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ORIGINAL RESEARCH ARTICLE

Theoretical principles of modeling for the regeneration process of cation exchanger

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ABSTRACT

Optimization of a cation-exchange softening plant requires linking reagent demand with the working capacity of the ion exchange layer. This, in turn, requires solving two preliminary problems: establishing the distribution of hardness ions across the depth of the layer after completion of the loosening stage and determining the change in concentration at the entrance to the layer when regenerating and washing water is supplied. A new combined mixing scheme is proposed, in which the solution entering the filter is mixed with a water cushion located above the filter bed. At the same time, the volume involved in the mixing changes over time. An analytical expression is obtained for the change in concentration of the solution entering the upper layer of the filter bed during both the regeneration and backwash stages. Obtained is an equation that allows us to determine the transit time with maximum concentration through exchanger load.

Keywords: cation exchanger; regeneration solution; dilution; modeling

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1. Introduction

Improving the efficiency of cation exchange units, as well as the design of new ones, depends on solving optimization problems aimed at producing water of the required quality at the lowest possible operating costs[1-5]. Currently, such optimization is no longer possible without computer-aided mathematical description and modeling of the main process stages[6-10]. The development of technology for the regeneration of sodium cation exchangers using a sodium sulfate solution also requires a similar approach[11-13]. Among all the stages of softening, regeneration is the most complex from a physicochemical point of view, the most difficult to formulate mathematically, and has the greatest economic significance[12,13]. Therefore, a consistent description of regeneration should be based on the nature of the distribution of retained ions across the depth of the filter bed and the change in the concentration of the regenerating substance supplied to the upper bed layer.

The shape of the regeneration output curves is determined by the distribution of sorbed ions within the layer[14-18]. Rregeneration of the cation exchange resin is preceded by a loosening (fluidization) stage, which serves to flush out fine particles formed during operation and disrupt channels formed within the resin layer. Both stages contribute to the efficient performance of subsequent regeneration. The fluidization process is carried out with softened water or with the last portions of washed off water got after the regeneration of exchangers. The agitation flow rate in industrial filters exceeds the fluidization velocity. This causes the movement of solid particles and changes the distribution of adsorbed ions across the filter bed. Consequently, the resulting distribution will differ from the original one obtained during water softening. The definition of true distribution of adsorbed ions on the charge of the exchanger after the fluidization stage is an important and essential task for ion exchangers.

The presence of water cushion above the charge layer during the feeding into the ion exchanger of the regeneration solution causes its dilution. The growth of concentration of regeneration solution at the entrance of ion exchanger as well as the change of concentration during the supply of washing out water into the exchanger is calculated by the equation of ideal swift[19]. The calculation method of the regeneration process supposes the constancy of regeneration solution concentration. That's why for calculating industrial exchangers, the averaged value of concentration of regeneration solution flowing directly to the exchange charge is used. Such kind of simplification also distorts the view of the diagram. Research purpose Finding the diagram of the regeneration process by calculation.

It requires:

1. to obtain a graph of the distribution of sorbed ions across the bed depth after completion of loosening (fluidization).

2. to determine how the concentration of the regenerating agent entering the top layer of the bed changes during regeneration and washing, taking into account the water cushion located above the bed.

2. Materials and methods

2.1. Distribution of total hardness ions by bed depth before and after fluidization

Determining the distribution of retained ions by bed depth is only possible if the sample can be taken from the desired depth without disturbing the bed layers. Traditional samplers for loose granular materials inevitably mix the bed and do not guarantee that the sample is taken from the desired depth. The tight internal geometry of the industrial column further limits the use of bulky devices, and cutting an additional inspection hatch in the filter shell is expensive and damages its anti-corrosion coating. To overcome these limitations, a hydraulic flush sampler was developed that operates within the confined space of the column and collects a sample from a selected depth without disturbing the bed structure[20].

The eluate formed during sampling was collected, and its total hardness was measured. The amount of ions retained at each depth in the sodium cation exchanger was calculated based on the amount of hardness ions removed from the sample bed and the volume of the corresponding sample fraction. Tests were conducted on a full-scale filter with a diameter of 3.0 m and a bed depth of 2.0 m, equipped with a standard drainage system (**Table 1**). The sodium cation exchangers under study were filled with CM-1 sulfonated carbon.

