Desalination 254 (2010) 75–79

Contents lists available at ScienceDirect

Desalination

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

The vaterite saturation index can be used as a proxy of the S&DSI in sea water desalination by reverse osmosis process

J. Peña [a,*], B. Buil [a,1], A. Garralón [a,2], P. Gómez [a,3], M.J. Turrero [a,4], A. Escribano [a,5], G. Garralón [b,6], M.A. Gómez [c,7]

[a] Unit of Engineering and Geological Barriers, Department of Environment. Ciemat. Avd. Complutense, 22 - 28040 Madrid, Spain
[b] Departamento I+D+i. CADAGUA, S.A. Gran Vía 45, 7ª planta, 48011 Bilbao, Spain
[c] Department of Civil Engineering. University of Granada. Campo de Fuentenueva s/n 18071 Granada, Spain

ARTICLE INFO

Article history:
Received 18 August 2009
Received in revised form 1 December 2009
Accepted 3 December 2009
Available online 18 January 2010

Keywords:
S&DSI index
Vaterite
pH
Saturation index
Modelling

ABSTRACT

The Stiff and Davis solubility index (S&DSI) is widely used to predict the precipitation of calcium carbonate on seawater reverse osmosis membranes. Although this index is defined as the pH of the solution minus the value of the pH of the solution in equilibrium with calcium carbonate, the actual polymorph of calcium carbonate to which this index refers is not specified. In the present work, the geochemical significance of the S&DSI was examined by geochemical modelling. The pH of a number of solutions minus the pH of these solutions in equilibrium with different polymorphs of calcium carbonate (calcite, aragonite, vaterite and monohydrocalcite) was determined using PHREEQC software and then compared with S&DSI indices for the same solutions. This index was found to correspond to the pH of the solution minus the value of the pH in equilibrium with vaterite. The possibility that the pH, and concentration of Ca2+ and HCO3− ions, measured in the original experiment of Stiff and Davis were controlled by the solubility of vaterite is discussed. Further, it is proposed that in seawater reverse osmosis desalination plants, the saturation index of vaterite may be used as a proxy of the S&DSI index.

1. Introduction

In 1952, Stiff and Davis [1] published an article in which they extended the use of the Langelier saturation index (LSI) [2,3] to water of high salinity (>4000 ppm). This they achieved with the following expression:

$$SI = pH - pCa - pAlk - K \tag{1}$$

where *pH* is the pH of the water, *pCa* is the negative of the log concentration of calcium, *pAlk* is the negative of the log total alkalinity, and *K* is a constant the value of which value depends on the salinity and temperature. The saturation index (SI) of Eq. (1) is an index of stability that, when positive, indicates the possible precipitation of calcium carbonate — something of great use in reverse osmosis desalination plants. The index later became known as the Stiff & Davis saturation index (S&DSI), a name it has kept to the present day. If, in equilibrium, the SI is zero, the value of *K* would be:

$$K = pH - pCa - pAlk \tag{2}$$

The above authors [1] then performed an experiment involving solutions of different sodium chloride concentration, to which were added different solutions of calcium chloride and sodium carbonate until a calcium carbonate precipitate formed. At this point the pH was determined, along with the carbonate, bicarbonate, chloride and calcium concentrations, and the value of *K* for different ionic strengths was obtained. This was performed at 0°, 30° and 50 °C. The outcome was the table shown in Fig. 1; these curves have survived until the present day and appear, for example, in standard ASTM no. D4582 [4].

The S&DSI is an extension of the LSI; these indices are defined as [4,5]:

$$LSI = pH - pH_S \tag{3}$$

$$S\&DSI = pH - pH_S \tag{4}$$

where *pH* is the pH of the concentrate, and pH_S the pH at which the concentrate reaches saturation with calcium carbonate. Although some authors have defined pH_S as the pH at which saturation with

---

* Corresponding author. Tel.: +34 91 346 08 35; fax: +34 91 346 65 42.
E-mail addresses: javier.pena@ciemat.es (J. Peña), belen.buil@ciemat.es (B. Buil), antonio.garralon@ciemat.es (A. Garralón), paloma.gomez@ciemat.es (P. Gómez), mj.turrero@ciemat.es (M.J. Turrero), alicia.escribano@ciemat.es (A. Escribano), ggl@cadagua.es (G. Garralón), mgomezn@ugr.es (M.A. Gómez).
[1] Tel.: +034 91 346 61 83.
[2] Tel.: +034 91 346 61 87.
[3] Tel.: +034 91 346 61 85.
[4] Tel.: +034 91 346 61 835.
[5] Tel.: +034 91 346 08 34.
[6] Tel.: +34 94 481 73 60; fax: +34 94 481 73 61.
[7] Tel.: +34 958 24 80 16; fax: +34 958 24 30 94.

