

# ANALYSIS, APPROACHES, AND MODELS FOR THE RELEASE OF CARBON DIOXIDE, NITROGEN, OXYGEN, AND ARGON IN EVAPORATORS

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## Summary

The main features of the oxygen (O<sub>2</sub>), nitrogen (N<sub>2</sub>), argon (Ar), and carbon dioxide (CO<sub>2</sub>) release processes in desalination distillers are summarized and the gas release model developed at the University of Bremen, Germany is presented for the case of MSF distillation. The model permits a stage-by-stage computation of the bicarbonate ion HCO<sub>3</sub><sup>-</sup>, carbonate ion CO<sub>3</sub><sup>2-</sup>, and dissolved molecular CO<sub>2</sub> concentrations as well as the pH value of the brine on its path through the pre-heaters and flash chambers and determines the release rates of O<sub>2</sub>, N<sub>2</sub>, Ar, and CO<sub>2</sub> during flash evaporation in MSF distillers. The release of O<sub>2</sub>, N<sub>2</sub>, and Ar is treated as physical desorption, while the release of CO<sub>2</sub> is treated as a problem of chemical desorption. The coupling of mass transfer and chemical reaction kinetics is investigated and the rate-controlling steps in the CO<sub>2</sub> release process are determined. The performance of the model is discussed with respect to some influencing parameters of the non-condensable gas release.

## 1. Introduction

As described in *The Problem of Non-Condensable Gas Release in Evaporators* (See:

The Problem of Non-condensable Gas Release in Evaporators), the release of non-condensable (NC) gases, essentially oxygen (O<sub>2</sub>), nitrogen (N<sub>2</sub>), argon (Ar), and carbon dioxide (CO<sub>2</sub>), from the evaporating brine in desalination distillers affects the heat transfer for condensation, energy consumption, operation, and material lifetime of the distillers. In the past, the problems caused by NC gases were managed by costly design precautions or even neglected. Furthermore, they were often wrongly attributed to other phenomena. For example, the reduction of heat transfer for condensation due to NC gas interference was often attributed to fouling. In MSF distillers disturbances in the brine flow caused by NC gases were sometimes wrongly explained by incorrect adjustment of interstage brine transfer devices.

Due to previous ignorance of the problem and its complexity, the predictive simulation of NC gas release in desalination distillers, particularly of CO<sub>2</sub> release, has been scarcely investigated and given little attention in the desalination literature. Thus, considerable uncertainty exists in predicting the total CO<sub>2</sub> release rates in distillers and the distribution of these between the individual stages. The first investigations (e.g. Ciba-Geigy 1978; Watson Desalination Consultants 1979) into CO<sub>2</sub> release relied on simple reaction models and sparse experimental data. Only chemical reactions in the brine were considered. Mass transfer processes were completely neglected. In practice, these investigations serve as the basis for the different approaches employed by plant manufacturers and other experts to determine the CO<sub>2</sub> release rates for the dimensioning of the design venting rates or for simulation purposes. The various design methods for predicting the CO<sub>2</sub> release rates in multistage flash (MSF) distillers are summarized in Design Data for Non-condensable Gas Release Rates in Flash Chambers (See: Design Data for Non-condensable Gas Release Rates in Flash Chambers).

Lukin and Kalashnik (1982) and later Seifert (1989) and Seifert and Genthner (1991) developed the first physical models that allowed the calculation of the CO<sub>2</sub> release rates in individual MSF distiller stages. The models are based on the assumption that mass transfer phenomena in the brine rather than the reaction kinetics control the desorption process. The chemical reactions were considered to be fast.

In recent work on CO<sub>2</sub> release the following approaches have been applied.

- (a) Rigorous electrolyte thermodynamics were applied to the simulation of MSF distillers by Watzdorf and Marquardt (1997). The brine is considered as a multicomponent electrolyte system of varying complexity. Scale formation and CO<sub>2</sub> release are predicted assuming equilibrium conditions. The proper description of the electrolyte system and the equilibrium state in a thermodynamic model are considered to serve as a limiting case or as a prerequisite of any rate-based model.
- (b) The release of CO<sub>2</sub> in MSF distillers is treated as a problem of chemical desorption by the authors of this chapter (Glade 1999). The coupling of mass transfer and chemical reaction kinetics is investigated and the rate-controlling steps in the CO<sub>2</sub> release process are determined. This approach is presented in the following.

