ENERGY CONSUMPTION AND ECONOMIC EVALUATION OF WATER DESALINATION BY HYDRATE PHENOMENON

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ABSTRACT

The required energy for seawater desalination based on a proposed hydrate formation process has been estimated. In addition, economic evaluation and cost estimation of produced potable water have been presented.

A computer program has been prepared for simulation of the proposed process and was used to estimate the total capital investment, operation and maintenance costs and total product cost.

A comparison study of desalination cost by different methods has been performed and the results are presented. The effect of the hydrate formation promoters on energy consumption and economic parameters has also been presented.

Keywords: Energy, Economy, water desalination, Gaseous Hydrate, Modeling

1. INTRODUCTION

When a gas mixture containing water vapor at high pressure is cooled to temperatures in the vicinity of 0°C, solid crystals like snow or loose ice in appearance may form. In other words, in the presence of small hydrocarbon molecules or some non-hydrocarbon compounds in gas or liquid phases, host water molecules can form cage structures that these guest compounds

are entrapped in. This is called "gas hydrates" and belongs to the category known as clathrates.

The clathrate, thermodynamically, is solid solutions. This lattice-like structure is formed because of water molecule hydrogen bonding and known as empty hydrate lattice structure and in the presence of suitable size molecules and certain conditions of pressure and temperature, well above the triple point of water, the hydrate crystals can be formed. The appearance of hydrate is ice-like and they consist of a framework of hydrogen bonded water molecules

Although gas hydrate could be formed by a pure gas or mixture of gases, some compounds such as acetone and 1,4-dioxine are also entrapped in hydrate lattice. These compounds have a promoting effect on hydrate formation, i.e. increasing the hydrate formation temperature or decreasing the hydrate formation pressure.

The main industrial interest in hydrates lies in preventing their formation and subsequent plugging of gas transmission lines. On the other hand some new industrial applications of gas hydrates are as follows: It is now well known that huge deposits of natural gas in the form of hydrates are present in the marine sediments throughout the world and also in the oil deposits and permafrost regions. These are the new source of natural gas and future energy. Transportation of these deposits from the ocean floor and production of natural gas are the new fields for investigators.

Removal of carbon dioxide from atmosphere and converting to the hydrate form is another application. On the other hand, however, decomposition of gas hydrates might also enhance the greenhouse effect. Water desalination, Knox et al. (1961), Kubota et al. (1984) and gas separation and storage, Miller and Strong (1946), are other application of the hydrate phenomenon. These applications explain why investigators pay attention to this matter more than before. This paper presents the application of hydrate formation in the desalination of seawater, for a proposed process.

2. PROPOSED PROCESS

Knox et al. (1961) proposed a process for desalination of the seawater to produce potable water and setup a pilot plant to study this process. But suitable theories and models for prediction of the hydrate formation conditions for pure water and saline water and evaluation of the enthalpies and entropies of different streams were unavailable at that time. The purpose of this work is to study the effect of hydrate former, promoter and other design parameters, such as seawater salinity and temperature, on the process and its economics by computer simulation. The economic evaluation could be achieved by a computer program written based on the mathematical modeling of the mass and energy balances.

Figure 1 presents a simple flow sheet of the proposed process for seawater desalination. This flow sheet is a modification of the process presented by Knox et al. (1961).

As shown in Figure 1, seawater pumped into the reactor is cooled in heat exchanger I by exchanging heat with potable water and brine streams. The produced slurry of the reactor which contains the hydrate crystals is filtered and washed in the separator and is then divided into two streams; brine and washed hydrate crystals. The brine stream, after exchanging heat with inlet seawater and the refrigerant (i.e. excess of hydrate former) of the refrigeration cycle, is discharged from the process. And the washed hydrate crystals are transported to the decomposer, where potable water and gaseous hydrate former are produced. Potable water is removed from the process in the same manner as brine, after exchanging heat in heat exchangers I and II.

The liquid hydrate-former after passing through a throttling valve is vaporized in the reactor removing partial heat from the formation of hydrate crystals, and then takes part in hydrate structure.

