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In elucidating the genesis of uranium-ore deposits and in planning prospecting work by the hydrogeochemical method, it is necessary to know the conditions for the precipitation of uranium compounds from various types of natural waters. The most important form of precipitation is the hydroxides, since the most widespread and industrially valuable uranium minerals belonging to the oxide group—uraninite, pitchblende, and uranium blacks—under low-temperature conditions separate from aqueous solutions and inevitably pass through the hydroxide stage. The present work gives the results of investigations completed in 1955 and devoted to the conditions of precipitation of hexavalent uranium hydroxide.

The hydrolysis of the uranyl ion and its precipitation from solutions by alkalis have been considered in a number of works (1–15). Various schemes of hydrolysis have been proposed with the participation of the ions UO_2OH^+ (3,14), $U_2O_5^{2+}$ (2), and other polymers with $n = 3$ (5,9), $n = 4$ (4), up to $n = 6$ (10). The number of hydroxyl groups entering into the polymeric ion varies from 0 to 5, and the charge of the ion from +2 to −3. There are also considerable discrepancies in the estimate of the solubility product $L_{UO_2(OH)_2}$: from $7.4 \cdot 10^{-12}$, corresponding to a solubility $S_{UO_2(OH)_2} = 0.16$ g/l (16), to $2 \cdot 10^{-23}$ (17).

Let us establish the relation between the pH value at which hydroxide precipitation begins, its solubility product, and the initial concentration of metal ions in solution. Taking into account the formation of soluble basic salts at the first stage of hydrolysis, we have:

$$Me^{n+} + m\,OH^- leftarrows Me(OH)_m^{(n-m)+}; \quad Me(OH)_m^{(n-m)+} + (n-m)\,OH^- leftarrows Me(OH)_n$$

Then the solubility product corresponding to the real scheme of dissociation is equal to:

$$L_1 = [Me(OH)_m^{(n-m)+}][OH]^{n-m} \gamma_{Me(OH)_m^{(n-m)+}} \gamma_{OH^-}^{n-m}. \qquad (1)$$

We use the expression for the ionic product of water:

$$K'_B = [H^+][OH^-]\frac{\gamma_{H^+}\gamma_{OH^-}}{a_{H_2O}} = K_B\frac{\gamma_{H^+}\gamma_{OH^-}}{a_{H_2O}}. \tag{2}$$

Introducing ionic exponents and substituting into (1) the value of $[OH^-]\gamma_{OH^-}$ from (2), we obtain:

$$pL_1 = p\,Me(OH)_m^{(n-m)+} - (n-m)\,pH + (n-m)\,pK_B -$$

$$-\lg\gamma_{Me(OH)_m^{(n-m)+}} - (n-m)\lg(\gamma_{H^+}\gamma_{OH^-}). \tag{3}$$

The solubility of the hydroxide $S = [\mathrm{Me(OH)}_m^{(n-m)+}] = \dfrac{1}{n-m}[\mathrm{OH}^-]$ is readily derived from (3):

$$\mathrm{p}S = \frac{1}{n-m+1}\left[\mathrm{p}L_1 + (n-m)\lg(n-m) + \lg\gamma_{\mathrm{Me(OH)}_m^{(n-m)+}} + (n-m)\lg\gamma_{\mathrm{OH}^-}\right]. \tag{4}$$

The "total" solubility product $L_2 = [\mathrm{Me}^{n+}][\mathrm{OH}^-]^n\gamma_{\mathrm{Me}^{n+}}\gamma^n_{\mathrm{OH}^-}$ has, in the present case, only a formal meaning and can be defined through S:

$$L_2 = n^n S^{n+1}\gamma_{\mathrm{Me}^{n+}}\gamma^n_{\mathrm{OH}^-}. \tag{5}$$

Taking logarithms and substituting pS from (4), and then p$L(1)$ from (3), after collecting like terms we obtain:

$$\begin{aligned}\mathrm{p}L(2) = &\frac{1}{n-m+1}\Big[(n+1)\,\mathrm{pMe(OH)}_m^{(n-m)+} - (n-m)(n+1)\mathrm{pH} + \\ &+ (n-m)(n+1)\mathrm{p}K_\mathrm{B} - (n-m)(n+1)\lg(n-m) - n(n-m+1)\lg n \\ &- (n-m+1)\lg\gamma_{\mathrm{Me}^{n+}} - m\lg\gamma_{\mathrm{OH}^-} - (n-m)(n+1)\lg(\gamma_{\mathrm{H}^+}\gamma_{\mathrm{OH}^-})\Big].\end{aligned} \tag{6}$$

