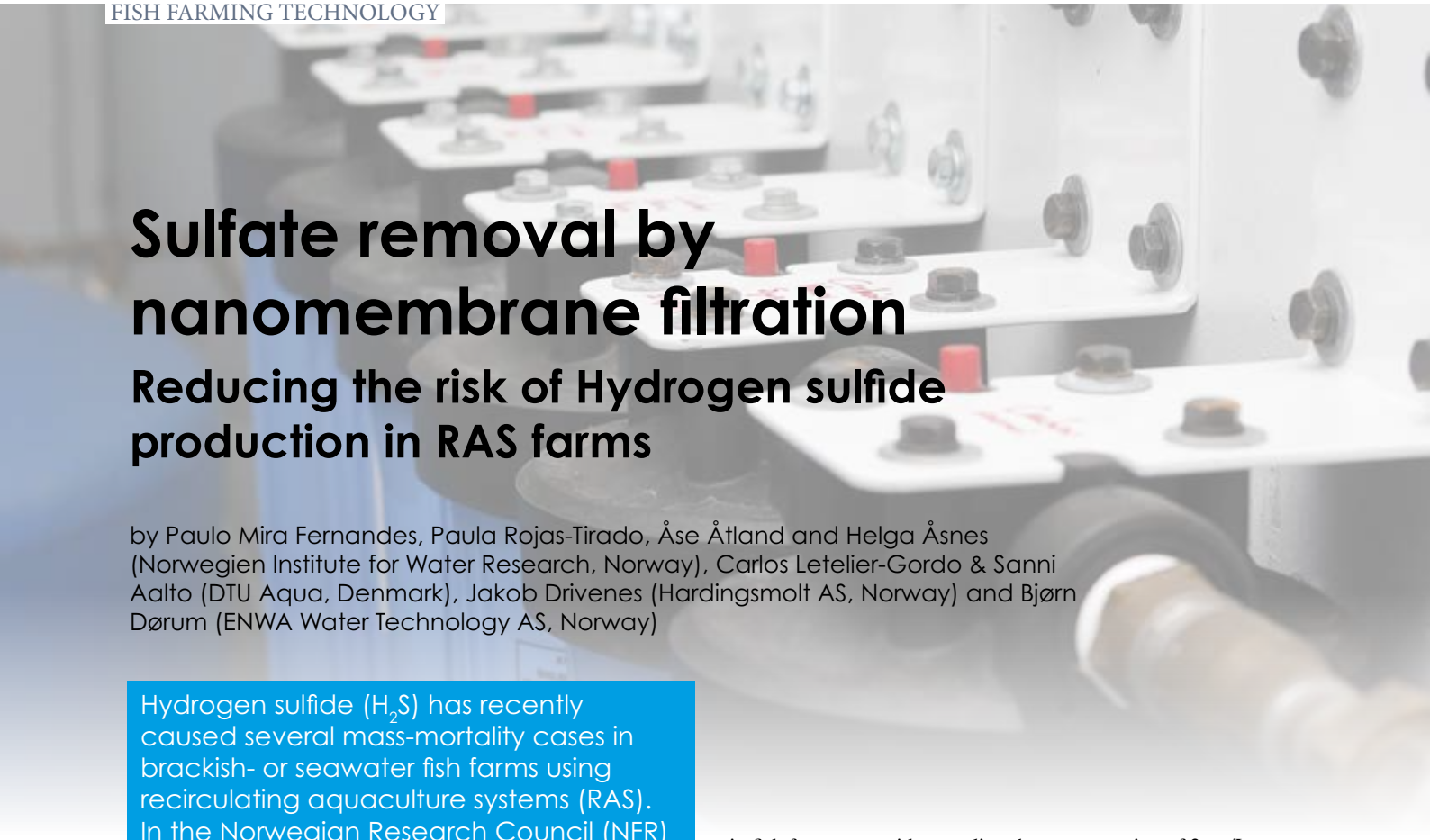

Sulfate removal by nanomembrane filtration

Reducing the risk of Hydrogen sulfide production in RAS farms

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Hydrogen sulfide (H_2S) has recently caused several mass-mortality cases in brackish- or seawater fish farms using recirculating aquaculture systems (RAS). In the Norwegian Research Council (NFR) project "Aquasulfat", they investigate the possibility of reducing the risk of H_2S production by removing sulfate from the intake water with nanomembrane filtration.

Hydrogen sulfide (H_2S) is a volatile gas and is extremely toxic to both humans and fish. In aqueous environments, sulfate-reducing bacteria (SRB) produce dissolved sulfide by degrading organic matter using sulfate (SO_4^{2-}) as electron donor.

