

STEADY-STATE MODEL

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Summary

A steady-state model for the MSF desalination plant is described, containing model equations for a flash stage, interstage brine flow, brine heater, and splitter. Auxiliary equations for calculating various properties for supporting model equations are presented as an appendix.

1. Literature Review

Process modeling has become an important task in process engineering activities. Models based on first principles are useful in the assessment of a plant's operability and performance optimization in the early design stage, so that necessary modifications can be incorporated. Another major area of application of rigorous models is in the design of linear and non-linear process control systems. For the above reasons, both steady-state and dynamic models of the multistage flash (MSF) desalination plants are of great interest.

At the simplest modeling level, the MSF plant consists of heat recovery and heat rejection sections, a brine heater, a deaerator, and a venting system, as shown in Figure 1. The heat recovery and heat rejection sections consist of a series of flash stages. In each stage, the flashing brine enters at the bottom through an inlet orifice, flows over the stage length, and leaves through an exit orifice. During its flow, the brine superheated with respect to the pressure prevailing in a particular stage flashes and the vapor generated condenses over a tube bundle through which the cooling brine flows. In between, a demister eliminates any liquid carry over along with the vapor. Depending on the location of the stage, the stage vapor space is connected either directly to the

venting system or cascaded to the next stage, in order to remove non-condensable gases and maintain the desired pressure within the stage.

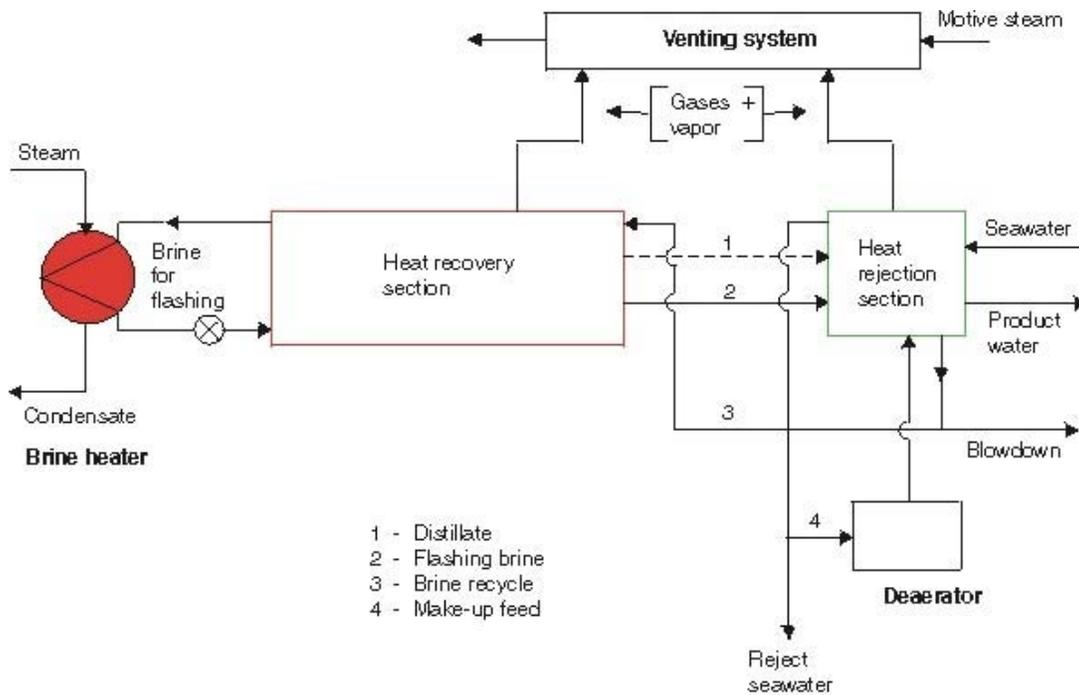


Figure 1. MSF desalination plant.

The flow sheet shown in Figure 1 contains a recycle of brine which, drawn from the last stage (in the rejection section), flows through the tube bundle in the recovery section as a coolant before entering the first stage (in the recovery section) for flashing. In an alternative process known as the "once-through" process, there is no recycle brine. Instead, the total amount of seawater flows in the tubes as the coolant before getting flashed. Since a majority of MSF plants operate with the recycle stream, only this process (Figure 1) will be dealt with here.

