ELSEVIER

Desalination 119 (1998) 199–204

DESALINATION

Increasing conversion in membrane filtration systems using a desupersaturation unit to prevent scaling

Ingrida Bremere[a*], Maria D. Kennedy[a], Amayo Johnson[a],
Rani van Emmerik[a], Geert-Jan Witkamp[b], Jan C. Schippers[a,c]

[a]*International Institute for Infrastructural, Hydraulic and Environmental Engineering, IHE, P.O. Box 3015, 2601 DA Delft, The Netherlands, , Tel.: +31 (152) 151767; Fax: +31 (152)122921;email: bre@ihe.nl*
[b]*Laboratory for Process Equipment, Delft University of Technology, Leeghwaterstraat 44, 2628 CA Delft*
[c]*Kiwa Research and Consultancy, P.O. Box 1072, 3430 BB Nieuwegein, The Netherlands*

Received 15 July 1998

Abstract

A desupersaturation unit (DU), placed between the stages of either RO or NF systems is aimed at reducing the degree of supersaturation in the concentrate stream thus preventing membrane scaling in the last stage of a membrane filtration system while allowing conversion to be maximized up to design limits (>90%). Barium sulfate desupersaturation in an up-flow fixed bed reactor was demonstrated for ca. 200 h (Concentrate A). However, barium removal in the DU was shown to be source dependent and early break-through of the DU occurred with Concentrate B after ca. 30 h. Calculations showed that barium sulfate deposition in the DU was affected by natural organic matter (NOM). Blocking of seed crystal surface by rapid adsorption of certain NOM fractions hindered crystal growth and was believed to be the main reason for break-through in the DU. Recycling of these naturally occurring organic molecules as "natural antiscalants" to maximize the conversion of RO (NF) systems may be possible if they can be isolated and characterized.

Keywords: Desupersaturation; RO system; Scale prevention; Barium sulfate; NOM

1. Introduction

The conversion of membrane filtration systems is frequently limited to 80% or lower, due to scaling problems, i.e. precipitation of sparingly soluble salts, such as calcium carbonate, barium sulfate and calcium sulfate on membrane surface. The existing approach to nanofiltration (NF) systems has limited sensitivity and thus scaling remains undetected until the rate of precipitation is high and the membrane surface is significantly covered with the layer of precipitated salt. At this stage replacement of membranes may be necessary. This results in a significant cost increase as the membranes are one of the most expensive components of RO and NF plants [1].

The conventional approach to achieve high conversions in RO/NF systems through the addition of acid and/or antiscalant has many limitations, i.e. antiscalant toxicity concerns

---

*Corresponding author.

Presented at the Conference on Membranes in Drinking and Industrial Water Production, Amsterdam, September 21-24, 1998, International Water Services Association, European Desalination Society and American Water Works Association

PII S0011-9164(98)00152-0

towards environment and potential membrane bio-fouling leading to increased operational costs because of increased cleaning frequency [2]. Although, physical antiscale pretreatment methods (magnetic, electrostatic, ultrasonic) are intensively studied for scale prevention as an attractive simple approach they are not completely accepted due to the lack of scientific explanation of the mechanism of scale inhibition, controversial results and inconsistent operation [3,4].

From thermodynamic considerations, supersaturation is the first requirement for crystallization (scale) to occur and is the driving force for both nucleation and growth [5], however, precipitation is a stepwise process which involves nucleation, i.e. creation of a new crystal, and growth. The nucleation processes include primary (homogeneous and heterogeneous) and secondary nucleation which results from the presence of crystallization surface in solution. Generally, the critical value of supersaturation for the different nucleation processes can be expressed in a decreasing order as $S_{c,\ homo}>S_{c,\ hetero}>S_{c,\ surface}>1$ (solubility) [6]. The presented order of critical supersaturation suggests, that in RO/NF systems precipitation of scaling agents, e.g. barium sulfate can be induced on seeds from supersaturated concentrates which are referred to as stable for spontaneous precipitation.

Removal of scaling agents before the last stage of a membrane filtration system by desupersaturation of membrane concentrate in a separate unit will result in the reduction of supersaturation in membrane concentrate and, consequently, higher conversions may be achieved without the risk of scaling. A crystallization unit incorporated into a membrane filtration system (RO, NF) has been cited as a part of a "zero discharge" approach to saline waste water treatment [7,8]. However, the application of the desupersaturation (crystallization) unit in processing moderately saline surface water is new and therefore has to be optimized yet.

