GEOLOGIJA. 2006. Vol. 55. P. 66–73

Hidrogeologija • Hydrogeology • Гидрогеология

Formation of iron compounds in the Quaternary groundwater of Lithuania

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Diliūnas J., Jurevičius A., Zuzevičius A. Formation of iron compounds in the Quaternary groundwater of Lithuania. *Geologija.* Vilnius. 2006. Vol. 55. P. 67–74. ISSN 1392-110X

The article focuses on the formation of iron concentrations in groundwater of Lithuanian Quaternary sediments. The vertical and horizontal distribution of iron concentrations, zonality, forms of compounds and conditions of equilibrium and mineral saturation were determined employing the WATEQ4F computer program. The main factor determining the formation and stability of iron compounds in groundwater is the aquifer–atmosphere interaction, i.e. the degree of confinement of a water-bearing system. There are three types of hydrogeological systems distinguished: open, semi-open and closed. Two factors – the dissolution process and the thermodynamic environment (pH, Eh) of the aquifer – predetermine iron concentrations. Fe^{2+} and $Fe(OH)_3$ are the main migration forms of iron. The investigation was aimed at substantiating the most effective methods of iron elimination from water intended for household consumption.

Key words: aquifer, computer program WATEQ4F, groundwater, Lithuania, iron, migration forms, saturation

Received 2 May 2006, accepted 5 June 2006

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INTRODUCTION

Iron is the basic chemical component affecting the quality of Lithuanian groundwater. About 87% of all investigated resources and 55% of supplied groundwater do not meet hygienic requirements for iron content in water (≥0.2 mg/1) (Diliūnas, Jurevičius, 1998; Diliūnas, Jurevičius, 1999; Diliūnas, Sakalauskas, 1996). The purpose of the current research was to reveal the major factors and thermodynamic conditions of the formation and migration forms of iron compounds in the groundwater of Quaternary aquifers.

METHODS

This study was designed as an investigation of factors affecting the hydrogeochemistry of iron, such as the concentrations of Fe^{2+}, Fe^{3+}, CO_2, O_2, H_2S and fulvic acid and the level of pH and redox potential (Eh). The role of iron bacteria and sulphate reducing bacteria was also evaluated. The forms of occurrence and speciation of chemical elements in groundwater and their impact on migration processes were determined by the method of thermodynamic computation. The modelling was based on the WATEQ4F computer program (with thermodynamic data BASIC). Saturation conditions (Ω) are expressed as the ratio of ion activity product (IAP) and solubility constant (K) (Appelo, Potsma, 1993):

$$\Omega = \frac{\mathrm{IAP}}{\mathrm{K}}.$$

The basic parameters characterizing the state of iron in groundwater and its changing conditions are pH and redox potential (Eh). The types of iron speciation, occurring as inorganic compounds, were determined on the basis of the Eh–pH diagram.

Data representing iron concentrations under typical hydrogeological conditions were assessed in accordance

