MULTIPLE-EFFECT EVAPORATION IN ALUMINOSILICATE TECHNOLOGY[#]

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[#]This paper is dedicated to Professor Roman Modic at his 90th birthday

Received 30-05-2001

Abstract

The article presents an engineering approach to the development of an alternative production with the existing equipment. Zeolite production is becoming an alternative to the old "Bayer" process for aluminum hydrate production. By applying appropriate know-how old equipment was used for an economically as well as ecologically acceptable production. In this equipment adaptation among other production steps the multistage evaporation battery was the most critical part of the process. We applied semi empirical approach on the basis of Z. Rant ideas to find heat transfer coefficients and to determine which equipment elements are more relevant for efficient performance and need serious maintenance.

Introduction

In late 80′s and early 90′s aluminosilicate – zeolite applications and productions spread rapidly worldwide, mainly for environmental reasons. The environmental reasons affect both the production and the application side. Many old extraction (leaching) processes had to be abandoned and one of the current alternatives is a restructuring process for synthesizing of zeolite from silicate and aluminum compounds in an alkaline medium. In the case discussed here the equipment of an over 50 years old »Bayer« aluminum hydrate production process was adapted to achieve economical zeolite production. It was mainly the economical reason that directed this decision. Relatively low and still falling world prices of zeolite disabled many new investments and old processes can now offer economical production. Fig. 1 presents the basic process principles of zeolite production. From the economic and environmental points of view, a crucial part of the process is concentration of dilute NaOH (cca 6%) solution by evaporation. Disposal of 50 m^3 of the solution per hour is ecologically impossible, and recycling can not be economically efficient. The solution to this is a multistage evaporation process. The purpose is how to test, evaluate and set the parameters of old equipment for the new product. Here we present a concept and the principles of solution, which enables economical operation of the equipment in question.

