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POWER ENGINEERING RECEPTION OF THE BORIC ACID IN THE SUBACIDIC SOLUTION

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The power engineering of reception process of a boric acid in a reactor is investigated. Process carried out by hydrolysis tetraborate anions, contained in breccia mud volcanos. For reaction of hydrolysis change of free energy Gibbs and a constant of balance are calculated. Account factors are determined and material and thermal balances of process are made.

Products of eruption of mud volcanos are so-called breccia, including various minerals [1] including a significant amount drills $Na_2B_4O_7 \cdot 10H_2O$. It is established, that breccia solutions of the mud volcanos which have been cast out in Gobustan and Binagadi (Azerbaijan) contain ~ $4 \cdot 10^{-3}$ mole/l tetraborate anions $B_4O_7^{2-}$. At hydrolysis tetraborate anions in the subacidic medium the boric acid is formed [2].

Experiments have shown, that boron–containing breccia such quality with success can be used for reception of a boric acid in industrial scale. In comparison with known ways, reception of a boric acid by hydrolysis tetraborate anions, contained in breccia, has significant advantages. Other reagents in this case are not applied, except for mineral acids, are not formed harmful waste products and sewage and there are no excited mediums.

According to the skilled data during breccia dissolution, containing tetraborate sodium, in a subacidic solution in a reactor there is a consecutive two-phasic process of hydrolysis [3]. Breccia used in experiences were as cemented breeds in the size ~ 1 cm. First arrives the tetraboron acid then there the hydrolysis of tetraborate anions is happen. As a result of hydrolysis tetraborate anions in weak solutions H_2SO_4 the boric acid $B(OH)_3$ is formed:

$$Na_2B_4O_7 + H_2SO_4 + 5\,H_2O = Na_2SO_4 + 4\,B(OH)_3 \qquad (1)$$

For reaction (1) the change of free Gibbs energy under standard conditions have defined:

$$\Delta G^0_p = \Delta G^0_{f,\,298}(Na_2SO_4) + \Delta G^0_{f,\,298}[4\,B(OH)_3] - \\ - \Delta G^0_{f,298}(Na_2B_4O_7) - \Delta G^0_{f,\,298}(H_2SO_4) - \Delta G^0_{f,\,298}(5H_2O) \qquad (2)$$

Thus used values $\Delta G^0_{f,298}$ substances [4] participating in reaction of a boric acid reception. The thermodynamic data of substances of reaction (1) are given in tab.1.

Computed value of change of free Gibbs energy of reaction (1) from equation (2) $\Delta G^0_p = -184$ kJ/mole specifies that in standard conditions in acid solutions reaction of hydrolysis tetraborate anions with reception of a boric acid spontaneously flows to the right.

Usually alongside with chemical interaction between initial substances there is also an interaction between products of reaction. Such balance of process is characterized by a constant K^0_b. Value K^0_b allows judging the attitude of concentration of reagents and products at balance. At changes of temperature value K^0_b can change, but it does not depend on concentration of reagents and products. The K^0_b is the important size allowing also defining, whether spontaneously given reaction will proceed.

Table 1. Thermodynamic constants of the substances participating in reaction (1) receptions of a boric acid

Substance	$-\Delta H^0_{f,298}$ kJ/mole	$-\Delta G^0_{f,298}$ kJ/mole	$C^0_{p,298}$ J/(mole·K)	Literature [3,4]
$Na_2B_4O_7$	3300 3276.6	3292.3 3081.6	357	
H_2SO_4	814.2 811.3	690.3	137	
H_2O	285.83	237.24	75	
Na_2SO_4	1388.5 1384.6	1270.8 1266.8	126.4	
$B(OH)_3$	1094	968.8	98	

A constant of balance K^0_b for reaction (1) have defined. The ΔG_r change is connected to a constant K^0_b the following equation:

$$\Delta G_r = RT \ln (a_p / a_i) - RT \ln K^0_b \quad (3)$$

Where R – is universal gas constant; T–temperature; a_p and a_i – activity of reaction products and initial substances. In a condition of balance $\Delta G_r = 0$. Then the equation (3) will become:

$$\Delta G_r = RT \ln (a_p / a_i) - RT \ln K^0_b = 0 \quad (3a)$$

$$a_p / a_i = K^0_b \quad (3b)$$

For a standard equilibrium case at $a_p / a_i = 1$ equation (3) will become:

$$\Delta G^0_r = - RT \ln K^0_b \quad (4)$$

From (4) under standard conditions for a constant of balance of reaction (1) we shall receive:

$$\Delta G^0_r = - 8.314 \cdot 298 \cdot 2.3 \lg K^0_b = - 5698 \text{ J/mole} \cdot \lg K^0_b \quad (5)$$

In view of value $\Delta G^0_b = - 184$ kJ/ mole for a constant of balance of reaction (1) on the equation (5) we shall receive $K^0_b = 10^{32}$.
According to principle of La Chatele the change of balance always reduce the influence of external effects. Since direct reaction (1) is exothermic then at temperature rise the value K^0_b = = 10^{32} should decrease.
On experimental data for an equilibrium outlet of a boric acid the optimum temperature interval is 323÷343 K.