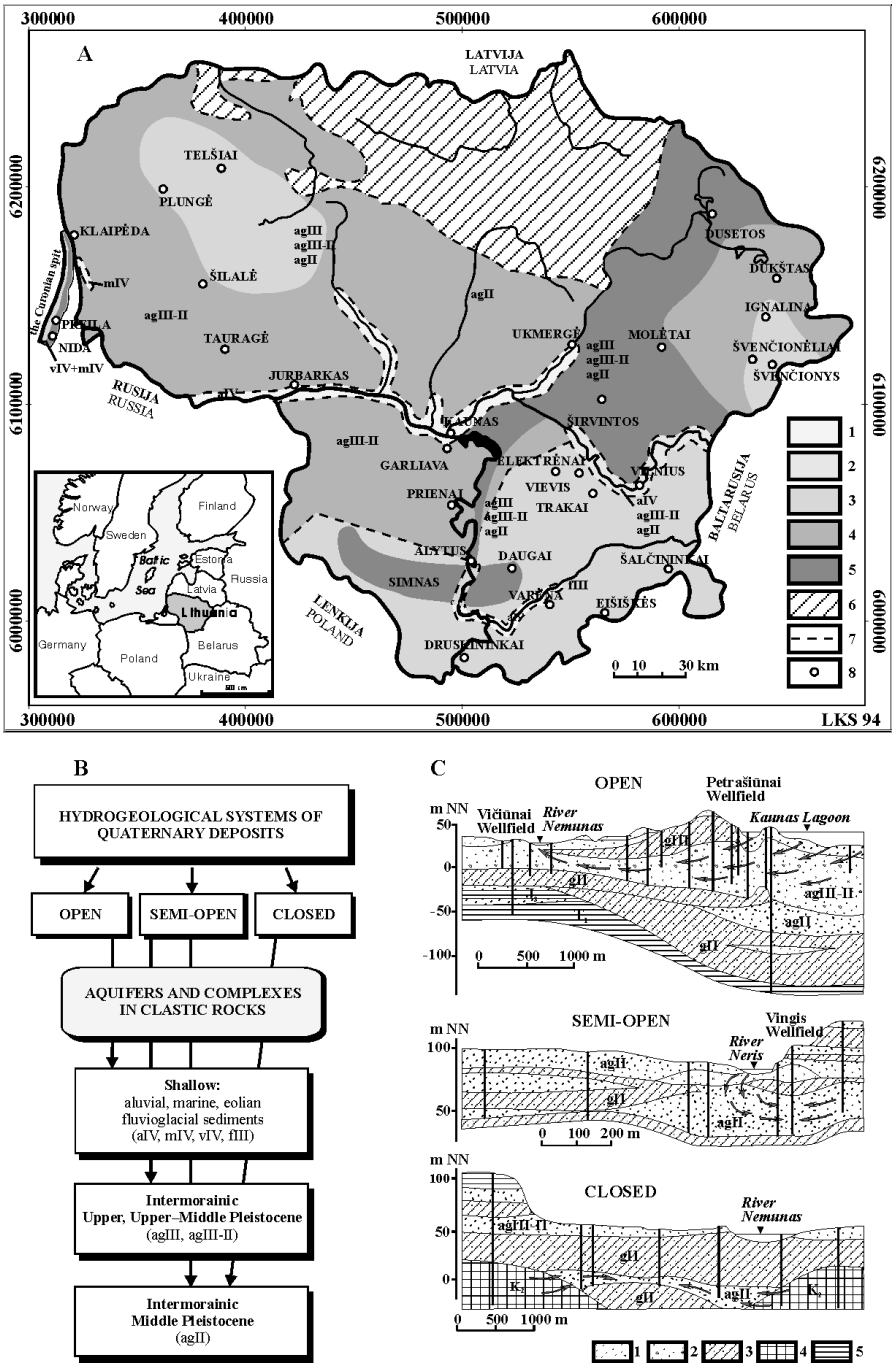

Fig 1. ***A***. Iron distribution in Quaternary groundwater: *1–5* – iron concentration (iron content zone): *1* – <0.3 mg/l (I); *2* – 0.3–1.0 mg/l (II); *3* – 1.0–2.0 mg/l (III); *4* – 2.0–3.0 mg/l (IV); *5* – >3.0 mg/l (V); *6* – no representative aquifers; *7* – aquifer boundaries, *8* – towns with water supplied from Quaternary aquifers. ***B.*** Classification of fresh groundwater systems in Quaternary sedimentary complexes (main aquifers for water supply). ***C.*** Profiles of typical hydrogeological systems: *1* – sand, *2* – gravel, *3* – loam, *4* – chalk, *5* – clay

1 pav. ***A***. Geležies pasiskirstymas kvartero požeminiame vandenyje: *1–5* – geležies koncentracija (geležingumo zona): *1* – <0,3 mg/l (I); *2* – 0,3–1,0 mg/l (II); *3* – 1,0–2,0 mg/l (III); *4* – 2,0–3,0 mg/l (IV); *5* – >3,0 mg/l (V); *6* – nėra svarbių vandeningųjų sluoksnių, tinkamų centralizuotam vandentiekiui; *7* – vandeningųjų sluoksnių ribos, *8* – kvartero požeminiu vandeniu aprūpinami miestai. ***B.*** Kvartero nuosėdinės dangos požeminio vandens hidrogeologinių sistemų klasifikacija (vandentiekai svarbiausi vandeningieji sluoksniai). ***C.*** Tipinių hidrogeologinių sistemų profiliai: *1* – smėlis, *2* – žvyras, *3* – priemolis, *4* – kreida, *5* – molis

with the system analysis principles and mathematical statistics. The distribution of iron concentrations in the groundwater of the main exploited aquifers and aquifer complexes is reflected in a special hydrogeochemical map (1:500 000) of Quaternary deposits (Fig. 1a).

The defined boundaries of the total iron concentrations in groundwater are based on the most frequent ranges of iron contents (mg/1): zone I Fe ≤ 0.3; zone II 0.3 < Fe < l.0; zone III 1.0 < Fe < 2.0; zone IV 2.0 < Fe < 3.0; and zone V Fe > 3.0. In each groundwater iron concentration zone distinguished within the limits of aquifers and aquifer complexes, the characteristics of iron concentrations were analyzed using the hydrogeochemical information about Lithuania and methods of mathematical statistics.