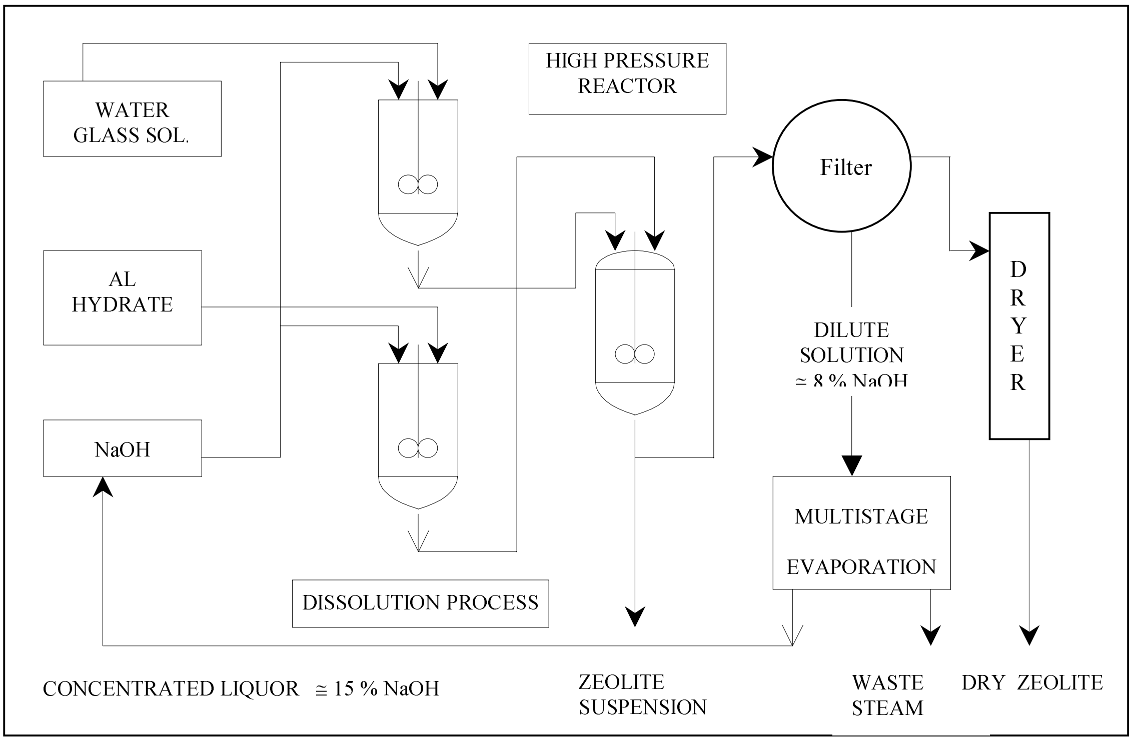

Figure 1. Principal process flow chart of zeolite production

Theoretical principles and concepts

The basic principles and equations can be found elswere,[2-5] but here we limit the discussion to the critical relations and parameters necessary to understand the basic concept. Thermodinamic potential of the process is defined with the condensation temperature of fresh steam in the first stage and the boiling temperature of the solution in the last stage,[8] while the boiling–point elevation (ebullioscopic) - BPE of the increasingly concentrated solution lowers the available temperature difference. The BPE of the boiling temperature, due to the more concentrated solution in the boiling chamber, can be expressed as:

$$\Delta T_e = K_e * \frac{m_2}{m_1 * M_2} \qquad K_e = \frac{R * T_{b1}^{0.2} * M_1}{\Delta H_1} \tag{1}$$

Number 1 indicates the solvent (water) and 2 the solute, m is mass, M denotes molecular weight and ΔH the latent heat of evaporation, T_b is the boiling temperature. From equations 1, the relationship can be expressed:

$$\Delta T_e = f(C_2, P_{abs}) \tag{2}$$

The relationship is used to understand the basic relations between the lost BPE, the pressure and the concentration of the solution boiled. We found BPE data by the help of **Duhring′s** rule, which states that the boiling point of a given solution is a linear function of the boiling point of water at the same pressure. The rule is applicable mainly to the strong inorganic solutions, what is also the situation under consideration.

Besides the thermodynamical potential, heat transfer is the most important factor influencing the capacity of the evaporation system. In the discussed case, heat transfer rate is a limiting process for the whole system. Heat flows from the warmer to the colder fluid separated by a solid wall. In this process convection and conduction play the mayor role and thus have become the object of this study. Typical situation is presented on Fig.2.

While mayor part of the equipment and process parameters are not known a semi-empirical approach to model the process is applied.[4] The model should enable to analyze the existing equipment configuration, to define the process limitations and to optimize the process parameters. The approach is based on a method of Z. Rant,[1] where it is necessary to establish the relationship ΔT = f (q) for a used range of heat flow – q. With this result the temperature gradient from a condensing steam side to the boiling solution side is found. By the help of equations the heat transfer from the surface to the boiling solution and the heat transfer from the steam to surface in film condensating regime the limiting heat transfer side and the corresponding heat flux is determined. On the basis of heat flux and total available temperature difference, heat transfer through the tube wall and the scale (usually on the boiling side) can be determined. From these results it is possible to calculate the total heat transfer coefficient in the equipment or, backwards from known or estimated heat transfer, it is possible to establish the scaling thickness on the equipment. Such an approach also implies simultaneous calculation of heat and mass balance, because it is very difficult to get all necessary data for separate calculations.[8]

Close attention has to be paid to the scaling and fouling processes because some silicon dioxide alkali products are present in NaOH feed exceeding trace quantities. The effects of scaling and fouling can be monitored through the deviation from initial process parameters and through different model scenarios.