Seul and Lee (1990, 1992) proposed a rigorous two-dimensional, steady-state model for non-isothermal two-phase flow of the flashing brine in the stage. However, such a model is far too complex to be used in plant simulations. Since the temperature difference across a stage is comparatively small and the brine's highly irregular pattern does not account for the spatial dependence of the state variables, the flashing brine can safely be assumed to be perfectly mixed. This assumption means that the local mass transfer is averaged by using representative values of the variables.

The state of perfect equilibrium is never reached in any real system; however, it is frequently assumed to describe two-phase systems and the non-equilibrium phenomenon is accounted for by introducing an empirical efficiency factor. Such an approach is well-established for modeling multicomponent multiphase systems (Luyben 1990). In the case of the desalination process, a non-equilibrium temperature loss or non-equilibrium allowance is commonly used in addition to other losses (Rimawi et al.

1989).

Non-equilibrium Allowance

A large number of empirical correlations are reported for estimating the non-equilibrium allowance of the flashing brine, mostly by the designers of MSF plants. Lior (1986) tested 12 well-known correlations and found them excellent but only in their specific regions of applicability. Beyond those limits, their extrapolation can lead to significant errors because these correlations do not include the effect of factors such as stage geometry, aperture shape and size, type of chemical treatment given to the brine, etc.

A correlation from the Oak Ridge National Laboratory (ORNL), USA, relates the non-equilibrium temperature loss to the brine level, brine inlet temperature, and flashdown temperature difference. Marquardt (1996) recently tested this against the non-equilibrium allowances calculated from the plant data; it was found that the results were not close to each other, nor was the trend in the experimental and the correlated data the same.

Gopalkrishna et al. (1987) correlated the vaporization rates from the liquid pools in terms of dimensionless groups such as Jakob number, Prandtl number, dimensionless hydrostatic head, and salt concentration in the temperature range 25-80°C, from which the non-equilibrium allowance can be calculated. However, these conditions are not suitable since the hydrodynamic phenomena occurring in the MSF plant stage are different from those in the experimental set-up.

A few investigations (Fujii et al. 1976; Miyatake and Hashimoto 1980; and Miyatake et al. 1983a,b 1992) have reported on adopting a rigorous approach for evaluating the non-equilibrium allowance, either experimentally or numerically, in which the flow behavior of the flashing brine in a stage is considered. These studies, however, were limited to single-phase isothermal flashing liquid and the models suggested consist of partial differential equations.

Brine Level

In most MSF plants, sluice gate-type orifices are provided for the interstage brine flow. Maintaining proper brine levels in the flash stages is important to the plants operation. Levels that are too high can result in carry over of the salt to the product trays and higher thermodynamic losses, whereas levels that are too low lead to vapor blowthrough from one stage to the other. The net head at the orifice depends on the liquid levels and vapor pressure difference between the connecting stages. In turn, the vapor pressures depend on the flashdown and operating temperatures. Over the operating temperature range of a typical MSF plant, the vapor pressure difference corresponding to the flashdown varies by a factor of 24 over the whole plant. As a result, very small changes in the operating temperatures at the high temperature end of the plant can have large effects on the brine levels. In reality, a two-phase flow occurs in the orifice. However, in most of the reported work, single-phase flow is assumed for

the sake of simplicity. The open channel single-phase flow is usually characterized by the Froude number ($Fr = v^2/gh$), which is the ratio between viscous and gravitational forces. When $Fr = 1$, the flow is called critical, while for $Fr < 1$, the flow is subcritical and for $Fr > 1$, it is supercritical. For example, the transition from supercritical to subcritical happens at the hydraulic jump. Thus, for a given steady-state flow there can be two equilibrium depths with the same total (energy) head ($H = h + v^2/2g$), resulting in any of the four different flow regimes shown in Figure 2. Out of these, only the submerged jet flow is desirable. The first and last types of flow involve blowthrough and the jump flow condition is unstable and temporary.

