Changes in chemical composition of drilling waste water in taiga zone of Western Siberia (the Russian Federation) on the basis of thermodynamic approach

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Abstract. Condition and process change modeling of chemical composition of liquid drilling wastes has been performed in waste pits located in the boggy areas of Western Siberia. Dissolved substance migration and waste water saturation indexes were calculated in relation to a number of minerals and organic-mineral compounds. It was shown that reclamation of disturbed land can be made with the use of substrate produced by mixing liquid drilling wastes, high-bog (mostly at a technical stage) and low-bog (for forest reclamation) peats.

1. Introduction

Western Siberia (the Russian Federation) is known for production of large amount of oil and gas. It results in emission of a great deal of waste water and drilling wastes into the environment that defines the relevance of research in both ecosystem conditions – sites of oil and gas industrial facilities, and processes of storage, refining, utilization, and treatment of waste water and refinery wastes. The key feature of the regional environment is its extremely high bogginess achieving 30 % or more in some areas [1, 2]. Besides, at present in taiga zone of Western Siberia rather a high rate of bog formation – up to 2.62 mm/year vertically and ten thousands of hectares horizontally is observed [3, 4]. Bogs are distinguished by elevated concentration of organic matter and some transformation products including very toxic ones, which define general conditions of bog ecosystem functions as extremely specific and unfavorable for many species of plants and animals [5, 1, 6]. One might assume that waste waters and drilling wastes (taking into account their chemical composition) can be used in forest reclamation of boggy areas, that conditions the goal of the research, namely, forecast evaluation of chemical composition changes in waste waters which are accumulated in reservoirs («waste pits») in the course of drilling operations. In particular, the conditions of waste water self-purification in waste pits formed at exploration well drilling. The basic assumptions: 1) waste water and drilling wastes inflow the waste pits on a tight schedule; 2) drilling operations and infrastructure building are to be performed within a year, after which disturbed land is remediated. Usually, reclamation reduces to site surface leveling (technical stage), fertilizer treatment, and seeding (biological stage).

The general purpose of reclamation is natural condition recovery. However, in case of site reclamation located in oligotrophic bogs such actions lead to development of a new, quite sustainable body, the properties of which are close to those of eutrophic bogs. One more question raised in the course of reclamation in Western Siberia consists in expedience of wetland restoration that replaces forest ecosystems rapidly. In this case industrial activity often contributes to, but not prevents, bog formation. Actually, this fact is not described in the nature protection strategy of the region.

2. Initial data and research methods

As a research object we chose a boggy area of the Cluch River catchment (an element of «the Kluch River – the Bakchar River – the Chaya River – the Ob River – Kara Sea» river system) within the South taiga subzone of Western Siberia. A brief hydrometeorological characteristic of the river is presented in Table 1, more detail information including the technique of water balance calculation, – in works [7, 8].

Table 1. Climatic and hydrologic characteristics of the Cluch River and its catchment area (an element of «the Kluch – the Bakchar – the Chaya – the Ob» river system) [8]

Indicator	I	II	III	IV	V	VI	VII	VIII	IX	X	XI	XII	Total
T_a, °C	-20	-18	-10	1	9	15	18	14	9	0	-11	-18	-1
T_w, °C	-28	-24	-12	1	10	16	18	12	6	-3	-16	-26	-4
v_w, m/s	3.1	3.3	3.6	3.7	3.7	3.2	2.5	2.6	3	3.7	3.7	3.3	3.3
P_{sa}, mm	18	14	15	26	45	67	74	84	46	42	31	23	485
P_{la} mm	1	0	2	6	42	67	74	84	46	26	7	1	356
O_{sn}, mm	0	0	0	90	22	0	0	0	0	17	0	0	129
$P_{la} + O_{sn}$, mm	1	0	2	96	64	67	74	84	46	43	7	1	485
E_{ws}, mm	3	5	11	21	53	64	75	62	75	38	6	4	417
E_{sn}, mm	3	5	11	0	0	0	0	0	0	0	6	4	29
E_{sw}, mm	0	0	0	58	101	147	161	126	83	0	0	0	676
Y, mm	0	0	0	11	37	12	3	1	1	2	1	0	68

Note: T_a – average monthly air temperature; T_w – calculated temperature of water surface; vw – wind velocity; P_{sa} – total amount of precipitation; P_{la} – liquid precipitation (rain); O_{sn} – water yield of snow cover; $P_{la} + O_{sn}$ – actual total catchment moisture; E_{ws} – total evaporation of catchment surface; Esn – evaporation from snow cover (a part of total evaporation from catchment surface); E_{sw} – evaporation from water surface; Y – total (surface and underground) runoff.

