

FORMS OF CHEMICAL ELEMENTS MIGRATION IN UNDERGROUND WATERS OF THE RIVER KATUN BASIN IN ITS AVERAGE CURRENT

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The characteristic of chemical elements condition in underground waters of the river Katun basin (Mountainous Altai) is shown; the main forms of migration of chemical macro- and microelements are allocated: Na^+ , Mg^{2+} , Ca^{2+} , Mn^{2+} , Fe^{2+} , Pb^{2+} , Cu^{2+} , Zn^{2+} . Statistical calculations, which purpose was confirmation of results of complex-formation process modeling, are carried out.

Introduction

Foreign and domestic researchers in different years were engaged in researches of forms of element migration in natural waters, such as: R.M. Garrels, C.L. Krayst, S.L. Schvartsev, S.R. Kraynov, V.M. Shvets, G.B. Naumov, B.N. Ryzhenko, P.N. Linnik, B.I. Nabivanets and others. Achievements of these researchers allow us to solve problems at modeling of formation processes of underground waters structure.

The purpose of the given work is allocation of the main forms of migration of a number of components in underground waters of the river Katun basin (Mountainous Altai) in the average current.

The dissolved condition of chemical elements in natural waters is extremely various. Some elements are inclined to form only rather simple compounds, others – complex associates, including with organic ligands. The basic forms of element migration depend not only on properties of the element (cations or anions), but also on external factors of migration (pH, Eh of the environment, active concentration of ions-complex-formators complexing compounds, etc.).

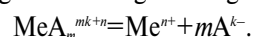
S.R. Kraynov and V.M. Shvets think that «migration of elements in underground waters in the form of complex ionic and molecular associates has very important consequences. Different compounds of the same elements have various thermodynamic parameters (free energy, factors of ionic and molecular diffusion). Therefore, the processes of mass transfer, dissolution-crystallization, ionic exchange and other, making the basis of the process of *chemical compound formation in underground waters*, it is impossible to interpret and predict correctly without the knowledge of forms of element transfer. These forms define an opportunity and geological importance of processes, as well as their kinetics. At formation of steady complex compounds there is a displacement of equilibrium in geochemical processes (in dissolution, desalination, precipitation and co-precipitation, sorption, ionic exchange, oxidation-restoration) towards the water phase» [1. P. 33].

Physical and chemical calculations play the role of a reference point at hydrogeochemical researches, their results can be used for a rough estimate and probabilistic forecasting of real geochemical processes. However, these calculations are frequently based on the *analytical* data on water composition summarizing free and connected forms of elements, which is not quite lawful at an attempt to recreate processes taking place in the real system.

The material for the researches were the data obtained as a result of approbation of water objects in the region, which were carried out by employees of Tomsk Branch of the Institute of Oil-and-Gas Geology and Geophysics of the Siberian Branch of the Russian Academy of Sciences and employees of Tomsk Polytechnic University with participation of the authors (2005).

The technique of physical and chemical researches of complex-formation is in [1–3]. Base positions of the theory consist in the following.

The so-called complex compounds are formed at interaction of ion-complex-forming agent (Me) and ligands (A) of organic or inorganic origin:



Характеристикой комплексного соединения служит константа устойчивости K_y –

The constant of stability K_y serves as a characteristic of the complex compound –

$$K_{y(T,P)} = \frac{[\text{MeA}_m^{mk+n}]}{[\text{Me}^{n+}][\text{A}^{k-}]^m},$$

where $[\text{Me}^{n+}]$ is molar concentration of an element with the charge $n+$ in the non-complexed form; $[\text{A}^{k-}]$ is molar Addend concentration A with the charge $k-$; $[\text{MeA}_m^{mk+n}]$ is molar concentration of the complex compound, with the total charge $mk+n$.

Dissociation of the complex compound, as a rule, occurs in steps under the typical scheme: $\text{Me(A)}_m \rightleftharpoons \text{MeA}^{n+} + \text{A}^{k-} \rightleftharpoons \text{Me}^{2+} + 2\text{A}^{k-}$, therefore, both full constants of stability and step constants are used. In equilibrium standard conditions (at 25 °C and 0,1 Pa) the constant of stability of the complex compound K_y is connected with free Gibbs energy by the expression $\Delta G^0 = -1,364 \cdot \lg K_y$, where $\Delta G^0 = \sum \Delta G_{\text{prod}}^0 - \sum \Delta G_{\text{init}}^0$.