0011-9164/$ – see front matter © 2009 Elsevier B.V. All rights reserved.
doi:10.1016/j.desal.2009.12.011

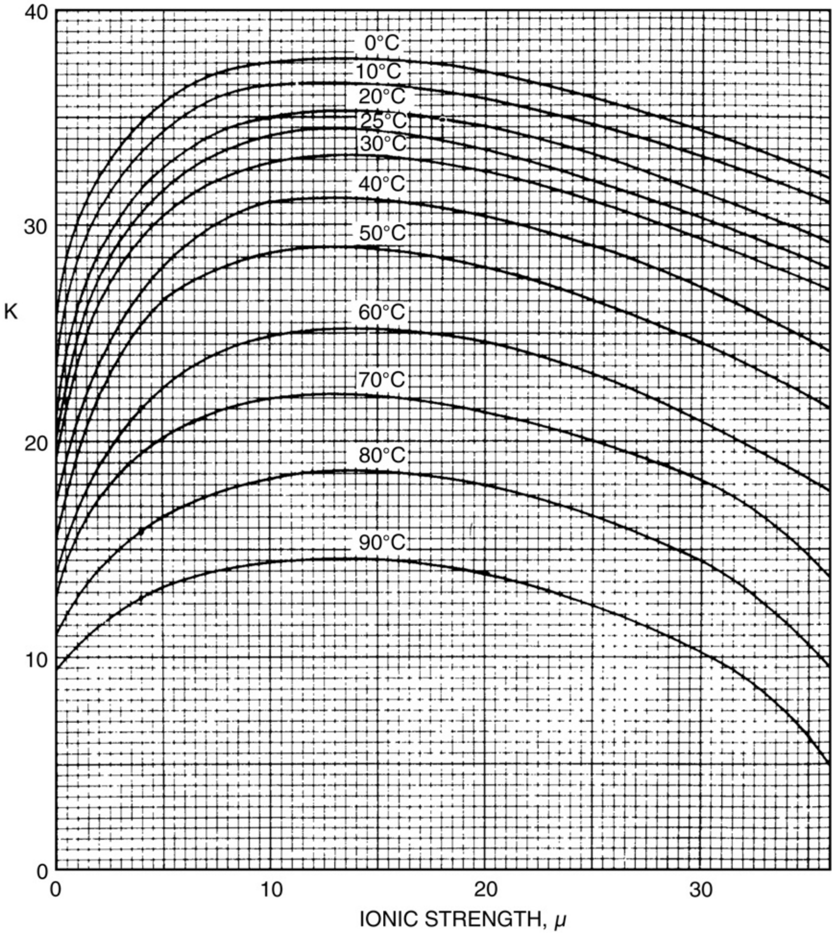

Fig. 1. Values of *K* at different ionic strengths. From [1].

calcite is reached [6], the mineral phase is not generally expressed but rather the generic term 'calcium carbonate' used.

Calcium carbonate is known to exist naturally in six forms [6–8], three of which are anhydrous crystalline polymorphs – calcite, aragonite and vaterite – and three of which are hydrated forms — amorphous calcium carbonate (ACC), calcium carbonate monohydrate (MCC, also known as monohydrocalcite), and calcium carbonate hexahydrate (CCH, also known as ikaite). The aim of the present work was to identify to which of these forms the generic value of pH_S used in the definition of S&DSI refers.

2. Methodology

PHREEQC software [9] is designed for use in a wide range of geochemical calculations under low temperature conditions. Very important in the present work is the ability of this software to calculate the speciation of the components dissolved in an aqueous solution, and to determine the saturation indices of a solution with respect to different mineral phases. PHREEQC makes use of an aqueous ion association-type model, employing Debye–Hückel-type equations (the Debye–Hückel equation, the Davies equation, the extended Debye–Hückel equation and the Truesdell–Jones equation) to take into account the non-ideal nature of aqueous solutions. This type of model is valid at low ionic strengths, but can fail in the range of the ionic strength of sea water or above. For water of high ionic strength, aqueous models involving ionic interaction should be used that bear in mind binary interactions between species of the same sign, as well as simultaneous interactions (ternary interactions) between three or more ions, two or more of which may have the same sign [10]. The most widely accepted model of this nature is the Pitzer model [11]. Since version 2.12, PHREEQC has included the Pitzer formulae for the calculation of activity coefficients. This simply requires the use of the "pitzer.dat" thermodynamic database.

To understand the significance of the S&DSI index in reverse osmosis, and its relationship with some of the anhydrous (calcite, aragonite and vaterite) and hydrated (monohydrocalcite) forms of calcium carbonate, the pH at equilibrium of a series of solutions of these phases was calculated using the PHREEQC software. The $pH-pH_S$ values of these solutions were then compared with the S&DSI values of the same solutions.

The PHREEQC calculations were made using the chemical composition data shown in Table 1 [12], and those determinated at a reverse osmosis pilot plant. The pilot plant has two lines of pretreatment of 384 m3/day capacity each, using an industrial scale membrane.

For these latter solutions, ROSA (Reverse Osmosis System Analysis) 6.1.5. software (DOW Chem.) was used to calculate the S&DSIs. For the solutions of Table 1 the S&DSIs from Al-Shammiri and Al-Dawas (1998) [12] were used.

For the calculation of pH at equilibrium for the different mineral phases, the solubility constants shown in Table 3 were used [7,8].

3. Results and discussion

Figs. 2 and 3 shows the value of the S&DSI index versus the values of the calcite LSI (CLSI), the aragonite LSI (ALSI), the vaterite LSI