Analysis of the measurements shows that after fluidization, the bed layers are mixed, and the sorbed hardness ions are distributed almost uniformly throughout the entire bed depth.

The loading of the cation exchange filter before regeneration can be represented as two sections. The main (upper) section has a height (H_0-H_{pr}), with a concentration of sorbed ions E, and the protective (lower) section has a height H_{pr} with a concentration of sorbed ions of $0.5E$[21]. Therefore, taking into account the volumes of the sections, the average value of sorbed hardness ions can be determined using the formula[21]:

$$E_{av} = \frac{(H_0 - H_{pr}) \cdot E + 0{,}5 \cdot H_{pr} \cdot E}{H_0} \tag{1}$$

where,

H_0 - total exchanger load height, m;

H_{pr}– ion exchanger protective layer height, m;

E – stiffness of content at the loading corresponding to the ion exchange constant, g-eq./ m^3.

Table 1. Concentrations of sorbed ions by bed depth.

The depth of taking samples, m	Quantity of ions of hardness on the charge g-eq./m^3	
	Before fluidization	**After fluidization**
0.00	600.0	512.5
0.50	-	450.0
0.60	512.5	-
1.00	-	500.0
1.10	444.4	-
1.40	-	456.3
1.50	400.0	-
1.60		450.0
1.75	300.0	500.0
		$E_{cp} = 478.1$

E is calculated according to the Nikolski equation[22,23]. The constant of ion exchange is taken from most adsorbed ion. The height of the protective layer is calculated according to the formula[21]

$$H_{pr} = 0{,}04V \cdot d^2 \cdot lnh_t \tag{2}$$

where:

V – soft water flow rate, m^3/h;

d - grain diameter of the load, mm;

h_t - total hardness of softened water, g-eq./m^3.

The average amount of hardness ions retained on the layer, calculated using equation (1) and obtained experimentally, is 486 ± 28 g-eq./m^3 at a confidence level of 0.95 (i.e. ±2 standard deviations). Thus, the relative error of the average content of sorbed ions along the resin layer does not exceed 6%.

2.2. Change in regenerant solution concentration during Na feeding to the cation exchanger and during rinsing

The change in regenerant solution concentration at the inlet to the top of the bed is determined by taking into account the volume of the water cushion above the bed and the solution flow rate. The data presented below demonstrate that estimating this dilution using the classical law of ideal mixing does not reproduce the actual concentration of the solution entering the bed surface[19]. Therefore, a combined model is more appropriate. In this model (**Figure 1**), the volume in which ideal mixing occurs changes as the process progresses, since only a portion of the water cushion is involved in mixing at any given time. Considering the mass balance equation for the amount of substance entering the water cushion yields:

$$q^r \cdot \Delta t \cdot C_r = C \cdot q^r \cdot \Delta t + \Delta C \cdot W \tag{3}$$

where q^r- regeneration solution discharge, m^3/h;

Δt - time interval, hour;

C_r- concentration of regeneration solution, g/m^3;

C - salt concentration in water cushion after being averaged, g/m^3;

ΔC - the change of the salt concentration in the water cushion, g/m^3;

W - volume participating in mixing, m^3.