It was assumed that waste pit (a reservoir for drilling waste and drilling waste water storage) is located in the site, which possesses the following typical parameters: pit volume – 800 m³ (average volume of waste pit per one well), volume of liquid flowing into the pit per one time (with regard for moisture 70 %) – 560 m³; average depth – 2.5 m [9, 10]. Chemical composition of waste, rain (Table 2), and bog waters was taken in terms of the results of previous research [11-14].

The research technique includes:
1) calculation of annual liquid balance in simulated waste pit using data on precipitation and evaporation from water surface (at assumed negative temperature of water surface the evaporation from snow was taken into account);
2) calculation of annual hydrochemical balance using the formula (1);
$$C_x \cdot (V_{dr} + P_{la} + O_{sn} - E_{sn} - E_{sw}) = C_{dr} \cdot V_{dr} + C_{la} \cdot P_{la} + C_{sn} \cdot O_{sn}, \qquad (1)$$
where V_{dr} is the waste pit volume; P_{la} is liquid precipitation (rain); O_{sn} is the water yield from snow cover; E_{sn} is evaporation from snow surface; E_{sw} is evaporation from water surface; matter concentration in: C_{dr} – in waste pit water; C_{la} – liquid precipitation; C_{sn} – melt water; the balance is defined for the substances from Table 2;
3) evaluation of change in waste pit water concentration by means its single mixing with high and low bog peat with the assumption that matter balance is described by the equation (2):
$$M \cdot k_a \cdot C_{x,s} + V_l \cdot C_{x,s} = V_l \cdot C_{x,0}, \qquad (2)$$
where M is the mass of sorbent; V_l is the liquid volume; k_a is a coefficient; $C_{x,0}$ and $C_{x,s}$ are the matter concentration in the initial liquid and after mixing liquid and sorbent [15]; the value k_a is determined

by matching the data on chemical composition of uncontaminated water in oligotrophic and eutrophic bogs [12] with the assumption that the impact of contamination source is limited by the site of up to 500 m in length; average depth of peat deposit is taken as 1.95 m in size, the peat moisture is 90.1 %;
4) calculation of migration conditions and saturation index L of waste pit water in relation to a number of minerals; negative magnitudes of index L indicate the potential undersaturation, whereas positive ones – solution oversaturation in relation to a number of minerals that can form or be present in the research medium [16];
5) simulation of chemical composition change towards minimization of Gibbs energy in «water – rock» system; thermodynamic calculations were performed by means of software Solution+ based on the method of constant [17].

Table 2. Average chemical composition of waste pit water and precipitation

Indicator	Waste pits [Bleuten et al., 1999; Savichev, Bernatonis, Bernatonis, 2011]	Snow [Savichev, Ivanov, 2010]	Rain [Savichev, Ivanov, 2010]
pH	8.00	6.10	6.50
Sum of principle ions	7211.80	23.10	50.90
Ca^{2+}	248.40	3.10	5.40
Mg^{2+}	31.80	0.70	2.00
Na^+	2124.80	1.90	2.30
K^+	202.20	0.70	0.90
HCO_3^-	338.30	12.10	29.10
SO_4^{2-}	388.10	2.30	8.00
Cl^-	3874.40	2.40	3.20
NO_3^-	4.96	0.98	0.01
NO_2^-	0.026	0.030	0.960
NH_4^+	1.60	0.74	1.23
PO_4^{3-}	0.68	0.14	0.72
Si	7.32	0.28	0.15
COD	364.69	4.00	4.00
Fe	19.277	0.090	0.110
Cu	0.0072	0.0046	0.0096
Zn	0.0336	0.0125	0.1390

Note: COD – chemical oxygen demand

    When performing the thermodynamic calculations we took into account the presence of fulvic acids (PA) (3) and humic acids (HA) in the solution (4), concentration of which was determined depending on chemical oxygen demand COD:

$$PA=0.3122 \cdot COD, \ R^2=0.57, \qquad\qquad (3)$$
$$HA=0.0832 \cdot COD, \ R^2=0.59, \qquad\qquad (4)$$

where R^2 is the square of correlation ratio. In case of thermodynamic calculations just for waste pit water we assumed that fulvic and humic acids flow into the waste pit mostly with precipitations, but in case of peat – with bog water.

