USE OF MINERALIZED WATERS IN TECHNICAL WATER SUPPLY

Abstract. The article presents the results of studies of the qualitative regularities of the process of Mg-Na zeolite softening of wide class mineralized water in order to use their huge reserves instead of fresh water in technical water supply system of the industrial enterprises. The mathematical model of the Mg-Na-zeolite softening process is obtained allowing to study and optimize the process, solve practical problems of calculation and design of water treatment plants.

Key words: mineralized water, zeolite softening, cation exchange capacity, ionic composition of water, mathematical model, height of the protective layer of cationite.

It is known that one of the technological processes of the oil chemistry, characterized by large water consumption is the pyrolysis process. Currently the amount of water steam supplied to the reaction tubes of the furnace is 50 up to 100% (on raw material). High process temperature (750-850°C) leads not only to coke formation, but also to the appearance of scale (scale formation).

In this regard, an alternative task to ensuring pyrolysis is the use of sea water instead of fresh, possible for coastal enterprises. To use huge stocks of mineralized waters instead of fresh water in technical water supply systems of industrial enterprises, scientific-technical tasks solving is required.
The most important of them is prevention of the scale formation by heating and during of water evaporation.

One of the effective methods solving of this task is magnesium-sodium zeolite softening.

Purpose of this work – is research of the base qualitative regularities of the Mg-Na-zeolite softening process the wide class of mineralized waters (with salt content from 2.5 up to 35 g/l); development of the mathematical model of the process for research and optimization the technology as a whole.

In the figure 1 in the most general form, the nature of the change in the output sorption curves for cationite KU-2 for water with ion content (in mg-equiv/l) is shown:

$C_{Ca} = C_{Mg} = 15, C_{Na} = 170$.

As follows from the figure, the filter operation is characterized by the formation of two volume fronts. In the first third (=12 liters of filtrate) there is a decrease not only in calcium but also in magnesium hardness (up to 2 mg-equiv/l). The magnesium (Mg) is replaced by more selective calcium cations (Ca). Specific output of water before the (Mg) breakthrough was 26 l/l of cationite and before the Ca- breakthrough – 46 l/l. Cation exchange capacity – 680 g-equiv/m$^3$, residual calcium concentration – 0.2 mg-equiv/l. Thus almost 99% calcium removal was achieved.

High technological indices are possible also by Mg-Na zeolite softening of other types of mineralized waters, covering class in question.

Results on experiments with counter current ionization of water, given in the table 1, testify to this. Here as process output indices are: cation exchange capacity for calcium ($E_{Ca}$; g-equiv/m$^3$); specific water production (d, m$^3$/m$^3$); residual concentrations of calcium and magnesium ($C_{res}^{Ca}, C_{res}^{Mg}$ mg-equiv/l) and also amount of initial water salts, which may be used for regeneration (g-equiv/l).

<table>
<thead>
<tr>
<th>Initial water</th>
<th>$C_{Na}$</th>
<th>$C_{Ca}$</th>
<th>$C_{Mg}$</th>
<th>$g$</th>
<th>$E_{Ca}$</th>
<th>d</th>
<th>$C_{res}^{Ca}$</th>
<th>$C_{res}^{Mg}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>50</td>
<td>5</td>
<td>5</td>
<td></td>
<td>7.7</td>
<td>640</td>
<td>128</td>
<td>0.02</td>
<td>2</td>
</tr>
<tr>
<td>100</td>
<td>10</td>
<td>10</td>
<td></td>
<td>6.7</td>
<td>670</td>
<td>67</td>
<td>0.10</td>
<td>6</td>
</tr>
<tr>
<td>170</td>
<td>15</td>
<td>15</td>
<td></td>
<td>8.4</td>
<td>710</td>
<td>47</td>
<td>0.22</td>
<td>8</td>
</tr>
<tr>
<td>188</td>
<td>16</td>
<td>60</td>
<td></td>
<td>7.0</td>
<td>525</td>
<td>33</td>
<td>0.20</td>
<td>48</td>
</tr>
<tr>
<td>248</td>
<td>13</td>
<td>59</td>
<td></td>
<td>9.9</td>
<td>400</td>
<td>31</td>
<td>0.35</td>
<td>46</td>
</tr>
<tr>
<td>470</td>
<td>20</td>
<td>110</td>
<td></td>
<td>11.0</td>
<td>380</td>
<td>15</td>
<td>0.03</td>
<td>75</td>
</tr>
</tbody>
</table>

As follows from the data received, even for waters with a high content of counterions high values of specific output of water are reached with a degree of removal of calcium 97% or more.