CO<sub>2</sub> release and alkaline scale formation, which is linked to the CO<sub>2</sub> release through chemical reactions, were investigated experimentally. Shams El Din and Mohammed (1994) studied the chemistry of alkaline scale formation in industrial MSF distillers by

extracting and analyzing brine samples from the water boxes and flash chambers. Moore et al. (1995) carried out corresponding investigations on CO<sub>2</sub> release. Shams El Din and Mohammed (1988, 1989) as well as Al-Sulami and Hodgkiess (1997) performed laboratory studies on the mechanism and rates of chemical reactions in aqueous bicarbonate solutions with respect to alkaline scale formation. A new experimental approach was applied by the authors of this chapter. For determining the CO<sub>2</sub> release rates in the individual stages of MSF distillers, the CO<sub>2</sub> concentrations were measured on-line and continuously in the parallel vents of industrial MSF distillers by means of a mass spectrometer. At the same time, the total vent flow rates, temperature, and pressure of the vents were measured. The measurements were carried out on two distillers from different manufacturers in a wide range of operation conditions. Some of the results of these measurements are presented in Design Data for Non-condensable Gas Release Rates in Flash Chambers (See: Design Data for Non-condensable Gas Release Rates in Flash Chambers).

As described above, the problem of CO<sub>2</sub> release has mainly been investigated in MSF distillers, but electrolyte thermodynamics and the chemical desorption theory can also be applied to the other thermal desalination processes, namely multiple-effect (ME) and vapor compression (VC) distillation.

In the following, the main features of the O<sub>2</sub>, N<sub>2</sub>, Ar, and CO<sub>2</sub> release processes are summarized and the gas release model developed at the University of Bremen, Germany, is presented for the case of MSF distillation.

## **2. Fundamentals of Desorption with and without Chemical Reaction**

The desorption of a dissolved gas from a solution without reacting is called "physical desorption". When the dissolved gas reacts chemically with other components of the solution, the desorption of the gas is called "chemical desorption".

In general, the phenomenon of desorption with a chemical reaction is made up of a number of elementary steps, which may be summarized as follows (Astarita 1967).

- (a) Chemical reaction of the dissolved gas within the liquid phase.
- (b) Mass transport of the dissolved gas from the bulk of the liquid to the interface.  
Physical equilibrium may be assumed to prevail at the interface.
- (c) Mass transport of the gas from the interface to the bulk of the gas phase.

Steps (a) and (b) may take place simultaneously and, thus, mutually interfere. The overall phenomenon resulting from steps (a) and (b) takes place in series with step (c). If step (c) is rate controlling, the overall rate is not influenced by the chemical reaction and the process may be regarded as a simple mass transfer phenomenon which is not influenced by the reaction rate. Of course, the chemical reaction may itself be the cause of an overall high mass transfer rate within the liquid phase and, therefore, for step (c) is rate controlling. In the case of physical desorption without chemical reactions step (a) does not occur.

The occurrence of the chemical reactions has two distinct effects on the desorption

process.

- (a) Chemical reactions affect the concentration of the molecularly dissolved gas in the bulk of the liquid. During desorption the chemical reactions continuously produce the component to be desorbed, thus providing a certain concentration of it in the bulk of the liquid and, hence, a certain driving force for the mass transfer.
- (b) The second effect is more subtle. At a given level of driving force, the actual rate of mass transfer may be very significantly larger when chemical reactions are taking place than it would be in the absence of chemical reactions. The rate enhancement may be very large, up to two orders of magnitude or even more. The enhancement may be so large as to actually reduce the mass transfer resistance in the liquid phase to the point at which it is negligible as compared to the resistance in the gas phase.

The first effect of the chemical reactions on the desorption of CO<sub>2</sub> in desalination distillers, i.e. the influence on the concentration of the molecularly dissolved CO<sub>2</sub> in the bulk of the seawater, is shown in section 4.1.3 of this chapter. In the following, the second effect of the chemical reactions on the mass transfer is discussed.

In the classical chemical desorption theory, different asymptotic regimes have been identified (Astarita 1967; Danckwerts 1970; Shah and Sharma 1976): the slow-reaction regime subdivided into the kinetic and diffusional regime, the fast-reaction regime, and the instantaneous reaction regime. In addition to these asymptotic cases, transition regions are known to occur.