3. Results and discussion

If we assume the absence of additional water inflow in waste pit and correlation of evaporation from water surface and waste pit water, the decrease in total liquid volume of waste, drilling waste water, and precipitation is to be observed during a year (Fig. 1). In particular, in case of simulated waste pit

the liquid volume decreases from 560 m³ to 490 m³ during a year due to evaporation (despite precipitations). Due to solution concentration it is possible to increase concentration of some substances (Fig. 1, Table 3). This results in changes of conditions in «water – rock» system including fall-outs of some slightly soluble compounds and, as a consequence, decrease in concentrations of soluble substances (Table 4).

Additional decrease in a number of substances in waste pit water can be potentially achieved by means of its mixing with peat, mostly with high-bog one (Table 3). It does not preclude mixing with low-bog peat, but changes the technique of the substrate obtained. Taking into account higher content of uncomplexed ions of Na^+ and Cl^- in waste pit water after its mixing with low-bog peat (consequently – lower concentration in the substrate), it is reasonable to apply the obtained substrate for forest reclamation of disturbed boggy areas. The use of high-bog peat for sorption would presumably allow the efficient decrease of substance concentration in liquid waste, but the substrate based on it is better to be applied at the technical stage of land reclamation due to elevated concentrations in the absorption complex.
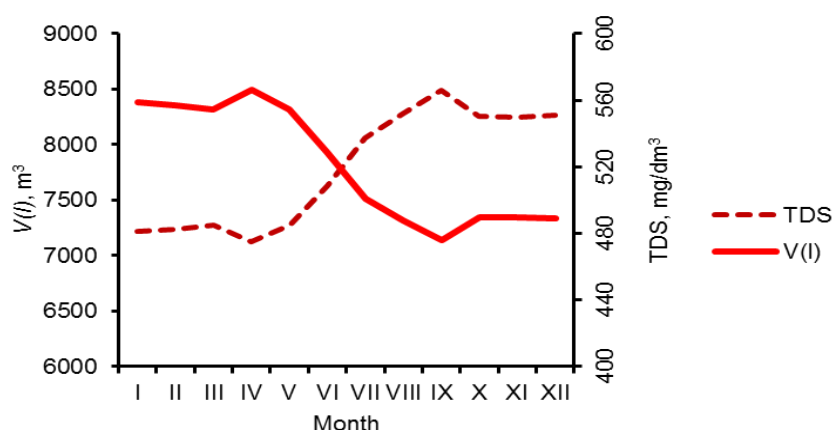

Fig. 1. Change of liquid volume in waste pit during a year (V(l)) and sums of dissolved substances in it (TDS)

Table 3. Calculated concentrations of uncomplexed ions in waste pit water, mg/dm³

Ion	Alternate design					
	I	II	III	IV	V	VI
Ca^{2+}	228.7	94.9	256.1	109.1	253.6	232.9
Mg^{2+}	29.4	12.2	33.3	14.1	33.5	31.8
Na^+	2105.6	811.6	844.9	928.6	1490.0	569.4
K^+	201.6	77.2	230.8	88.5	167.3	118.0
HCO_3^-	313.8	321.8	374.0	373.6	374.0	356.6
CO_3^{2-}	0.6	0.6	<0.1	<0.1	<0.1	<0.1
SO_4^{2-}	347.5	148.2	394.8	170.4	313.7	336.3
Cl^-	1740.6	1479.9	1694.2	1693.2	1692.5	622.4
Сумма	4967.9	2946.4	3828.3	3377.6	4324.5	2267.5

Note: I – calculation of migration conditions without taking into account waste pit water dissolving with precipitations (Table 2); II – simulation of chemical composition change towards minimization of Gibbs energy in «water – rock» system» without taking into account waste pit water dissolving with precipitations (based on design I); III – calculation of migration conditions taking into account waste pit water dissolving with precipitations; IV – simulation of chemical composition change towards minimization of Gibbs energy in «water – rock» system» taking into account waste pit water dissolving with precipitations (based on design III); V – concentration after waste pit water mixing

with low-bog peat (based on design III); VI – concentration after waste pit water mixing with high-bog peat (based on design III)

Judging by the saturation index calculation (Table 4), it should be noted that more efficient decrease in concentration of some metals (with the exception of Na and K) might be achieved by additional introduction of humic acids in waste pit due to slightly dissolved compound formation.