An important task any ion exchange technology is development of the mathematical model of process.

It is important for forecasting of the technological indices of the process, depending on water ion composition, sorption and regeneration conditions.

These technological indices include: working exchange capacity of cationite by Ca$^{2+}$ ions and residual content of these cations in treated water.

There are several approaches to solving such problems [1]:

$\Rightarrow_1$ development of the functional (experimental-statistical) model, describing process without considering its mechanism;

Figure 1. Output curves of the Mg-Na-zeolite softening of the water

1- $CCa = f(V)$; 2 - $CMg = f(V)$; 3 - $CNa = f(V)$; 4 - $A_{Mg}^{in} = C_{Ca}^{in}$
development of the semi-empirical models which describe the whole process and reflect individual aspects of the mechanism of the studied process;

- development of purely deterministic models, reflecting sufficiently fully the mechanism of the studied process.

The latter approach is the most effective and at the same time the most complex.

Semi-empirical approach is based on the following initial formula, used for calculation of the base technological index of the process-working exchange capacity of cationite (E_w):

\[ E_w = \alpha_p \cdot E_{eq}\left[1 - h_{p,1}(1 - \delta)/h_0\right], \text{g-equiv/m}^3 \] (1)

where:
- \( \alpha \) – is regeneration efficiency coefficient;
- \( E_{eq}\) – is the full equilibrium exchange capacity of cationite by calcium cations, g-equiv/m^3;

\( h_{p,1} \) – is height of the cationite protective layer, m;

\( h_0 \) – is total height of the cationite layer, m.

According to calculation of the ion equilibrium, the Ca^{2+} residual concentrations, reliably eliminating CaCO\(_3\) and CaSO\(_4\) precipitation by heating and evaporation of mineralized water are 0.1-0.3 mg-equiv/l.

Deeper Ca^{3+} removal is achieved by filtration in the second stages.

Therefore, by development of the mathematical model of the process, can be limited to obtaining a system of ratios, allowing to calculate working exchange capacity of cationite, turning on the depth of Ca^{3+} removal in the category of indices, to which restrictions are imposed.

Analysis of the formula (1) indicates its universality (from the point of view of solution of applied tasks in particular – suitability for calculating the ionization process of mineralized waters of arbitrary composition).

### Levels and intervals of factors variation

<table>
<thead>
<tr>
<th>Levels</th>
<th>C(x) (mg-equiv/l)</th>
<th>H(x) (mg-equiv/l)</th>
<th>ΔCa (x)</th>
<th>( v (x) ) (m/h)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Upper (+)</td>
<td>300/550</td>
<td>120/200</td>
<td>0.5/0.5</td>
<td>20/20</td>
</tr>
<tr>
<td>Lower (-)</td>
<td>40/200</td>
<td>10/30</td>
<td>0.2/0.2</td>
<td>5/5</td>
</tr>
<tr>
<td>zero</td>
<td>120/375</td>
<td>20/75</td>
<td>0.35/0.35</td>
<td>12.5/12.5</td>
</tr>
</tbody>
</table>

Note: in numerator – the value of the factors on brackish waters, in the denominator – on salt water.

Determination of the \( h_{p,1} \) value for every experiment carried out according to the methodic [2].

Since the equation (2) is linearized after logarithm, then processing the results of calculation was carried out, by logarithm received values of \( h_{p,1} \).

\[ y = 1.36 + 0.079x_1 + 0.146x_2 + 0.0445x_3 + 0.0824x_4 \] (2)

Therefore, research came down to getting functional dependences \( \alpha_p, h_{p,1}, E_{eq} \) from the determining factors of the process.

- total salt content of initial water (C_0);
- total hardness (H_0);
- calcium share in total hardness (\( \Delta\text{Ca} \));
- rate of water filtration (\( \vartheta \)).

The object of research were mineralized waters with salt content from 2.5 up to 35g/l, by hardness 30÷120 mg-equiv/l, calcium component 20÷50% of total hardness. On base of preliminary experiments it was area accepted to break down the studied area into two parts within each of which a more accurate approximation of the desired functional dependences is possible.