Under certain conditions the desorption and reaction may conform to the slow-reaction regime. The gas reacts in the bulk of the liquid and is transported through the boundary range to the phase interface without reacting. Thus, the processes of chemical reaction and mass transfer become two steps in series for a slow reaction. The desorption rate in this case is almost unaffected by the chemical reaction. If the reaction is so slow that the overall driving force is almost entirely used up by the reaction, i.e. the difference between the gas concentration in the bulk and the equilibrium concentration is much greater than the difference between the gas concentration in the bulk and the concentration at the phase interface, then the desorption will take place in the kinetic regime. If the reaction rate is high enough to keep the gas concentration in the bulk of the liquid practically to its equilibrium value, the desorption will take place in the so-called diffusional regime.

The desorption accompanied by a chemical reaction is considered to be in the fast-reaction regime when the desorption rate is considerably affected by the chemical reaction. In the fast-reaction regime both reaction and mass transfer occur in parallel within the boundary range at the phase interface and the mass transfer is enhanced by the reaction rate.

The instantaneous regime is the case where the chemical reactions are so fast that chemical equilibrium prevails at all points in the liquid phase, i.e. in the bulk as well as in the boundary range and at the phase interface. Therefore, chemical reactions take place at whatever rate the reactants are brought together by diffusion. The instantaneous regime represents an upper bound to the rate enhancement, since all resistance to

desorption due to chemical kinetics has been reduced to zero. The increase in desorption rate due to the chemical reactions would be a maximum in this situation.

In some cases, a wide spectrum of regimes, e.g. from the kinetic, to the diffusional, to the fast-reaction regime, may be encountered in a process, according to the operating conditions (Astarita 1967).

When a gas is desorbed from a quiescent liquid, it is transported from the bulk of the liquid to the phase interface by diffusion alone. In an agitated liquid the dissolved gas is transported mainly by convective motion. The situation in any but an artificially simplified, agitated system is a very complicated one. The concentrations of the various species are not constant or uniform when measured over short time and length scales. Convection, diffusion, and reaction proceed simultaneously. The nature of the convective movements of gas and liquid are ill-defined and any attempt to describe them completely would encounter intolerable complications. Several useful predictions have been performed to describe the behavior of highly complicated absorption and desorption processes with chemical reactions by using simplified models which simulate the situation sufficiently well for practical purposes without introducing a large number of parameters to which it is difficult to assign values. These are the film and surface renewal models (Astarita 1967; Danckwerts 1970; Shah and Sharma 1976).

### **3. Release of Oxygen, Nitrogen, and Argon**

Extending the work of Seifert (1989) and Seifert and Genthner (1991) the authors of this chapter developed an analytical model for the computation of the O<sub>2</sub>, N<sub>2</sub>, Ar, and CO<sub>2</sub> release rates in the individual flash chambers of MSF recycle and once-through distillers.

The gases O<sub>2</sub>, N<sub>2</sub>, and Ar are only molecularly dissolved in seawater and are mainly released in the deaerator or, in plants without deaerators, during evaporation. The release of these gases can be treated as physical desorption, because they do not react chemically in seawater.

Since no reactions take place that might enhance the mass transfer of O<sub>2</sub>, N<sub>2</sub>, and Ar in the brine and the solubility of these gases in seawater is relatively low, it is assumed that the liquid-side mass transfer controls the desorption process. The mass transfer resistance in the gas phase is neglected.

For calculating the O<sub>2</sub>, N<sub>2</sub>, and Ar release rates during flash evaporation, the mass transfer processes in the brine as well as the phase equilibrium at the brine/vapor interface are described for a "slice" of brine in the cross-section of a flash chamber. The release rate in one stage is obtained by following this volume element through the stage from the entrance to the exit orifice and adding up the release rates.

The bulk of the brine is assumed to be homogeneously mixed through turbulence, flashing and flow obstacles. Thus it is assumed that, locally, the bulk of the volume element has a uniform concentration of the dissolved gas. Only in a boundary range near the brine/vapor interface does the concentration of the NC gas fall from its value in

the bulk to its value at the brine/vapor interface. The resistance to mass transfer lies within this boundary range. The rate of desorption of the NC gas, i.e. O<sub>2</sub>, N<sub>2</sub>, or Ar, is given by:

$$\Delta \dot{n}_{\text{NC,R}} = \beta \Delta A_{\text{Ph}} (c_{\text{NC,B}} - c_{\text{NC,Ph}}) \quad (1)$$

with

$$\Delta \dot{n}_{\text{NC,R}}$$

as the molar release rate of the NC gas,  $\beta$  the mass transfer coefficient,  $\Delta A_{\text{Ph}}$  the phase interface area,  $c_{\text{NC,B}}$  the concentration of the NC gas in the bulk of the brine, and  $c_{\text{NC,Ph}}$  the concentration of the NC gas at the phase interface.