According to equation (3), in order to find L_1 and L_2 it is necessary: (a) to establish the value of m, which is determined by the actual hydrolysis scheme; (b) to determine experimentally the equilibrium pH at which precipitation begins; (c) to use the values of $\gamma_{\mathrm{Me}^{n+}}$, $\gamma_{\mathrm{Me(OH)}_m^{n-m+}}$, and $f = (\gamma_{\mathrm{H}^+}\gamma_{\mathrm{OH}^-})$. The initial concentration of metal ions and the ionic product of water are specified by the experimental conditions.

Fig. 1. Curves of potentiometric titration of a solution of $\mathrm{UO_2(ClO_4)_2}$ hydrate with sodium hydroxide, obtained by the usual method. Uranium concentrations $C_{\mathrm{UO2^{2+}}}$: A $-0.1\,M$, $-0.01\,M$, $-0.001\,M$, $-0.0001\,M$, $-0.00003\,M$,

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Procedure. The principal method of work was potentiometric titration of perchlorate solutions of uranyl salts with NaOH solutions, with measurement of pH by a glass electrode. Uranyl perchlorate solutions were prepared from $UO_3 \cdot 1.96H_2O$, purified by the peroxide method, by dissolving it in $HClO_4$. Alkali solutions containing no carbonates were obtained by dissolving metallic sodium in degassed bidistillate (pH 6.5-6.8). The titrations were carried out in a stream of nitrogen purified from CO_2 and O_2, in a closed cuvette mounted on a stirrer imitating the motion of the hand during titration.

Dependence of the pH at the onset of hydroxide precipitation on the initial uranium concentration. Series I of titrations of $UO_2(ClO_4)_2$ solutions from 0.1 to 0.00001 *M* was carried out by the usual method. The curves obtained (Fig. 1) are close to the data of Satton[5] and of many other authors; however, we did not observe the constancy of the ratio $[OH^-]/[{UO_2}^{2+}]$, equal in Satton' s work to 1.66 for all concentrations, which indicates the incorrectness of the hydrolysis scheme proposed by him. It was found that, for uranyl salts, during titration with alkali beginning with the ratio

for $[OH^-]/[UO_2^{2+}] > 1$, equilibrium is established slowly: over hours and days, so that ordinary titration with readings after 1 min cannot be used. Therefore, the following method was used subsequently. A definite volume of $UO_2(ClO_4)_2$ solution was poured into a series of test tubes, and then a certain amount of alkali was added, so that the ratio $[OH^-]/[UO_2^{2+}]$ from the first to the last test tube varied from 0 to 3.0; after this the test tubes were closed, shaken at 20° for the required time, and the pH was measured in them periodically, while visual observations of precipitate formation were also made. In Fig. 2 the data obtained for a 0.1*M* initial solution are presented. For other concentrations the same character of changes is observed. It is evident that time, as it were, "develops" the titration curve, revealing on it distinct horizontal sections corresponding to the precipitation of uranyl hydroxide and its conversion into sodium diuranate. The usual titration curves (see Fig. 1) have sections corresponding to metastable phases. From Fig. 3 it is seen how the precipitation conditions

Fig. 2

Figure 2: Fig. 2

change as a function of the initial uranium concentration. At the beginning of precipitation only singly charged uranium ions are present in the solution, i.e. $m = 1$.

