Study of the Influence of Groundwater Impurities on the Iron Oxidation Rate

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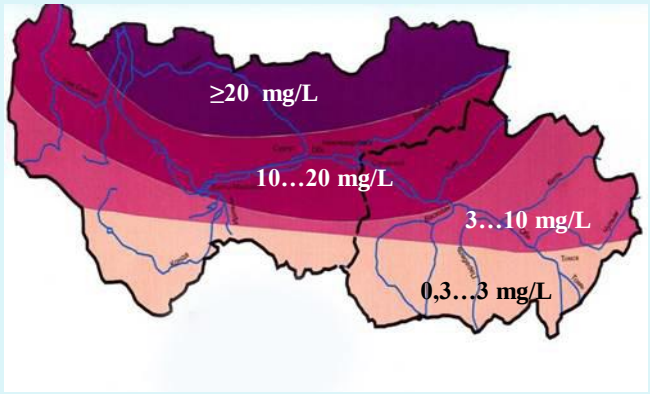
The parameters of the West Siberian Groundwater

Parameter	Units	Indicator value		MPC according to SanPiN 2.1.4.1074-01
		Water II type North West Siberian region	**Water I type** South West Siberian region	
pH		6.0…7.0	6.8…7.7	6…9
Color	grad	30…150	10…45	20
Total iron	mg/L	1.0…25.0	0.88…27.0	0.3
Manganese	mg/L	0.03…0.75	0.10…1.35	0.1
Total water hardness	^{0}Ж	0.5…6.0	4.5…13.0	7.0
Hydrocarbonate	mg/L	30.0…360.0	280.0…800.0	not standardized
Silicon	mg/L	10.0…28.0	4.5…16.0	10.0
Permanganate oxidizability	mgO/L	3.0…14.0	0.9…3.0	5.0

Iron
3 to 30 mg/L



Technology:
Aeration –
Sedimentation –
Filtration

Problem:
which stage is the limiting one?

The purpose is to study the kinetics of the iron oxidation process depending on the composition of groundwater**.**

Background:

1. Emmanuel et al, (1984), Belopolsky et al, (1948), Getskin et al, (1956), Smotraev et al., (2016), Morgan and ets., (2007) founds that the oxidation of iron (II) ions by atmospheric oxygen in water proceeds with a decrease pH of the solution.

2. The authors of the work (Getskin et al., 2956) assume that dissolved oxygen is adsorbed on the surface of iron (III) hydroxide precipitates and it is activated.

$$Fe^{2+} + O_{адс-} + 2H_2O = Fe(OH)_3 + H^+.$$

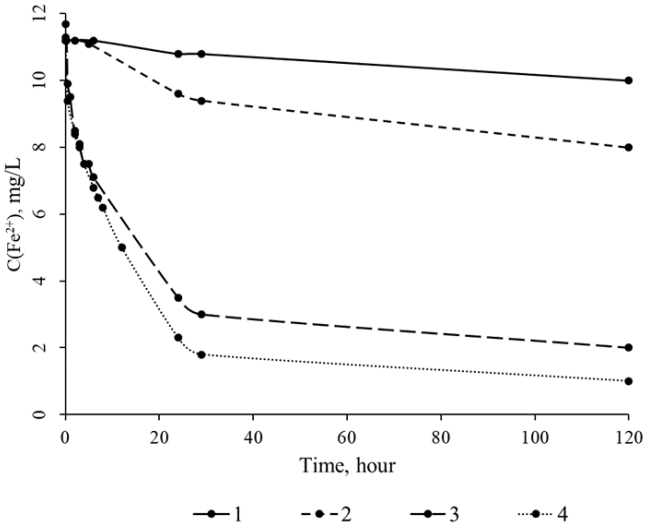
3. In the work (Smotraev et al, 2016) it was found that the oxidation of iron (II) ions proceeds most fully during the oxidation of iron (II) hydroxide with oxygen according to the reaction:

$$2Fe(OH)_2 + ½\ O_{2(g)} + H_2O = 2Fe(OH)_3.$$

Table 1. Basic reactions in the system Fe^{2+} - Fe^{3+} - H_2O – NH_4^+ - O_2 and их their equilibrium constants at 20^0C.

