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Nitrification and alkalinity – the basics

This article is all about nitrification in sewage plants and, in particular, the relationship between nitrification and alkalinity. It won't be a detailed treatise on the minutiae of nitrification theory and nor will it be a rigorous explanation of what a nitrifying plant looks like or how one works. What we'll do here is show that basic theory, when applied sensibly, has real, practical benefits to a real, working sewage plant. Readers with an academic interest in the source of the small amount of theory we include here might like to follow that up using the footnotes.

A touch of theory

The term nitrification defines :

"..the biological oxidation of ammonium, with nitrate as the end product"[1]

As we've said, we're not going in to the theory of nitrification in any real detail. It's sufficient for our current purposes to know that nitrification is essentially a two-step reaction. In the first step, ammonium is oxidised to form nitrites by bacteria of the *Nitrosomonas* species. In the second step, bacteria from the *Nitrobacter* family convert nitrites to nitrates.

The stoichiometry of nitrification can be analysed[2] to arrive at some useful and practical figures. Two of the most important are:

4.57 mg O_2 per mg N

7.14 mg $CaCO_3$ per mg N

The figure on the left tells us that oxidising 1 mg of ammoniacal nitrogen requires (theoretically) 4.57 mg of oxygen. The figure on the right shows that oxidising 1 mg of ammoniacal nitrogen *consumes* 7.14mg of alkalinity expressed as calcium carbonate. Bear in mind we're not going in to the complexities of the different types and sources of alkalinity, or the variations in these figures you find in text books and papers. We're keeping it simple for now! That's enough theory for the time being; let's look at how we applied this recently to a working sewage treatment plant.

[1]*Handbook Biological Waste Water Treatment: design and optimisation of activated sludge systems, Adrianus van Haandel and Jeroen van der Lubbe, Quist Publishing, pp. 87, 2007.*
[2]*Ibid., pp. 93.*

A practical example

The site of interest has a small sewage treatment plant serving a commercial premises. The plant has two stages of biological treatment, preceded by a primary tank and followed by a final settling tank. The final treated discharge is pumped to a watercourse

The plant had performed variably for some time. In particular, ammonia removal (i.e. nitrification) was intermittently poor, leading to failures of the site's discharge consent. It was concluded that dosing sodium carbonate would increase the alkalinity and so improve nitrification. Although the correct equipment was installed, it was not used particularly carefully or rigorously. This meant nitrification was still variable and data showed a classic trend whereby the following happens:

- alkalinity is not maintained and pH decreases
- a pH is reached which inhibits nitrification and ammonia removal decreases
- alkalinity begins to increase, which raises pH and hence improves nitrification
- return to step one and repeat

We were asked to develop an operating strategy for the plant. Here's where our simple-but-effective theory comes in.

Alkalinity, pH and carbon dioxide

It is possible to estimate alkalinity if you know the pH and concentration of dissolved carbon dioxide in a sample. The usual caveats about ideal samples and conditions apply but the theory is useful, as we'll see. Here's the equation[3]:

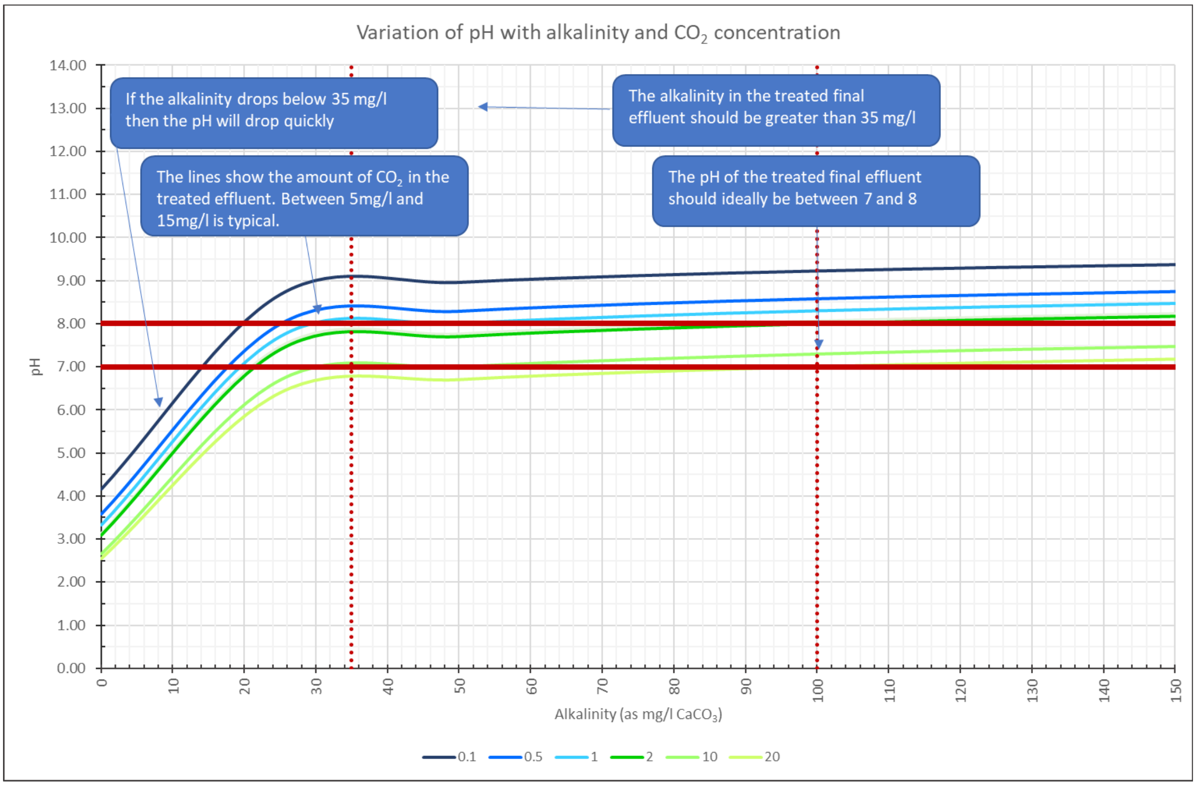
$$\mathrm{Alk} = [\mathrm{CO_2}]10^{\mathrm{pH}-\mathrm{pk}^{*}1}(1 + 2 * 10^{\mathrm{pH}-\mathrm{pk}^{*}2}) + 10^{\mathrm{pH}-\mathrm{pk}^{*}w} - 10^{-\mathrm{pH}}$$