Dependence \( h_{p,1}(C_0, H_0, \Delta\text{Ca}, \vartheta) \) can be approximated with high accuracy by the power equation of the type:

\[ h_{p,1} = a \cdot C_0^{\alpha_1} \cdot H_0^{\alpha_2} \cdot \Delta\text{Ca}^{\alpha_3} \cdot \vartheta^{\alpha_4} \] (3)

where: \( a, \alpha_1, \alpha_2, \alpha_3, \alpha_4 \) - are the empirical coefficients.

Research were carried out on the cationite KU-2 by method of mathematical planning of experiment. Factors affecting the height of cationite protective layer and its levels are presented in the table 2.

The following expression was used to transition the equation (3) to natural scale [3].

\[ X_i = \frac{2(\lg \xi_i - \lg \xi_i^*)}{\lg \xi_i^* - \lg \xi_i} + 1 \] (4)

where \( \xi_i \) - is coded value of \( i \) – factor;

\( \xi_i^*, \xi_i^* \) – are natural values of the upper and lower level of \( i \)-factor.

As a result of the transition from coded values of factors to natural, it was obtained:

\[ \lg Y = 0.0678 + 0.234 \lg C_0 + 0.524 \lg H_0 + 0.325 \lg \Delta\text{Ca} + 0.33 \lg \vartheta \] (5)
After potentiation:

\[ h_{p.e.} = 1.17 \cdot C_0^{0.23} \cdot H_0^{0.52} \cdot \Delta C_a^{0.33} \cdot \theta^{0.33} \] (5)

Similar formula but with other empirical coefficients was derived for salt waters:

\[ h_{p.e.} = 1.19 \cdot C_0^{0.35} \cdot H_0^{0.24} \cdot \Delta C_a^{0.15} \cdot \theta^{0.38} \] (6)

Interpretation of the obtained formulas showed that for brackish waters \( h_{p.e.} \) value is changed within 10÷50 cm for salt waters – 40÷90 cm, i.e. doubled on average.

The nature of the influence of all factors on \( h_{p.e.} \) is the same: the rise of each of them contributes to growth of \( h_{p.e.} \).

At the same time for both types of waters from 4 considered factors total hardness of water has a more noticeable effect on \( h_{p.e.} \).

Dispersion analysis showed that by research of effect of the base factors on coefficient of effectiveness of cationite regeneration \( (a_2) \) in the study area, significant for the regeneration of cationite are 3 factors: \( C_0, C_a \) and specific salt consumption.

This dependence may also be approximated by equation of power type:

\[ E_{eq} = 4.27 - 2 \cdot C_0 + 0.1H_0 + 49H_0 \cdot \Delta C_a + 46.3H_0 \cdot \Delta C_a \] (9)

for salt waters:

\[ E_{eq} = 238 - 0.77 \cdot C_0 + 2.8 \cdot H_0 + 149 \cdot \Delta C_a + 7.7H_0 \cdot \Delta C_a - 0.76C_0 \cdot \Delta C_a \] (10)

Analysis of the equations (10) and (11) shown that the \( E_{eq} \) values are changed within 450÷1300 g-equiv/m³ in field of the brackish waters and within 240÷1200 g-equiv/m³ in field of salt waters. By the significance of the influence on \( E_{eq} \) value, factors are arranged in the following order: \( \Delta C_a, C_0, H_0 \).

Totality of equations (1) and (2) represent mathematical model of the process of Mg-Na-zeolite softening of wide class mineralized water.

Taking into account the features of the organization of the process in periodic filters and for reasons of technological expediency this model is supplemented by a system of restrictions:
- rate of water filtration \( (\dot{g}) \);  
- height of cationite layer \( (h_0) \);  
- specific consumption of the magnesium and sodium salts on regeneration of cationite \( (g) \);  
- residual content of calcium ions \( (C_{a_{res}}) \)

Two calculation formulas were obtained:

a) for brackish waters

\[ a_2 = 0.6 \cdot C_a^{0.04} \cdot g^{0.24} \cdot C_0^{-0.057} \] (7)

b) for salt waters

\[ a_2 = 0.65 \cdot C_a^{0.043} \cdot g^{0.31} \cdot C_0^{-0.078} \] (8)

In the first case: \( C_a = 5÷15, C_0 = 40÷200 \) mg-equiv/l, in the second – 10÷50 and 200÷60 mg-equiv/l respectively.

For the whole range \( g = 4÷10 \) g-equiv/l of cationite. Calculation by above formulas show that in studied are \( a_2 \) values are changed within 0.7÷0.97 and the most significant of the considered factors is specific salt consumption.

