O}$

If the nitric acid produced during nitrification is not immediately bound by buffer substances in the wastewater, the pH value quickly drops to values below 7.0. Since the optimal pH range for the nitrificants is 7.5 - 8.5, when the pH value falls, the nitrification slowly but surely comes to a standstill. In water with a low acid capacity, such as the Forchheim wastewater treatment plant, the pH value would regularly fall below 6.5 without the addition of a buffer substance. This would severely impair the rate of nitrogen degradation. If the pH value falls below the mentioned range, this leads to a decrease in the efficiency of the nitrificants. The use of oxygen and the formation of sludge flakes are then severely impaired. The addition of carbonates or basic substances becomes necessary. If 1.0 mg/L of NH₄-N is converted into NO₃-N, 7.1 mg/L of alkalinity are consumed for this. De-nitrification in turn recovers 3.6 mg/L of alkalinity. Phosphorus elimination also has a negative effect on alkalinity. The overall result is always negative (see Tab. 2).

Process	Change in alkalinity [mg/L]	Per mg/L
Ammonification of organic nitrogen	+ 3.6	Hydrolysis of organic nitrogen
Nitrification	- 7.1	Ammonia-N oxidation
De-nitrification	+ 3.6	Nitrate-N reduction
Phosphorus elimination	- 5.6	Addition of aluminium
Phosphorus elimination	- 2.7	Addition of iron

Tab. 2: Influence of acid capacity on biological wastewater treatment

Effects of acid capacity on sludge management

If a plant suffers from a lack of acid capacity, this can additionally lead to problems regarding sludge management. Sludge loss often occurs mainly during hydraulic shocks, such as heavy rainfall events or snow melting. If you then look at the activated sludge under the microscope, you will notice that the sludge consists of many small, light flakes. These are carried away even by slight turbulence. Such an unfavourable sludge structure results from the dissolution of calcium carbonate particles from the activated sludge. If there are no compact flakes, filamentous organisms very often grow out and the settling behaviour of the activated sludge deteriorates. Nitrificants in particular like to grow here. Despite this problem, the sludge volume index is often good. Despite a good sludge volume index, there may be a disturbance in the flocculation. In the case of sludge loss, this in turn leads to a considerable loss of nitrificants, and the sludge age decreases.

In combination with an insufficient acid capacity, nitrification may come to a standstill. This effect can be prevented by dosing with calcium carbonate. The Ca/Na ratio should be greater than 0.6. According to the DWA, a residual acid capacity of 1.5 mmol/L should be ensured in the biological stage effluent [1].

Establishing a dosing strategy

For 10 years now, AZV Breisgauer Bucht has been using various CaCO₃ products (also OMYA Optical) to control the alkalinity concentrations in the biological stage. For the operator, simple and safe handling as well as uncritical behaviour in the event of a possible overdose of CaCO₃ are essential characteristics of such products. The product is dosed in powder form into the activation influent, after pre-precipitation. Until now, the control variable was the pH value in the activation influent and effluent.

The pH value is determined by the concentration of the H⁺ ions in the water. If a hydraulic thrust is expected, the aeration is ramped up at an early stage. This leads to increased CO₂ stripping and suggests an increase in the pH value. If this process is controlled via the pH value, this leads to a reduction of the dosing quantity, even though this should be increased at this moment. To avoid this effect, the alkalinity – which is the more independent parameter – should be used as the control variable.