Gibbs energy, calculated by such researchers as I.L. Shok, H.K. Helgeson, P.N. Linnik, B.I. Nabivanets, I.I. Volkov, G.A. Solomin, I.K. Karpov, et al. for various compounds, is included into the database. On the basis of Gibbs energy and the data on physical conditions of reaction, the constants of stability of the element complex are calculated. But quantitative parities between conditions of any present in the water element-complex-forming-agent depend not only on constants of stability of its compounds, but also on concentration of addends. A special value for complex-formation is rendered by fulvic acids, since the ability to complex-formation of humic and other organic acids is much weaker.

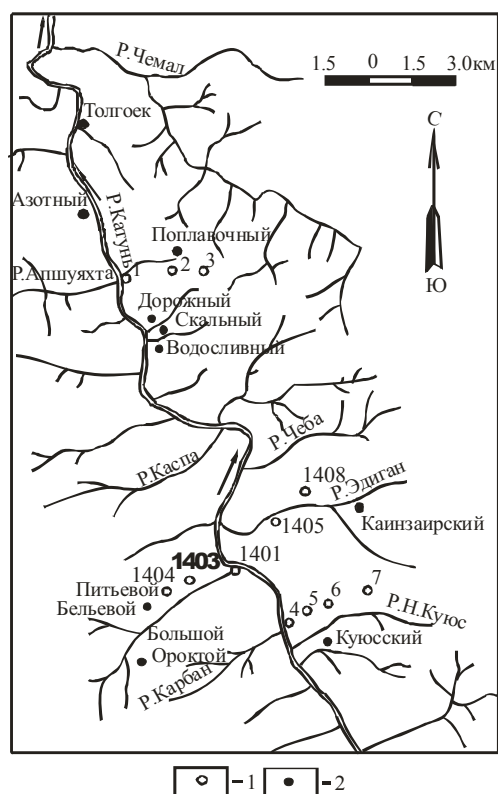


Fig. 1. The scheme of observation points distribution: 1) observant (regime) hydro-geological wells; 2) springs and their numbers.

Explanation to Fig. 1: р. Чема – river Chema; Толгоок – Tolgoek; Азотный – Azotniy; Поплавочный – Polavochniy; р. Апшухта – river Apshuyakhta; р. Катунь – river Katun; Дорожный – Dorozhniy; Скальный – Skalniy; Водосливный – Vodoslivniy; р. Каспа – river Kaspa; р. Чеба – river Cheba; р. Эдиган – river Edigan; Каинзаирский – Kainzairskiy; Питьевой – Pityevoy; Бельевой – Belyevoy; Большой Ороктой – Bolshoy Oroktoy; р. Н. Куюс – river N. Kuyus; Куюсский – Kuyusskiy

Calculation of concentrations of various forms of element migration in underground waters was made by means of the program module for PC HydrGeo (author – M.B. Bukaty, Tomsk Branch of the Institute of Oil and Gas Geology and Geophysics of the Siberian Branch of the Russian Academy of Sciences) [4].

Description of the research object

The basin of the average current of the river Katun (Mountainous Altai) occupies the area from the mouth of the river Koksy up to the mouth of the river Smulta. Hydro-geological conditions are defined by significant breaks of the relief, active water-exchange and presence of two water-bearing complexes of rocks – alluvial formations dated to valleys of the rivers, and fractured bed-rocks, mainly Paleozoic, rocks that are broken by disjunctive tectonic destructions which actively influence the course of underground waters. Waters of these infringement zones are poorly revealed and studied. Waters of fracture of bed-rocks and alluvial sediments are of a great importance.