The research is directed at testing the long-term application of fixed and fluidized bed reactors used for precipitation of sparingly soluble salts, e.g. barium sulfate, calcium carbonate from supersaturated concentrate in membrane filtration systems. The efficient operation of the desupersaturation unit can be achieved by modeling and optimizing design parameters, e.g. mode of operation, concentrate flow and crystal growth conditions. This paper focuses on precipitation of a model compound: barium sulfate in a desupersaturation unit which may be incorporated in RO membrane system for potable water production.

2. Principle of a desupersaturation unit

Seeded growth technique which is based on the inoculation (seeding) of a supersaturated solution with crystals of the precipitating salt is the principle used in desupersaturation unit aimed to remove scaling agents, e.g. barium sulfate before the last stage of membrane filtration system (Fig. 1).

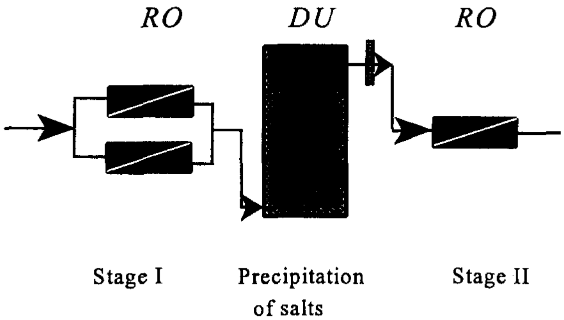

Fig. 1. Incorporation of a desupersaturation unit between I and II stage of an RO system.

A concentrate stream (50 to 80% conversion) which is supersaturated with respect to the precipitant salt is introduced at the lower part of a crystallizer where seed crystals of the same material as the crystallizing salt (barium sulfate) are present. Advantages of desupersaturation include: (i) rapid desupersaturation of the membrane concentrate on large crystallization surface available, (ii) controlled outgrowth allowing the controlled sludge production, and

(iii) easy operation as the precipitation is a self-conducting process. However, the efficiency and performance of crystal growth will depend on: (i) The supersaturation, which is the driving force for crystallization. (ii) The condition of seeds, i.e. surface area available and reactivity. The available seed crystal surface area can be easily manipulated by the amount of added crystals, however, the reactivity of crystals may decrease during the continuous crystallization process due to poisoning of seeds by other substances present in water, e.g. inorganic ions, biological and (natural) organic matter and/or perfection and outgrowth of the crystalline structure (aging). In addition, the condition of the seeds may be influenced by pH. The maximum desupersaturation which can be reached is dependent on the solubility of the salt to be removed.

3. Experimental

Laboratory scale desupersaturation unit: comprised a plastic storage vessel (100 l), variable speed peristaltic pump and barium sulfate seeds contained in a perspex plastic tube (column) with openings for influent and effluent. Columns of three different sizes were employed: 1.5 m high and 50 mm diameter, 0.7 m high and 34 mm diameter, 0.7 m high and 25 mm diameter, respectively. Hydraulic loading was varied between 9 to 1 l/h depending on the column size, respectively, while the empty bed contact time of 20 min and a concentrate contact time with seeds of 8 min were kept constant for all examined columns. The loading rate per effective seed surface area was kept as 5.1 l/h m^2 (unless stated differently).

Seed crystals: mineral barite crystals (white, black and brown) (supplier: Aquatechniek) were crushed in laboratory, size grade of 2.0 to 3.15 mm was separated by sieving (BS), washed with deionized water and filled in fixed bed column as barium sulfate seeds. Scanning Electron Microscopy coupled with X-ray Spectroscopy (JSM-6400F, Pioneer) analysis revealed Sr (white), Cu and Zn (black), and Na, Al, Si, Fe and Cu (brown) traces present in seeds.

RO concentrates (80–85% conversion) were collected from surface water processing Pilot Plant RO systems with different applied feedwater pretreatment techniques: (i) coagulation, rapid filtration and ultrafiltration (Concentrate A) and (ii) ozonation, GAC filtration and slow sand filtration (Concentrate B). Investigated concentrates had similar total ionic strength (*ca.* 0.05 M), solution pH (ca. 7) and similar supersaturation ratio (SR of ca. 3), calculated using Eq. (1):

$$SR = \sqrt{\frac{\gamma_{Ba^{2+}}[Ba^{2+}]\gamma_{SO_4^{2-}}[SO_4^{2-}]}{K_{sp}}} \qquad (1)$$

where γ_i – barium and sulfate ion Pitzer activity coefficient which accounts for the effect of possible ion associations (calculated according to the method [9]), [i]–concentration of barium and sulfate ion in corresponding concentrate (mol/l), and K_{sp}–thermodynamic solubility product for corresponding type of RO feedwater ($K_{sp}=1.34\times10^{-10}$ mol^2/l^2) [9].