Equation one Relating pH, CO_2 and alkalinity

Dissolved CO_2 isn't something that's measured commonly in treated sewage (I've never seen measurements of it in 20+ years in the water industry). Consequently, equation one is more useful if we make assumptions about the amount of CO_2 and then use it to estimate pH when we know the alkalinity. This is straightforward to do in a spreadsheet using a function such as Goal Seek in Excel®. We end up with a family of curves such as those in graph one.

We've added some notes to the graph. *These are our personal opinion based on our experience*. Each plant is different and the figures we show in graph one should only be taken as guidance and not as definitive rules.

[3] *Ibid., pp 98.*



Graph one How pH varies with CO_2 and alkalinity

You can see that pH decreases rapidly when the alkalinity is less than about 30 mg/l. A good range of pH for nitrification is *generally* between about 7 and 8. Again, many variations of this are possible but we find this range to be conducive to successful nitrification. This range is shown by the solid horizontal red lines. The two vertical dashed red lines show a relatively fixed lower limit for alkalinity (35 mg/l in this case) and an arbitrary upper limit of 100 mg/l. The blue and green coloured lines show the variation of pH for various concentrations of carbon dioxide, with those values shown in the key on the graph in mg/l. This all looks very nice but how can it be used in practice?

A bit of practice

Our client began to take measurements of pH and alkalinity in the treated sewage. We've overlaid these on graph one. Green markers show where the plant complied with its ammonia consent and red show where it failed the consent. It's very clear that, at this particular sewage works, the plant struggles to meet its ammonia consent when the alkalinity in the treated effluent is below around 25 mg/l. When alkalinity in the treated effluent is more than about 35 mg/l then nitrification is much better and the plant is compliant with its consent. We can't show the actual values of ammonia on this graph for reasons of confidentiality but the concentration increases as the alkalinity decreases. This gave the client a simple but well-founded approach for monitoring compliance but how do we set the dose of sodium carbonate to make sure the alkalinity is exactly where we need it to be?

