VAPOR INFUSION WITH NANOBUBBLES TO MITIGATE HEAT EXCHANGER FOULING AND REDUCE ITS ENVIRONMENTAL IMPACT

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ABSTRACT

Heat exchangers are foundational devices in many industrial processing systems, and the need to minimize or prevent heat exchanger fouling is imperative. Fouling on the cooling water side may render exchangers inefficient and, in the extreme, ineffectual. Even minimal fouling can reduce functionality. The lower the heat exchanger efficiency, the higher the energy demand through additional fuel burn, correlating with excessive carbon expression.

Methods to prevent heat exchanger fouling have been studied over decades to reduce costs. More recently, the relationship of fouling to global warming has become apparent. Numerous methods to help reduce carbon dioxide expression, termed Net Zero, are being proposed. Key to the commercial acceptance and adoption of any technology is its effectiveness, ease of integration, and financial and tangential benefits.

Vapor infusion is an antifouling technology that reduces fouling and carbon expression through creation of a chemically and mechanically induced nanobubble formation. This paper reviews vapor infusion and nanobubble science, development, and commercial application.

INTRODUCTION

Cooling water used in the heat exchange processes may contain dissolved, sedimentary, or planktonic fouling agents. They will attach to heat transfer surfaces, forming intrusive, insulating beds through adhesion and solidification that impede water flow and heat transfer. This type of fouling impacts the mechanical or electrical system associated with the heat exchanger. Responding to reduced heat transfer or elevated pressure drop often means compensatory action to increase water flow, which in turn necessitates additional energy draw that, through fuel burn, elicits elevated carbon presentation [1, 2].

Greenhouse gases including carbon dioxide, sulfur dioxide, and others are released into the atmosphere through energy generation. Higher greenhouse gas concentrations in the atmosphere capture solar energy and thus raise the earth's temperature. Net Zero methods are intended to reduce greenhouse gas emissions from human activity. These methods may be grand (such as output/capture protocols) or minor (such as industrial technologies that minimally decrease CO_2 emissions). To achieve global Net Zero goals, companies need to reduce CO_2 emissions, especially any "low hanging fruit" such as reducing energy waste by improving heat exchanger efficiency within their facilities. Furthermore, the potential non-environmental benefits derived from functional improvement, such as cost or labor savings, contribute to a better value proposition.

Heat exchangers are a vital component in most industrial process systems, and carbon expression associated with heat exchanger fouling could account for a significant amount of atmospheric discharge. Any achievable improvement could offer broad impactful environmental and energy saving benefits. Providing a sufficient water supply, without fouling, is key to this endeavor.

RELATIONSHIP BETWEEN FOULING AND GREENHOUSE GASES

Optimized heat transfer is vital for industrial processes such as energy propulsion or reaction kinetics in materials processing. When conditions that hinder heat transfer are detected, they require a remedial response to allow for a return to designed functionality. Although eventually mechanical cleaning may be required, as an interim measure, the system's response is to increase pump output to increase the water flow through the system to compensate for the loss in heat transfer efficiency. Even a marginal increase in head loss, applied continually, leads to a significant increase in energy usage.

Studies have shown that fouling in a heat exchanger leads to additional energy demands and is directly related to greenhouse gas emissions [1], as indicated in Fig. 1, and potentially to other environmental consequences [2]. The loss of heat recovery and the additional energy for pumping represent a loss of thermal efficiency. The increase in energy supply, whether created on site or drawn from a local utility, is through additional fuel burn.

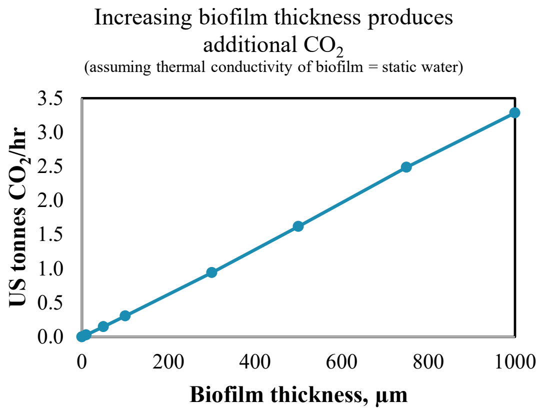


Fig. 1. Correlation between the biofilm thickness atmospheric release of CO_2 [1].

Although mechanical or chemical cleaning may return functionality to an exchanger, it will not prevent the progression of functional decline due to continuous fouling. A clean heat exchanger begins to foul immediately after being brought online. Therefore, continuous prevention of foulant formation and progression is a prudent approach. Treatment that is imparted in situ with the cooling water as its vehicle and applied during exchanger use offers both heat transfer efficiency and environmental benefits.