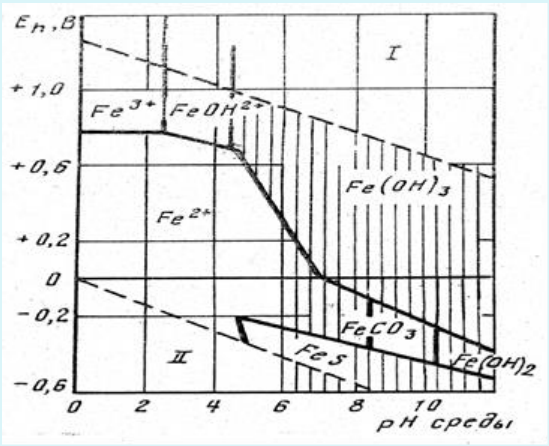
№	Реакции	$lg(K_p^{20})$
1	$H_2O=H^++OH^-$	-14.160
2	$NH_4^++H_2O=NH_4OH + H^+$	-9.200
3	$NH_4OH=NH_4^++OH^-$	-4.750
4	$2Fe^{2+}+1/2O_{2(g)+}H^+=2Fe^{3+}+OH^-$	0.969
5	$2Fe(OH)_2+1/2O_{2(g)}+H_2O=2Fe(OH)_3$	17.698
6	$2Fe^{2+}+1/2O_{2(g)}+H_2O=2Fe^{3+}+2OH^-$	-6.111
7	$2Fe^{2+}+1/2O_{2(g)}+2H^+=2Fe^{3+}+H_2O$	8.049
8	$4NH_4^++3O_2= 2N_2+6H_2O+4H^+$	14.468
9	$4NH_3+3O_2=2N_2+6H_2O$	0.228

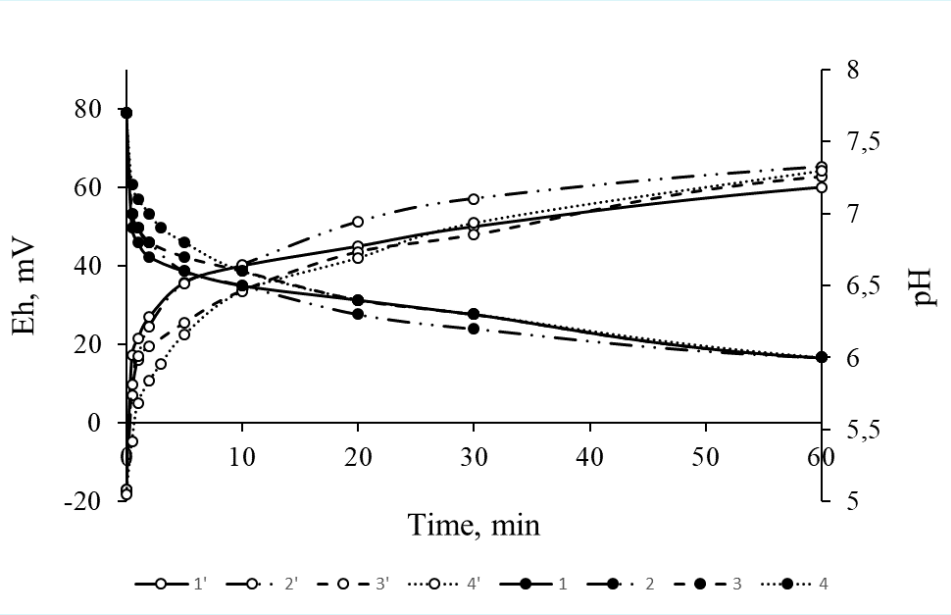
Oxidation of iron (II) ions in distilled water



pH: 1 − 5.4; 2 – 6.0; 3 – 7.0; 4 – 8.0

Figure 1 Dependence of the concentration of iron (II) on the reaction time at different pH values