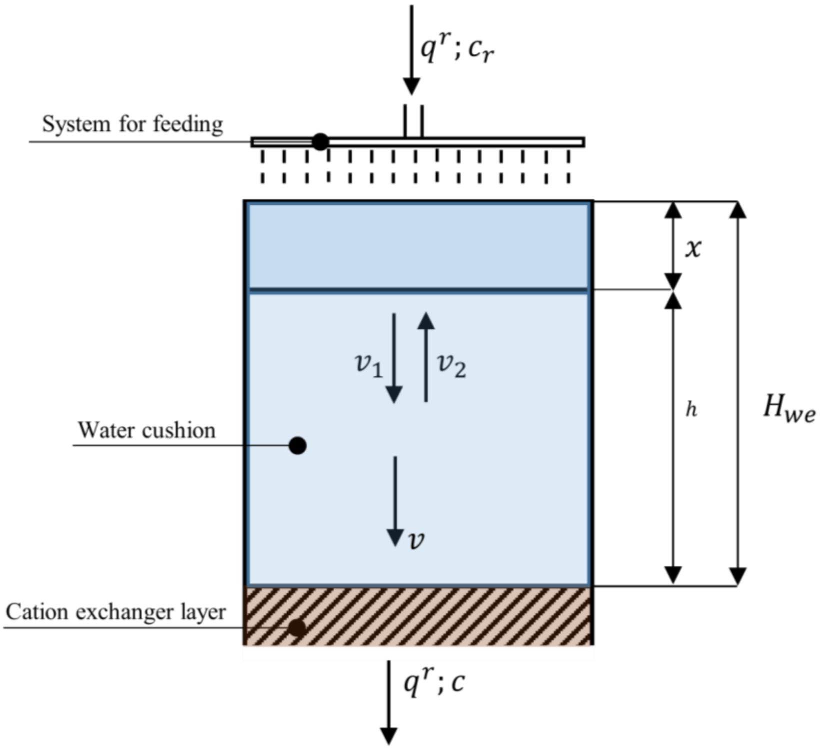

Figure 1. Schematic diagram of the combined model used to describe the change in solution concentration at the inlet to the upper loading layer. H_{WC}- the height of the water cushion layer; x - ; h - ; v – the speed of the solution movement over the ion exchanger; v_1– speed of the front movement of maximum concentration; v_2– the speed of the penetration of regeneration solution into volume participating in ideal mixing.

The equation of the material balance is the following:

$$C_r - C = \frac{W}{q^r} \cdot \frac{\Delta C}{\Delta t} \tag{4}$$

After conversion and integration within the limits from 0 till t and from initial concentration C_W till C we get:

$$\int \frac{q^r}{W} \cdot dt = \int \frac{dC}{C_r - C} + A \tag{5}$$

or

$$\frac{q^r}{W} \cdot t = -ln(C_r - C) + A \tag{6}$$

where, C_w - concentration of salts in the water cushion before feeding the regeneration solutionб g/m^3.

Under initial conditions $t = 0$ and $C = C_W$ (before the start of the regeneration process),

$A = \ln(C_r - C_W)$

With the account of above given, we get:

$$-\frac{q^r\cdot t}{W} = ln\frac{(C_r - C)}{(C_r - C_W)} \tag{7}$$

Hence

$$(C_r - C) = (C_r - C_W)\cdot \exp\,(-\frac{q^r\cdot t}{W}) \tag{8}$$

Consequently, the nature of the change in the concentration of the solution entering the top layer of the bed takes the following form:

$$\frac{C}{C_r} = 1 - \left(1 - \frac{C_W}{C_r}\right)\cdot \exp\,(-\frac{q^r\cdot t}{W}) \tag{9}$$

The volume of the water cushion involved in mixing is determined by the ratio:

$$W = m\cdot f\cdot H_{WC} \tag{10}$$

where, m - a part of water cushion participating in ideal mixing;

f - the area of the ion exchanger, m^2;

H_{WC}- the height of the water cushion layer, m.

m - the fraction of the capacity of the water cushion that participates in ideal mixing.

At the same time the volume participating in mixing is variable quantity.

$$W = m\cdot f\cdot H_{WC} - f\cdot x = f(m\cdot H_{WC} - v_1\cdot t) \tag{11}$$

where v_1– speed of the front movement of maximum concentration, m/h;

$$v_1 = v - v_2 \tag{12}$$

v – the speed of the solution movement over the ion exchanger, m/h;

v_2– the speed of the penetration of regeneration solution into volume participating in ideal mixing (or, this is equal to the difference of the speed of the solution movement above the ion exchanger and the speed of the front movement with maximum concentration.)

The regenerating solution, which enters the water cushion, partially participates in the mixing. Denoting the proportion of the regenerating solution as α, we determine the velocity v_2 using the formula:

$$v_2 = \frac{\alpha\cdot q}{f} = \alpha\cdot v \tag{13}$$

So, with the account of (12) and (13) we get:

$$v_1 = v(1-\alpha) \tag{14}$$

Substituting dependencies (12) – (14) into the material balance equation and simplifying, the relationship describing the change in the concentration of the regenerating substance entering the upper layer of the load takes the form:

$$\frac{C}{C_r} = 1 - \left(1 - \frac{C_W}{G_r}\right)\exp\,(-\frac{v\cdot t}{m\cdot H_{WC} - v\cdot t(1-\alpha)} \tag{15}$$