Fig. 2: EZ4004 online titrator from Hach

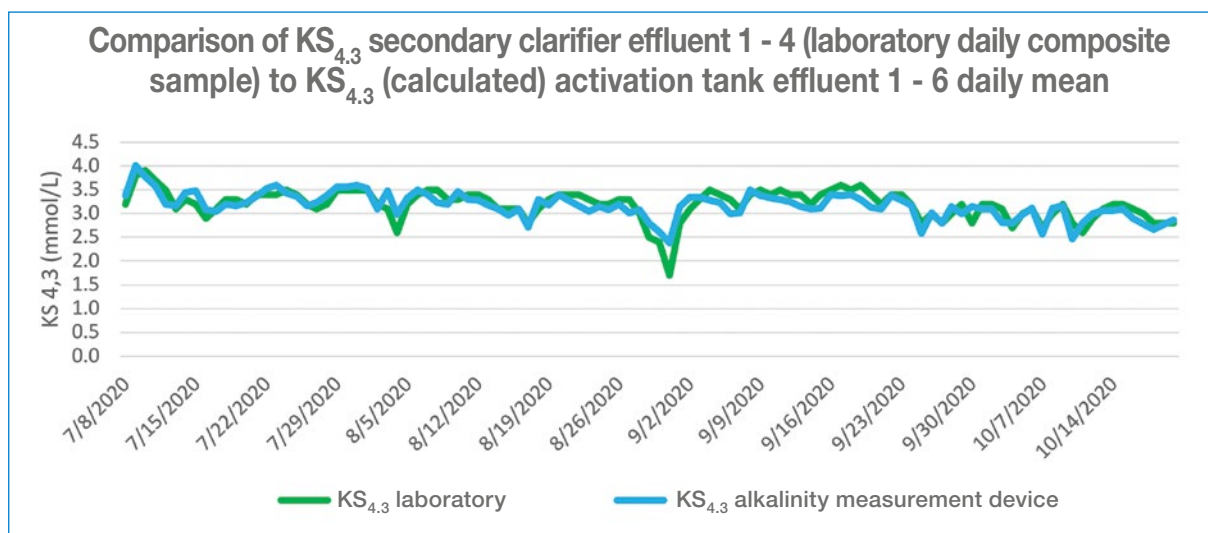


Fig. 3: Comparative measurements of the daily composite sample in the laboratory against the online analyser

Regulation or control?

Due to the very high volumes of the activation and the associated time delay, the EZ series alkalinity analyser was initially placed in the activation influent. The titrator measured the alkalinity of the filtered sample after pre-precipitation. In addition, the consumption of alkalinity in the biology was estimated using continuously measured NH_4-N and NO_3-N values based on the relationships explained above, and the expected alkalinity value in the effluent was predicted.

The $CaCO_3$ dosage was then controlled according to the calculated alkalinity value in the effluent. Alkalinity-guided control has already improved the situation considerably compared to control by means of pH. After the process could be shown in a stable way, an attempt was made to further increase the simplicity and thus the operational reliability. To do this, the analyser was implemented in the activation effluent. The dosing station in the activation influent after pre-precipitation has not been changed. This made it possible to establish effluent-controlled regulation without the need for complex calculations. As mentioned at the beginning, this was the best way to design the process and additionally reduce the $CaCO_3$ consumption by about 30%.

The measurement results were regularly checked by means of a titration in the AZV Breisgauer Bucht laboratory (Fig. 3).

Summary

At AZV Breisgauer Bucht, a number of factors come together that have a negative impact on acid capacity. On the one hand, there is the very soft water with a hardness < 10 dH. On the other hand, there is a rather poor C/N ratio, which has a negative effect on denitrification, which in turn has a negative effect on the acid capacity. Large volumes of mixed water and hydraulic shocks load the system with a lot of rainwater and low acid capacity. Due to very low P_{total} values in the effluent, large quantities of acid precipitants have to be added. The only structurally possible doing point for the calcium carbonate is the return activated sludge pump station. Dosing directly into the nitrification is not possible.

Despite this initial situation, two goals were defined at the beginning. On the one hand, the Ca/Na ratio should be raised to greater than 0.6, which leads to more stable flakes in the activation. This also improves the settling capacity of the activated sludge. In addition, the risk of filamentous organisms forming is reduced. On the other hand, the acid capacity should be adjusted to around 2.5 mmol/L. This corresponds to around 125 mg/L of $CaCO_3$. Due to the aforementioned negative influencing factors, the DWA's recommendation was increased.

Fig. 4 shows an excerpt from the PLC of AZV Breisgauer Bucht. The wastewater treatment plant influent can be seen in purple, the addition of the carbonates in light blue and the measured value of the alkalinity analyser in green. A correlation between rainfall events and a decrease in alkalinity is very clearly recognisable. Despite maximum carbonate dosing, the alkalinity first drops to < 2.0 mmol/L of $CaCO_3$. The reason for this is the hydraulic residence time between the measuring and dosing point and the limited performance of the dosing screw. However, this turned out to be uncritical during operation.

In conclusion, it can be said that by measuring the alkalinity concentration in the biological stage effluent, regulation of the acid capacity, taking into account the wastewater volume, can be implemented very well and very precisely. During heavy rainfall events, short-term downward outliers do occur, but on average the acid capacity could be set relatively stably at 2.9 mmol/L. Furthermore, regulation of the acid capacity via continuous alkalinity measurement enabled great savings to be achieved, which quickly recovers purchase costs.