RESULTS AND DISCUSSION

Iron is an element of multiple valency that can migrate in the form of elementary ions and generate various ionic or colloidal complex compounds with OH_3^-, HCO_3^-, CO_3^{2-}, SO_4^{2-}, HS_3^-, S_2^-, and organic matter. These migration types depend on the state of the thermodynamical system and its parameters. An important role in iron stability and its speciation forms is played by the occurrence of CO_2, HCO_3, H_2S, organic matter, phosphorous compounds, and iron bacteria in water, as well as by the temperature and solubility of rocks. Under the Lithuanian hydrogeochemical conditions, the main factor determining the formation and stability of iron compounds in groundwater is the aquifer–atmosphere interaction, i.e. the degree of confinement of a water-bearing system.

There are three types of hydrogeological systems distinguished: open, semi-open and closed (Figs. 1b and 1c).

Fresh groundwater for urban water supply is taken from eight

Table 1. **Hydrogeochemical indexes of typical Quaternary hydrogeological systems (values: *1* – limiting, *2* – extremes occuring in water with centralized management)**
1 lentelė. **Tipinių hidrogeologinių sistemų hidrocheminiai rodikliai (reikšmės: *1* – ribinės, *2* – pasitaikančios ekstremalios centralizuotai eksploatuojamame vandenyje)**

Index	Dimension	Hydrogeological systems					
		Open		Semi-open		Closed	
		1	2	1	2	1	2
Fe	mg/l	0.05÷1.5 (8.0*)	2.0 (13.0**)	0.1÷2.7	5.5	0.1÷5.0	10.0
Mn	mg/l	0.002÷0.4 (0.9*)	0.6 (1.9*)	0.005÷0.5	1.0	0.004÷0.4	0.9
Dry residuals	mg/l	100÷500	660	120÷550	700	130÷640	820
Ca^{2+}	mg/l	7÷100	130	10÷120	150	20÷130	170
Mg^{2+}	mg/l	1÷42	64	3÷45	72	5÷50	97
Na^{+}	mg/l	1÷38	51	5÷40	67	5÷45	95
K^{+}	mg/l	0.1÷8	27	0.1÷10	28	0.2÷13	42
HCO_3^-	mg/l	50÷360	490	80÷450	530	100÷500	560
SO_4^-	mg/l	2÷80	168	2÷140	420	2÷160	520
Cl^-	mg/l	2÷60	150	2÷75	240	2÷90	270
Total hardness	mg-ekv/l	1.0÷8.4	11.6	1.0÷9.0	12.0	1.4÷9.5	16.0
Alkalinity	mg-ekv/l	0.8÷6.0	8.0	1.0÷7.4	8.7	2.0÷8.2	9.2
Permanganate value	mgO_2/l	0.5÷7.0	9.0 (20**)	0.3÷4.0	8.0	0.3÷5.0	9.0
P total	mg/l	0.01÷0.06 (0.2*)	0.08 (3.1**)	0.01÷0.09	0.16	0.01÷0.13	0.25
PO_4^{3-}	mg/l	0.001÷0.09 (0.6*)	0.18 (4.7**)	0.01÷0.16	0.30	0.02÷0.18	0.33
NH_4^+	mg/l	0.01÷1.0 (4.5**)	1.5 (11.5**)	0.01÷1.7	3.2	0.01÷2.6	5.0
NO_3^-	mg/l	0.01÷30.0	80.0	0.005÷20.0	50.0	0.01÷10.0	40.0
O_2	mg/l	0.06÷3.6	6.0	0.06÷2.1	4.5	0.02÷1.3	3.1
CO_2 free	mg/l	4÷40	69	5÷54	83	5÷60	95
H_2S	mg/l	0.0÷1.4	1.7	0.0÷1.2	1.7	0.0÷0.3	1.1
pH		6.2÷8.2	8.8	6.6÷8.3	9.0	6.6÷8.3	8.9
Eh	mV	80÷380	2	70÷320	-60	-10÷290	-85
t	°C	4÷16	19	6÷11	12	6÷13	15
Iron bacteria	Th cell/l	0.3÷300	1000 (11000**)	0.5÷400	2000	0.9÷2000	11000
Huminic acids	mg/l	0.02÷0.04 (0.16*) (0.8**)	(1.8**)	0.02÷0.05	0.06	0.02÷0.06	0.09
Fulvoacids	mg/l	0.02÷0.05 (0.16*) (2.3**)	0.09 (0.8*) (4.2**)	0.01÷0.06	0.09	0.01÷0.14	0.20

Anomalous values at waterworks: * Petrašiūnai (aIV+agIII-II), ** Nida, Preila (vIV+mIV).

Quaternary aquifers and aquifer complexes. Their general characteristics are given in Table 1.

The calcium–magnesium–bicarbonate water type prevails in all hydrogeological systems of Lithuania. With increasing the confinement of aquifers, the salinity, the concentration of dissolved chemical components and the number of iron bacteria increase, while the concentration of dissolved oxygen goes down. Consequently, the oxidation conditions deteriorate with iron concentrations increasing in more closed hydrogeological systems.

