Chemical Engineering Journal 244 (2014) 505–513

Contents lists available at ScienceDirect

Chemical Engineering Journal

journal homepage: www.elsevier.com/locate/cej

# Ozonation of phosphonate antiscalants used for reverse osmosis desalination: Parameter effects on the extent of oxidation ☆

Lauren F. Greenlee [a,*], Benny D. Freeman [b], Desmond F. Lawler [c]

[a] Applied Chemicals and Materials Division, National Institute of Standards & Technology, 325 Broadway, MS 647, Boulder, CO 80305, United States
[b] The University of Texas at Austin, Department of Chemical Engineering, Center for Energy and Environmental Resources, 10100 Burnet Road, Building 133, Austin, TX 78758, United States
[c] The University of Texas at Austin, Department of Civil, Architectural and Environmental Engineering, 301 E. Dean Keeton St. Stop C1786, Austin, TX 78712, United States

## HIGHLIGHTS

- Phosphonate antiscalants are oxidized by ozone and hydrogen peroxide.
- Extent of oxidation varies with antiscalant molecular structure.
- Coordination with dissolved calcium ions results in greater phosphonate oxidation.
- Orthophosphate is measured to evaluate the extent of antiscalant oxidation.
- Ozone doses as low as 1 mg/L resulted in significant antiscalant oxidation.

## ARTICLE INFO

*Article history:*
Received 7 November 2013
Received in revised form 30 January 2014
Accepted 1 February 2014
Available online 7 February 2014

*Keywords:*
Phosphonate
Antiscalant
Ozone
Hydroxyl radical
Reverse osmosis desalination
Calcium complexation

## ABSTRACT

The recovery of usable product water in brackish water reverse osmosis (RO) desalination is limited by the potential for membrane scaling. This limited recovery results in high costs of disposal of the concentrate (waste) stream. Concentrate treatment to improve recovery is vital, and treatment that includes antiscalant oxidation prior to precipitation and solid/liquid separation might allow increased precipitation through antiscalant deactivation. Ozone and hydrogen peroxide were used to oxidize phosphonate-type antiscalants under varying conditions of water composition, pH, ozone dose, and antiscalant type; orthophosphate (P) is an oxidation product and was used to measure the extent of oxidation. Antiscalant oxidation increases with ozone dose (1–10 mg/L $O_3$) and in the presence of calcium, from 1 mg/L P to 7 mg/L P for an antiscalant concentration of 27 mg/L as P. The addition of hydrogen peroxide causes only minor increases in antiscalant oxidation. The extent of oxidation varies with pH as a function of metal–ligand speciation, with the doubly-protonated metal–ligand species dominating the reactivity of the antiscalant. In the presence of calcium, the primary oxidation pathway for phosphonate antiscalants is through direct reaction with ozone (70–80% of measured P). In the absence of calcium, ozone and hydroxyl radicals appear to contribute relatively equally to oxidation. These results suggest phosphonate antiscalants can be oxidized with relatively low ozone doses, thereby deactivating the chelating behavior of the antiscalant and allowing increased precipitation of scaling salts such as calcium and magnesium.

Published by Elsevier B.V.

## 1. Introduction

Antiscalants, or scale inhibitors, are used in many applications to prevent salt precipitation [1]. A primary target precipitate is calcium carbonate ($CaCO_3$); however, several other precipitates of calcium, barium, and strontium, as well as silica, can be problematic. Multiple precipitates can form during reverse osmosis (RO) membrane desalination of brackish water (between 1 and 10 g/L total dissolved solids, TDS) [2], and salt precipitation can occur on the membrane surface even if no bulk precipitation occurs [3]. Calcium

---

*Abbreviations:* ATMP, aminotri(methylene phosphonic acid); DOC, dissolved organic carbon; DTPA, diethylenetriamine-pentaacetate; DTPMP, diethylenetriamine penta(methylene phosphonic acid); HDTMP, hexamethylenediamine tetra(methylenephosphonic acid); K, formation (protonation) constant; NOM, natural organic matter; RO, reverse osmosis; t-BuOH, tert-butanol; TDS, total dissolved solids; TOC, total organic carbon.