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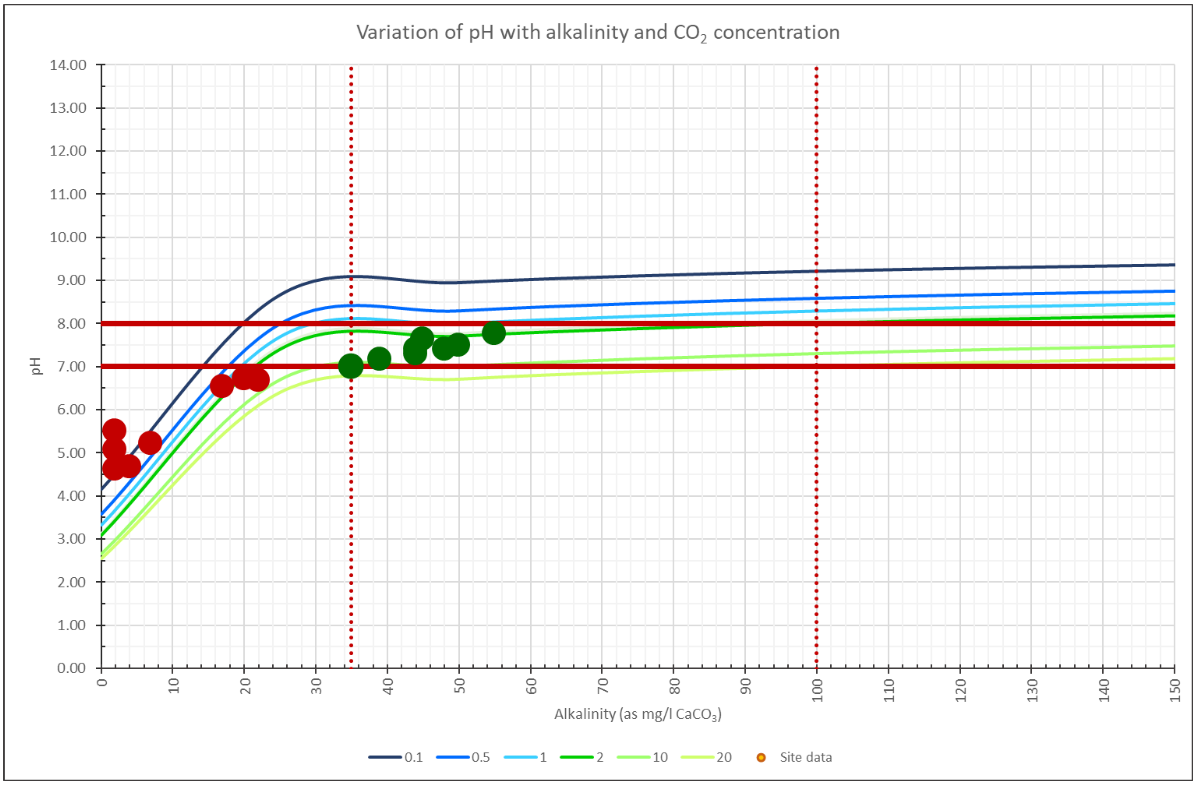


Graph two Our pH-alkalinity-CO_2 curves with real site data overlaid.

Let's go for a swim

We found an excellent article which describes how to calculate the amount of a chemical needed to increase alkalinity by a specified amount. Help can come from the oddest of places and this came from an article about swimming pool maintenance[4].

We won't delve into the stoichiometric calculations but what we find is that if we know the following:

- the volume of wastewater into which sodium carbonate is to be dosed
- the strength of the sodium carbonate solution
- the amount (in mg/l) by which we want to raise the alkalinity

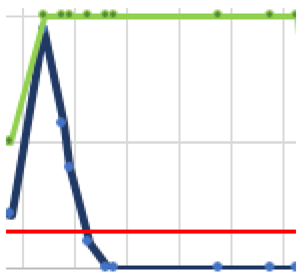
we can estimate the volume of liquid sodium carbonate needed. We use the word “estimate” advisedly. Bear in mind this calculation procedure comes from a swimming pool application. Swimming pool water and sewage are (hopefully) two very different things. There are many things in sewage which could consume alkalinity so these calculations are a guide at best. Nevertheless, coupled with experience they are a *useful* guide.

The client's site suffered a mechanical problem. The pumps that feed fresh sewage to the plant tripped and telemetry was temporarily out-of-order. Nobody knew about the problem until an engineer turned up for a routine visit. Oh dear. On top of this, the sodium carbonate is only dosed when the feed pumps operate. Since

[4]*Doses for adjusting alkalinity, Kim Skinner and J. Que Hales, J. Swimming Pool & Spa Industry, Vol. 1, No. 1, pp. 14-20, 1996.*

the feed pumps had tripped, no sodium carbonate was dosed. Oh dear again. A sample of treated effluent revealed it was well out of consent and alkalinity was very low. We used our calculation procedure to estimate the dose of sodium carbonate needed to boost the alkalinity and hence the nitrification process.

Again, confidentiality means we can't show the actual figures so we've taken this snap-shot from a trend of the final effluent ammonia at the site.



Graph three A snap-shot of ammonia, the consent and the dose of soda ash

In graph three, ammonia is shown by the blue line, the consent by the red line and the volume of sodium carbonate dosed by the green line. It's clear that nitrification was badly affected and ammonia increased quickly. We estimated an increased dose of sodium carbonate and had it implemented on site. The increased dose of soda ash increased pH and brought about conditions that favoured nitrification. The ammonia in the final effluent decreased to a level that was well below the consent (the dose of sodium carbonate was reduced once we were sure the plant was back on track).

What does this tell us?

As we've alluded to, the theory of nitrification and managing such a plant can be complex. The plant mentioned in this article is relatively simple and so is the theory we've applied but the results are self-evident. Collecting the right data is incredibly important too: before we were asked to optimise this plant, data about alkalinity and pH had not been collected. Consequently the dose of sodium carbonate was effectively set on nothing better than a gut feeling. Some simple theory has added much needed rigour and, more importantly, it has brought a plant that was failing part of its discharge consent back in to compliance.

Blackwell Water Consultancy Ltd provide consultancy about all aspects of sewage treatment, industrial effluent treatment and water efficiency.

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