Open hydrogeological systems comprise shallow sand and gravel aquifers and aquifer complexes in river valleys and watershed areas. Three characteristic hydrogeological and hydrogeochemical groups can be categorized on the basis of iron speciation and its stability in groundwater: (1) aquifers of fluvioglacial deposits in watershed areas recharged by atmospheric precipitation; (2) alluvial aquifers recharged mainly by river water in the case of water extraction; and (3) aquifers of marine sediments rich in organics.

Groundwater in fluvioglacial, alluvial and marine sediments. Under oxidizing conditions with oxygen content exceeding the iron content, bivalent iron oxidizes into trivalent one: $Fe^{2+} \rightarrow Fe^{3+} + e^-$. During hydrolysis iron oxide precipitates: $Fe^{3+} + 3\ 0H^- \rightarrow Fe\ (OH)_3 \rightarrow$ $\rightarrow FeOH_s$. In water containing no dissolved organic matter and the oxygen content exceeding 1.2 mg/1, all dissolved iron would be oxidised. The prevailing iron concentrations range within 0.05–0.33 mg/1. Maximum concentrations are related to organic compounds: the permanganate value of water reaches 5–8 $mgO_2/1$. The basic migrational type of iron compounds is Fe^{2+} and $Fe(OH)_3$ while groundwater is saturated with minerals of iron oxide (Tables 2 and 3).

Complex of alluvial and intermorainic aquifers. A distinctive feature is an intense discharge of ground-

Table 2. **Basic iron compounds in Quaternary groundwater (average values)**
2 lentelė. **Svarbiausi geležies junginiai kvartero požeminiame vandenyje (vidurkinės reikšmės)**

Hydro-geological system	Aquifer and complex	Iron content zone	Fe total mg/l	Fe^{2+}	$Fe(OH)_3$	$FeHCO_3^+$	$Fe(OH)_2^+$	$FeCO_3$	$FeSO_4$	$FeHPO_4$
				% rom Fe total						
Open	fIII		0.29	54.5	18.6	13.0	9.2	3.5	0.6	0.06
	aIV	I	0.23	57.9	15.9	11.2	8.8	3.2	1.2	0.02
	mIV		0.24	65.4	7.2	16.9	3.4	4.6	1.1	0.05
	aIV+agII	II	0.49	50.4	19.9	15.9	9.8	3.5	1.5	0.02
	aIV+agIII-II*		0.59	57.7	14.4	15.8	6.4	4.1	1.1	0.14
	mIV+vIV	III	1.35	70.9	11.8	9.3	9.8	1.8	1.3	3.2
	mIV+vIV**	V	4.22	64.7	5.8	14.1	6.4	1.7	1.4	3.4
Semi-open	agIII,	II	0.79	55.3	13.9	16.5	6.8	3.9	1.3	0.04
	agIII-II, agII	III	1.27	38.8	14.0	19.6	7.1	4.0	0.7	0.02
Closed		IV	2.54	54.6	8.8	24.8	6.8	4.0	0.6	0.02
		V	3.45	46.1	17.2	20.5	11.4	3.8	0.5	0.01

Waterworks: * Petrašiūnai (aIV+agIII-II), ** Nida, Preila (vIV+mIV).

Table 3. **Groundwater saturation with iron minerales in Quaternary aquifers**
3 lentelė. **Požeminio vandens prisotinimas geležies mineralais kvartero vandeninguosiuose sluoksniuose**

Hydro-geolo-gical system	Aquifer and complex	Iron content zone	Saturation state / Minerals: Subsaturation $\Omega < 1$	Equilibrium $\Omega = 1$	Supersaturation $\Omega > 1$
Open	fIII				
	aIV	I	Siderite $FeCO_3$, Strengite $FePO_4 \cdot 2H_2O$		$Fe_3(OH)_8$, $Fe(OH)_{2,7}Cl_{0,3}$, Ferrihydrite $Fe(OH)_3$, Goethite FeOOH, Hematite Fe_2O_3, Maghemite Fe_2O_3, Magnetite Fe_3O_4, Cupric Ferrite $CuFe_2O_4$, Cuprous Ferrite $CuFeO_2$
	mIV				
	aIV+agII	II	Vivianite $Fe_3(PO_4)_2 \cdot 8H_2O$		
	aIV+ag III-II*				
	vIV+mIV	III	Jarosite K $KFe_3(SO_4)_2(OH)_6$		
	vIV+mIV**	V		Siderite	Strengite, Vivianite, Siderite,
Semi-open					
	agIII,	II	Vivianite $Fe_3(PO_4)_2 \cdot 8H_2O$	Siderite	
Closed	agIII-II,	III	Melantarite $FeSO_4 \cdot 7H_2O$,	Strengite	Siderite
	agII	IV	Jarosite Na $NaFe_3(SO_4)_2(OH)_6$,		
		V	Jarosite H $(H_3O)Fe_3(SO_4)_2(OH)_6$, Jarosite ss $[K_{0,77}Na_{0,03}(H_3O)_{0,2}]Fe_3(SO_4)_2$	Jarosite K	Strengite