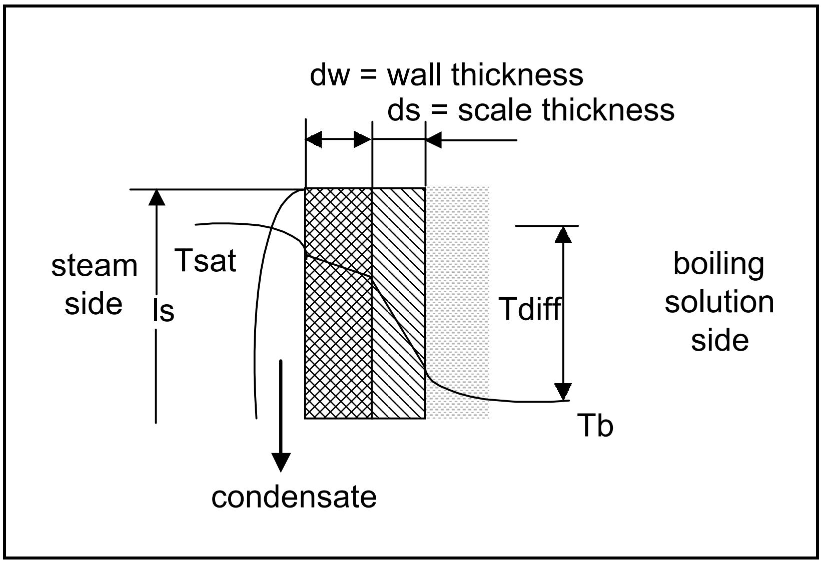

Figure 2. Heat transfer profile

Calculation procedure

To calculate the model we used MathCAD program. Calculations were preceded step-by-step, starting with an approximation.[9]

In the first step, concentration distribution among evaporators was calculated to find out the evaporated steam flow in each stage. The feed of dilute NaOH was 52 t/h and it contained 8,3% of NaOH, the final concentration should have been 14,5 % of NaOH. It was necessary to evaporate 22.3 t of water per hour in all stages. Heat transfer areas of all four stages were the same (Fig 3). The calculation began with an equal distribution of evaporated water from each stage but the final results gave: 1.00, 0.74, 0.31 and 0.80 in the last fourth stage. From these results concentration distribution was calculated: 12,14 %, 14,5% at second (exit) stage, 8,7% at the third (input) stage and 9,95% at the fourth stage were the results.

In the second step, the thermodynamic situation in the evaporation process was evaluated. With the help of Duhring′s rule: Tbsol = f (Tbwater, Csol), reverse Antoine′s equation for steam condensation temperature, the latent heat of water evaporation at different temperatures and enthalpy of steam at different temperatures enabled us to calculate pressure distribution among stages. The pressures should have been: 2.3, 1.6, 0.9 and 0.2 bar respectively. At this step, all parts of the lost ΔT can be calculated. The first one was BPE, then hydrostatic pressure (the pipes are 2.4 m high), and transport ΔT is estimated to be approx. 1 deg on each stage. Finally the temperature differences lost in each stage were computed: 6.6, 8.4, 6.8 and 14.8 degrees. The whole ΔT available (netto) for all stages was 42.3 degrees and represented the thermodynamic potential for heat transport.