Barium was analyzed by inductively coupled plasma (ICP) spectrometry (Spectroflame 21/016) calibrated using barium standards 0–700 μg/l. Standards were prepared in laboratory from a solution of 1000 mg/L barium (Baker) using calibrated Eppendorf pipettes, concentrated HNO_3 (INSTRA-Analyzed, Baker) and deionized water. The accuracy of calibration was checked with the certified barium standard of 100 μg/l (Perkin Elmer), the calibration was unacceptable if the standard deviation of the certified standard was greater than 5%.

Sampling started when the corresponding RO concentrate entered the crystallization column. Periodically 10 ml samples in duplicate were taken for barium analysis for influent (blanks) and effluent from the column using a plastic syringe (Becton Dickinson) with a 0.22 μm filter (Sartorius) rinsed with 0.2 M HNO_3 prior to use. The first 2 ml of sample filtered was discarded and the following 8 ml of filtrate collected in plastic sample bottles (25 ml) pretreated by soaking in 7 M HNO_3 for 24 h, and rinsing three times with deionized water, prior to use. To preserve the collected sample, a drop of concentrated (14 M) HNO_3 (INSTRA-Analyzed, Baker) was added to each sample prior to barium analysis by ICP.

4. Results and discussion

4.1. Choice of a desupersaturation unit (DU) design

Certain criteria have to be met before either a fixed or fluidized bed reactor can be incorporated between the stages of an RO unit for scaling prevention, i.e. safe operation of the last stage of the membrane filtration system with no danger of crystal wash-out from the DU. An upflow fixed bed reactor was the choice for desupersaturation of RO concentrate with respect to barium sulfate, because of the efficiency of desupersaturation and absence of crystal wash-out from the column. The barium concentration in RO concentrates from potable water treatment plants tested was low (<500 ug/l), and as a result the expected outgrowth of barium sulfate crystals was very small and the chance of cementing the crystallizer was negligible.

4.2. Desupersaturation of RO concentrates

Barium removal was tested using two surface water pilot plant RO concentrates (80-85% conversion) with similar levels of supersaturation. The principle of desupersaturation, i.e. rapid decrease from a high concentration in the column influent to a low barium concentration in the desupersaturated effluent was demonstrated for at least 200 h with Concentrate A (Fig. 2). The influent supersaturation ratio of the RO concentrate (80% conversion) SR=3.2 (concentration of barium ca. 190 μg/l and sulfate ca. 650 mg/l) rapidly decreased to SR=1.6 (concentration of barium ca. 50 μg/l) in the effluent, suggesting that barium sulfate crystallization took place on the column seed crystals. However, maximum desupersaturation, i.e. SR=1 (solubility) was not reached possibly due to the presence of organic matter and particles in the concentrate which may influence crystal growth conditions, and/or slow growth kinetics approaching equilibrium and therefore contact time (8 min) may have been insufficient

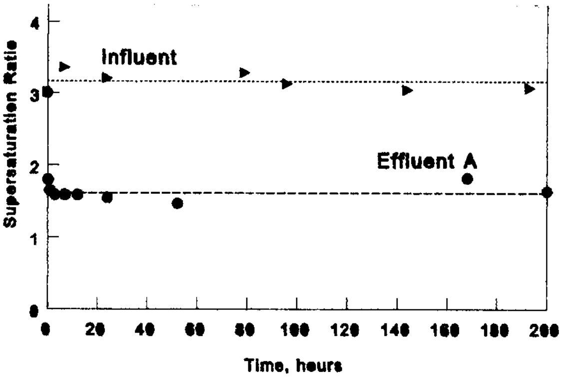

Fig. 2. Desupersaturation of Concentrate A.

A typical desupersaturation curve was also found initially for Concentrate B (Fig. 3), i.e. a rapid drop in supersaturation from SR=3.2 (concentration of barium ca. 440 μg/l and sulfate ca. 290 mg/l) to ca. 1.2 (concentration of barium ca. 60 μg/l) within 20 min for the first 20 h. Unexpectedly, an apparent decline was observed in the barium removal efficiency after 30 h of operation, indicating loss of seed activity possibly due to poisoning of the seed crystal surface by inorganic ions, organic molecules and/or biological material. Blocking of barium seed crystals by inorganic ions appears unlikely, because efficient desupersaturation for at least100 h was observed with synthetic concentrate (similar to Concentrate B) prepared by dissolving the corresponding concentration of inorganic salts in deionized water in the absence of organic matter. Natural organic matter may act as a natural antiscalant, inhibiting crystal growth. However, the efficiency depends on the type and strength of the chemical bonds formed with the crystal surface [10]. The adsorption of highly polar NOM molecules (present in Concentrate B) on positively charged barium sulfate crystals is believed to be the major reason for break-through in the DU. The barium sulfate removal is apparently source dependent implying that the nature and composition of the RO concentrate and applied pretreatment techniques may influence the crystal growth kinetics and the breakthrough.

