Lakshtanov L.Z. Acid-basic differentiation of hydrothermal solutions during filtration through the porous media

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In a number of previous experimental and theoretical studies (Alyokhin et al., 1981; Lakshtanov, Kopylov, 1985, etc.), we investigated in detail the major mechanisms and regularities of the salt rejection. However, there are some unsolved problems related to the acid-base differentiation of a filtrating solution (the acid-basic filtration effect).

We present the major statements of the model of the acid-base differentiation of an electrolyte solution at unidimensional isothermal filtration, as well as a comparison with the experimental results on variations of pH of a solution during filtration through diverse porous media.

The following statements were admitted in the model: the constant of water dissociation is infinitely large (local equilibrium), salt concentration (phonic electrolyte) is much more larger than that of proton (hydroxyl-ion). Thus, for example for 0.1 M NaCl, this admittance is acceptable for the interval 2<pH<12. The following admittance is an independence of phenomenological transport coefficients of electrolyte ions on pH. However, a dependence of pH on charge (and potential) of solid surface is taken into account.

The proton concentration in the filtered-up solution was calculated numerically from equation

$$\int_{c_0}^{c''}\int_{0}^{r} \frac{\exp(-\varphi)+K_w \dfrac{D_{OH}}{D_H}\dfrac{\exp(\varphi)}{c^2}}{\dfrac{1}{D}\tanh(\varphi)\left[D_H c\exp(-\varphi)+K_w D_{OH}\dfrac{\exp(\varphi)}{c}\right]+\left[c\exp(\varphi)-K_w\dfrac{\exp(\varphi)}{c}\right]+\dfrac{K_w}{c''}-c''}\,dxdc = Pe,$$ where

$$\varphi = 2\ln\left[\frac{1+\Phi\exp(-\kappa x)}{1-\Phi\exp(-\kappa x)}\right], \qquad \Phi = \frac{\exp\left(\dfrac{F\varphi_0}{2RT}\right)-1}{\exp\left(\dfrac{F\varphi_0}{2RT}\right)+1},$$

$\varphi_0 = \varphi_0(pH)$ - surface potential, which is accepted to be equal to the ζ-potential,

$\kappa = \sqrt{\dfrac{0.2F^2 I}{\varepsilon_0 \varepsilon RT}}$ - the inverse Debye length, I – ionic strength of a solution,

D, D_H, D_{OH} - diffusivities of electrolyte, proton, and hydroxyl-ion.

$Pe = \dfrac{vl}{D_H}$ - the logitudinal Peclet criterion, ν - filtration velocity, l – length of a filter.

The results of the calculations are shown in Figures 1-6. The principally different character of the acid-base differentiation in dependence on a composition of a solid phase, which defines the position of the zero-charge point (pH_{pzc}) (Figs. 1-3), is clearly seen.

Consider the major regularities of pH variation during filtration of the solution through the porous quartz media. There are experimental data on the ζ-potential of quartz in the wide temperature interval. The zero-charge point of quartz ($pH_{zcp} = 2$) is located in the region, which is characteristic for many minerals and rocks (orthoclase, albite, andesite, gabbro, granites, granodiorites).

The most impressive feature is the strong effect in the acid region (Figs. 1 and 4). At given parameters, the salt rejection does not exceed 10 %, while the pH variation is up to 3 units. That correspond to the proton retention more than 99.9 %. It is unusual that at high filtration velocities, the effect of separation is significant even in relatively coarsely porous media. The reason of such differentiation is a significant exceeding of the electromigrational flux of proton over its contrary convection flux because of high mobility.

Three regions of pH can be distinguished on the plots of Figures 1 and 4: the region of constant retention of proton; the buffer region (pH of the filtered-up solution is practically constant and does not depend on pH of the starting solution); the region of constant retention of hydroxyl-ion. In the region of constant retention of proton, reaction of water dissociation does not play any role, and the proton behavior is similar to the behavior of highly mobile counter-ion. Then the proton concentration in the filtered solution becomes close to 10^{-7} M, dissociation of water contributes its action, and transition to the buffer region occurs. In the region of domination of hydroxyl-ion (this region begins at pH>7 for negatively charged surfaces), their retention occurs. However, the effect is not so significant comparing to the proton retention in the acid region. The reason is common (in contrast to proton) direction of the electromigrational and the convection fluxes of hydroxyl-ion.

If pH_{zcp} of the solid phase is about 5 (Fig. 2), as it is in anorthosite and dunite, acidifying of the filtered-up solution occurs. The interval of the proton retention is narrower in comparison to quartz and is confined by 5 and 8. At pH>8, the situation is similar to quartz, i.e. in finely porous media acidifying of the solution occurs.