Fig. 2. Change with time in the potentiometric titration curve of $0.1\,M$ $UO_2(ClO_4)_2$ solution with sodium hydroxide. 1—$t = 0$; 2—curve A of Fig. 1, $t = 2$ min; 3—$t = 1$ day; 4—$t = 3$ days; 5—$t = 6$ days; 6—$t = 8$ days; 7—$t = 13$ days; 8—$t = 60$ days; 9—$t = 107$ days; arrows indicate the beginning of visually observed precipitation.

Determination of ion activity coefficients. Since the only literature data we encountered, those of Robinson and Lim (^{18}), on activity coefficients refer to more concentrated solutions of uranyl salts, these coefficients ($\gamma_{\mathrm{UO2^{2+}}}$ and $\gamma_{\mathrm{UO2OH^+}}$) were determined by us experimentally. If the precipitation of uranyl hydroxide proceeds in the absence of complexing agents in two solutions with the same uranium concentration and with different ionic strengths μ_1 and μ_i, then the pH at the beginning of precipitation will differ only owing to different activity coefficients. From equation (1) we have:

$$\lg\gamma_{\mathrm{UO2OH}^+_{(\mu_i)}} = \lg\gamma_{\mathrm{UO2OH}^+_{(\mu_1)}} + \Delta p[\mathrm{UO_2OH^+}]_{(\mu_i-\mu_1)} - \Delta \mathrm{pH}_{(\mu_i-\mu_1)} - \Delta\lg(\gamma_{\mathrm{H^+}}\gamma_{\mathrm{OH^-}})_{\mu_i-\mu_1}. \tag{7}$$

An analogous expression can also be obtained for $\gamma_{\mathrm{UO2^{2+}}}$. If μ_1 is sufficiently small, the first term of equation (7) can be calculated by the Debye–Hückel formula; the second term is determined by the experimental conditions (dilution), ΔpH is determined experimentally, and the 4th term is calculated from tabulated data. It can be shown that the curves of potentiometric titra-

solutions of uranium with different ionic strength are equidistant, which makes it possible to reduce the experimental determination of $\gamma_{\mathrm{UO_2OH^+}}$ and $\gamma_{\mathrm{UO_2^{2+}}}$ to potentiometric titration, up to the beginning of hydroxide precipitation, of a neutralized uranyl perchlorate solution with a solution of $NaClO_4$, which changes the ionic strength. The data obtained by this method are presented in Fig. 4.

Determination of the solubility product of uranyl hydroxide. By substituting the data obtained into equations (1) and

[Fig. 3 and Fig. 4 graphs]

Fig. 3. Dependence of the precipitation conditions of $UO_2(OH)_2$ on the uranium concentration

Fig. 4. Dependence of the activity coefficients of UO_2OH^+ and UO_2^{2+} on the ionic strength of the solution

(3), the following were calculated for uranyl hydroxide: $L_1 = 1.3 \cdot 10^{-11}$, $L_2 = 6 \cdot 10^{-18}$ and $S = 3.3 \cdot 10^{-4}$ g/l ($\mu < 0.001$) at $t = 20°$. Direct determinations of $S_{\mathrm{UO_2(OH)_2}}$ give overestimated results (16) because of the exceptional tendency of the hydroxide to form colloidal solutions. To determine the temperature dependence of $L_{\mathrm{UO_2(OH)_2}}$, the shift in the pH at the beginning of hydroxide precipitation due to temperature change was determined, and L_{t_i} was calculated from the equation derived from (1):

$$\mathrm{p}L_{t_i} = \mathrm{p}L_{t_1} + \Delta\mathrm{pH} - \Delta pK_B + \Delta \lg \gamma_{\mathrm{UO_2OH^+}} + \Delta \lg(\gamma_{\mathrm{H^+}}\gamma_{\mathrm{OH^-}}). \qquad (8)$$

The temperature dependence of L (2) was determined analogously. These dependences are expressed by the equations:

$$\mathrm{p}L_1 = 12.16 - 0.0141\, t, \qquad (9)$$

$$\mathrm{p}L_2 = 17.65 - 0.2156\, t. \qquad (10)$$

The data obtained in this work make it possible to calculate the conditions for precipitation of hexavalent uranium from certain types of natural waters.

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