The excess hydrate former is used as a refrigerant to provide the cooling duty required for hydrate formation in the reactor. The excess hydrate former is compressed in the compressor and after cooling in the decomposer (and destroying the hydrate crystals), is passed through heat exchangers III and II, and a second throttling valve. This excess hydrate former provides the rest of required cooling duty in the reactor. A computer program developed for the simulation of this process is used to determine the ratio of the number of moles of the hydrate former to moles of seawater. This ratio is evaluated by energy balance and will be discussed in the following section.

The gaseous hydrate former has two roles in the process: it takes part in the hydrate structure; and it acts as direct heat exchange agent. Figure 2 presents the qualitative phase diagram for a pure hydrate former. Although the operating pressure of the decomposer in the proposed process is higher than the reactor, as shown in Figure 2, they should operate on the right-hand side and left-hand side of the hydrate line, respectively.

For every mole of seawater fed to the process the following parameters are introduced:

y, number of moles of the potable water produced by the process.

R, number of moles of the hydrate former.

If we assume that the reactor is a mixed type, the molalities of different salts in the effluent brine will become:

$$m_{i_{out}} = \frac{m_i}{1-y}$$
 i=1, no. of salts (1)

which is obtained from this fact that for every mole of seawater fed to the reactor, y moles take part in the hydrate lattice. Thus the reactor salt concentration will increase according to the above equation.

These molalities should be used for prediction of hydrate formation conditions in the reactor. On the other hand, the number of molecules of the hydrate former per water molecules in the hydrate lattice can be evaluated by the following equation:

$$F = \sum_{m=1}^{2} v_m \theta_m \tag{2}$$

where v_m is the ratio of the no. of type m cavities to no. of water molecules in the hydrate phase and θ_m is the fraction of the type m cavities which is occupied by hydrate former molecules, Parrish and Prausnitz, (1972). Two types of cavities exist in hydrate structure: large and small. Summation over these two types will yield the number of the hydrate former molecules per water molecules in the hydrate lattice.

It should be noticed that this parameter is reciprocal of the hydrate number, n, and it is always less than one. In other words, the hydrate former molecules are entrapped in a cage structure composed of water molecules. Therefore, the number of moles of the hydrate former in the hydrate lattice, and the number of moles compressed in the compressor per mole of seawater fed to the process are: yF and R-yF, respectively.

Also the number of moles of brine and the number of moles of the hydrate former passing through throttling valve I and II per seawater fed to the reactor are: y, R-yF and yF, respectively.

The hydrate formation process could be represented by the following equation:

(1 mole)
$$H_2O + (F \text{ moles})$$
 Hydrate Former \rightarrow (1 mole) Hydrate Crystal (3)

The heat of formation of one mole hydrate crystal could be evaluated by the following equation, Pieroen (1955):

$$\Delta H = H \big|_{Hydrate \ Crystal} - H \big|_{Hydrate \ Former} - \frac{1}{F} H \big|_{H_2O} \tag{4}$$

where H is the enthalpy of the defined species. This reaction is exothermic and the heat of formation can be evaluated by the model presented by Javanmardi et al. (1998). This model predicts the heat of formation in the presence of electrolytes directly.

Applying the first law of thermodynamics to the reactor, it could be shown that for every mole of seawater fed to the reactor we have:

$$\begin{aligned} & (R)H|_{Hydrate \ former \ at \ T_{reactor} \ and \ P_{reactor}} + (yF)\Delta H|_{at \ T_{reactor} \ and \ P_{reactor}} \\ & + C_p|_{water} \left(T_{reactor} - T_{seawater}\right) - (R - yF)H|_{Hydrate \ former \ at \ T_{H-E \ II}} \ and \ P_{Decompser} \\ & - (y)H|_{Hydrate \ former \ at \ T_{decomposer}} \ and \ P_{decomposer}} = 0 \end{aligned}$$

$$(5)$$

In this equation it is assumed that the enthalpy of the brine is equal to the pure water enthalpy and depends only on temperature and that the reactor operates adiabatically. For the decomposer, ignoring the effect of pressure on the hydrate crystal enthalpy, the following equation could be used:

$$\begin{aligned} & (R - yF)H|_{Hydrate \ former \ at \ T_{out} \ and \ P_{compressor}} \\ & - (R - yF)H|_{Hydrate \ former \ at \ T_{compressor} \ and \ P_{compressor}} - (yF)\Delta H|_{at \ T_{reactor} \ and \ P_{reactor}} \\ & - (yF)\left(H|_{Hydrate \ former \ at \ T_{decomposer} \ and \ P_{decomposer}} - H|_{Hydrate \ former \ at \ T_{reactor} \ and \ P_{reactor}}\right) \\ & + (y)C_{p}\Big|_{water} \left(T_{decomposer} - T_{reactor}\right) = 0 \end{aligned}$$

$$(6)$$

Where T_{out} is the temperature of the refrigerant (hydrate former) out of the decomposer heat exchanger. It should be noticed that an approach temperature equal to 6 °C was used in all heat exchangers.

The models developed by Parrish and Prausnitz (1972) or Holder et al. (1980) could be used to predict the hydrate formation conditions in the presence of pure water. The equilibrium conditions in the presence of mixed aqueous electrolyte solutions and promoters such as acetone could be estimated using models proposed by Javanmardi and Moshfeghian, (2000) and Mainusch et al. (1997), respectively. The heat of formation of hydrate crystals in the presence of pure water, mixed aqueous electrolyte solutions and acetone have been given by Moshfeghian and Maddox (1993), Javanmardi et al. (1998) and Mainusch et al. (1997), respectively. These parameters are needed for performing the energy balances as shown in Equations (5) and (6).

3. SELECTION OF HYDRATE FORMER AND PROCESS CONDITIONS

As mentioned above, the reactor and decomposer must operate at the left-hand side and righthand side of the hydrate equilibrium curve, respectively. Moreover, the highest temperature for hydrate formation of pure gaseous hydrate former is the upper quadruple point of the hydrate former, i.e. the intersection of condensation and the hydrate formation curves. Therefore, the most feasible condition for the reactor and decomposer is near the quadruple point, Figure 2. On the other hand, in this process, the hydrate former operates as a direct heat exchange agent. Thus, the condition of the hydrate former after heat exchanger II must lie on the right-hand side of quadruple point and in liquid region, Figure 2.

Based on the above discussion, it is concluded that for minimizing the energy consumption of the process, the hydrate former should have condensation and hydrate equilibrium curve with the following specification:

- 1. The upper quadruple point of hydrate former or the operating conditions of the reactor and the decomposer should occur at more feasible condition which is low pressure or high temperature.
- 2. The heat of vaporization of hydrate former near its quadruple point must be considerable. In other words for a desirable hydrate former, its quadruple point must be far from its critical point as much as possible.

To illustrate the above comments consider propane and carbon dioxide as a hydrate former which also have the role of the refrigerant in the proposed process. The quadruple point and critical point pressures for propane are: 562.07 (kPa) and 4247.36 (kPa), respectively. The corresponding values for carbon dioxide are: 4757.06 (kPa) and 7371.47(kPa), respectively. A close look at their phase diagrams, Figures 3 and 4, and based on the above comments one expects that the required work per potable water for propane to be much less than that of carbon dioxide. This point has been verified using the computer program for simulation of the process. The results are shown in Table 1,

4. ECONOMIC EVALUATION

4.1. Total Capital Investment

The shortcut methods, presented by Douglas (1988) could be used to estimate the installed costs of heat exchangers, compressor, reactor and decomposer for the process shown in Figure 1.

Estimation of the compressor power and heat loads of the heat exchangers is required for this purpose, which could be obtained using the developed computer program.

The onsite costs, Douglas (1988), correspond to the installed equipment costs for the items shown on the Figure 1 could be estimated directly from Guthrie's correlations, Guthrie (1969).

The installed cost of the heat exchangers could be obtained from the following equation, Douglas (1988):

Installed
$$\cos t$$
, $= \left(\frac{M \& S}{280}\right) 101.3 A^{0.65} [2.29 + (F_d + F_P)F_m]$ (7)

Where A is the heat exchanger area in ft^2 , and 200<A<5000. For brine streams, the proper value of the parameter F_m should be used.

The overall heat transfer coefficient, U, equal to 100 Btu/(hr.ft².°F) is used for estimating the heat exchangers area.