Fig. 1. Variation of pH in dependence on pH of starting solution (quartz, 0.1M NaCl, 25°C).

Fig. 2. Variation of pH in dependence on pH of starting solution (anorthosite, dunite, 0.1M NaCl, 25°C).

Fig. 3. Variation of pH in dependence on pH of starting solution (boehmite, 0.1M NaCl, 25°C).

Fig. 4. Dependence of pH of the filtered-up solution on pH of starting solution (quartz, 0.1M NaCl, 25°C).

Fig. 5. Dependence of pH of the filtered-up solution on pH of starting solution (collodion membrane, Pe=0.5, 25°C).

Fig.6. Variation of pH during filtration in dependence on pH of starting solution (0.001M NaCl, 25°C). *Symbols denote the experimental data, lines are results of calculation.*

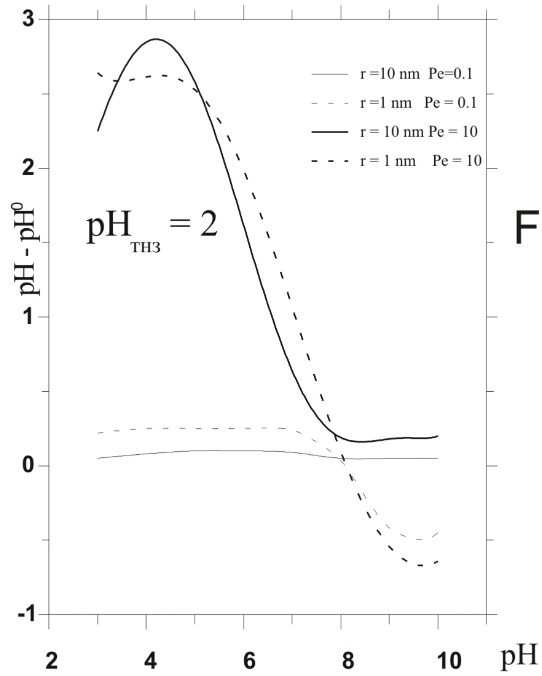

Fig.1

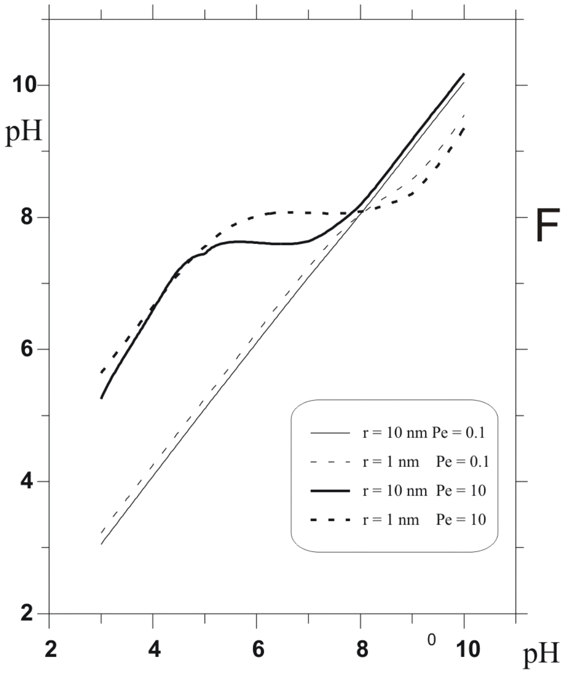

Fig.4

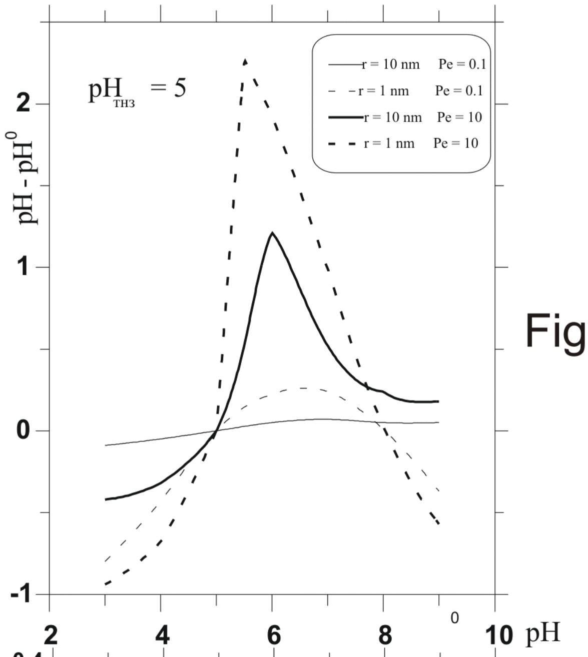

Fig.2

