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Abstract

Full Text

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Soda Formation as a Result of Sorption of the Sulfate Ion

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The removal of sulfates from water with the formation of bicarbonates is usually explained by the action of anaerobic sulfate-reducing bacteria (^1).

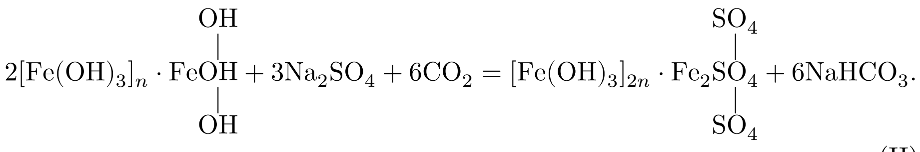
One of us indicated (^2) that the existing hypotheses of soda formation cannot explain how artesian alkaline waters were formed in the North Caucasian steppe over the area from the Sea of Azov to the Caspian Sea. A comparison of the salt composition of surface sodium sulfate waters and deep sodium bicarbonate waters led to the following reaction, based on the simultaneous sorption of divalent calcium and sulfate ions:

$$Ca(HCO_3)_2 + Na_2SO_4 + \;\; = \begin{matrix} \cdots\ Ca \\ \cdots\ SO_4 \end{matrix} + 2NaHCO_3, \tag{I}$$

where Γ denotes a finely dispersed clayey rock.

This reaction was verified in the laboratory, including with the use of the radioactive isotopes Ca^{45} and S^{35} (^3).

Repeating the experiments of Pelouze and Fremy (^4) and of V. A. Kistyakovskii (^5) on the interaction of sodium sulfate solutions with metallic iron led us (^6) to the conclusion that the authors mentioned had not taken into account the adsorption of the SO_4 ion by freshly formed iron oxides, and that in a sodium sulfate solution in contact with metallic iron an irreversible transformation of sulfate into sodium bicarbonate takes place under the influence of atmospheric carbon dioxide. We proposed a reaction based on a colloid-chemical process:



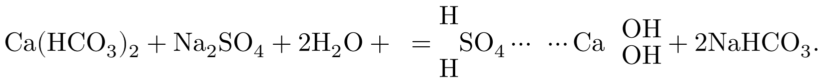
$$2[Fe(OH)_3]_n \cdot Fe\begin{matrix} OH \\ | \\ OH \\ | \\ OH \end{matrix} + 3Na_2SO_4 + 6CO_2 = [Fe(OH)_3]_{2n} \cdot Fe_2\begin{matrix} SO_4 \\ | \\ SO_4 \\ | \\ SO_4 \end{matrix} + 6NaHCO_3. \tag{II}$$

We assumed that the divalent SO_4^{2-} ions displace monovalent hydroxyl ions from the diffuse layer of colloidal ferric hydroxide micelles. The latter interact with carbon dioxide from the air, forming the bicarbonate ion:

$$OH^- + CO_2 = HCO_3^-.$$

Both in reaction (I) and in reaction (II), soda (sodium bicarbonate) was formed "by residues."

Subsequently we introduced an addition into reaction (I), on the basis that the adsorption of calcium and sulfate ions occurs non-equivalently and is accompanied by a change in the pH of the solution (⁀7), which indicates the participation of water ions:



$$Ca(HCO_3)_2 + Na_2SO_4 + 2H_2O + \;= \begin{matrix}H\\ \\ H\end{matrix}SO_4\cdots\;\cdots Ca\begin{matrix}OH\\ OH\end{matrix} + 2NaHCO_3. \qquad (III)$$

If calcium absorption predominates, then the pH of the solution decreases, which indicates the entrainment of hydroxyl ions as counterions. With predominant adsorption of the sulfate ion, the pH increases, which indicates participation in the adsorption of counterions H^+.

Reaction (III), first, drew our attention to the role of the counterion in ionic adsorption and, second, led to experiments on soda formation without the participation of calcium salts. In these experiments the initial materials were sodium sulfate solutions saturated with carbon dioxide gas, and the adsorbents used were either freshly precipitated ferric hydroxide or the usual chromatographic reagent, aluminum oxide, washed free of water-soluble substances. The results of the experiments are shown in Table 1.

Table 1

Adsorbent	Experimental conditions	Na_2SO_4	$NaHCO_3$
$Fe(OH)_3$	Initial solution, 0.01 *N* Na_2SO_4	100	0
$Fe(OH)_3$	Shaking with adsorbent	38.4	61.6
$Fe(OH)_3$	Repeated shaking with a new portion of adsorbent	5.1	94.9

Adsorbent	Experimental conditions	Na_2SO_4	$NaHCO_3$
$Fe(OH)_3$	Fourfold shaking with adsorbent	3.0	97.0
Al_2O_3	Initial solution, 0.02 *N* Na_2SO_4	100	0
Al_2O_3	CO_2 pressure, atm: 0.04	87.1	12.9
Al_2O_3	CO_2 pressure, atm: 1	15.5	84.5
Al_2O_3	CO_2 pressure, atm: 3	11.7	88.3
Al_2O_3	CO_2 pressure, atm: 5	10.6	89.4
Al_2O_3	CO_2 pressure, atm: 10	9.1	90.9
Al_2O_3	CO_2 pressure, atm: 20	7.2	92.8

Carbon dioxide promotes soda formation by increasing the concentration of hydrogen ions required as counterions in the adsorption of $SO_4{}^{2-}$ according to the reaction:

$$Na_2SO_4 + 2CO_2 + 2H_2O + \;=\; \cdots SO_4{}^{\cdots H}_{\cdots H} + 2NaHCO_3. \tag{IV}$$

The shift in the equilibrium of water ions: $H_2O \rightleftharpoons H^+ + OH^-$ is compensated by a shift in the equilibria: $CO_2 + H_2O \rightleftharpoons H_2CO_3 \rightleftharpoons H^+ + HCO_3^-$, which leads to an increase in the concentration of the bicarbonate ion.

At first, solutions of sulfate with the adsorbent were shaken for one hour; later it was established that a contact time of 6-7 min was sufficient to obtain the same results.

The rate of the adsorption process, measured in minutes, makes it possible to suppose that in nature, in the presence of finely dispersed clayey substances rich in oxides of aluminum and iron, saline-alkaline waters may form according to the above reaction (IV), such as, for example, the sulfate-free medicinal waters of Essentuki and the waters of Pyatigorsk with a reduced sulfate content.

Atmospheric precipitation carries along dust and aerosols; thus its composition, along with carbon dioxide, always contains finely dispersed substances—potential adsorbents. This may facilitate the conversion of sodium sulfate into bicarbonate and explain to us the presence of soda in atmospheric precipitation.

According to the determination of N. E. Fedorova ([8]), about 18% of atmospheric precipitation belonged to class V alkaline waters (sodium bicarbonate waters).

It has been established that, for the formation of sodium bicarbonate (soda) in aqueous solution, the presence of sodium sulfate, dissolved carbonic acid, and an adsorbent absorbing the sulfate ion is sufficient. As the content of CO_2 increases, the degree of conversion of sodium sulfate into bicarbonate increases. The proposed reaction of soda formation can proceed also under oxidizing conditions, does not require the participation of microorganisms, and can explain the formation of sulfate-free mineral saline-alkaline waters, as well as the content of sodium bicarbonate in a substantial portion of atmospheric precipitation.

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