For centrifugal gas compressor, the following equation could be used to estimate the installed cost.

Installed
$$\cos t$$
, $= \left(\frac{M \& S}{280}\right) 517.5 bhp^{0.82} [2.11 + F_c]$ (8)

Where bhp is the brake horse power, 30<bhp<10000. In the above calculations it is assumed that the compressor efficiency is equal to 0.8.

The Marshal and Swift cost index, M&S, is used for updating the cost correlations. This parameter is given by Douglas (1988) and Park et al. (1997).

As shown in the flow sheet of the proposed process, Figure 1, the reactor and the decomposer act as heat exchanger. Therefore, equation (7) could be used for estimating their costs.

After estimating the total installed costs of equipment, the total capital investment in M\$ could be obtained from the following equation, Douglas (1988).

Tot. Inv.=2.36(Onsite)

4.2. Operation and Maintenance Costs

In order to estimate the operation and maintenance, O&M costs, the following equation has been suggested by Douglas (1988).

$$O \& M = 1.031 (\text{Raw Matl. + Util.}) + 0.186 (\text{Onsite}) +2.13 (\text{Operating Labor}) + 0.0256 (\text{Revenue})$$
(10)

In this work, it is assumed that the labor cost per day per person is about \$60.00.

Moreover, it is assumed that the electricity cost is about \$0.04/kWhr. The required "manhour/day-processing step" could be estimated by the following equation, Peters and Timmerhaus (1981),

$$Operating \ Labor = \exp(2.791 + 0.234\ln(Capacity))$$
(11)

where the capacity is in m^3 of potable water per day. It is assumed that in the suggested process shown in Figure 1, one processing step is required, Wessel (1952). Considering four shifts in each day and eight hours operation per day for each shift and dividing equation (11) by six yields the required man per day.

Substituting the above parameters in equation (10) yields the O&M costs in US dollars per day. It should be noted that for this purpose, the onsite costs obtained in the previous section should be divided by the plant useful life.

4.3. Amortized Total Capital Investment

Assuming 20 years useful life of the plant and continuous discount rate, i, equal to 8%, the amortized total capital investment is obtained by following equation.

Amortized Tot. Inv. =
$$\left(\frac{\exp(0.08 \times 20)}{\sum_{i=0}^{19} \exp(0.08 \times i)}\right) / (365 \times Capacity) Tot. Inv.$$
 (12)

The above parameter is in US dollars per ton. The economic life equal to 20 years has been chosen by many investigators such as Park et al. (1997) for multi-stage flash distillation (MSF), multi-effect distillation (ME) and reverse osmosis (RO) processes. Better comparison of the economic parameters of the proposed process and the above processes needs using the

(9)

same economic life and discount rate. Furthermore, the operational temperature in the proposed process is less than about 30 °C, where in the common MSF or ME processes the operational temperature equal to the normal boiling point of water is a common practice. Obviously, the low operational temperature of the proposed process decreases the corrosion problems considerably.

4.4. Amortized O&M Costs

As mentioned above, the O&M costs obtained in the previous sections is in US dollars per day. Therefore, the amortized O&M costs could be obtained in US dollars per ton by using the following equation.

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Amortized O \& M = O \& M / Capasity (13)
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Finally, the total product cost is the summation of the above two terms.

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Total Product Cost = Amortized Tot. Inv. + Amortized O&M (14)
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5. RESULTS

Figure 5 shows the effect of yield, y, on economic parameters. Also the other economic parameters described in the previous sections are shown in this figure. This figure indicates that increasing the yield, or number of moles of potable water per mole of seawater fed to the process, will decrease the total energy consumption and the total product cost. Total work as a function of yield for this system is shown in Table 2. Based on the discussion in the previous sections for selection of the suitable hydrate former and suitable process conditions, the following operation conditions have been assumed for this system:

Hydrate former: Propane

Reactor pressure: 450 kPa, Decomposer pressure: 650 kPa Discharge pressure of the compressor: 1400 kPa, Seawater temperature: 300K Molality of seawater, M_{NaCl} : 1, Capacity: 1000 m³ of potable water per day