Case study: EZ alkalinity at a municipal sewage treatment plant

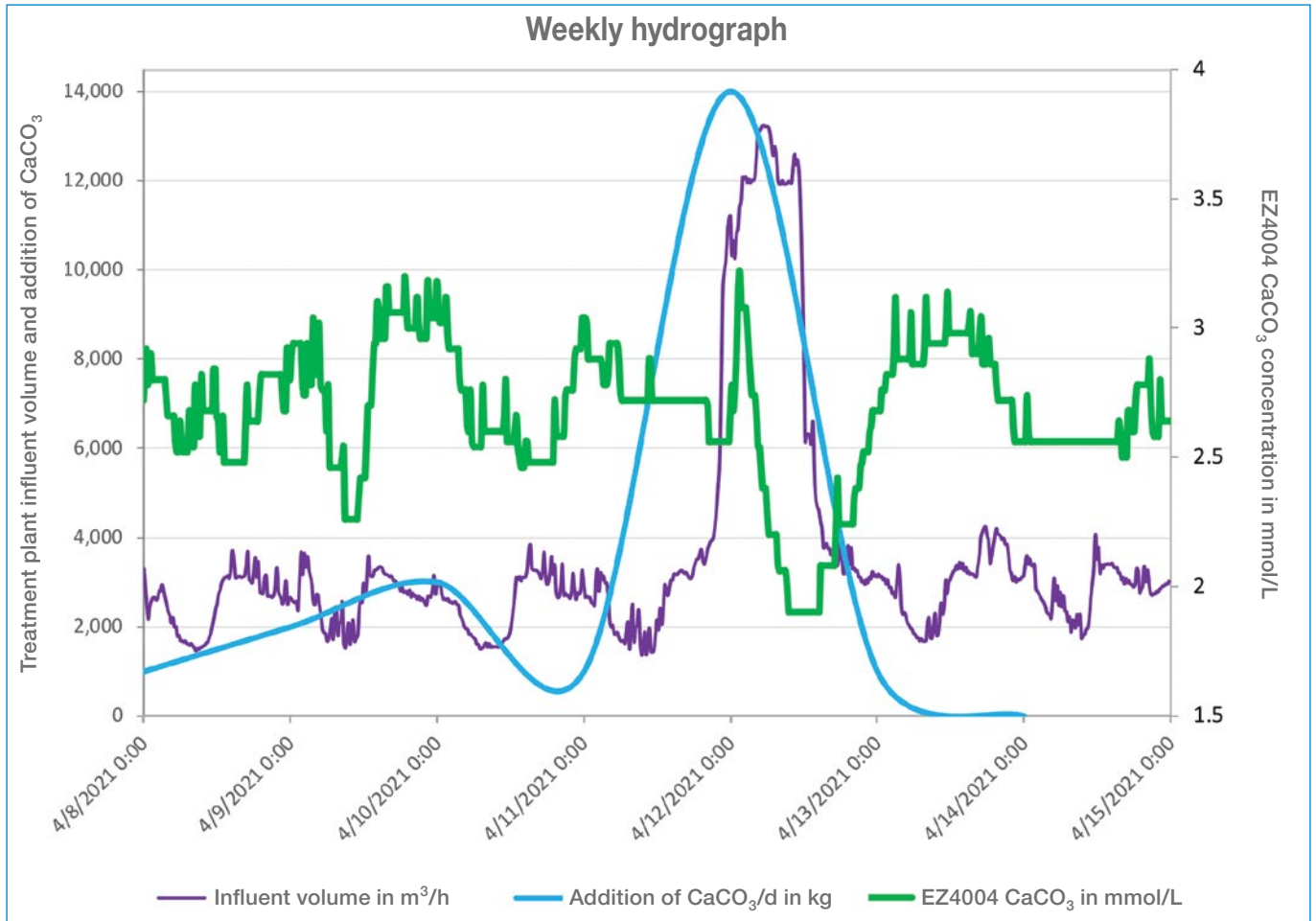


Fig. 4: Representation of a hydraulic shock, excerpt from PLC of AZV Breisgauer Bucht

[1]. (Source: Page 67; https://www.expoval.de/sites/default/files/download/T4-2016_Bemessung_von_Klaeranlagen_in_Klimazonen_Nov_2017.pdf)

Section on OMYA:

Omya International AG Omya is a leading global producer of calcium carbonate and distributor of speciality chemicals.

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