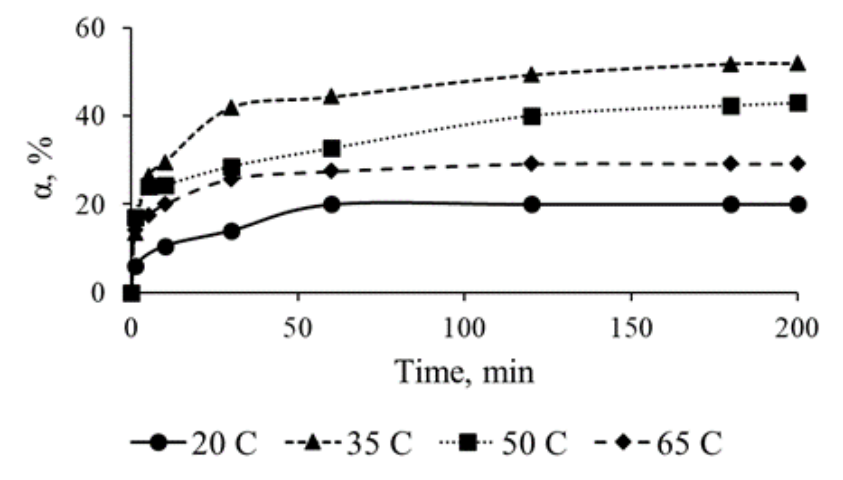


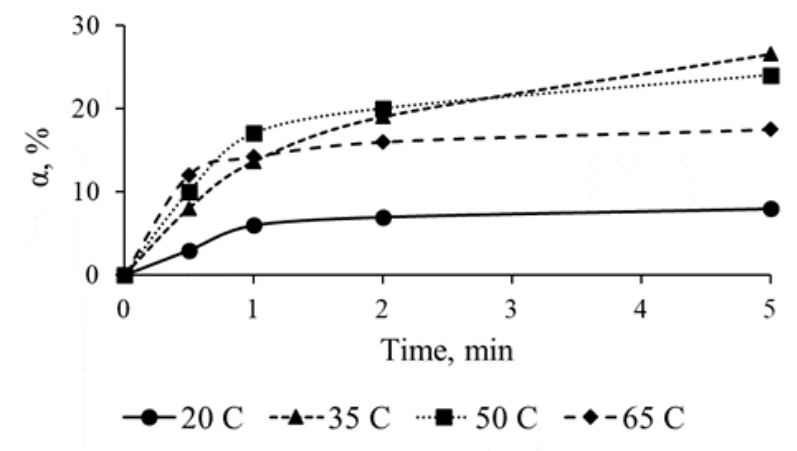


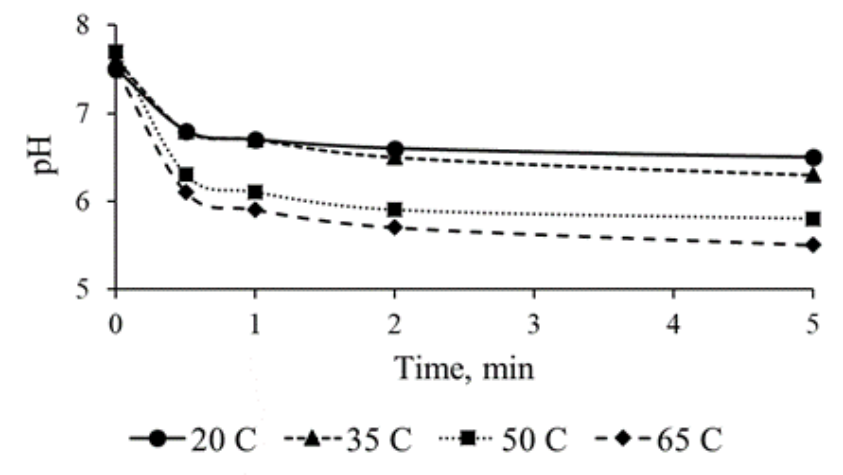
pH: 1 – without NH_4^+; CNH_4^+ (mg/L): 2 – 3.8; 3 – 4.8; 4 − 9.1
Eh: 1′ – without NH_4^+; CNH_4^+ (mg/L): 2′ – 3.8; 3′ – 4.8; 4′ − 9.1

Figure 2 Dependence of pH and Eh of the reaction medium on the reaction time of the oxidation of iron (II) ions