☆ Contribution of NIST, an agency of the US government; not subject to copyright in the United States.

* Corresponding author. Tel.: +1 303 497 4234; fax: +1 303 497 5030.
*E-mail address:* lauren.greenlee@nist.gov (L.F. Greenlee).

http://dx.doi.org/10.1016/j.cej.2014.02.002
1385-8947/Published by Elsevier B.V.

carbonate can be largely controlled by lowering the pH, but antiscalants are used in most RO operations to further control precipitation and increase the product water flux. RO feed water is typically lowered to approximately pH 6, and during membrane desalination, the pH of the concentrate (RO waste stream) slowly increases.

Antiscalants allow higher recovery in an RO system; recovery is the fraction of the feed flow that becomes the permeate (product water). However, even with antiscalants, brackish water RO recovery is typically limited to 75–85%. Inland brackish water sources are an important alternative water resource, but reverse osmosis treatment is currently limited by the cost and technical feasibility of concentrate disposal [4] and requires an alternative approach to increase recovery above 90%. A significant decrease in the volume of RO concentrate by increasing recovery would help reduce the size of downstream processes to achieve zero liquid discharge, such as evaporation ponds or thermal treatment. For concentrate disposal, increased recovery and decreased concentrate volume would result in decreased costs.

Recent research has focused on using multi-stage treatment of the concentrate to increase recovery [5]. The primary approach is to perform a controlled precipitation step on the concentrate and remove salts that are likely to precipitate, followed by a solid/liquid separation step (typically microfiltration) and secondary RO treatment. The product of concentrate treatment is a highly saline, but of low scaling propensity, water that can be desalinated, resulting in less concentrate and more product (drinking) water.

Antiscalants are dosed to RO feed water, typically in the concentration range of 1–15 mg/L, and are concentrated in the concentrate during RO desalination. For an RO recovery of 80%, the antiscalant feed concentration would increase approximately by a factor of five. Therefore, these compounds are present during subsequent concentrate treatment and are likely to hinder a concentrate treatment process that includes precipitation. If antiscalants in the concentrate could be degraded prior to precipitation, more precipitation might occur, which would further lower the scaling propensity of the concentrate and enable higher overall recovery. Many antiscalants are phosphonate-based synthetics that are not easily degraded, and a strong oxidant is needed.

The goal of this study was to determine the specific parameters and parameter ranges that influence the oxidation of phosphonate antiscalants. In this study, ozone, with and without hydrogen peroxide, was used as the oxidant. The parameters examined included pH, water composition, antiscalant type, ozone dose, and hydrogen peroxide concentration. In particular, this paper focuses on the effect of specific cations typically present in brackish water on antiscalant oxidation and on the relative importance of reactions with ozone and with hydroxyl radicals in the reaction pathway. Antiscalant oxidation was examined within a pH range relevant to the expected pH range of an RO concentrate (pH 6–8).

## 2. Materials and methods[1]

All inorganic salts, acids, and bases used in experiments were ACS grade. Unstabilized hydrogen peroxide (30%) was obtained from Sigma–Aldrich Co. (St. Louis, MO, USA). 0.1N potassium permanganate ($KMnO_4$) was used to determine the hydrogen peroxide concentration [6].