Provided that physical equilibrium prevails at the phase interface and the gas solubilities and partial pressures are small, the concentration of the dissolved gas at the interface is governed by Henry's law, i.e. the concentration of the gas in solution is proportional to its partial pressure in the gas phase as follows:

$$c_{\text{NC,Ph}} = H_{\text{NC}} p_{\text{NC}} \quad (2)$$

with  $c_{\text{NC,Ph}}$  as the concentration of the dissolved NC gas in the brine at the phase interface,  $p_{\text{NC}}$  the partial pressure of the NC gas in the gas phase, and  $H_{\text{NC}}$  the Henry's law constant of the NC gas in seawater.

The Henry's law constant, for any given solute and solvent, depends upon the temperature of the solution and its ionic strength. In seawater with a salinity of 35 g kg<sup>-1</sup> equilibrated with the atmosphere at 25°C, the concentration of dissolved N<sub>2</sub> is about 11 mg kg<sup>-1</sup>, the O<sub>2</sub> concentration about 7 mg kg<sup>-1</sup>, and the Ar concentration 0.4 mg kg<sup>-1</sup>. The Henry's law constants of O<sub>2</sub>, N<sub>2</sub>, and Ar in water and hence the solubilities decrease with increasing temperature, reach a minimum (for example, O<sub>2</sub> in water at approximately 112°C), and increase again at higher temperatures. Furthermore, the solubilities decrease with increasing ionic strength of the solution.

The partial pressures of O<sub>2</sub>, N<sub>2</sub>, and Ar in the gas phase are calculated on the assumption that the non-condensable gases are vented continuously so that no accumulation occurs in the vapor above the brine. The partial pressures thereby depend on the local vapor release rates.

The prediction of the local mass transfer coefficient  $\beta$  as well as the analytical description of the interface area  $A_{\text{Ph}}$  are a particular problem in the model. Due to Eq. (1), obviously the product ( $\beta A_{\text{Ph}}$ ) strongly affects the gas release rates.

The mass transfer coefficient  $\beta$  is calculated on the assumption of an analogy between heat and mass transfer. The function for the Stanton number of heat transfer is then identical to that for mass transfer. An empirical correlation developed by Lior and Nishiyama (1983) is used for the Stanton number of heat transfer.

The interface area  $A_{Ph}$  comprises not only the bulk flow surface of the brine, including waves and water jets, but mainly the interface between the brine and the vapor bubbles.

Since the NC gases are released from the brine by the same interface as the vapor, the interface area that releases the vapor generated in the volume element has to be determined. An energy balance over the volume element yields the effective release area  $\Delta A_{Ph}$  in the element:

$$\Delta A_{Ph} = \frac{\dot{m}_b|_y c_{p,b}}{\alpha} \ln \left( \frac{T_b|_y - T_s}{T_b|_{y+\Delta y} - T_s} \right) \quad (3)$$

with

$$\dot{m}_b|_y$$

as the local brine mass flow rate at position  $y$  in the flash chamber,  $c_{p,b}$  the specific heat capacity of the brine,  $\alpha$  the heat transfer coefficient,  $T_s$  the saturation temperature of the brine,

$$T_b|_y$$

the local brine temperature at position  $y$  in the flash chamber, and

$$T_b|_{y+\Delta y}$$

the local brine temperature at position  $y + \Delta y$  in the flash chamber.

#### 4. Release of Carbon Dioxide

The discussion of the release of dissolved gases from the brine in the previous section was concerned with those which do not react in seawater. In contrast,  $CO_2$  reacts chemically in seawater and is involved in its pH buffer system (Skirrow 1975; Millero 1996).

As a new approach for predicting the  $CO_2$  release, the authors of this chapter consider the release of  $CO_2$  from the flashing brine in MSF distillers as a problem of chemical desorption and examine to which reaction regime the desorption of  $CO_2$  conforms (Glade 1999).

The mechanism of the reaction, the rate-determining steps in the mechanism, the kinetic order of the reactions, the degree of reversibility and the reaction rate constants, the mass transfer coefficients without reaction, and the brine residence times are analyzed.

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