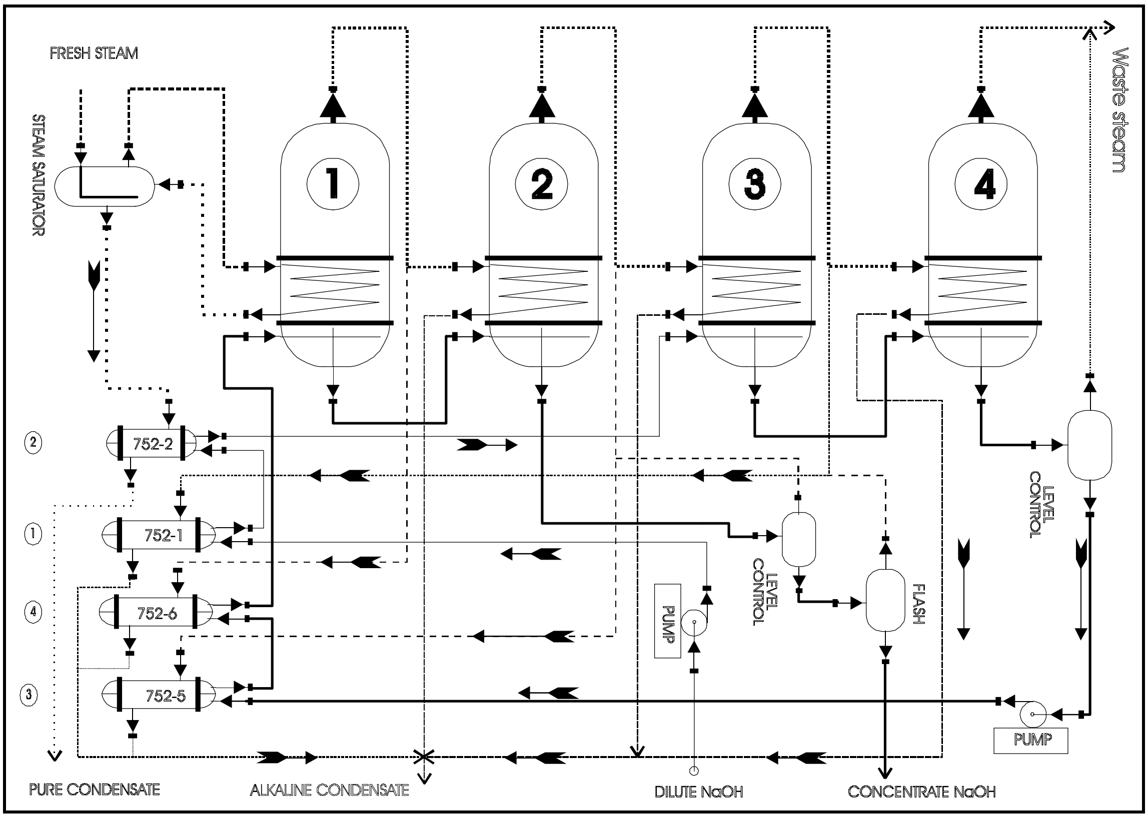

Figure 3. Flowchart of four-stage evaporation process

In the third part, the heat transfer was estimated. As we mentioned with regard to the principle published by Z. Rant[1] ΔT had to be established as a function of heat flux. According to presented process the computation scheme started with heat flux value 5.4

GJ/h up to 160 GJ/h. From the heat flux we calculated the corresponding water condensate flow and then the Reynolds number[2] for a different heat flux. With the known Re heat transfer coefficient α from the steam to the heat exchanger tube wall, following was established (film condensing regime):[2,6]

$$\alpha_{steam} = 1{,}47 \cdot \mathrm{Re}^{-\frac{1}{3}} \cdot \lambda_{cond} \cdot \left(\rho_{cond}^{2} \cdot \frac{g}{\eta_{cond}^{2}} \right)^{\frac{1}{3}} \tag{3}$$

In the eq. (3) λ is heat conductivity, ρ is specific gravity, η viscosity and *cond* denotes (water) condensate.

From the heat transfer coefficient α and known specific heat flux through the tube surface, the corresponding temperature differences on the steam side were calculated. This was the first set of data for the construction of a graph ΔT = f (q).

As heat flowed from the surface of the tube wall through the metal wall (Fig. 2), the temperature drop on a base of heat conductivity was calculated. We got a second set of data ΔT = f (q). Almost the same situation was on the scale layer in the heat exchanger tubes. This represented the third set of data ΔT = f (q).

Finally, it was necessary to calculate ΔT for the convection heat transfer to the solution. For pure water the heat transfer coefficient α was calculated using an equation by Kruschlin:[1] $\alpha_W = 1.95 * q^{0.72} * p^{0.24}$ and corrected with factor ϕ for solution at the same conditions. The correction factor ϕ was computed using an equation proposed by Kirschbaum:[1]

$$\phi = \frac{\rho_{sol}}{\rho_w} \cdot \left[\frac{\left(\frac{\lambda_{sol}}{\lambda_w}\right) \cdot \left(\frac{C_{p,sol}}{C_{p,w}}\right)}{\left(\frac{\sigma_{sol}}{\sigma_w}\right) \cdot \left(\frac{\Delta H_{evap,sol}}{\Delta H_{evap,w}}\right)} \right]^{0,5} \cdot \left[\left(\frac{\rho_{sol,gasphase}}{\rho_{w,gasphase}}\right) \cdot \left(\frac{\eta_{sol}}{\eta_w}\right) \right]^{-0,25} \tag{4}$$

In the eq. (4) λ is heat conductivity, ρ is specific gravity, η viscosity, C_p specific heat, ΔH is heat of evaporation, σ is surface tension, *w* denotes water, *sol* denotes solution and *gasphase* means properties of gas phase in equilibrium above liquid.