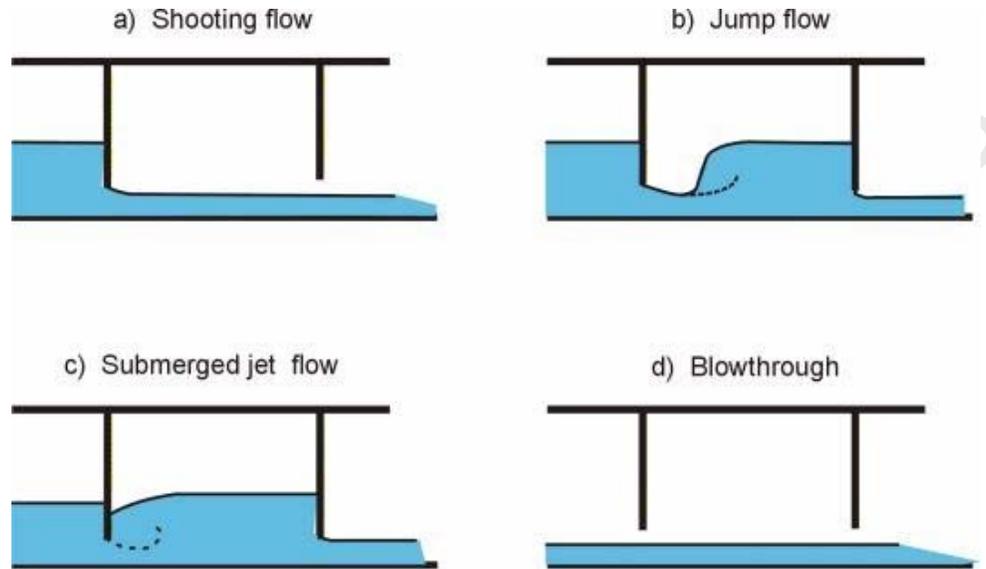


Figure 2. Flow regimes prevailing in MSF plants.

For the single-phase submerged flow, the standard energy conservation equation for liquid flow through the orifices in closed pipes or conduits can be applied. The discharge coefficient in the resulting equation is a complex function of flows; Hömig (1978) gave an empirical relation to evaluate this coefficient and Ball (1986) discussed in detail the difficulties in evaluating brine levels in a stage using the orifice pressure drop equation.

In general, the flow out of the orifice will be supercritical, but due to obstacles placed in the flow path (to enhance flashing) the flow will have a hydraulic jump downstream of the orifice. In a "sudden expansion" model, the unknown brine level at the vena contracta is related to the tail brine level at the exit of the stage by means of a momentum balance for the hydraulic jump. Thus, in this model two balances are made, namely (a) the Bernoulli equation for the mechanical energy from a point well upstream of the orifice to the vena contracta and (b) a momentum balance from the vena contracta to downstream of the hydraulic jump. However, application of this model to an experimental two-phase flow data did not provide satisfactory results (Ball et al. 1971). In an "enhanced sudden expansion" model developed by Reddy et al. (1995), the impact of the kick-plate is taken into account by including one additional momentum balance

to calculate the brine level downstream of the kick-plate, which is assumed equal to the level upstream of the orifice of the subsequent stage.

A parametric model for the brine level hydraulic was developed at the ORNL from extensive plant tests using a three-stage evaporator (Wichner 1970), which was equipped with simple orifice-type brine gates without baffles, weirs, or any flashing enhancement devices. This model is entirely empirical and does not involve any physical considerations.

Perhaps the single-phase models cannot accurately predict the brine levels due to the complex flow mechanism prevailing in the flash stages. For that reason a parametric model has been suggested by Marquardt (1996), with adjustable parameters for correlating the experimental data. In deriving this model, the Bernoulli balance equation is written from a point upstream of the orifice to a point upstream of the subsequent orifice, by accounting for all pressure drops, i.e. of orifice, hydraulic jump, and kick-plate. The drag coefficient is the adjustable parameter in the model. In a simpler version of the model as applied by Von Watzdorf and Blum (1995) and Maniar and Deshpande (1996), the kinetic energy terms are dropped, being similar on both sides. Furthermore, to have more flexibility in correlating the experimental data, the drag coefficient can be expanded in the Taylor series. In a "damped" hydraulic flow relation, the pressure drop coefficient is made dependent on the brine level, As a result, large deviations from the Bernoulli-type flow laws with a constant pressure drop coefficient can be avoided.