Oxidation of iron (II) ions in distilled water





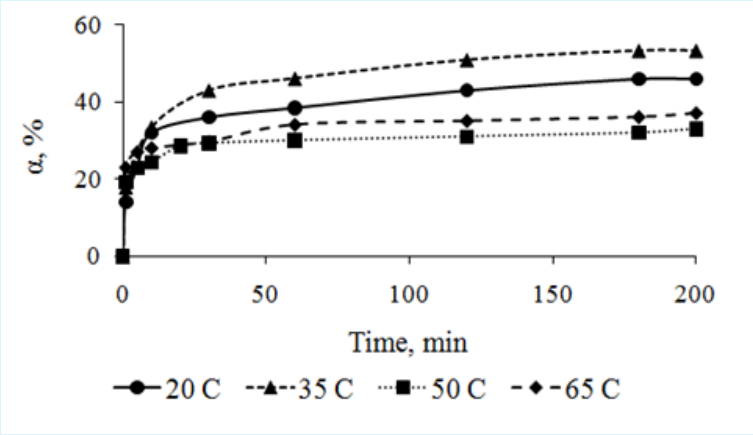


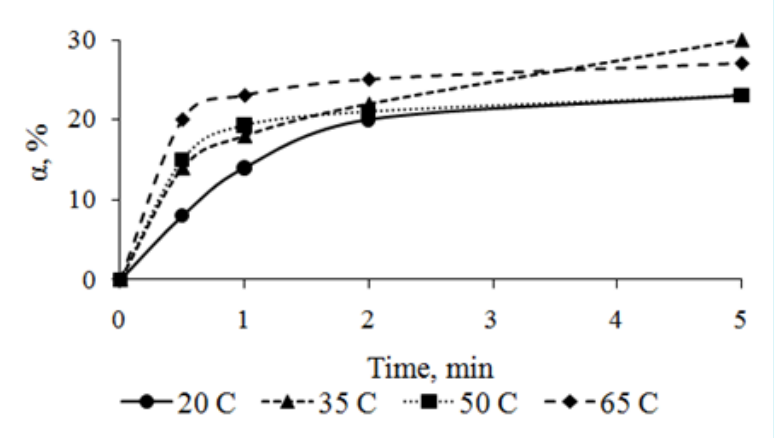
t, ^{0}C	1/T, K^{-1}	$k_{эф}$, c^{-1}	ln $k_{эф}$
20	0,0034	0,0010	-6,9078
35	0,0032	0,0024	-6,0323
50	0,0031	0,0035	-5,6550
65	0,0030	0,0043	-5,4491

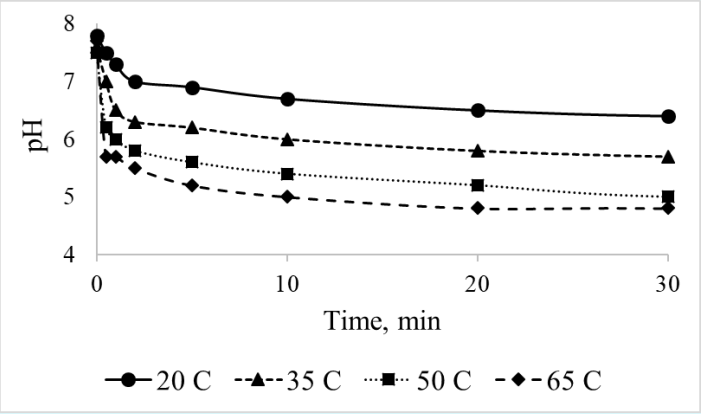
For the first stage ($\tau < 60$ s)