Table 1. The data used in calculations on composition of underground waters of the basin of the average current of the river Katun (based on the results of analyses of Tomsk Branch of the Institute of Oil-and-Gas Geology and Geophysics and TPU, 2005, except for CO_3^{2-} – 1999; Hg^{2+} – 2003)

Parameter	Measurement unit	Points of sampling – springs					
		Tolgoek	Dorozhniy	Skalniy	Kainzairskiy	Pityevoy	Kuyusskiy
		1	2	3	4	5	6
pH		7,9	7,8	7,7	7,7	7,6	8
Ionic force	mol/l	0,01	0,01	0,01	0,01	0,01	0,01
Mineralization		360,0	350,0	390,0	290,0	370,0	290,0
Na^+	mg/l	3,50	4,00	7,00	0,80	8,00	5,00
Ca^{2+}		44,0	56,0	60,0	60,0	72,0	52,0
Mg^{2+}		9,80	20,70	25,60	12,20	9,80	10,50
K^+		1,50	1,10	1,20	1,50	0,80	0,90
Fe^{2+}		0,8	0,01	0,05	0,08	0,07	0,03
Fe^{3+}		2	0,1	0,02	0,02	0,02	0,02
Mn^{2+}		68,70	18,60	20,40	12,00	10,40	12,70
NH_4^+		0,10	0,08	0,10	0,10	0,07	0,06
Al^{3+}		0,25	0,25	0,25	0,25	0,25	0,25
Cl^-		1,56	1,42	1,42	3,55	2,84	1,28
HCO_3^-		268,4	292,8	366,0	268,4	329,4	244,0
F^-		0,15	0,12	0,56	0,10	0,22	0,18
NO_2^-		0,39	0,01	0,01	0,01	0,01	0,01
NO_3^-		4,03	3,33	5,90	17,24	16,91	3,25
SiO_2^-		3,70	3,70	3,35	4,15	4,15	4,80
CO_3^{2-}		0,4	1,2	0,4	0,6	0,4	0,4
Pb^{2+}	mkg/l	2,73	1,25	1,09	0,46	–	0,17
Cu^{2+}		10,6	1,98	3,28	0,75	–	0,03
Cd^{2+}		0,11	0,1	0,09	0,03	–	0,07
Li^+		9,00	7,00	9,00	8,00	–	9,00
Zn^{2+}		29,2	49,3	26,7	0,7	–	1,93
Hg^{2+}		0,002	0,002	0,001	0,003	–	0,001

In this connection, the process of their chemical compound formation proceeds in various conditions. The module of the underground flow amounts to 3,2...4,0 l/s·km² in the region. The afflux is within the limits of 0,1...0,4 km³/year [5]. The interval of approbation in wells mainly amounts to 100 m from daily surface (the maximal depth of wells is 160 m).

Underground waters of the considered territory are fresh with mineralization of 70...700 mg/l, as a rule, neutral or weakly alkaline (pH 7,0...8,8); in structure they are hydrocarbonate- sulfate. More detailed characteristic of geologic-hydrogeological conditions and geochemistry of underground waters of the basin of the average current of the river Katun is given in publications [6–9].

The results of researches of migration forms of the main macro- and microcomponents, especially carefully normalized without taking into account element-organic forms, are stated in the given work. The scheme of distribution of approbation points is shown on Fig. 1; initial data for calculations – in table 1, calculation results are presented in table 2.

Results of physical-chemical calculations

Table 2 shows calculations of complex-formation in waters of the tested regime springs which allow drawing the following conclusions.

Table 2. Calculation results of the basic forms of microcomponent migration in underground waters, %