MSF Plant Model

The model for the MSF plant comprises the models for all the process units, namely flash stages, brine heater, condensers, mixers and splitters, valves and pumps, deaerator, and ejectors. The model equations are to be supported by the physical and thermodynamic properties of the brine, distillate, and water vapor, as well as the heat transfer coefficients. For stage modeling, as previously mentioned, an equilibrium approach is assumed, then corrected with a non-equilibrium temperature loss. This provides a reasonably accurate model for the steady-state operation of the MSF plant, which consists of a set of non-linear algebraic equations. The simplest way to solve these equations is to linearize them by neglecting variations of properties of various streams in the process and using a linear rate expression for heat and mass transfer. However, this approach will lead to serious errors in the calculated results since variations in properties are considerable in the operating range of the MSF plant.

The alternative approach is to solve the non-linear equations as such. A simpler way is to adopt a sequential iterative method as followed in conventional distillation column calculations (Lewis and Matheson 1932; Thiele and Geddes 1933). Using such an approach, Glueck and Bradshaw (1970), Beamer and Wilde (1971), Hayakawa et al. (1973), Rautenbach and Buchel (1980), and Omar (1983) applied one optimization technique or the other to minimize stage to stage computational effort, while Montagna et al. (1991) applied partition and tearing techniques.

The non-linear equations of the MSF plant model can be solved more effectively by applying matrix methods as done in multicomponent distillation calculations (Thiele

and Geddes 1933; Naphthali and Sandholm 1971; Husain 1985). Along these lines, Helal et al. (1986) developed an iterative tridiagonal matrix (TDM) method for solving the MSF model, which is a fast and more stable algorithm. This method has been modified by Husain et al. (1994) to represent realistic situations in the plant practice.

Mutaz and Soliman (1989) used the orthogonal collocation method to solve the MSF process model by selecting a few stages (not all) which fall at the roots of the orthogonal polynomial. Though they claimed the method to be twice as fast as the TDM model, it is not possible to estimate brine levels in the stages. In an alternative approach, all the model equations were solved simultaneously by Husain et al. (1993, 1994) using a commercially available simulation package, SPEEDUP (Aspen Tech 1991b), which is based on an equation-oriented procedure.

Non-condensable Gases

Atmospheric gases such as oxygen, nitrogen, and argon are molecularly dissolved in the seawater and liberated mainly in the deaerator. On the other hand, carbon dioxide reacts chemically with the seawater to form carbonic acid which, in turn, dissociates into bicarbonate and carbonate ions. In acid-treated plants, CO₂ is removed in the carbonator. On the other hand, in the additive-treated MSF plants, CO₂ is released in the flash chambers and should be extracted adequately by venting; otherwise, heat transfer rates will be significantly reduced. Due to their large Henry coefficients, non-condensable gases (NC) make an appreciable contribution to the vapor space pressure. Moreover, CO₂ and oxygen corrode the shell side of the condensers and lead to tube leakages.

A great deal of uncertainty prevails in determining the release rates of CO₂ in the MSF distillers due to a lack of knowledge about the kinetics of the chemical reactions involved, as well as the influence of the mass transfer process. For that reason, design information varies widely as far as CO₂ release rates are concerned.

Seifert (1988) proposed a semi-empirical model for the release of NC gases in MSF plants, in which the main emphasis was on the mass transfer resistance hindering the release of such gases. The model proposed by Genthner and Seifert (1991) included the dissociation of water and CO₂ according to the following equilibrium reactions:



In their model, all other species were represented in terms of the ionic strength of the solution and not accounted for individually. The activities of all ionic species were approximated by the Debye-Huckel equation and equilibrium constants by temperature-dependent correlations. The ionic strength was determined by using an empirical

expression in terms of the total dissolved solids. Scale formation and solid precipitation were not considered. Upon implementation of the Seifert-Genthner model, Marquardt (1996) noted several inconsistencies; therefore, he used a different set of correlations (Hancke 1994) to calculate the equilibrium constants.