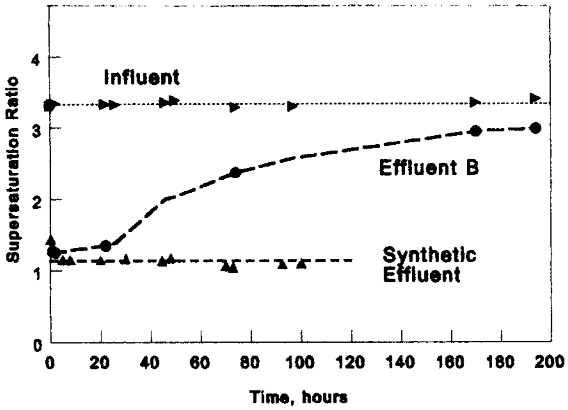

Fig. 3. Desupersaturation of Concentrate B and synthetic concentrate.

4.3. Desupersaturation efficiency

Desupersaturation efficiency, η (%), was calculated as presented below Eq. (2):

$$\eta = \frac{100\,(SR_i - SR_t)}{(SR_i - 1)} \tag{2}$$

where SR_i and SR_t represent the barium sulfate supersaturation ratio in the influent and effluent at any given time. A comparison of the two concentrates (Fig. 4) showed that high desupersaturation efficiency ca. 70% was observed with Concentrate A over the entire test period (200 h). However, for Concentrate B, the initial efficiency was excellent, i.e. ca. 95% but declined after 50 h and decreased to ca. 20% after 200 h. Organic matter present in Concentrate B was shown not to affect barium solubility [9], and hence the high driving force for crystallization (supersaturation ratio) coupled with the large barium sulfate seed surface area available in DU during the initial hours of experiment resulted in efficient barium desupersaturation. Progressive reduction of the available crystal surface area, i.e. "poisoning" of seed crystals via adsorption of organic matter led to low removal efficiencies in the DU. The excellent removal efficiency, i.e. >90% observed in the case of synthetic concentrate (without organics) for at least 100 h, supports the hypothesis that the loss of desupersaturation efficiency in the DU column is caused by organic matter.

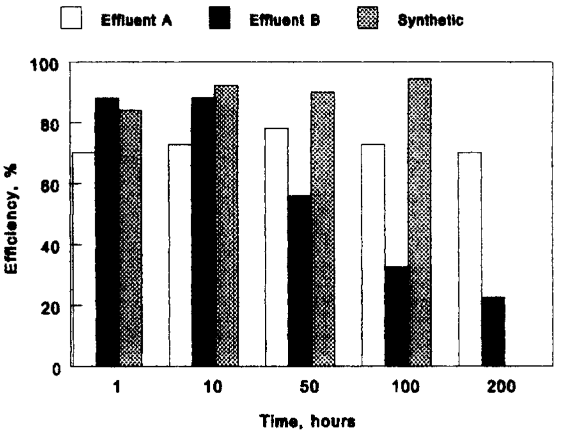

Fig. 4. Barium sulfate desupersaturarion efficiency in a fixed bed DU.

The supersaturation ratio in the last stage RO concentrate determines how far the RO system conversion can be increased without the risk of barium sulfate scaling. The strategy behind the DU is rapid desupersaturation of the concentrate (as close as possible to SR=1, solubility level) before it enters the last stage of the RO system. In this way, the last stage can be operated at higher conversions due to the low initial supersaturation ratio, without the risk of barium sulfate scaling.

4.4. Modelling of barium sulfate deposition in DU column

The barium sulphate deposition rate D_R (m/h) which is related to crystal growth kinetics was calculated via Eq. (3):

$$D_R = \frac{M(C_i - C_j)Q}{\rho\, A_T(o)} \tag{3}$$

where M – molecular weight of barium sulfate (0.233 kg/mol), C_i and C_j are influent and effluent concentrations (mol/m^3), Q – column hydraulic loading rate (m^3/h), ρ_b - barium sulfate density (4500 kg/m^3) and A_T(o) - seed crystal surface area (0.57 m^2).The main assumptions in modeling the deposition rate include: (i) only barium sulphate precipitated on the seed crystals (no precipitation of other salts), (ii) the change in effective crystal surface area over time is negligible due to low outgrowth of barium sulphate, (iii) crystals are spherical and have a uniform size.