The ozone generator used was OzoneLab™ Model OL80W/FM100VT. The oxygen flow to the ozone generator was controlled by a digital mass flow meter and controller (Mass Flo© Model 1179A-01522CS1BV). The flow meter was calibrated for oxygen flow at room temperature (20 °C); all experiments were performed at room temperature. The ozone offgased was captured by catalytic ozone destructors. All experiments were performed using an aliquot of ozone stock solution [7]. The stock solution was made by bubbling gaseous ozone through deionized water in a gas washing bottle. The gas washing bottle was placed in a bucket of ice to increase the solubility of ozone in water; the oxygen gas flow was set to 40 mL/min. The gas washing bottle had a volume of 500 mL. The aqueous ozone concentration was measured on a UV/visible spectrophotometer (Agilent model 8453) at 258 nm in a one centimeter quartz cuvette. To prepare a sample for measurement, an aliquot was removed from the stock solution and added to 5 mM phosphate buffer (pH 3) to stabilize the ozone. The sample was measured within approximately 30 s on the spectrophotometer. All experiments were dosed with a specific volume of aqueous ozone based on the measured ozone concentration in the stock solution, and the same glass pipet was pretreated with ozone and used for aqueous ozone addition. The stock solution had an ozone concentration between 1.25 mM (60 mg/L) and 1.66 mM (80 mg/L). Ozone concentrations used in experiments included 1 mg/L, 5 mg/L, and 10 mg/L $O_3$. Hydrogen peroxide ($H_2O_2$) was added from a working solution of 1,000 mg/L. All experiments were performed in glass bottles with a volume of 250 mL and screw caps with Teflon-lined inserts. After addition of the oxidants, samples were allowed to react for 30 min under constant stirring; no residual ozone was detected at the end of 30 min. The absence of residual ozone was an expected result based on previous work performed on waters with similar or lower levels of organic carbon [8–10], where the organic carbon quickly reacts with ozone. All experiments were performed at least three times.

Antiscalant samples were obtained from Dequest Water Management Additives. The antiscalants, shown in Fig. 1, included DQ2006, the penta-sodium salt of aminotri(methylene phosphonic acid); DQ2054, the hexa-potassium salt of hexamethylenediamine tetra(methylene phosphonic acid); and DQ2066, the hepta-sodium salt diethylenetriamine penta(methylene phosphonic acid). Total organic carbon (TOC) and total solids analysis were used to determine the organic carbon and mass concentrations of all the antiscalants. TOC was measured on a Teckmar-Dohrman Apollo 9000 Combustion Analyser, where, first, $CO_2$ (inorganic carbon) was removed from each sample through addition of 21% phosphoric acid and subsequent oxygen sparging. The sample then passed through a catalyst and was oxidized in a furnace at 680 °C. Raw data counts from the detector, a Nondispersive Infrared (NDIR) sensor, were correlated to organic carbon concentration through a calibration

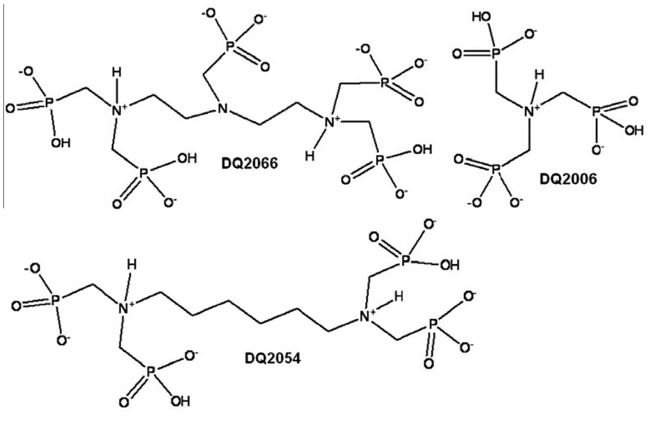

**Fig. 1.** Phosphonate antiscalants in appropriate protonated form at pH 6.0.

---

[1] Commercial equipment, instruments, or materials are identified only in order to adequately specify certain procedures. In no case does such identification imply recommendation or endorsement by the National Institute of Standards and Technology, nor does it imply that the products identified are necessarily the best available for the purpose.

Download English Version:

https://daneshyari.com/en/article/147781

Download Persian Version:

https://daneshyari.com/article/147781

Daneshyari.com