According to the same procedure on the steam side, the last set of data ΔT = f (q) for the boiling solution side was calculated.

When all individual ΔT = f (q) functions were known, a summation graph was formed (Fig 4.).

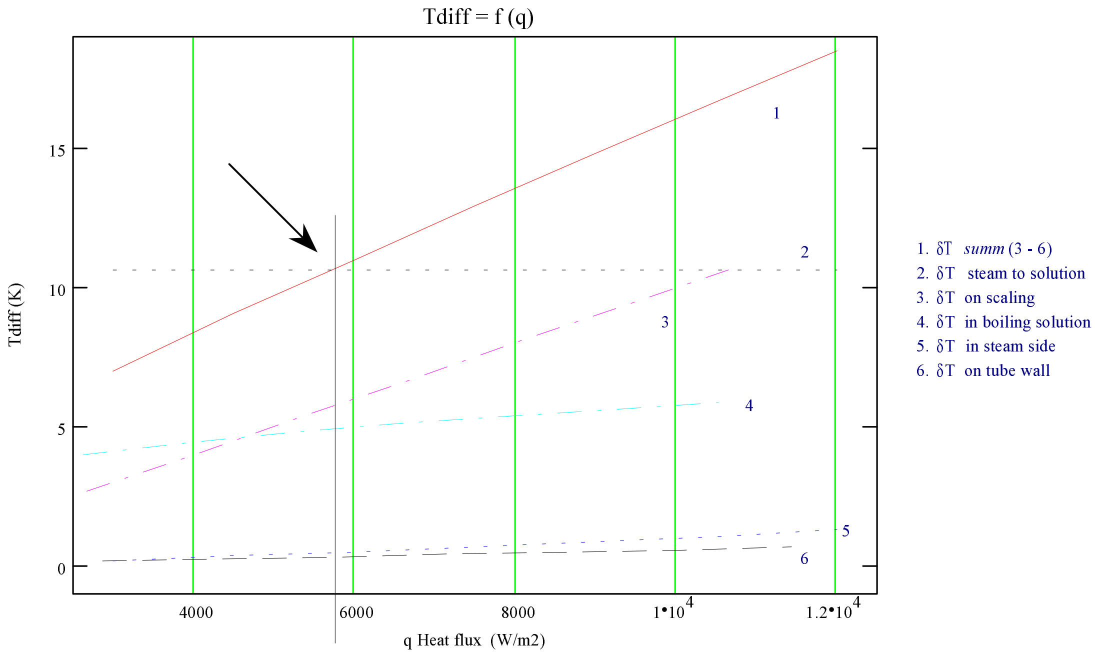

Figure 4. Summation graph of the ΔT = f (q) functions

As the temperature difference (between the steam condensing temperature and the temperature of solution boiling) was known (11K), from the summation function heat flux was determined. With known heat flux (5900 W/m^2), individual heat transfer coefficients were calculated and finally the overall heat transfer coefficient for the calculated stage was found. Because all individual temperature differences were calculated from measured data backwards the thickness of the scale could be assumed. This procedure was very important at the beginning, in order to find out the effect of scaling and fouling. The last (third) part of calculation was evaluated separately for each stage.

Results and discussion

The calculated overall heat transfer coefficients with the assumed 1 mm of scale thickness with the model were: 951 in the first evaporator, 1062, 800 and in last fourth stage 346 W/m^{2}K. These results were used only for comparison to some data of other equipment and to estimate the magnitude of heat transfer. As all evaporators were of the same geometry (63 mm inner diameter pipes, 2.4 m long, 2.9 mm thick walls and 800 pipes in a bundle) the heat coefficients were surprisingly different. The influence of process parameters was very great and should have been monitored carefully. With the simulation of scaling-fouling, we found that its influence was important and that a general cleaning procedure was necessary. Later we modified the process with an online periodically repeated cleaning procedure to keep the evaporation capacity of the system constant.