Waterworks: * Petrašiūnai (aIV+agIII-II), ** Nida, Preila (vIV+mIV).

water from Quaternary intermorainic aquifers and the transportation of organic matter from rivers when water is extracted from a complex. The most important factor regulating the iron concentration is organic matter, especially fulvic acids, their concentrations in some pumping periods reaching 0.8 mg/1. The prevailing iron concentrations range within 0.25–0.75 mg/1.

Shallow groundwater in marine and eolian sediments of the Curonian Spit (mIV+vIV). The characteristics of iron speciation depend on abundant organic matter contained in sand and the intrusion of water from the Curonian Lagoon into the aquifer. The elements determining the physicochemical state of iron compounds are humic and fulvic acids, their maximum concentrations reaching 1–4 mg/1. Formation of complex iron compounds in water may also depend on other organic substances when their components reach 6–13 mgO_2/l (permanganate value) and 3.0 mg/1 (total phosphorus), respectively. The inner hydrogeochemical zone (III) is characterized by more oxidative conditions (Eh = 100 mV) and a lower permanganate value and iron bacteria content (about $9 \cdot 10^5$ cell/1), thus causing lower iron concentrations.

Semi-open intermorainic aquifers. There aquifers occur most frequently in river valleys, but are rather rare in watershed areas. In places, the impervious Quaternary

deposits covering the aquifers are eroded. The hydrogeological systems of intermorainic aquifers are characterized by oxidative conditions: the redox potential (Eh) about 180 mV, and CO_2 concentration below 40 mg/1, while the residual oxygen content in water usually exceeds the iron content. The prevailing iron concentration in groundwater ranges within 0.4–1.1 mg/1 (75% of the values). Iron migrates as Fe^{2+}, $Fe(OH)_3$ and $FeHCO_3$ (Table 2).

Closed hydrogeological systems are spread along the entire Lithuania. There hydrogeological systems can be grouped according to the specificity of hydrogeochemical conditions almost unaffected by the stratigraphical position of the aquifers. With increasing the confinement level of the aquifers, reductive conditions gradually develop: the content of CO_2 and organic matter and the number of iron bacteria increase. During oxidation, organic matter is rapidly consumed by oxygen, its residual content in water being below 0.5 mg/1, i. e. 3–7 times lower than the iron concentration. The basic types of migrational iron are Fe^{2+} and $FeHCO_3$.

CARBONATE EQUILIBRIUM OF IRON

Clayey and carbonate deposits are the most important source of iron in groundwater. The iron content in water with a low oxygen content is determined mostly by the solubility of iron carbonate. About 40–60% of iron migrates as Fe^{2+} ions, which usually are in equilibrium with the iron carbonate system. The compounds and ions such as CO_2, H_2CO_3, H^+, HCO_3^-, CO_3^{2-} and Fe^{2+} take part in this equilibrium system. Their state of occurrence can be described by the following carbonate equilibrium:

CO_2 (atmospheric)

$\updownarrow$

CO_2 (in water) + $H_2O \leftrightarrow H_2CO_3 \leftrightarrow H^+ + HCO_3^- \leftrightarrow 2H^+ + CO_3^{2-}$,

$FeCO_3$ (in sediments) + CO_2 (in water) + $H_2O \leftrightarrow Fe^{2+} + 2H^+ + CO_3^{2-}$.

$\updownarrow$

$FeCO_3$ (in rocks, deposits).

Any change of a component of a system affects the other ones. During extraction, groundwater is separated from the iron source, i. e. carbonate rocks. As a result, the carbonate equilibrium is disrupted, and iron is partly precipitated as $FeCO_3$. The process of iron settling accelerates emission of CO_2^- into the atmosphere. Moreover, Fe^{2+} ions in aerated water are easily oxidised to trivalent iron. The latter hydrates and precipitates as $Fe(OH)_3$ sediments.

The state of the iron carbonate system depends on the saturation state $\Omega(_{FeCO_3})$, i.e. the ratio Fe^{2+} and CO_2^- activity products of and iron carbonate solubility. At $\Omega_{FeCO_3} = 1$, there is an equilibrium between iron carbonate mineral and solution, hence no solution or precipitation of $FeCO_3$ take place. All bivalent iron dissolved in the water is bound with the iron carbonate system. This maximum amount of iron enclosed in the carbonate system under the present conditions will be referred to as equilibrium iron.