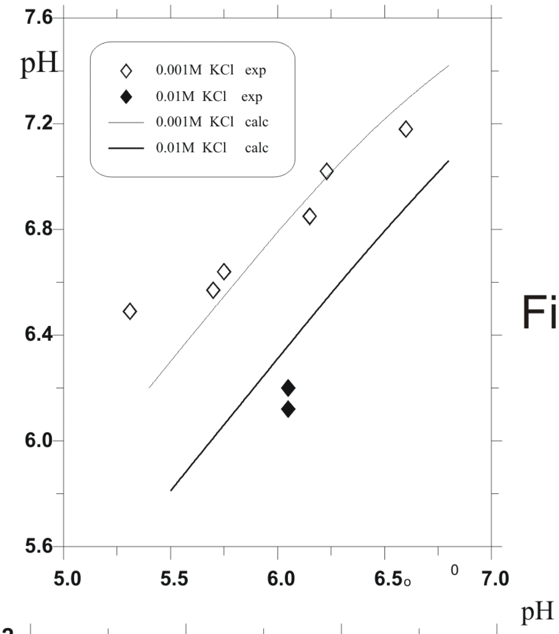

Fig.5

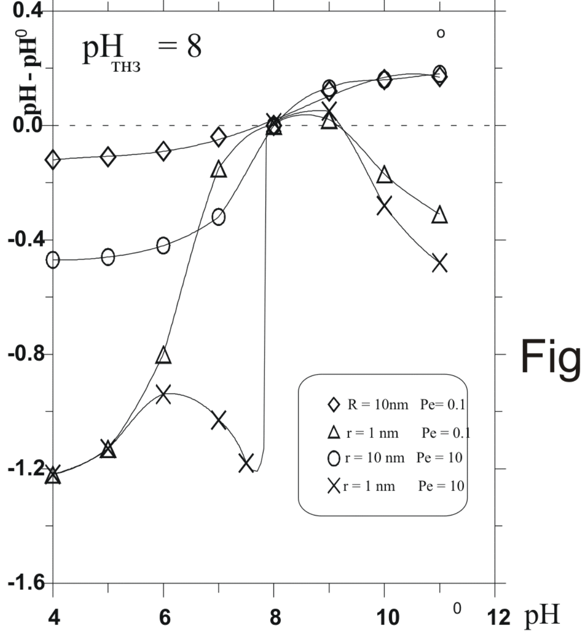

Fig.3

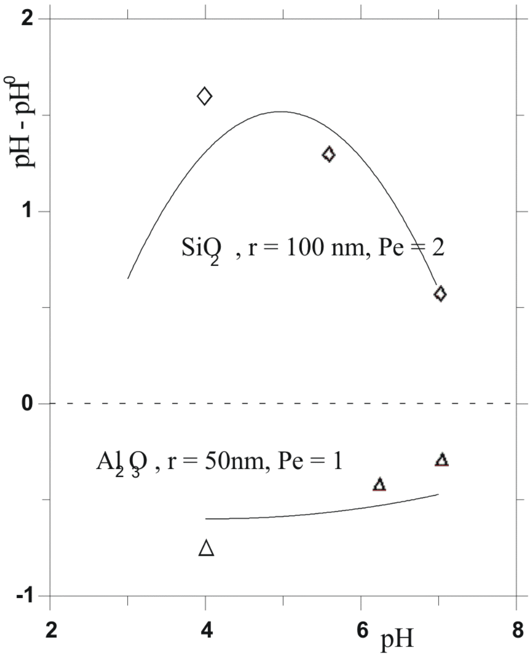

Fig.6

If the solid phase is iron or/and aluminum oxides, pH_{zcp} is located at 8 (Fig. 3). At $pH<pH_{zcp}$, an appreciable acidifying is observed, especially in finely porous media. At $pH> pH_{zcp}$, the situation is similar to quartz again.

Figures 5 and 6 show the results of calculations compared with the experimental data on pH variation of the solution filtered through collodion membrane, as well as through synthetic filters from ceramic silicate (99 % of SiO_2) and sintered Al_2O_3. It is evident that the model of the acid-base filtration effect satisfactorily predicts the pH value during filtration of solution through porous media of strictly different nature, with different structural and surface characteristics.