Finally the most important economic factor was the specific consumption of steam (steam consumption / evaporated water). We found from the model that this factor was 0.41 but in practice the average coefficient was found to be 0.42.

We believe that the presented case shows how the equipment of an old process can be applied to the production of a new product by implementation of the appropriate engineering know-how. Almost eight years later, the equipment is still in operation.[9]

Nomenclature

K_e - ebullioscopic constant
ΔT_e - ebulioscopic BPE
BPE - boiling-point elevation
m_1 - mass of solvent-water
m_2 - mass of solute-NaOH
ΔH_1 - latent heat of evaporation
T_b - boiling temperature
C_2 - cocncentration of solute
P_{abs} - absolute preassure
q - heat flux (W/m^2)
T_{sat} - temp. of saturated steam
T_b - boiling temp. of solution-NaOH
g - gravity constant
T_{diff} - temperature difference
α_w - heat transfer coefficient
p - pressure of saturated steam

References and Notes

1. Rant, Z. *Verdampfen in theorie und praxis*; Verlag Theodor Steinkopff, Dresden, 1977.
2. McCabe, W. L.; Smith J. C.; Harriot, P. *Unit operations of Chemical Engineering* - 4th ed.; McGraw-Hill, Singapore, 1985, chapter 13.
3. Golob, J.; Modic, R.; Černetič, J. *Mathematical model for sizing multiple effect evaporator, Computers in Chemistry* **1975**, Conference in Bled Slovenia.
4. Billet, R. *Verdampfung und ihre technischen anwendungen*; Verlag Chemie GmbH, Weinheim, 1981.
5. Geankoplis, C. J. *Transport processes - momentum, heat, and mass*; Allyn and Bacon, Massachusetts, 1983.
6. Perry, R.H. *Chemical engineers handbook*- 6th Ed.; McGraw-Hill, 1984.
7. Schweitzer, P.A. *Separation techniques for Chemical Engineers* - 2nd Ed.; McGraw-Hill, 1988.
8. McAdams, W. H. *Heat transmission* - 3rd Ed.; McGraw-Hill, 1988.

9. Klinar, D.; Golob J. *Štiristopenjska vakuumska uparilna baterija za zeolitni NaOH*, Research report, 1993, »SILKEM d.o.o.« Kidričevo Slovenia.

Povzetek

Vse večji ekološki interes za širitev uporabe zeolitov je ponudil priložnost za prenovo starega Bayerjevega procesa proizvodnje glinice iz boksita. Pri uvajanju novega izdelka se je pokazalo uparevanje odpadnega NaOH kot ključna rešitev, ki je omogočala rešitev ekologije (recikliranje) kakor ekonomike proizvodnje. Poglobljen inženirski pristop je omogočil revitalizacijo in učinkovito obratovanje več kot 50 let starega postrojenja. Uporabili smo polempiričen pristop na osnovi ideje Z. Ranta ter nekatere preizkušene empirične enačbe različnih avtorjev. Ideja je, da najprej izračunamo funkcije $\Delta T = f(q)$ za posamezen prehod ali prestop (iz pare na steno cevi, skozi steno cevi, skozi oblogo in v vrelo raztopino) nato pa vsoto vseh funkcij – sumarni graf (SLIKA4.) za vsak uparilnik posebej, takšen graf nam nato omogoča določiti q glede na lahko merljiv ΔT med nasičeno paro in vrelo raztopino. Znan q nam omogoča izračun posamičnih koeficientov prenosa toplote končno pa tudi celotnega koeficienta prenosa toplote na posameznem uparilniku. Metoda omogoča tudi obraten pristop. Na osnovi merjenih temperaturnih razlik je mogoče simulirati debelino obloge, kajti le ta ima največji vpliv na ΔT. Tako smo določili učinek vpliva oblog na delovanje uparilnikov ter spoznali, da je nujno njihovo redno odstranjevanje. Izdelani model je omogočil optimirati proces in določiti metode za spremljanje obratovanja kakor tudi določiti ukrepe za njegovo izboljšanje. Po skoraj osmih letih proces še vedno uspešno obratuje.