The process takes places in the absence of free dissolved oxygen, such as in anoxic conditions, as SRB are outcompeted by other heterotrophic bacteria using dissolved oxygen (O_2) or nitrite (NO_2-) and nitrate (NO_3-) to degrade organic matter.

Depending on the pH, temperature and salinity of the receiving water, the dissolved sulfide can occur in the form of hydrogen sulfide (H_2S), bisulfide (HS-) or sulfide (S_2-) (See Figure 1).

At the natural pH in fresh- or seawater (6-8.5), most of the dissolved sulfide will be in either H_2S or HS- form. In salmonid aquaculture systems, approximately 50 percent of the total dissolved sulfide occurs as H_2S, since the normal operational pH is between 6.5 and 7.5. tolerance levels. Little is known about the acute and chronic effects of fish exposure to H_2S.

The scientific literature states that H^2S is acutely lethal to fish in the 20-50 µg/L range, while for chronic exposure the level can be as low as 2 µg/L. Even though the toxicity limits and exposure to H_2S varies between fish species and their life stages, it is important that H_2S does not accumulate in fish farms to avoid exceeding the concentration of 2 µg/L. The concentration of SO4, the precursor of H_2S, is 2700 mg/L in seawater and < 100 mg/L in freshwater, which means that H_2S is toxic at a minute fraction of natural SO_4^{2-} levels. Therefore, obtaining reliable and accurate measurements of the SO_4^{2-} and H_2S concentrations in the production waters is of critical importance.

Table 1. Selected water quality parameters of normal (raw) or filtered (with the nanomembrane filtration apparatus) at Hardingsmolt AS.
b.d.l. = below detection limit

Parameter	Unit	Normal	Filtered
Salinity	ppt	16	15
pH	-	7.6	7.7
SO42-	mg/L	1059	102
Al3+	µg/L	23	19
Ca2+	mg/L	200	84
Cl-	g/L	9.1	9.0
Cu2+	µg/L	1.5	3.0
Fe3+	mg/L	b.d.l.	0.2
K+	mg/L	180	190
Na+	g/L	4.9	5.3
Mg2+	mg/L	580	97
Mn2+	µg/L	11	b.d.l.
Zn2+	µg/L	21	13

Production of H_2S in RAS

In short, sulfide is produced when water movement is halted or hydrodynamics are poor, there is no oxygen and nitrate present and there is enough organic matter to sustain SRB activity. More sulfide, and consequently more H_2S, is produced when more SO_4^{2-} and dissolved or easily degradable organic matter is sufficiently available.

Therefore, the risk of H_2S production is higher in seawater than in freshwater environments. However, the connection between presence, activity, and location of SRB's is also important.

In a study within the Research Norwegian Council-sponsored project "Aquasulfat" (RCN no. 296545) published in 2021, Rojas-Tirado et al, observed that the highest risk for H2S production in a brackish water (15-17 ppt) RAS environment is in the biofilter (as illustrated in Figure 2).

The authors studied the potential production of H_2S with internal microorganisms and carbon sources from the biofilter, system water, and sludge collected in a salmon smolt Norwegian RAS facility in closed environments for 26 days.

The production of H_2S started earlier in a sludge-based environment, but due to limitations with carbon sources and

bacterial activity, and the highest H_2S concentration obtained with sludge was much lower than the one obtained with biofilter biomedia.

The high H_2S production potential of biofilter biomedia could be due to the higher bacterial production and activity in biofilters, which, coupled to the abundance of SO_4^{2-} in brackish water, led to a higher production of H_2S and for a longer period in biofilters than in sludge environment.

General recommendations to prevent H_2S incidents in aquaculture systems, and RAS in specific, are to maintain Nitrate nitrogen (NO_3)- levels high, to avoid dead zones as much as possible, to keep biomedia aerated and agitated, to degas efficiently, and to improve hydrodynamics and biofilter/reactor design.

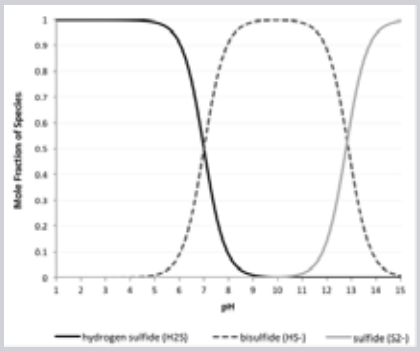

Figure 1: Dissociation of sulfide species in aqueous solutions according to PH.

Removal of sulfate by nanomembrane filtration

One possibility to decrease H_2S-related incidents in aquaculture is via the removal of SO_4^{2-} from the rearing water. To test this, a nanomembrane filtration apparatus (80 nm, Figure 3) was installed at Hardingsmolt AS (Tørvikbygd, Norway) to filtrate divalent ions from the intake seawater, and use in post-smolt salmon rearing at 15-17 ppt.