Air Bubbles in Heat Exchangers

Numerous papers report the actions of air bubbles when applied within a heat exchanger. Air bubbles have been shown to both disrupt fouling [3] and potentially improve heat transfer [4, 5, 6]. Micro and macro bubbles, when presented to a flow stream, can mechanically sparge fouling bodies or disrupt sedimentary masses and improve heat transfer by moving heat away from surfaces through the creation of wake waves. In one study, the convection heat transfer rate between hot and cold fluid streams was studied both with and without the generation of nanobubbles in the hot fluid. The study noted that fluid with nanobubbles offered a 10 – 12% increase in the heat transfer rate [7].

Unfortunately, studies also indicate that introducing air bubbles alone may increase the dissolved oxygen, potentially inducing biofouling and corrosion of materials in seawater [8] and within metallic piping systems [9]. Furthermore, cavitation due to micro or macro bubble presentation remains a concern.

Vapor infusion uses a chemical vapor and mechanical presentation to create nanobubbles. This treatment can help heat exchangers avoid potential pitfalls such as increasing fouling formation while it also limits dissolved oxygen, cavitation, or macro bubble incursion.

Nanobubbles

Nanobubbles are tiny vapor-filled structures with a diameter of less than about 1 μm and are potentially 2500 times smaller than a single grain of sand. Tens of millions fit within a micro bubble and offer an extremely large surface area. They may exist either as surface nanobubbles or dispersed in bulk liquid. Fluid-borne nanobubbles have a very long life in water due to their neutral buoyancy and low-rise velocity, possibly persisting for more than two months [10]. Their characteristics are due to strong surface charges, internal pressures [11], and surface tension. Nanobubbles undergo Brownian motion within a fluid which enables them to continuously stimulate physical, biological, and chemical interactions and allow for a long perseverance within a fluid [12].

Nanobubbles have been shown to induce the removal of fouling mineral sites held together by minerals such as calcium carbonate [13] and provide the cleaning of stainless-steel surfaces [14]. The formation of nanobubble-nanoparticle clusters induces mineral disruption, calcite crystal inhibition and dissolution [13]. Thus, nanobubble technologies hold the potential for anti-fouling capabilities [15] and offer positive physiochemical properties in water [16]. In one study, nanobubbles were shown to accelerate the transition from vaterite to calcite as a result of nanoparticle-nanobubble coagulation [17].

Nanobubbles were determined to alleviate and resolve pitting caused by sulfate-reducing bacteria in a study performed with pipe sections and service water from the secondary cooling water system at Three Mile Island Nuclear Power Station [13, 18]. The studies showed that nanobubbles could eliminate pipe surface nodules that protect bacteria. Two samples of water pipe were treated by receiving water that either contained or did not contain nanobubbles. After eight months of exposure, the pipe samples were sectioned and examined to measure corrosion pit depth. The results revealed that the mean pit depth was approximately 50% greater in the control pipe (which did not receive nanobubbles) than in the sample exposed to nanobubbles. Further study indicated that nanobubbles have been shown to reduce calcified plaque in *ex vivo* pericardial tissue [19].

Nanobubble Generation Methods

For small-scale scientific investigation or low-volume applications, such as radio contrast agents, the method of nanobubble creation is determined by the bubble size desired. To generate nonspecific high-volume bulk fluid nanobubbles for use in large commercial applications such as antifouling in heat exchangers, various methods have been utilized [20]. These may include liquid flow generators that use membranes, static mixing, swirling liquid flow [21] and pressurized dissolution to create nanobubble emulsions of significant density. These techniques for nanobubble creation require a liquid pump which can produce a gas-liquid two-phase fluid. This fluid is introduced into a static mixer and swirling flow chamber that crushes the bubbles into nanobubbles due to shear stress. This method requires both significant time and water volume as the gas-liquid fluid circulates between generator and sample tank numerous times to create the desired volume.

Another method to create bulk nanobubbles is ultrasonic irradiation [22, 23]. When ultrasound is directed at water, fine bubbles occur within the fluid. Due to acoustic pressure fluctuations, these bubble nuclei grow and collapse. Termed *acoustic cavitation*, this method can create relatively small nanobubbles with a diameter of 90 – 100 nm in a significant concentration of 1.5×10^9 mL^{-1}.