At $\Omega_{FeCO_3} < 1$, water is subsaturated with iron carbonate and there are good conditions for iron to dissolve. The water contains less bivalent iron than the carbonate equilibrium requires, i.e. the iron content is lower than the equilibrium amount. The deficit of bivalent iron can be caused by oxidation processes. When $\Omega_{FeCO_3} > 1$, the water is supersaturated with iron carbonate. The water contains iron in amounts too high for carbonate equilibrium to be achieved. This amount of bivalent iron exceeding the equilibrium iron remains stable in dissolved state due to other factors.

According to the degree of water saturation with iron carbonate (siderite), the zones of iron concentration levels of aquifers and complexes are grouped into three categories with different weight and percentage equilibrium and above-equilibrium iron amounts characteristic of a carbonate system (Table 3): I – subsaturated with iron carbonate, II – in equilibrium with iron carbonate, III – supersaturated with iron carbonate. The lowest level of saturation of water with iron carbonate (<1) is found in the aquifers occurring under oxidation conditions of open shallow systems of Quaternary alluvial, fluvioglacial and marine sediments. The highest oversaturation with iron carbonate (>1) is found in the Quaternary intermorainic aquifers.

CHARACTERISTICS OF DISTRIBUTION OF IRON CONCENTRATION IN GROUNDWATER

It is known that the geochemical features of iron are regulated by the pH and redox potential (Eh) of groundwater. Components determining the Eh value at the same time are considered to control the electric potential. Under the conditions described, three systems are thought to regulate the electric potential. These are the concentrations of oxygen, organic matter and iron. They all act in a neutral or weakly alkaline medium (pH mean range within 6.8–7.7). Under certain conditions, the sulphur system can also determine the electric potential.

The oxygen system determines the oxidative conditions and iron content in separate hydrogeological systems (iron-level zone I) in groundwater at a low content of humic acids. The average amount of dissolved oxygen ranges from 1.1 to 2.4 mg/1 and Eh is > 250 mV, while iron concentrations are 10 times lower than those of oxygen. Iron occurs as Fe (III) hydroxides.

The second groundwater iron-level zone (iron range 0.3–1.0 mg/1) is an expression of two systems (oxygen and organic matter) regulating the redox potential. Both

systems should manifest themselves under conditions of decreasing oxygen and increasing organic matter and CO_2 contents. In this zone, the oxygen system prevails, determining the basic type of iron ($Fe(OH)_3$) in groundwater. Deeper aquifers usually contain iron as Fe^{2+}. Iron and oxygen concentrations are similar. Eh is about 130–180 mV on average. An important role in the formation of redox conditions is played by organic matter. Organics are actively transformed by biochemical micro-organisms which, depending on the processes of consumption or release, can be oxidizers or reducers.

In the third iron-level zone of groundwater (iron range 1.0–2.0 mg/1), the systems regulating the potential should be of transitional type: organic matter and iron. Iron concentrations here exceed almost twice the residual dissolved oxygen and are similar to those of organic matter (half of permanganate oxidation). The prevailing Eh values are 100–160 mV. In many cases, the content of carbon dioxide, a product of micro-organic activities of organic matter, has the most obvious impact on the content and distribution of iron. Fe^{2+} is the prevailing iron species. Under these conditions, after artificially increasing oxygen content in the aquifers, Fe^{2+} is oxidised and hydrolysed as $Fe(OH)_3$ precipitate. Iron bacteria play the basic role in this process. They are able to mineralise iron into complex compounds resistant to chemical oxidation. The iron oxidation rate under biochemical processes is significantly higher than that caused by chemical oxidation. For instance, when iron concentration does not exceed 5 mg/1 (Eh < 250 mV), Fe^{2+} oxidation rate is 200 times higher than that in the case of abiogenic oxidation.

With an increase in iron content in groundwater and a decrease in dissolved oxygen (zones IV and V), the iron system should regulate the redox potential. Under the conditions when Fe exceeds 2.5 mg/1, O_2 < 0.3–0.4 mg/1, NH_4 = 0.8–1.2 mg/1, permanganate value reaches 3.5–5.5 mgO/1, CO_2 > 65–75 mg/1, and Eh is 85–130 mV, iron migrates as Fe^{2+}.

There is a rather complicated situation with the redox potential in the shallow groundwater of marine sediments of the Curonian Spit. According to the generally known principles, the iron system should define the electric potential (Крайнов, Швец, 1987). Rather high concentrations of organic matter, first of all humic acids (reaching 1 mg/1), determine the formation of complex organic compounds of iron. The concentrations of Fe^{3+} in the shallow groundwater exceed 1.0 mg/1. This deteriorates the oxidative capability of the system (Eh is about 80 mV). The redox conditions can be affected by two components, iron and organic matter, which regulate the potential. The reductive medium where iron migrates as Fe^{2+} prevails.

