

Introduction

The chemistry of the chlorination of seawater is more complex than many people realise and, although the measurement of chlorine residuals is possible in seawater (and therefore automatic control of chlorine dosing), better results will be obtained if this is fully understood.

Chlorination Chemistry of Seawater



Seawater contains about 65-80ppm dissolved bromides¹ most of which are sodium bromide. When you put chlorine in water it displaces the bromine from the bromide (because it's more reactive) and becomes a chloride. So for up to about 70ppm of total chlorine dosed, what you actually have in the water is free bromine and combined bromine (NOT free and combined chlorine), so it is the total bromine that actually does the disinfection². So why does everyone call it chlorination when technically it is bromination? Mainly because most people don't know about the chemistry. So what? Normally it makes no difference as total bromine is an effective disinfectant, however there can be a lot of confusion when it comes to monitoring residuals and controlling dosing. Choosing the correct sensor to control the dosing is crucial. The table below shows the concentrations of ions in Seawater.

The table was taken from http://www.ocean.washington.edu/courses/oc400/Lecture_Notes/CHPT4.pdf



At salinity (PSS 1978): S = 35.000%				
	g/kg	ppm (mg/l)	mmol/kg	mM
Na ⁺	10.781	10781	468.96	480.57
K ⁺	0.399	399	10.21	10.46
Cl ⁻	19.353	19353	545.88	559.4
Br ⁻	0.0673	67	0.844	0.865
F ⁻	0.0013	1	0.068	0.07

Table shows concentration of the major constituents in surface seawater.

Free Chlorine and Total Bromine

Due to the confusion on what is being measured, it is easy for an engineer to specify the wrong equipment and calibrate it incorrectly. For example, it is common for a free chlorine sensor to be specified for seawater chlorination control. Most electrochemical free chlorine sensors will react to free bromine (not all so be careful!) but this isn't necessarily what you need for bromination control. Most authors agree that whilst the disinfection capability between free chlorine and combined chlorine differs, when it comes to free bromine and combined bromine both forms of the chemical are equally good at disinfection and so a better measurement would be total bromine, which requires a total bromine sensor.

DPD and Seawater Chlorination

To add to this already confusing environment we need to look at calibrating online sensors. DPD is used extensively to measure chlorine residuals and it also reacts to bromine so can be used for both, however, DPD 1 measures FREE chlorine or TOTAL bromine. There is no easy way of measuring free bromine.

The situation can therefore arise where you have an online instrument specified as a free chlorine, actually measuring free bromine and calibrated as a total bromine (against DPD 1). An online DPD instrument must be specified for seawater (bromine) or the results it gives you will be poor.

Typically the best results are obtained by specifying a total bromine (total chlorine) sensor and calibrating it using DPD 1.

Estuarine Water

Many seawater chlorination applications are estuarine in nature (partly seawater and partly fresh water) and it is the degree of dilution which determines which sensor and which electrolyte you should use. Seawater has approximately 70ppm bromides and so up to 70ppm chlorine the replacement will be 100%. If the sea water is 50% fresh water then up to 35ppm chlorine will give 100% displacement. For example, if we looked at a 2ppm residual then the water could be only 3% seawater and 97% fresh water and you would still be measuring bromine, so a total bromine sensor calibrated with DPD 1 would be appropriate.

Because bromine is heavier than chlorine, 1mg/l of chlorine is the same as approximately 1.6mg/l of bromine³ so it is important to understand what you are measuring. DPD kits can be used in three ways for the chlorination of seawater.

- 1. A chlorine DPD 1 kit will measure total bromine but will report the concentration as chlorine equivalent. If this is used to calibrate a Pi sensor, it should be a Pi total chlorine probe that will also then report in mg/l of chlorine equivalents.**
- 2. A chlorine DPD 1 test kit can be used and the mg/l can be multiplied by 1.6 to give a total bromine reading, and if this is used to calibrate a Pi sensor it should be a Pi total bromine sensor.**
- 3. A bromine DPD 1 test kit is the same as a chlorine test kit except that it does multiply internally and outputs as mg/l of total bromine. If the kit is used to calibrate a sensor, it should be a total bromine sensor.**

References

1. Goosen, M. F. A. & Shayya, W. H. Water management, purification, and conservation in arid climates. Volume 2: Water purification. (Univ. of Sultan Qaboos Univ.(OM), 1999).
2. Wiley, White's Handbook of Chlorination and Alternative Disinfectants, 5th Edition. (page 874, pages 122-129).
3. Wieser, M. E. et al. Atomic weights of the elements 2011 (IUPAC Technical Report). Pure Appl. Chem. 85, 1047–1078 (2013).