Table 4. Magnitudes of waste pit water saturation index L in relation to some minerals and organo-mineral complexes

River point	Alternate design					
	I	II	III	IV	V	VI
$CaCO_3$ (calcite) = $Ca^{2+}+CO_3^{2-}$	0.13	-0.09	-1.18	-1.17	-8.53	-8.45
$CaCO_3$ (calcite)$+CO_2+H_2O = Ca^{2+}+2 \cdot HCO_3^-$	0.69	0.47	-0.29	-0.62	0.10	-0.71
$CaMg(CO_3)_2$ (dolomite)$= Ca^{2+}+Mg^{2+}+2 \cdot CO_3^{2-}$	0.39	-0.05	-2.23	-2.21	-16.91	-16.71
$CaMg(CO_3)_2$ (dolomite) $+ 2 \cdot CO_2 + 2 \cdot H_2O = Ca^{2+}+Mg^{2+}+4 \cdot HCO_3^-$	1.51	1.07	-0.45	-1.11	0.35	-1.22
$Ca(\Gamma K) = Ca^{2+}+\Gamma K$	1.28	0.99	1.37	1.03	1.35	1.43
$Mg(\Gamma K) = Mg^{2+}+\Gamma K$	1.11	0.81	1.20	0.86	1.19	1.32
SiO_2 (quartz) $+ 2 \cdot H_2O = H_4SiO_4^0$	0.49	0.07	0.56	0.14	0.55	0.54
$CaAl_2Si_2O_8$ (anorthite) $+ 3 \cdot H_2O + 2 \cdot CO_2 = Al_2Si_2O_7 \cdot 2 \cdot H_2O$ (kaolinite) $+ Ca^{2+} + 2 \cdot HCO_3^-$	-256.2	-256.4	-258.5	-258.8	-257.6	-259.3
$2 \cdot NaAlSi_3O_8$ (albite) $+ 11 \cdot H_2O + 2 \cdot CO_2 = 2 \cdot Na^+ + 2 \cdot HCO_3^- + Al_2Si_2O_7 \cdot 2 \cdot H_2O$ (kaolinite) $+4 \cdot H_4SiO_4^0$	-4.36	-6.71	-7.18	-8.74	-5.84	-8.47
$3 \cdot KAlSi_3O_8$ (microcline) $+ 2 \cdot H^+ + 12 \cdot H_2O = KAl_3Si_3O_{10}OH_2$ (muscovite) $+ 2 \cdot K^+ + 6 \cdot H_4SiO_4^0$	-16.88	-20.13	-18.68	-22.01	-18.12	-20.29
$2 \cdot KAl_3Si_3O_{10}OH_2$ (muscovite) $+ 2 \cdot H^+ + 3 \cdot H_2O = 3 \cdot Al_2Si_2O_7 \cdot 2 \cdot H_2O$ (kaolinite) $+2 \cdot K^+$	4.63	3.84	2.41	1.59	2.98	0.86
$CaAl_2Si_2O_8$ (anorite) $+ 2 \cdot H^+ + 6 \cdot H_2O = Al_2O_3 \cdot 3 \cdot H_2O$ (gibsite) $+ 2 \cdot H_4SiO_4 + Ca^{2+}$	-3.36	-4.47	-5.49	-6.66	-4.65	-6.43
$CaAl_2Si_2O_8$ (anorite) $+ 2 \cdot H^+ + H_2O = Al_2Si_2O_7 \cdot 2 \cdot H_2O$ (kaolinite) $+ Ca^{2+}$	-19.47	-19.90	-23.94	-24.59	-22.28	-25.70
$NaAlSi_3O_8$ (albite) $+ 7 \cdot H_2O + H^+ = Al_2O_3 \cdot 3 \cdot H_2O$ (gibsite) $+ Na^+ + 3 \cdot H_4SiO_4^0$	-200.8	-202.4	-202.1	-203.3	-201.5	-202.8

4. Conclusions

Oil and gas production in Western Siberia has a sufficient impact on the environment [18, 19] that often can be estimated as regional and long-term. In most cases this impact may be decreased due to improvements in locations and reclamation of waste pits in boggy areas as well as more efficient use of natural conditions. Besides, it is possible to reduce the costs for nature protection measures without decreasing their performance. In particular, disturbed land reclamation can be performed using the substrate obtained by means of mixing drilling waste water, high-bog (mostly at the technical stage) and low-bog (for forest reclamation) peats.