An alternating magnetic field [13, 18, 19] has been shown to create emulsions of nanobubbles in flowing water. High strength rare earth magnets are arranged within the core of a tube that create nanobubbles in water that flows through alternating magnetic fields. The nanobubbles that are generated then persevere for an extended period. For commercial applications, these and other methods are scalable to provide large volumes of fluid containing effective nanobubble densities.

Vapor Infusion Nanobubble Formation

The task of treating cooling water in an environment such as a heat exchanger necessitates a simple, easily integrated approach. Vapor infusion is just such an approach and is capable of forming high nanobubble concentrations. Vapor infusion uses various methods to form nanobubbles, including mechanical, physical, and chemical means. These simple infusion techniques include bubble shearing [24], microbubble creation and collapse [25, 26] and use of varied gases [27, 28, 29] to potentially create bubble surfaces prone to shrinking, prevent dissolved oxygen mass transfer, and provide a chemical treatment.

Vapor infusion was originally developed using iodine vapor to inactivate fluid-borne microbes in dental and medical waterlines by infusing iodine vapor into treatment water flow streams. The elemental iodine bubbles provided a rapid and profound impact on high log counts of both planktonic and biofilm containing microbes [30]. When tested for iodine levels, the fluid registered only residual iodine at a low ppb incapable of disinfection. Researchers were unsure of the method by which the iodine was inactivating the microbes except through possible bubble membrane/microbe contact.

To test the possibility of this interaction, they imparted (bubbled) a 90-second iodine vapor into a static water volume containing planktonic (Table 1) or biofilm microbes (Table 2). As both results indicate, the microbes contained in the water were completely inactivated. Of further note, no microbial rebound occurred for 72 hours after the infusion. Of importance environmentally, the total iodine residue content in the infused water was less than 50 ppb, indicating minimal iodine mass transfer from the vapor-phase bubble to the surrounding water.

Table 1. Planktonic microbes 90-second infusion

Bacteria	**Concentration, Log CFU/mL**	
	Initial	**Final**
E. Coli K12	6.12	0.00
E. Coli 0157:H7	6.48	0.00
Salmonella	6.28	0.00
Enterococcus	6.56	0.00

Table 2. Biofilm microbes 90-second infusion

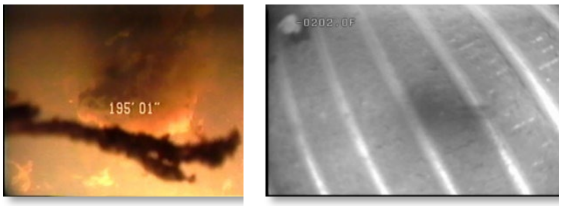
Biofilm treatment	**Time, s**	**Log CFU/mL**
None, A	—	7.05
None, B	—	7.09
None, C	—	7.35
Air, A	90	5.25
Air, B	90	5.63
Air, C	90	5.37
Iodine, A	90	0.00
Iodine, B	90	0.00
Iodine, C	90	0.00

During this study, another trial was performed to determine if the infused water retained any residual disinfection quality. A static fluid volume of water was inoculated with a 6 log10 mixed microbial inoculum. Water was infused once with iodine vapor bubbles for 90 seconds. After infusion, the water was determined to contain less than 50 ppb total iodine, too low to cause disinfection. Without further infusion, new microbial inoculum was added to the solution every hour, and the fluid was then tested for microbial viability. As indicated by Table 3, although some viability remained, most of the microbes were inactivated over time. It was suspected that the inactivation was due to iodine nanobubbles, and decreasing efficacy was due to consumption, coalescence, and gas off.

Table 3. Residual nanobubble disinfection in a sealed container.

Time, hr.	**CFU/mL**
0	0
1	20
2	480
4	5250
6	Too numerous to count

In 2005, a test of the technology was planned at the request of an electronics manufacturing plant that had a geothermal system suffering from severe biofouling in exchanger and recipient well screens, resulting in significant back pressure. After installation of an infusion system, the heat exchanger showed improved function and the back pressure was resolved in two months. The well screen fouling was resolved after six months of vapor infusion. Photos taken of the well screens prior to infusion indicated significant, gelatinous biofilms. After six months of infusion, only sand silt remained (Fig. 2). The supply well water contained high levels of mineral iron and iron-reducing bacteria which caused fouling within the exchanger and downstream well screens over 2000 feet away. The well screens received only pre-infused water from the exchanger and not direct infusion. This client did not need to clean the exchanger for an additional 16 years.



Before *After six months*

Fig. 2. Well screens before and after vapor infusion.