The effect of seawater temperature on economic parameters is shown in Figure 6. The total work of compressor and pumps are shown in Table 3 for this process. Other process conditions are as follows:

Hydrate former: Propane, Reactor pressure: 450 kPa, Decomposer pressure: 650 kPa Discharge pressure of compressor: 1400 kPa, Yield: 0.3 Molality of seawater, M_{NaCl}: 1, Capacity: 1000 m³ of potable water per day

6. THE EFFECT OF HYDRATE PROMOTERS

As mentioned in the previous sections, promoters cause an increase in the hydrate formation temperature. Increasing the hydrate formation temperature causes the reactor temperature to increase and therefore saving the energy consumption of the compressor. Obviously, this affects the total product cost considerably. The more the promoting effect of the promoter is, the less the total product cost will be. The effect of this phenomenon on the economic parameters is shown in Figure 7. For this purpose two cases are considered. In the first case it is assumed that the promoter increases only the reactor temperature. The cross symbols on Figure 7 show the results.

In the second case it is assumed that this reagent takes part in hydrate lattice and increases the decomposer temperature. The circle symbols in this figure show the results. Increasing the decomposer temperature causes the excess hydrate former passing through the decomposer not to condense. Therefore, for obtaining the required cooling duty the surface area and costs of heat exchangers increase. This explains the discontinuity in this curve. Other process conditions are as follows:

Hydrate former: Propane, Reactor pressure: 450 kPa, Decomposer pressure: 650 kPa Discharge pressure of compressor: 1400 kPa, Yield: 0.3 Molality of seawater, M_{NaCl}: 1, Capacity: 1000 m³ of potable water per day

7. COMPARISON OF DESALINATION COST BY DIFFERENT METHODS

Comparison between the product cost of common desalination processes such as multi-stage flash distillation (MSF), multi-effect distillation (ME) and reverse osmosis (RO) have been given by Park et al. (1997). Table 4 shows the economic parameters for some selected processes of the Park et al. (1997) data. It should be noted that all of these selected plants are located in the Middle East with the capacity equal to 1000 ton/day. These plants are in operation and therefore the economic parameters, especially amortized O&M costs, are not the same. Difference between the initial design of the plants and optimum conditions describes this disagreement.

The computer results of this work for two cases are also included in this table. Other process conditions for these two cases are as follows:

Case a: Hydrate former: Propane, Reactor pressure: 450 kPa, Decomposer pressure: 650 kPa, Discharge pressure of compressor: 1400 kPa, Yield: 0.20, Seawater temperature: 300K, Capacity: 1000 ton/day It was assumed that the seawater contains only NaCl with molality equal to 1.2,

Case b: Hydrate former: Propane, Reactor pressure: 450 kPa, Decomposer pressure: 650 kPa, Discharge pressure of compressor: 1400 kPa, Yield: 0.3, Seawater temp.: 300K, Capacity: 1000 ton/day It was assumed that the seawater contains NaCl and CaCl₂ with $M_{NaCl}=1$ and $M_{CaCl2}=0.5$ and, Hydrate formation temperature elevation in reactor equal to 4K. The total capital investment and therefore the amortized value, for the proposed process are greater than the other process. High installed cost of the compressor is the main reason. Corrosion problems, especially for thermal process, cause higher O&M cost for MSF and ME process in comparison with the proposed process. As mentioned above, the low operational temperature of the proposed process decreases the corrosion problems considerably. The maximum temperature of brine in the proposed process is about the seawater temperature whose corrosion rate in comparison with MSF or ME is insignificant.

8. CONCLUSIONS

Comparison between the available desalination process and that proposed in this work has been done in this paper. Under normal operating conditions the proposed process is not economical. However, by using a proper hydrate formation promoter, the total cost of the produced potable water drops drastically and makes the proposed process attractive. Therefore, research must continue to find effective hydrate promoters. It seems that in the presence of suitable promoter, the total product cost of this process is comparable with other process such as MSF, ME and RO. Of course, one of the basic properties of this reagent must be non-toxicity.