Migration forms	Sampling points					
	1	2	3	4	5	6
NH₄⁺	0,09 95,05	0,07 90,19	0,09 93,76	0,09 95,10	0,06 89,89	0,05 91,38
NH₄HCO₃	0,00	0,00	0,26	0,19	0,24	0,19
NH₄CO₃⁻	0,00	0,00	0,00	0,00	0,00	0,00
NH₄Cl	0,00	0,00	0,00	0,00	0,00	0,00
NH₄OH	0,00	-	0,39	0,41	0,38	0,39
(NH₄)₂CO₃	0,01	0,00	5,19	3,89	9,10	7,64
NH₃⁰	0,00	-	0,39	0,41	0,38	0,39
NO₂⁻	0,39 99,86	0,009 99,86	0,009 99,87	0,009 99,86	0,009 99,87	0,009 99,86
HNO₂	0,00	0,13	-	-	-	-
Mg²⁺	9,11 92,97	20,07 96,96	24,75 96,68	11,9 97,56	9,49 96,92	10,23 97,41
MgHCO₃⁺	1,33	0,56	3,07	2,27	2,87	2,42
MgCO₃	0,05	0,02	0,10	0,08	0,09	0,08
MgCl⁺	0,00	0,00	0,00	0,00	0,00	0,00
Mg(HCO₃)₂	0,06	0,03	0,09	0,05	0,09	0,06
MgCl₂	0,00	0,00	0,00	0,00	0,00	0,00
MgF⁺	0,00	1,15	0,04	0,03	0,02	0,01
MgOH⁺	0,00	-	0,00	0,00	0,00	0,00
Na⁺	3,45 98,58	3,98 99,43	6,96 99,37	0,79 99,54	7,95 99,40	4,98 99,52
NaHCO₃	0,37	0,07	0,61	0,44	0,59	0,47
NaCl	0,00	0,01	0,00	0,00	0,00	0,00
NaH₃SiO₄	0,00	0,00	0,00	0,00	0,00	0,00
NaHSiO₃	0,00	0,01	0,00	0,00	0,00	0,00
Al³⁺	0,00	0,00	0,00	0,00	0,00	0,00
(AlO₂)⁻	0,24 96,64	0,25 100,00	0,23 92,89	0,23 92,82	0,23 92,88	0,23 92,82
Al(OH)₃	0,00	0,00	0,00	0,00	0,00	0,00
(AlO(OH))₂⁻	3,6	0,00	7,11	7,18	7,12	7,17
SiO₂	1,81 48,91	1,81 48,91	1,64 48,91	2,03 48,91	2,03 48,91	2,35 48,91
(H₂SiO₄)⁻	0,11	0,11	0,11	0,11	0,11	0,11
H₂SiO₄	50,84	50,84	50,84	50,84	50,84	50,84
(HSiO₃)⁻	0,13	0,12	0,13	0,13	0,13	0,13
K⁺	1,37 91,71	1,09 99,41	1,19 99,36	1,49 99,54	0,79 99,39	0,89 99,51
KHCO₃	0,03	0,00	0,63	0,46	0,60	0,48
KCO₃	0,00	0,00	0,00	0,00	0,01	0,00
KCl	0,00	0,00	0,00	0,00	0,00	0,00
K₂CO₃	0,00	0,00	0,00	0,00	0,00	0,00
Ca²⁺	42,49 96,56	54,11 96,62	57,73 96,22	58,34 97,24	69,41 96,39	50,46 97,04
CaHCO₃⁺	2,98	0,85	3,28	2,45	3,20	2,61
CaCO₃	0,22	0,06	0,24	0,18	0,23	0,19
Ca(HCO₃)₂	0,15	0,08	0,18	0,09	0,17	0,11
Ca(CO₃)₂²⁻	0,00	0,00	0,00	0,00	0,00	0,00
CaNO₃⁺	0,08	-	0,07	0,02	-	0,03
CaCl⁺	0,01	0,04	0,00	0,00	0,00	0,00

CaCl₂	0,00	0,00	0,00	0,00	0,00	0,00
CaF⁺	0,01	0,36	0,01	0,01	0,00	0,00
Mn²⁺	48,11 70,03	14,45 77,67	15,53 76,33	9,74 81,19	8,03 77,17	10,18 80,19
(MnHCO₃)⁺	0,01	0,00	11,89	9,50	11,49	9,99
MnCO₃	0,01	0,00	10,74	8,69	10,39	9,15
Mn(HCO₃)₂	0,00	0,00	0,99	0,57	0,92	0,64
(MnCl)⁺	0,00	0,00	0,00	0,00	0,00	0,00
MnCl₂	0,00	0,00	0,00	0,00	0,00	0,00
MnOH⁺	0,00	-	0,03	0,03	0,03	0,03
Fe²⁺	0,72 90,56	0,009 94,66	0,05 94,26	0,076 95,63	0,066 94,51	0,029 95,37
(FeHCO₃)⁺	0,04	0,00	2,89	2,21	2,77	2,34
FeCO₃	0,03	0,00	2,09	1,62	2,09	1,72
Fe(HCO₃)₂	0,01	0,00	0,49	0,27	0,44	0,30
FeCl⁺	0,00	0,00	0,00	0,00	0,00	0,00
FeOH⁺	0,00	-	0,25	0,27	0,25	0,27
Fe³⁺	0,00	0,00	0,00	0,00	0,00	0,00
(FeOH)²⁺	6,23	4,79	3,26	2,80	2,82	3,06
(Fe(OH)₂)⁺	1,41 70,41	0,068 68,21	0,014 71,23	0,018 88,86	0,016 78,91	0,002 80,30
Fe(OH)₃	23,32	26,90	25,26	8,02	17,96	16,48
(Fe(OH)₄)⁻	0,10	0,19	0,35	0,43	0,43	0,29