A poster presenting the geothermal trial led to a US Navy vapor infusion study for use on shipboard heat exchangers [31]. In this case, vapor infusion reduced foulant formation within shipboard heat exchangers with minimal rise in seawater residual iodine and no increase of metallic ions in water effluent during the infusion study. The successful outcomes of this study led to several research projects with the US Navy's Undersea Warfare Division to investigate the impact of iodine vapor bubbles on ship hull fouling [32], based upon research that had shown that nanobubbles interfere with community biofilm formation [33].

Another indication of downstream bubble interaction was provided during the US Navy trial. Naval Facilities Engineering Systems Command (NAVFAC) wanted to determine if vapor infusion could provide sustainable bubbles for downstream shipboard seawater piping systems. NAVFAC designed a proof-of-concept study which pumped seawater from the sea water surface off Kona, Hawaii. The test pipes were clear PVC and over twenty feet long. Normally, ambient air bubbles should have coalesced over this distance, providing little wall surface interaction. The researchers compared a timed iodine vapor infusion with a non-infused control. After 45 days, the biofouling within the two pipes containing titanium coupons (as seen in Fig. 3 and 4) are noticeably different. This may have been the first indication of nanobubble formation.

Fig. 3. Control pipe after forty-five days.

Fig. 4. Pipe with vapor infusion after forty-five days.

Evidence of nanobubble formation using vapor infusion treatment chemicals was provided by the Earthman Labs at the University of California (UC) Irvine, CA. The purpose of the study was to determine if infusing iodine vapor into a fluid volume could create nanobubbles without the varied methods commonly used. Infused iodine vapor was used to create nanobubbles in a fluid volume. Dry, oil-free airflow was supplied from a compressed air source through an iodine-generating cartridge for three minutes and allowed to bubble within deionized water with a constant stirring. Two infusion devices consisting of a simple ¼-in. OD tube and a custom injection quill were used to determine if microbubble size influenced nanobubble formation and characteristics. After infusion, the fluids were left untouched for a period to indicate if any nanobubbles persevered. The fluids were then analyzed using a NanoSight instrument (Malvern Panalytical) [34]. This device can determine and register the concentration density of nanoscale objects within a solution using Nanoparticle Tracking Analysis (NTA). Additionally, it can determine the relative range of size of particles or bubbles between 10 nm and one µm.

The results (Table 4) indicate that infusing for three minutes, using a simple ¼-in. OD tube, created a significantly high density of relatively small (under 200 nm) bubbles. The concentration was like that achieved using ultrasonic irradiation, as previously described. Of significance was the persistence of bubbles 48 hours post-infusion, indicating the neutral buoyancy of the nanobubbles. This study also indicated that chemical treatment can be administered with nanobubble formation.

Table 4. NanoSight results after using an open-end ¼-in. OD tube to produce iodine vapor infused nanobubbles.

0.25-in. diffuser	
Persistence	48 hours
Concentration	1.28×10^8 mL^{-1}
Size	158 – 196 nm

The results given in Table 5 indicate that infusing with a custom injection quill through shearing creates much smaller nanobubbles. A majority of the nanobubbles had diameters between 50 and 60 nm, providing some verification that initial microbubble size and consequent shrinkage accounts for smaller nanobubble formation [25]. The concentration density was still significant even 192 hours post-infusion, indicating the neutral buoyancy of the nanobubbles.

Table 5. NanoSight results after using a micro diffuser to produce iodine vapor infused nanobubbles.

Micro diffuser	
Persistence	192 hours
Concentration	3.77×10^7 mL^{-1}
Size	53 – 62 nm

An example of the nanobubble analysis as provided by the NanoSight is shown in Figure 5, indicating bubble size distribution and concentration.

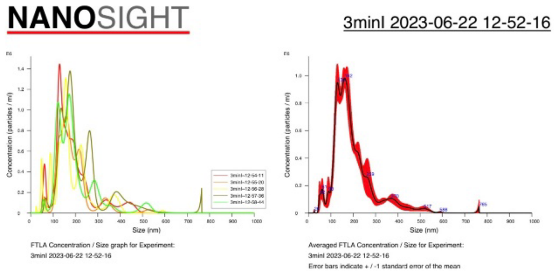


Fig. 5. Results from the NanoSight device for iodine vapor infused nanobubbles corresponding to the results listed in Table 4.

Nanobubbles created using the vapor infusion method may be added to the treatment protocol and provide further fouling protection. Vapor infusion offers a low residual chemical treatment in the cooling water while providing an expansive nanobubble active surface area. Nanobubbles may also have benefits when used concurrently with common biocidal treatments. They have been shown to enhance the chemical disinfection of waterline biocides against food pathogens without undue biocide levels [35].