LIST OF SYMBOLS

- A area, ft^2
- A the heat exchanger area, ft^2
- bhp brake horse power
- C_P heat capacity, J/gr mole.K
- *F* the number of molecules of the hydrate former per water molecules in the hydrate lattice
- F_c parameter corresponding to the compressor type in equation (8)
- F_d parameter corresponds to the heat exchanger type in equation (7)
- F_m parameter corresponds to the shell-and-tube material in equation (7)
- F_P parameter corresponding to the heat exchanger pressure in equation (7)
- H enthalpy, J/gr mole
- i continuous discount rate
- *m* molality, gr mole/1000 gr of solvent
- M&S Marshal and Swift cost index
- P pressure, kPa
- *R*, number of moles of the hydrate former per mole of seawater fed to the process
- T temperature, K
- U The overall heat transfer coefficient, $J/(s.m^2.K)$
- *y*, number of moles of the potable water produced by the process per mole of seawater fed to the process, yield

Greek

- ΔH heat of formation of hydrate molecule, J/gr mole
- θ_m fraction of the type m cavities which are occupied by hydrate former
- v_m ratio of the no. of type m cavities to no. of water molecules in the hydrate phase

Subscripts

in input out output

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Figure 1. Flow sheet for the proposed seawater desalination process



Figure 2. Typical phase diagram for a gaseous hydrate former



Figure 3. Hydrate and Condensation Curves for C_3H_8 . Quadruple Point Press. is: 562.07 (kPa), P_C =4247.36(kPa), T_C =96.82 (°C)



Figure 4. Hydrate and Condensation Curves for CO₂ Quadruple Point Press. is: 4757.06 (kPa) P_C=7371.47(kPa) ,T_C=31.10 (°C)



Figure 5. Effect of yield on economic parameters



Figure 6. Effect of seawater temperature on economic parameters



Figure 7. Effect of the hydrate formation temperature elevation in the presence of promoters, on economic parameters

| | C ₃ H ₈ | CO ₂ |
|------------------------------------------------|-------------------------------|-----------------|
| Reactor press., kPa | 450 | 4000 |
| Decomposer press., kPa | 650 | 5000 |
| Discharge press. of compressor, kPa | 1200 | 6800 |
| Seawater temp., K | 300 | 300 |
| Molality of NaCl as seawater electrolyte | 1 | 1 |
| Y (yield) | 0.3 | 0.3 |
| Total work, MJ/m ³ of potable water | 25.820 | 172.380 |

Table 1. the required total work per m³ of potable water for two different hydrate formers.

Table 2. Total energy consumption as a function of yield for the process described in Figure 5.

| Yield | 0.05 | 0.10 | 0.15 | 0.20 | 0.25 | 0.30 | 0.35 |
|--------------------|-------|------|------|------|------|------|------|
| Total work, MJ/ton | 125.8 | 67.8 | 48.5 | 38.9 | 33.3 | 29.6 | 27.1 |

Table 3. Total energy consumption as a function of seawater temperature for the process described in Figure 6.

| Temperature, °C | 15 | 17 | 22 | 25 | 30 | 32 |
|--------------------|------|------|------|------|------|------|
| Total work, MJ/ton | 26.8 | 27.2 | 28.4 | 29.1 | 30.5 | 31.1 |

Table 4. Economic parameters for some selected processes given by Park et al. (1997) and generated by computer program of this work.

| Process | Total cap. inv., M\$ | Amortized tot. cap. inv.,\$/ton | Amortized O&M, \$/ton | Total product cost, \$/ton |
|-------------------|-------------------------|---------------------------------|--------------------------|----------------------------|
| MSF | 2.67 | 0.75 | 1.81 | 2.96 |
| MSF | 2.33 | 0.65 | 1.72 | 2.74 |
| MSF | 2.93 | 0.82 | 2.00 | 3.26 |
| ME | 2.26 | 0.63 | 1.75 | 2.75 |
| ME | 2.62 | 0.73 | 2.17 | 3.34 |
| RO | 2.30 | 0.64 | 3.23 | 4.47 |
| RO | 2.31 | 0.65 | 0.19 | 0.97 |
| RO | 1.97 | 0.55 | 0.19 | 0.85 |
| This work, case a | 7.18 | 2.05 | 2.17 | 4.23 |
| This work, case b | 5.46 | 1.56 | 1.20 | 2.76 |