Following the same logic of reasoning for the beginning of the washing stage, the nature of the change in the concentration of the solution at the entrance to the upper layer of the load takes the form:

$$\frac{C}{C_r} = \frac{C_W}{C_r} - \left(1 - \frac{C_W}{G_r}\right) \exp\left(-\frac{v \cdot t}{m \cdot H_{WC} - v \cdot t(1-\alpha)}\right. \tag{16}$$

The change in the concentration of the solution at the inlet to the load was monitored by the salt content in the solution flowing out of the filter. During the passing of the solution through the grain charge the model of ideal displacement can be used[19]. The resulting effect is a time shift in the change in concentration without distortion of its shape. Total salt content was determined by the specific electric conduction of the solution. The substitution of sodium ion by calcium ion and magnesium and backwards insignificantly influences electric conduction of the solution as equivalent electric conductions of these ions are close: sodium ion 50.1; calcium ion 59.5; magnesium ion 53.0 S · m^2 · $mole^{-1}$[24].

3. Results and discussion

Experimental data yield a value of m = 0.45 for equation (15), determined graphically using the method recommended by V. V. Kafarov[25] (**Figure 2**). The same approach yields m = 0.6 for equation (16). The fraction of the water cushion participating in ideal mixing is itself a function of the incoming flow velocity, which is accurately reflected by the different values of m. From measurements carried out on the same industrial filter with sodium cations (diameter 3.0 m, layer depth 2.0 m), the most probable value of the coefficient α in equations (15) and (16) is 0.45. This coefficient represents the fraction of the incoming flow that enters the ideal mixing volume. During testing, the height of the water cushion above the bed was 1.5 m. The regeneration solution was supplied at a rate of 14 m^3/h, and the wash water at a rate of 28 m^3/h.

The agreement between the inlet concentration dependences calculated using equations (15) and (16) and the experimentally measured ones (**Figure 3**) was assessed using the χ^2 criterion. The proposed model reproduces the observed change in the concentration of the solution entering the top layer of the bed with an accuracy of better than 95%. The duration t_2 during which the maximum concentration plateau passes through the bed is derived from the substance balance equation.

$$q_1^r \cdot \int_0^{t_1} \left[C_r - (C_r - C_w) \cdot \exp\left(\frac{v_1 \cdot t}{0.5 \cdot H_{WC} - 0.55 \cdot v_1 \cdot t}\right)\right] dt + q_2^r \cdot t_2 \cdot C_r +$$
$$+ q_3^r \cdot \int_0^{t_3} \left[C_W - (C_r - C_w) \cdot \exp\left(\frac{v_3 \cdot t}{0.6 \cdot H_{WC} - 0.55 \cdot v_3 \cdot t}\right)\right] dt = W_r \cdot C_r \tag{17}$$

Hence, after the conversion we get:

$$t_2 = \frac{1}{q_2^r \cdot C_r} \cdot \left\{W_r \cdot C_r - q_1^r \cdot \left[C_r \cdot t_1 - (C_r - C_W) \cdot \int_0^{t_1} \exp\left(\frac{v_1 \cdot t}{0.5 \cdot H_{WC} - 0.55 \cdot v_1 \cdot t}\right) \cdot dt\right] - \right.$$
$$\left. - q_3^r \cdot \left[C_W \cdot t_3 \cdot (C_r - C_W) \cdot \int_0^{t_3} \exp\left(\frac{v_3 \cdot t}{0.6 \cdot H_{WC} - 0.55 \cdot v_3 \cdot t}\right) \cdot dt\right]\right\} \tag{18}$$

where W_r- regeneration solution capacity, m^3;

q_1^r- liquid discharge being supplied into the exchanger over a period t_1,m^3/h;

q_2^r- liquid discharge being supplied into the exchanger over a period t_2,m^3/h;

q_3^r-liquid discharge being supplied into the exchanger over a period t_3, m^3/h;

t_1- time during which maximum concentration of regeneration solution is reached at the entrance of ion exchanger layer, an hour;

t_3- time during which concentration of washing out water is reached, an hour;

v_1-the speed of liquid movement above the ion exchanger layer under the discharge q_2^r, m/h;

v_3– the speed of liquid movement above the ion exchanger layer under the discharge q_3^r, m/h.