Note: mg/l is the content of the component form in water, number in the denominator – %, falling on this content in water

Without taking into account compounds with organic radicals, mainly in the ionic form, ions Na, K, Ca, Mg, Cl, HCO₃, F, NO₂, NO₃, HCO₃, Fe and Mn migrate. They share makes, as a rule, more than 90 %, which is quite natural, considering near-neutral pH values of waters, oxidizing geochemical condition, low mineralization of solutions and low values of their ionic force (0,01...0,02).

Among the forms of microelement migration (table 2) complexes-associates with participation of dominating anions HCO₃⁻, CO₃²⁻ prevail; occasionally there are compounds with Cl⁻ and F⁻. Hydrooxidic migration forms are more characteristic for elements-hydrolyzates: H₄SiO₄ is the basic form of migration Si⁴⁺ (more than 50 %).

At the same time, practically unique migratory form for Al is products of dissociation Al (AlO₂⁻ и AlO(OH)₂⁻), since concentrations of Al are so small, that they are insufficient for formation of weakly soluble hydroxides Al³⁺, AlOH²⁺ or AlO(OH)₃. Si, containing in waters of Katunskiy range in quantities close to maximum permissible, is in the form of two basic forms of migration – dominating – H₂SiO₄ and subordinated – SiO₂, in quantity of 52 and 48 % respectively.

Based on calculation results, the basic migration forms for Mn were Mn²⁺ (more than 70 %), as well as MnHCO₃⁺, MnCO₃⁰ and Mn(HCO₃)₂.

A little bit different forms of migration are characteristic for Fe. In the given geochemical conditions, the basic form of Fe migration is Fe(OH)₂⁺ (more than 68 %), and secondary are Fe(OH)₃⁰, Fe(OH)₂⁺, Fe(OH)₄⁻. From compounds of Fe bivalent, the ion Fe²⁺ prevails, its secondary forms are FeHCO₃⁺, FeCO₃⁰, Fe(HCO₃)₂.