References

[1] Bazanov V A, Berezin A Ye, Savichev O G and Skugarev A A 2009 The phytoindication method for mapping peatlands in the taiga zone of the West-Siberian Plain *International Journal of Environmental Studies* **4** 473–484

[2] Zemtsov V A and Savichev O G 2015 Resources, regime and quality of surface waters in the Ob River basin: history, current state and problems of research *International Journal of Environmental Studies* **3** (Published online: 17 Mar 2015) DOI:10.1080/00207233.2015.1019299

[3] Neishtadt M I 1972 Bogs of Ob-Irtysh interstream area In: Zhukov, M.V. (Eds) *Natural conditions of Ob-Irtysh interstream area development* (Institute of Geography Publishing House) 322–346

[4] Pologova N N and Lapshina Ye D 2002 Accumulation of hydrogen in peat deposits of Large Vasyugan bog In: Kabanov M V (Eds.) *Large Vasyugan bog. Modern condition and development processes* (Tomsk, Atmosphere Optics Institute RAS SB Publishing House)174–179

[5] Liss O L, Abramova L I, Avetov N A, Berezina N A, Inisheva L I, Kurnishkova T V, Sluka Z A, Tolpysheva T Yu and Shvedchikova N K 2001 Bog ecosystems of Western Siberia and their nature protection significance (Tula: Grif i C°)

[6] Eckstein Y, Savichev O G and Pasechnik E Yu 2015 Two decades of trends in ground water chemical composition in The Great Vasyugan Mire, Western Siberia, Russia *Environmental Earth Sciences* **1** 3-15 DOI 10.1007/s12665-014-3908-z

[7] Savichev O G, Skugarev A A, Bazanov V A and Khanzhevskaya Yu A 2011 Water balance of boggy catchment areas of Western Siberia (by the example of the small river Kluch, Tomsk Oblast) *Geoinformatika* **3** 39 – 46

[8] Savichev O G, Bernatonis P V and Bernatonis V K 2012 Hydrological foundation of peat bog development (by the example of the River Kluch catchment, Western Siberia) *Bulletin of Tomsk Polytechnic University* **320:1** 155 – 162

[9] Regulation of engineering design of gathering, transportation, refining facilities of oil, gas, ans water at oil fields. VNTP 3-85 1986 (Moscow, Minneftprom SSSR)

[10] Instruction on nature protection at well construction on land at polycomponent hydrocarbon field including sulphur containing. RD 51-1-96 1998 (Moscow, IRC Gazprom)

[11] Bleuten W, Lapshina E, Ivens W, Shinkarenko V and Wiersma E 1999 Ecosystem recovery and natural degradation of spilled crude oil in peat bog ecosystems of westsiberia *International Peat Journal* **9** 73–82

[12] Savichev O G 2009 Chemical composition of bog water over the territory of Tomsk Oblast (Western Siberia) and its interaction with mineral and organic-mineral compounds *Bulletin of Tomsk Polytechnic University* **314:1** 72-77

[13] Savichev O G and Ivanov A O 2010 Precipitations in the Middle Ob River basin and their influence on hydrochemical river flow *Izvestia RAN. Series of Geography* **1** 63-70

[14] Savichev O G, Bernatonis P V and Bernatonis V K 2013 Hydrochemical conditions of drilling waste storage and utilization in peat-bog geosystems of Siberia *Tomsk State University Journal* **375** 183–186

[15] Zhukov A I, Mongait I L and Rodziller I D 1977 Methods of industrial waste water treatment (Moscow, Stroyizdat)

[16] Grenthe I and Puigdomenech I 1997 Symbols, standards, and Conventions *Modelling in aquatic chemistry* (Paris, Nuclear energy agency) 35 – 68

[17] Savichev O G, Kolokolova O V and Zhukovskaya E A 2003 Composition and equilibrium of bottom sediments of the River Tom with river water *Geoekologia* **2** 108-119

[18] Adam A M 2005 Evaluation of ecological conditions of the Western Siberia territory for the purpose of ecological safety in the context of sustainable nature use In: *Okhrana Pripody* (Ed. by A.Ye. Berezin) (Tomsk, NTL Publishing House) 3–12

[19] Savichev O G, Kolesnichenko LG and Saifulina E V 2011 The ecologo-geochemical state of water bodies in the Taz-Yenisei interfluve. *Geography and Nature Resources* 32. 4 333-336, DOI: 10.1134/S1875372811040056