According to present knowledge, reactions (2) and (3) describe the CO₂/seawater system at lower temperatures only. At higher temperatures, because of the evolution of molecular CO, the equilibrium between CO₂, HCO₃⁻, and CO₃²⁻ is disrupted. Moreover, additional CO₂ is formed due to thermally induced reactions. The primary reaction, which leads to further evolution of CO₂ and triggers alkaline scale formation, is the thermal decomposition of HCO₃⁻ ions, for which Langelier et al. (1950) suggested the following mechanism:



The carbonate ions, thus generated, can cause precipitation of calcium carbonate once its solubility limit is exceeded. At still higher temperatures, CO₃²⁻ ions may be partially or totally hydrolyzed and, as a result, the concentration of OH⁻ ions increases, leading to precipitation of magnesium hydroxide if sufficient Mg²⁺ ions are available in the solution to satisfy the solubility limit. In the case of total hydrolysis of CO₃²⁻ ions, more molecular CO₂ will form as follows:



Dooly and Glater (1972) suggested unimolecular decomposition of HCO₃⁻ instead of a bimolecular reaction (4) according to



However, the investigations carried out by Shams El Din and Mohammed (1989) confirmed the bimolecular decomposition of HCO₃⁻ according to reaction (4) and complete hydrolysis of CO₃²⁻ according to reaction (5).

The release of CO₂ in the MSF evaporators is thus influenced by the following factors.

- (a) Prevailing temperature and pressure profiles, particularly the maximum temperature.
- (b) Reaction kinetics, mass transfer rate, and, hence, residence time.
- (c) The HCO₃⁻ and CO₃²⁻ content of the make-up stream.
- (d) Deaeration effects, such as agitation of the brine.
- (e) The availability of Ca²⁺ and Mg²⁺ ions.
- (f) The presence of antiscalants.

In the various approaches proposed to compute CO₂ release rates in MSF distillers, the relative importance attached to the above parameters is controversial. The models suggested differ not only in the procedure for computing the total release rate of CO₂ but also its distribution among the individual stages.

The Ciba-Geigy (1978) model is based on reaction (4) for the CO_2 release rate, assuming that the hydrogen carbonate concentration in the seawater is approximately equal to the value of the total alkalinity (p.p.m. CaCO_3 of the make-up flow). Thus, this model does not take into account (a) the hydrolysis of CO_3^{2-} at higher temperatures in addition to HCO_3^- decomposition and (b) any effect of temperature, reaction kinetics, and mass transfer on the extent of decomposition reaction and, hence, the residual concentration of HCO_3^- ions in the brine of the last stage.

A semi-empirical model given by Watson Desalination Consultants (1979) for computing the CO_2 release rate is based on HCO_3^- measurements in the last stage, in which dependence of the HCO_3^- decomposition on the brine residence time is implicitly involved. In this model, CO_2 diffusion is not the determining factor in its release, which may be hindered by the reaction kinetics or mass transfer process. The Watson report further assumed the following stagewise pattern in the high temperature stages for the release of CO_2 from the thermal decomposition of HCO_3^- : stage 1, 85 per cent; stage 2, 10 per cent; stage 3, 5 per cent; and virtually no CO_2 is released from the fourth stage onwards.

Seifert's (1988) investigation showed that the chemical reactions occurring in the CO_2 /seawater system are faster than the mass transfer rate of CO_2 from the brine to the vapor. Therefore, the transfer resistance of CO_2 in the interface between brine and vapor is the determining factor in the CO_2 release rate.

In a recent study based on electrolyte equilibria, Marquardt (1996) found that the CO_2 formation rate depends strongly on the operating conditions. A reduction in the top brine temperature leads to a significant decrease in the CO_2 formation rate in the first few stages and a corresponding increase in the subsequent stages. The influence of the vapor flow rate is more involved; a reduction in the vapor flow rate results in a corresponding reduction in the CO_2 formation rate in the first stage only, while for all other stages it is enhanced. As reported by Marquardt (1996), almost all of the CO_2 is formed and released in the first four flash stages.

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Biographical Sketch

Asghar Husain received Master of Science degree in Applied Chemistry from the Osmania University, Hyderabad – India in 1948, Bachelor of Chemical of Engineering from the University of Michigan – U.S.A. in 1950 and Doctor of Science from the University of Indonesia in 1958 on submission of a thesis on batchwise distillation. This work has been abridged in *Chemical Engineers Handbook* by Perry in 4th to 6th edition, a McGraw Hill publication.

He taught at the Technical Faculty of the University of Indonesia at Bandung (1952 -1959) and at the Delhi Polytechnic, Delhi University (1959 – 1961). Then he joined as the Research Scientist in the Regional Research Laboratory (now known as IICT) in his hometown Hyderabad – India, a constituent of the Council of Scientific and Industrial Research (CSIR – Delhi).

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