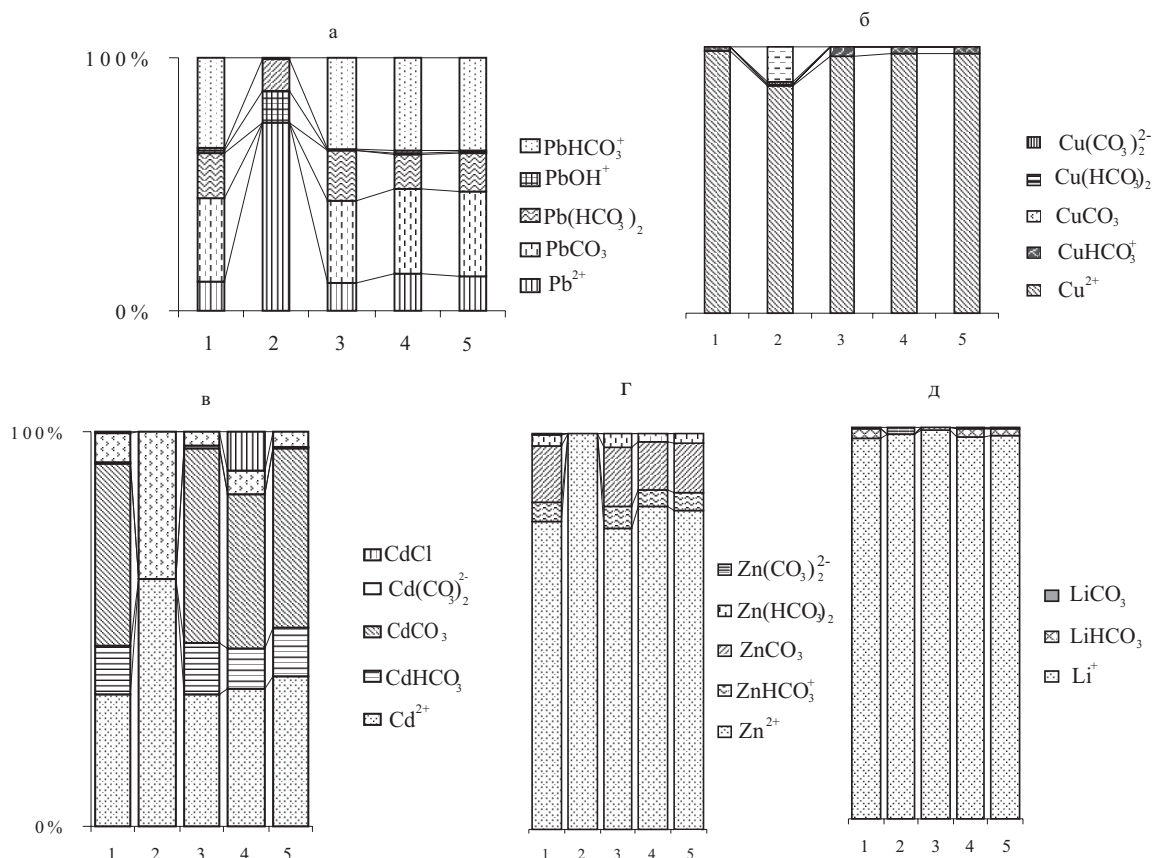


Fig. 2. Calculation results of the basic forms of microcomponent migration

Presented on Fig. 2 calculation results of the basic forms of *microcomponent* migration in waters of the basin of the river Katun, show that dominating in the solution are hydrocarbonate- and carbonate-complexes with ions Li, Cu, Zn, Cd and Pb.

Group OH^- gives secondary complexes Pb, Zn, Cu and Cd by way of reduction of the role of the given complex with the named elements, but on average the role of these complexes does not exceed 1...2 % in case of Zn, and 20...40 % in case of Pb.

Complexes of Hg migration, calculated by us, specify the prevailing role methylated mercury ($\text{Hg}(\text{NH}_3)_2^{2+}$ – cation hydrargium diammonium). It is obvious, that on the share $\text{Hg}(\text{NH}_3)_2^{2+}$ (cation hydrargium diammonium) of mercury there is no more than 1 % from its total quantity in the solution.

It is necessary to note that not considered by us interactions of ions of the solution with organic compounds can also influence both formation of element migration forms, and on processes mineral-formation. Another consequence of the presence of organic substances in the solution is primary linkage of microelements, while Ca^{2+} and Mg^{2+} form very weak compounds.

Fulvic acids are bound into strong organic-complexes from 0,0n up to 50 % of microelement content (especially Cd^{2+}). The minimal degree of ion linkage is characteristic for Li^+ and Zn^{2+} (0,0n %, Fig. 2, з, д), while fulvic-complexes are capable to link from 0,0 up to 16 % from the initial quantity of cations Pb^{2+} and Cu^{2+} (Fig. 2, а, б). And, at last, the maximal degree of connection is characteristic for Cd^{2+} , reaching from 3 up to 60 % (Fig. 2).

Basic conclusions

Components Ca, Na, K, Mg, Fe, Cl and F migrate mainly in the ionic form composing 95...99 % from their total amount. Among various forms of migration of such elements or compounds as Mn and NH_4 , the ionic form takes up only up to 80...95 %; for Cd, Pb – only 5...40 %, and for Cu, Zn and Li it takes up from 99...76 %. The maximal values of adhesiveness with fulvic acids are characteristic for Cd (3...60 %). At hydrogeochemical researches, it is necessary to consider the level of element adhesiveness in strong complex compounds, since the level of their adhesiveness noticeably affects the processes of migration, sorption, oxidation-restoration of elements or precipitation-dissolution of their compounds.

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