A low initial barium sulfate deposition rate ca. 1×10^{-9} m/h for both RO concentrates indicated that cementing of the column could be expected to occur in ca. 10000 h (assuming 0.1 mm distance between seeds in column). However, decreasing deposition rate over time was observed for both RO concentrates examined (Fig. 5.), indicating that NOM (colloids and/or particles) have a direct influence on the barium sulfate deposition rate by blocking (adsorption) available crystallization centres. In Fig. 5, two types of adsorption were identified: (i) fast adsorption (within ca. 10 h) which was only observed in the case of Concentrate B, and (ii) slow adsorption of NOM (for ca. 50 h) observed for both concentrates. The fraction of NOM responsible for the fast retarding of barium sulfate crystal growth (by ca. 0.1×10^{-9} m/h) was present in Concentrate B. If this fraction of NOM can be isolated and characterized (type, size, charge), these naturally occurring organic molecules may be used in membrane filtration systems as “natural antiscalants” to maximize the conversion.

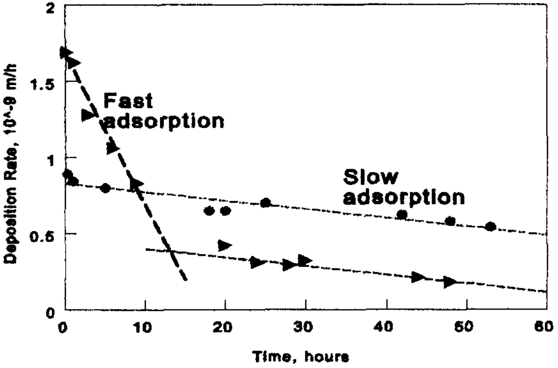

Fig. 5. Barium sulfate deposition rate in RO concentrates: • – Concentrate A, ▶ – Concentrate B.

5. Conclusions

A fixed bed DU for barium sulfate desupersaturation for RO concentrates was preferred to fluidized bed due to absence of crystal wash-out from the column. Successful operation of a fixed bed desupersaturation unit was demonstrated for 200 h where the supersaturation ratio was reduced from ca. 3 in the influent to ca. 1.5 in the effluent from DU and thus higher conversions could be applied without the risk of barium sulfate scaling. However, the barium sulfate removal was shown to be source dependent implying that the nature and composition of RO feedwater (concentrate) and applied pretreatment methods may influence the crystal growth kinetics, desupersaturation efficiency and the break-through in the DU. Early break-through of desupersaturation unit was attributed to blocking of active crystallization sites by adsorption of organic matter on seed crystals. However, work in this direction is on-going and directed at isolation and characterization of these organic molecules which may be used in membrane filtration systems as “natural antiscalants” to maximize the conversion.

Acknowledgments

The authors wish to acknowledge financial assistance from NOVEM (Netherlands Agency for Energy and Environment) within the Subsidy Programme of New Technology for Industry (MINT), and Amsterdam Water Supply (GWA), Overijssel Water Supply, Kiwa N.V. Research and Consultancy, Heineken, Hydranautics Europe and Advanced Treatment Processes Europe (ATP). We are also thankful to the Provincial Waters of North-Holland (PWN) for co-operation.

References

[1] J.C. Schippers, J.C. Kruithof, H_2O, 30 (1997) 179.
[2] J.P.van der Hoek, P.A.C.Bonné, E.A.M.van Soest and A. Graveland, Proc., AWWA 1997, Membrane Technology Conference, New Orleans, USA, pp. 1029–1041.
[3] K.W. Busch and M.A.Busch, Desalination, 109 (1997) 131.
[4] J.S.Baker, S.J.Judd and S.A.Parson, Desalination, 110 (1997) 151.
[5] A.S. Myerson and R.Ginde, In: A.S.Myerson, (Ed.), Handbook of Industrial Crystallization, Butterworth-Heinemann, 1993, pp. 33–63.
[6] J.A.Dirksen and T.A.Ring, Chem. Eng. Sci., 46 (1991) 2389.
[7] 7. R. Rautenbach and T.Linn, Desalination, 105 (1996) 63.
[8] B. Ericsson and B.Hallmans, Desalination, 105 (1996) 115.
[9] S.F.E. Boerlage, M.D.Kennedy, G.J.Witkamp, J.P.van der Hoek and J.C.Schippers, Proc., AWWA 1997 1997, pp. 745–759.
[10] M.C.van der Leeden and G.M. van Rosmalen, J. Colloid Interface Sci., 171 (1995) 142.