It is postulated that the vapor infusion treatment chemicals and shearing techniques facilitate the creation of microbubbles which shrink in size to nanobubbles. Vapor infusion currently uses elemental iodine, ammonium benzoate, and other vaporous chemicals, based on foulant type, system materials, and regulatory requirements. Research has shown that microbubbles of a certain size shrink and form nanobubbles [25]. In one study, a vapor infusion system used a shearing bubble injection quill to inject chemical vapor within a flow stream, creating small microbubbles which then rapidly shrank into nanobubbles. Once in the cooling water flow path, they further sheared through surface interaction and immediately filled the flow space within the heat exchanger.

Commercial Application

Infusion of chemical vapors in a manner as described in this work allows for the formation of bubble emulsions including nanobubbles of a desired volume and size for use in industrial settings. The vapor infusion system utilizes a chemical treatment in an easily replaceable cartridge. As oil-free air of a necessary flow rate and pressure is directed through the cartridge, the chemical vapor treatment moves with the airflow to the heat exchanger injection site. The chemical vapor flow is sheared by the infusion quill into the cooling water pipe before it enters the heat exchanger. The creation of smaller microbubbles due to shearing hastens the creation of nanobubbles for internal and downstream presentation. The bubble emulsion, including nanobubbles, moves through the heat exchanger. The nanobubbles move in a non-coalescing, Brownian motion driven cloud, contacting surfaces within the heat exchanger. As the bubble cloud including nanobubbles makes contact, the bubbles interact with fouling agents on heat transfer surfaces while imparting the chemical treatment. Vapor infusion occurs for a designed duration and frequency and does not require constant vapor presentation. The bubble emulsion then moves through the system for discharge. The results of several commercial applications bear out the efficacy of this protocol.

In one such application, a NCL Cruise Line ship was experiencing fouling within its engine coolers before infusion devices were installed. After installation, the aft engine cooler plates were opened for inspection onboard (Fig. 6) and clearly showed a lack of fouling after three years of infusion without any other antifouling treatment. During this time, the electro chlorination system was turned off. This system is in use on other ships for engine and flue gas scrubber applications with comparable success.

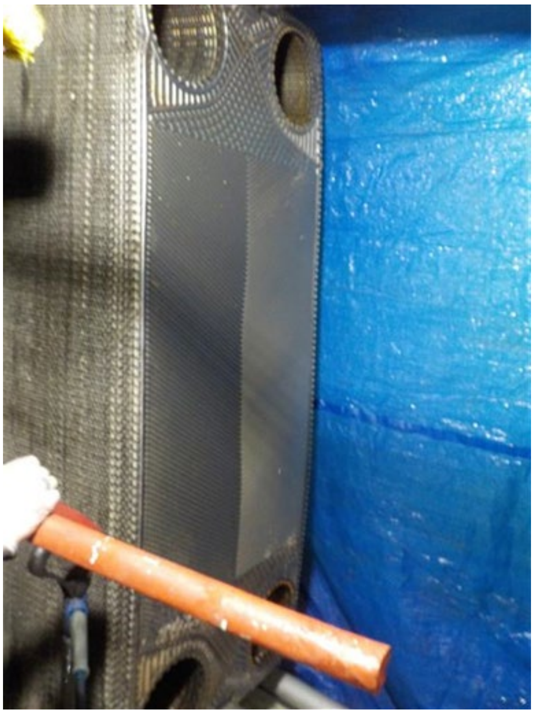


Fig. 6. Aft engine cooler three years post infusion installation.

CONCLUSION

Nanobubbles can be produced by different methods, including vapor infusion. Iodine vapor infused nanobubbles have been shown to offer improvement in various waterborne fouling applications. Evidence from both laboratory and commercial settings has demonstrated that nanobubbles have a stronger impact on heat exchanger fouling than first expected. Vapor infusion holds promise in maintaining heat exchanger performance and resultant environmental impact. Nanobubbles created with vapor infusion contribute additional improvements to a method that should be commercially acceptable and sustainable.

Improved nanobubble generation and implementation methods are key in their use for water and wastewater treatment processes. The relative ease of application and the lack of excessive chemical residue with vapor-infused nanobubbles enable improved efficiency and reduce the negative impact to the environment compared to other methods. Research into applications in areas such as wastewater treatment, flue gas scrubber function, and membrane fouling may also lead to efficiency gains and improved environmental impacts.

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