After two weeks of continuous membrane operation without significant downtime, the apparatus managed to reduce SO_4^{2-} concentration by approximately ten times as compared to the expected SO_4^{2-} concentration at 17 ppt (102 vs 1060 mg SO42-/L, as shown in Table 1).

To test H_2S production dynamics in an extreme scenario of halted biofilter media movement in filtered or non-filtered system water, biofilter, system and intake water samples were incubated in 2-L flasks in a similar fashion to Rojas-Tirado et al. (2021).

The reactors were monitored every second day for 42 days and spiked with acetate on day 26 to a final concentration of 180 mg/L, to simulate an extreme feed load scenario.

The first signs of H_2S production in the reactors occurred at day 4 in the raw water reactors and at day 8 in filtered water reactors. The production of H_2S reached its peak at day 12 in the raw water reactors and 14 in filtered water reactors. After day 14 in both reactor types, the concentration of H_2S slightly decreased, until the reactors were spiked

with acetate on day 26, after which H^2S concentration increased again, indicating the reactors were limited with organic matter substrate before day 26.

The timing and intensity of peak H_2S in each reactor type were different, and this could probably be attributed to differences in the SO_4^{2-} start levels. However, it is important to note that, even though SO_4^{2-} concentration was 10 times lower in the filtered

water reactors than in the raw water reactors, the filtered water had roughly four times more organic matter and NO_3- at the start of the trial.

Although H_2S was produced in all reactors in this trial, it is important to stress that the nanomembrane filtration apparatus significantly reduced the sulfate concentration in the intake water. Consequently, the production of H_2S was delayed, and at a lower level than in non-filtered water.

The use of nanomembrane filtration in the intake water to reduce sulfate levels is, hence, a potentially great benefit to those operating RAS; however, one key aspect of the membrane operation is the operational costs, which will be integrated into the analysis of this dataset in the upcoming future.

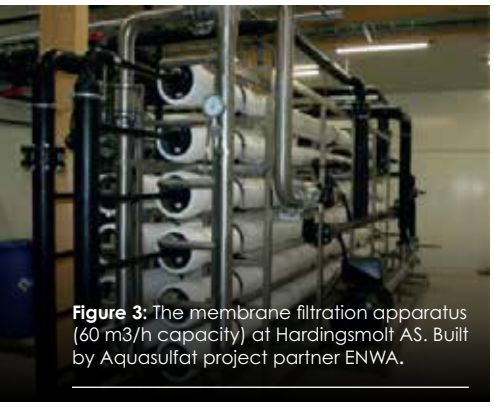

Figure 3: The membrane filtration apparatus (60 m3/h capacity) at Hardingsmolt AS. Built by Aquasulfat project partner ENWA.

With some extra effort, the membrane would probably have been able to remove the remaining sulfate, and those costs, and H_2S-related benefits, will be integrated into the cost-benefit model of the membrane utilisation.

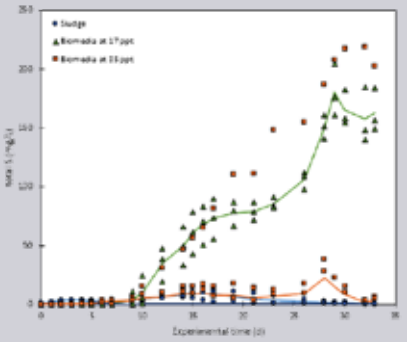

Figure 2: H_2S production in sludge (blue), biomedia in RAS water (grey), biomedia in seawater (yellow), or RAS water (orange). Results are standardised as total sulfide (H_2S+HS^-+$S2^-$) to minimise differences affected by pH.

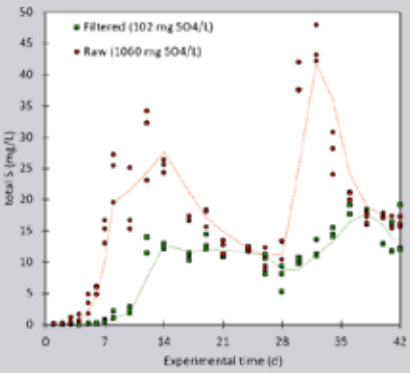

Figure 4: Total sulfide concentration profile in reactors with fixed biofilter biomedia inoculated with filtered (green) or raw (orange) water.

Going forward

The next steps within the "Aquasulfat" project are to determine the safe and optimal utilization of the nanomembrane apparatus. In this sense, the production of H_2S will be tapered, or at least delayed significantly so the installation and operational costs can justify the apparatus utilisation.

Secondarily, since the nanomembrane reduces the concentration of divalent and some monovalent cations and anions in the intake water, fish welfare and growth need to be studied in the filtrated water.