Adjusted the equation of reaction (1) have defined the account factors of raw material (breccia), a sulfuric acid and water on reception of a boric acid in a reactor at hydrolysis tetraborate anions. The made material balance on 1 t of the basic product, i.e. on a boric acid, is given in tab. 2. It is known, that for the majority of chemical manufactures 60 ÷ 70 % of the cost price fall to account factors on raw material. Proceeding from material balance, have computed the charge of raw material on formation 1 t of $B(OH)_3$. The breccia expense is 25 t on reception 1 t of $B(OH)_3$.

Table 2. Material balance on 1 t of $B(OH)_3$

Receipt		Expense	
Initial substance	kg	Product	kg
$Na_2B_4O_7 \cdot 10H_2O$ including:		$B(OH)_3$	1000
$Na_2B_4O_7$	812	Na_2SO_4	574
H_2O cryst.	728	H_2O (for reaction)	19762
2 % H_2SO_4 including:			
H_2SO_4 (monohydrate)	404		
H_2O (for desaturation of H_2SO_4)	19392		
Total:	21336	Total:	21336

Using the data of material balance and thermodynamic constants of substances (tab. 1) participating in reaction (1), have defined account thermal factors.
Proceeding from standard values of heat formation of substances [4] and in view of that the thermal effect of reaction is equal to a difference total enthalpy products and total enthalpy initial substances have calculated thermal effect of reaction (1). It is found, that during formation 1 t of a $B(OH)_3$ the thermal effect of exothermal reaction is $Q_1 = 241000$ kJ.
The heat amount, acting with initial substances of reaction (1) $Q_2 = 1097301$ kJ, (tab. 2) have defined from the data of material balance thermal capacities (tab. 1) for the appropriate substances on the equation

$$Q_2 = G\ C_p^0\ T \quad , \qquad (6)$$

where G - amount of substance (kg); C_p^0 - thermal capacity [J / (mole·K)]; T - temperature (K).

Thus, total heat arrival in reaction of hydrolysis $B_4O_7^{2-}$ anions in the sub acidic water medium with $B(OH)_3$ formation is $Q_{re} = Q_1 + Q_2 = 1338301$ kJ.

The heat charge for 1 t $B(OH)_3$ reception $Q_3 = 974919$ kJ was found from value of thermal effect of reaction with the account stochiometric factor and molecular weight $B(OH)_3$.

If to accept, that heat losses in medium Q_4 make 5 % from the total heat arrival, $Q_4 = 66915$ kJ.

Thus, total heat charge in reaction (1) is $Q_{ex} = Q_3 + Q_4 = 1041834$ kJ.

Proceeding of data of arrival and charge of heat of reaction (1) the thermal balance of $B(OH)_3$ reception have made (tab.3).

Table 3. Thermal balance on 1t $B(OH)_3$ reception

Receipt	kJ	Expense	kJ
Q_1	241000	Q_3	974919
Q_2	1097301	Q_4	66915
Total:	1338301	Total:	1041834

$$\Delta Q = Q_{re} - Q_{ex} = 1338301 - 1041834 = 296467 \text{ kJ (82 kWh)}$$

Thus, in view of surplus ΔQ = 296467 kJ or the specific charge of the electric power W = 82 kWh during hydrolysis $B_4O_7^{2-}$ anions with $B(OH)_3$ reception to system heating up to 323÷343 K the insignificant charge of the electric power is needed.

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ZƏİF MƏHLULLARDAN BORAT TURŞUSUNUN ALINMASI PROSESİNİN ENERQETİKASI

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Reaktorda gedən borat turşusunun alınması reaksiyasının enerqetikası tədqiq edilmişdir. Son məhsulun alınması üçün palçıq vulkanlarında olan tetraborat anionlarının hidrolizi reaksiyası aparılmışdır. Bu prosesin enerqetik parametrləri, o cümlədən, sərbəst Qibbs enerjisinin dəyişməsi ΔG^0_p = – 184 kC/ mol və tarazlıq sabiti tapılmışdır $K^0_{taraz} = 10^{32}$. İstifadə olunan maddələrin sərf olunma əmsalları, borat turşusunun alınmasının material və istilik balansları hesablanmış və nəticələr cədvəl şəklində verilmişdir.

ЭНЕРГЕТИКА ПРОЦЕССА ПОЛУЧЕНИЯ БОРНОЙ КИСЛОТЫ В СЛАБОКИСЛОМ РАСТВОРЕ

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Исследована энергетика процесса получения борной кислоты в реакторе. Процесс получения конечного продукта проводили путем гидролиза тетраборат анионов, содержащихся в брекчиях грязевых вулканов. Для процесса гидролиза определены энергетические параметры: изменение свободной энергии Гиббса ΔG^0_p = – 184 кДж / моль и константа равновесия $K^0_{равн} = 10^{32}$. Определены расходные коэффициенты, составлены и в виде таблице приведены материальный и тепловой балансы процесса получения борной кислоты в реакторе.