Method of mathematical planning was used also by study of dependence of the equilibrium exchange capacity of cationite on base factors [4].

On base of preliminary research an expediency of approximation of this dependence have been determined by equation of linear regression.

As a result, the following regression equations have been obtained:

for brackish waters:

\[ C_{a_{res}} = 5 \div \dot{g} \leq 25 \div 30 m/h \] (11)

\[ 1.5 \leq h_0 \leq 6 m \] (12)

\[ 2 \leq g \leq g_{coh}, g - \text{equiv/l} \] (13)

\[ C_{a_{res}} = 0.1 mg - \text{equiv/l} \] (14)

In the equation (14) disposable quantity of salts \( (g_{coh}) \) is calculated as follows:

\[ g_{coh} = k \cdot \frac{K_r}{H_0} \cdot C_0 \cdot 10^{-3} \] (15)

where \( k \) – is coefficient, taking into account reuse of the worked regeneration solution. Value of \( K_r \) are changed within 1.1÷1.4.
Адекватность полученной модели была подтверждена сравнением рассчитанных значений с эксперименタルными данными, за исключением упомянутых выше.

Вычисление констант в модели было проведено на компьютере, методом согласованной аппроксимации, а затем было проведено сравнение экспериментально полученных и расчетных значений.

**Таблица 3.**

<table>
<thead>
<tr>
<th>Initial water</th>
<th>E.e.q.</th>
<th>g</th>
<th>α</th>
<th>E2</th>
</tr>
</thead>
<tbody>
<tr>
<td>C0</td>
<td>G0</td>
<td>C4</td>
<td></td>
<td></td>
</tr>
<tr>
<td>60</td>
<td>10</td>
<td>5</td>
<td>906</td>
<td>10.8</td>
</tr>
<tr>
<td>120</td>
<td>20</td>
<td>10</td>
<td>898</td>
<td>10.8</td>
</tr>
<tr>
<td>200</td>
<td>30</td>
<td>15</td>
<td>964</td>
<td>11.8</td>
</tr>
<tr>
<td>312</td>
<td>76</td>
<td>26</td>
<td>690</td>
<td>8.3</td>
</tr>
<tr>
<td>320</td>
<td>72</td>
<td>13</td>
<td>518</td>
<td>12</td>
</tr>
<tr>
<td>380</td>
<td>130</td>
<td>20</td>
<td>445</td>
<td>12</td>
</tr>
</tbody>
</table>

Адекватность полученной модели была подтверждена сравнением рассчитанных значений с эксперименタルными данными, за исключением упомянутых выше.

Исходные свойства воды: 

- Определена роль антиотражающего покрытия на коэффициенты отражения и поглощения света видимой области спектра.
- Получено, что антиотражающее покрытие из SiO2 в кремниевых пластинах с пирамидальной текстурой может быть использовано.
- Предложены методы оценки адекватности полученной модели, включающие расчетные и эмпирические методы.

**СТИМУЛИРОВАНИЕ ОПТИЧЕСКИХ СВОЙСТВ КРЕМНИЯ ПУТЕМ ТЕКСТУРИРОВАНИЯ ПОВЕРХНОСТИ**

**Аннотация.** Приведены результаты расчетного анализа влияния геометрических размеров пирамидальной текстуры на коэффициенты отражения и поглощения света видимой области спектра. Определена роль антиотражающего покрытия из SiO2 в кремниевых пластинах с пирамидальной текстурой.

Известно, что оптические свойства кремниевых пластин, используемых в качестве базового материала для оптоэлектронных солнечных элементов (СЭ) являются важными показателями, определяющими их эффективность. Для улучшения оптических свойств пластин используются различные формы поверхностного текстурирования. В современных СЭ наибольшее применение получили пирамидальные текстуры, которые традиционно формируются методом щелочного анизотропного травления [1, 2]. Такая технология позволяет создавать неоднородные пирамидальные текстуры с геометрическими размерами 0,5 - 4 мкм на поверхности пластин кремния. Для достижения однородной поверхностной текстуры необходима предварительная обработка кремниевой пластини с целью удаления нарушенного слоя. В качестве текстурирующего реагента обычно используются водные растворы KOH или NaOH. Взаимодействие кремния и раствора щелочи, например гидроксида калия описывается химической реакцией:

\[
\text{Si} + 2\text{KOH} + \text{H}_2\text{O} = \text{K}_2\text{SiO}_3 + 2\text{H}_2
\]

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