In larger aquifer systems, both horizontal and vertical zonalities in iron concentration distribution are usually observed. The horizontal zonality of iron content is determined mainly by the hydrodynamical characteristics of aquifer complexes. Quaternary intermorainic aquifers contain groundwater with the iron content increasing in the direction of water flows from recharge to discharge areas.

CONCLUSION

The main factor determining the formation and stability of iron compounds in groundwater is the aquifer–atmosphere interaction, i.e. the degree of confinement of a water-bearing system. There are three types of hydrogeological systems: open, semi-open and closed. Two factors – the dissolution process and the thermodynamic environment (pH, Eh) of the aquifer – predetermine the concentrations of iron. Fe^{2+} and $Fe(OH)_3$ are the main migration forms of iron.

On the basis of the established conditions of formation of iron compounds in groundwater, their migration forms and the degree of water saturation with iron minerals, a choice of optimum technologies of iron removal is determined.

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GELEŽIES JUNGINIŲ SUSIDARYMO SĄLYGOS LIETUVOS KVARTERO NUOSĖDŲ POŽEMINIAME VANDENYJE

S a n t r a u k a

Geležis yra pagrindinis cheminis komponentas, darantis poveikį požeminio vandens išteklių kokybei Lietuvoje. Apie 87% išžvalgytų gėlo požeminio vandens išteklių viršijama higienos norma geležies atžvilgiu (Fe ≥ 0,2 mg/l). Tyrimų tikslas – atskleisti geležies koncentracijų ir migracijos formų susidarymą bei termodinamines sąlygas svarbiausių kvartero vandeningųjų sluoksnių ir kompleksų, naudojamų vandentiekiui, požeminiame vandenyje.

Ištirti visi geležies junginių formavimąsi veikiantys komponentai: Fe^{2+}, Fe^{3+}, CO_2, O_2, H_2S, fulvo rūgštys, geležies bakterijos, sulfatus redukuojančios bakterijos, pH, Eh ir kt. (1 lentelė). Cheminių junginių formos požeminiame vandenyje ir jų

poveikis migracijos procesams buvo nustatyti termodinaminio skaičiavimo (modeliavimo) metodu naudojant WATEQ4F kompiuterinę programą.

Gėlas požeminis vanduo Lietuvoje daugiausia hidrokarbonatinis, pagal pH yra artimas neutraliam. Pagrindiniai geležies šaltiniai požeminiame vandenyje yra priemolis ir karbonatinės uolienos. Pagal dažniausiai pasitaikančias geležies koncentracijų reikšmes požeminiame vandenyje išskirtos penkios geležingumo zonos: I – Fe ≤ 0,3, II – 0,3 < Fe ≤ 1,0, III – 1,0 < Fe ≤ ≤ 2,0, IV – 2,0 < Fe ≤ 3,0, V – zona Fe > 3,0 mg/l.

Geležies geochemines savybes lemia požeminio vandens pH ir oksidacijos-redukcijos potencialas (Eh). Aprašomomis sąlygomis oksidacijos-redukcijos potencialo reikšmę reguliuoja deguonies, organinės medžiagos, geležies, rečiau sieros, sistemos. Pirmoje geležingumo zonoje oksidacijos-redukcijos potencialą reguliuoja deguonies sistema (geležies koncentracija yra 10 kartų mažesnė už deguonies), antrojoje – deguonies ir organinės medžiagos, trečiojoje – organinės medžiagos ir geležies, ketvirtojoje ir penktojoje – geležies (deguonies koncentracija yra 3–7 kartų mažesnė už geležies).

Geležies koncentraciją mažai deguonies turinčiame požeminiame vandenyje reguliuoja geležies karbonato tirpumas. Čia apie 40–60% geležies migruoja Fe^{2+} jono pavidalu, esančio pusiausvyroje su geležies karbonato sistema. Pastarąją sudaro CO_2, H_2CO_3, H^+, HCO_3^-, CO_3^{2-} ir Fe^{2+}. Karbonatinės sistemos komponentų koncentracijos tarpusavyje susijusios – vienų jų pokytis sukelia kitų pokytį.

Siurbiant požeminį vandenį suardoma karbonatinė sistema ir dalis geležies nusėda $FeCO_3$ pavidalu, todėl CO_2 išsiskiria į atmosferą. Be to, išsiurbtas iš sluoksnio vanduo yra veikiamas atmosferos deguonies: ištirpusi geležis oksiduojasi ir Fe^{2+} jonas lengvai transformuojasi iki trivalentės geležies, kuri vėliau hidratuojasi ir nusėda $Fe(OH)_3$ pavidalu. Geležies karbonatinės sistemos būvis priklauso nuo prisotinimo geležies karbonatu laipsnio (Ω_{FeCO_3}) ir santykio tarp Fe^{2+} ir CO_2.