In the expression

$$\int_0^t \exp\,(-\frac{v\cdot t}{m\cdot H_{WC}-v\cdot t(1-\alpha)} \qquad (19)$$

After the substitution of variable by

$$Z=-\frac{a}{b\cdot(b\cdot t-a)}$$

where $a=-\frac{m\cdot H_{WC}}{v}$; $b=(1-a)$ an integral will be got

$$\frac{a}{b}\cdot\exp\,(\frac{1}{b})\cdot\int_{Z_0}^{Z_1}\frac{\exp\,(Z)}{Z^2}\cdot dz \qquad (20)$$

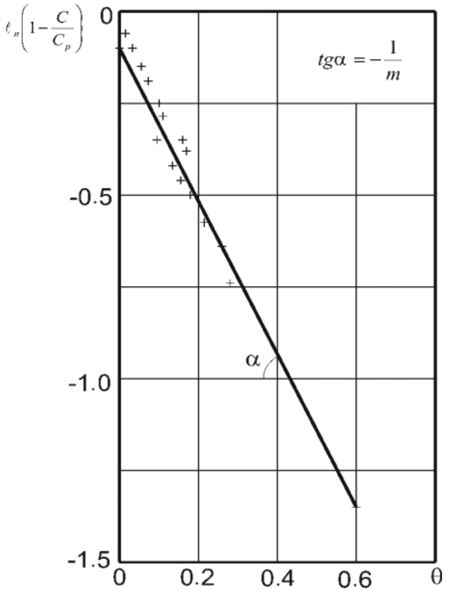

Figure 2. The plot for the definition of the coefficient *m* during the supply of the regeneration solution into the exchanger; $\theta=\frac{q^r}{w}\cdot t$ - dimensionless time.

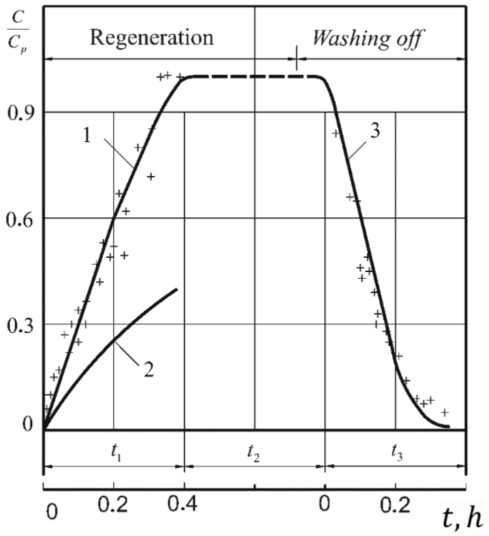

Figure 3. Change in the concentration of the regenerating solution at the entrance to the upper layer of the load during the complete regeneration and washing cycle: 1 - determined by equation (15); 2 - determined by the ideal mixing equation; 3 - determined by equation (16).

Which is equal

$$\frac{a}{b}\cdot\exp\left(\frac{1}{b}\right)\cdot\left(-\frac{\exp(z)}{Z}+ln|Z|+\frac{Z}{1!}+\frac{Z^2}{2\cdot 2!}+\frac{Z^3}{3\cdot 3!}+\cdots+\frac{Z^n}{n\cdot n!}\right)\Bigg|_{Z_0}^{Z_t} \tag{21}$$

$$(Z^2<\infty)$$

where $t=0$, the lower limit assumes the value $Z_0=-\frac{1}{b}$, and the upper level $Z_1=-\frac{a}{b\cdot(b\cdot t-a)}$.

The expressions obtained above are used to determine the input concentration of the solution entering the loading layers during the layer-by-layer calculation of the regeneration of sodium cation exchangers.

4. Conclusion

Both experimental measurements and theoretical analysis confirm that, after fluidization, retained hardness ions are distributed almost uniformly throughout the depth of the cation exchanger. Analytical relationships have been developed for calculating the concentration of the regenerating solution entering the upper layer of the bed. These relationships can be used in layer-by-layer regeneration calculations and as components of a complete mathematical model for the regeneration process of sodium cation exchangers.

Author contributions

Conceptualization, ZM and ID; data curation, ID and TJ; formal analysis, ID, TJ and ND; investigation, TJ and ND; project administration, ZM and VZ; resources, ZM, ND and ND; supervision, ZM and ID; writing—original draft, ID and VZ; writing — review and editing, ZM, VZ and TJ. All authors have read and agreed to publish version of the manuscript.

Conflict of interest

The authors declare no conflict of interest.

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