Pagrindinis veiksnys, lemiantis geležies junginių formavimąsi ir stabilumą Lietuvos kvartero nuosėdų požeminiame vandenyje, yra vandeningojo sluoksnio ryšys su atmosfera. Šiuo požiūriu išskiriamos trys hidrogeologinės sistemos: atviros, pusiau atviros ir uždaros. Geležies koncentracijų dydį lemia tirpumas ir aplinkos termodinamika (pH, Eh). Pagrindinės geležies migracinės formos požeminiame vandenyje yra Fe^{2+} ir $Fe(OH)_3$ (2 lentelė). Nustatytos geležies formavimosi požeminiame vandenyje sąlygos, junginių migracinės formos ir vandens prisotinimas geležies mineralais leidžia parinkti optimalias geležies šalinimo iš požeminio vandens technologijas esant tipinėms hidrogeologinėms sąlygoms.

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УСЛОВИЯ ФОРМИРОВАНИЯ СОЕДИНЕНИЙ ЖЕЛЕЗА В ПОДЗЕМНЫХ ВОДАХ ЧЕТВЕРТИЧНЫХ ОТЛОЖЕНИЙ ЛИТВЫ

Резюме

Железо – основной химический компонент, ухудшающий качество подземных вод питьевого назначения. Приблизительно 87% всех исследованных в Литве ресурсов пресных подземных вод превышает гигиенический норматив (0,2 мг/л). Цель представляемого исследования состояла в установлении главных факторов и термодинамических условий формирования концентрации и форм миграции железа в подземных водах основных для хозяйственно-питьевого использования водоносных слоев и их комплексов.

Исследовались основные компоненты, влияющие на формирование и состояние соединений железа в подземных водах: Fe^{2+}, Fe^{3+}, CO_2, O_2, H_2S, фульвокислоты, железобактерии, сульфат редуцирующие бактерии, pH, Eh и т. д. (табл. 1). Формы химических элементов в грунтовых водах и их воздействие на процессы миграции определены методом термодинамических вычислений с использованием компьютерной программы WATEQ4F.

Пресные (до 1 г/л) подземные воды в Литве главным образом гидрокарбонатного состава, по pH близки к нейтральным. Главным источником образования соединений железа являются глинистые и карбонатные породы. По концентрациям железа в подземных водах выделено пять зон: I – Fe ≤ 0,3, II – 0,3 < Fe ≤ 1,0, III – 1,0 < Fe ≤ 2,0, IV – 2,0 < Fe ≤ 3,0, V – Fe > 3,0 мг/л (рис. 1). Геохимические свойства железа подземных вод и ее концентрацию предопределяют pH и окислительно-восстановительный потенциал (Eh). В описанных условиях величину окислительно-восстановительного потенциала регулируют потенциалзадающие системы кислорода, органических веществ, железа, реже – серы. В первой зоне окислительно-восстановительный потенциал регулирует система кислорода – здесь концентрация железа в 10 раз меньше, чем кислорода, во второй зоне – потенциалзадающая система кислорода и органических веществ, в третьей – органических веществ и железа, в четвертой и пятой – железа (здесь концентрация кислорода в 3–7 раз меньше, чем железа).

В подземных водах с низким содержанием кислорода концентрацию железа регулирует растворимость карбоната железа. 40–60% железа мигрирует в ионной Fe^{2+} форме, которая обычно находится в равновесии с карбонатной системой. В этой системе равновесия принимают участие ионы CO_2, H_2CO_3, H^+, HCO_3^-, CO_3^{2-} и Fe^{2+}. Любое изменение компонента системы влечет за собой изменение концентрации других компонентов.

При извлечении подземной воды карбонатная система нарушается и часть железа оседает в форме $FeCO_3$, вызывая выделение CO_2 в атмосферу. Кроме того, извлеченная подземная вода подвергается воздействию атмосферы: железо окисляется и ион Fe^{2+} легко трансформируется в трехвалентную форму, которая в дальнейшем гидратируется и оседает в форме $Fe(OH)_3$. Состояние системы карбоната железа зависит от степени карбонатной насыщенности (Ω_{FeCO_3}) и отношения между продуктами Fe^{2+} и CO_2.

Главным фактором, определяющим формирование и стабильность соединений железа в подземных водах четвертичных отложений Литвы, является степень взаимодействия водоносного слоя с атмосферой.

Выделяются три типы гидрогеологических систем: открытые, полуоткрытые и закрытые. Главными миграционными формами железа в подземных водах являются Fe^{2+} и $Fe(OH)_3$ (табл. 2).

Установление условий формирования железа в подземных водах, миграционных форм соединений и насыщенности воды железистыми минералами (табл. 3) дает возможность выбора оптимальной технологии удаления железа при типовых гидрогеологических условиях.