E_a = 27 kJ/moL

Oxidation of iron (II) ions in distilled water with NH_4^+





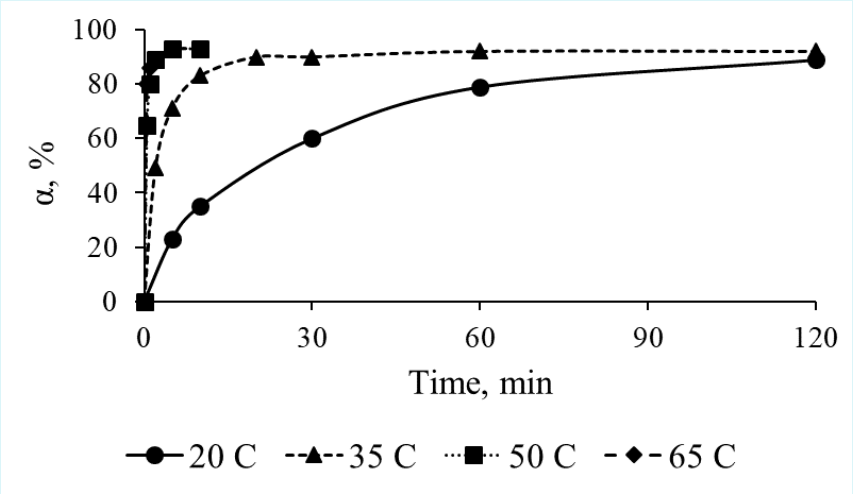


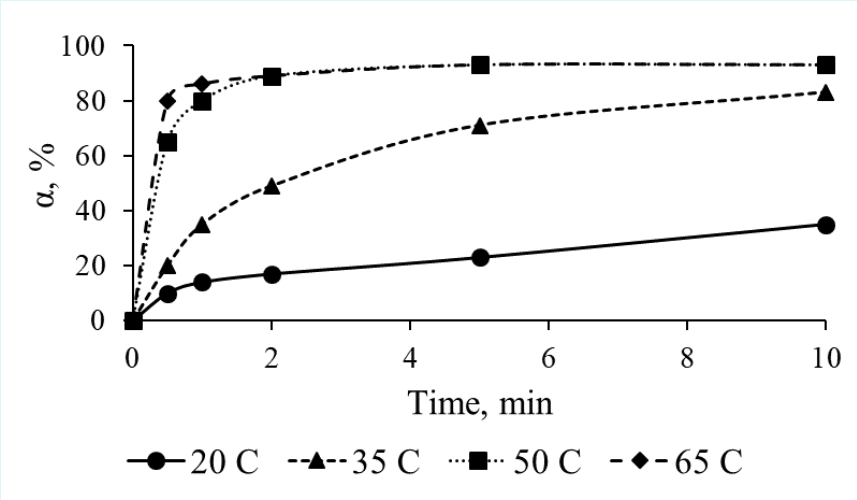
t, ^{0}C	1/T, K^{-1}	$k_{эф}$, c^{-1}	ln $k_{эф}$
20	0,0034	0,0025	-5,9915
35	0,0032	0,0033	-5,7138
50	0,0031	0,0036	-5,6268
65	0,0030	0,0043	-5,4491

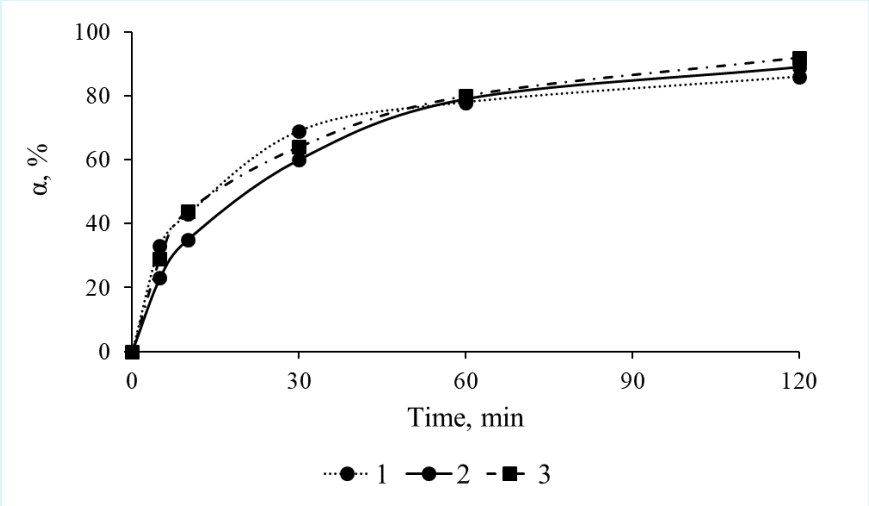
For the first stage ($\tau < 200$ s)

E_a = 10 kJ/moL

Oxidation of iron (II) ions in distilled water with hardness salts







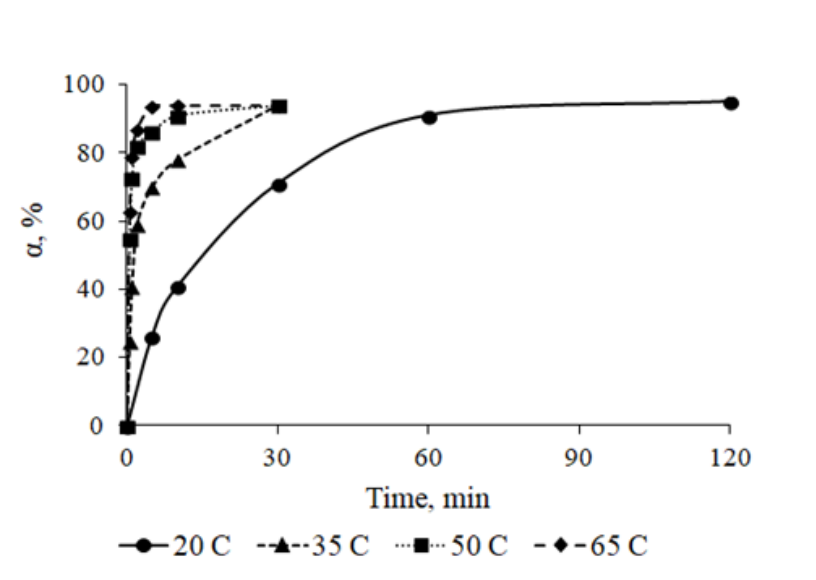
Hardness (^{0}H): 1 – 4.0; 2 – 9.0; 3 – 11.0

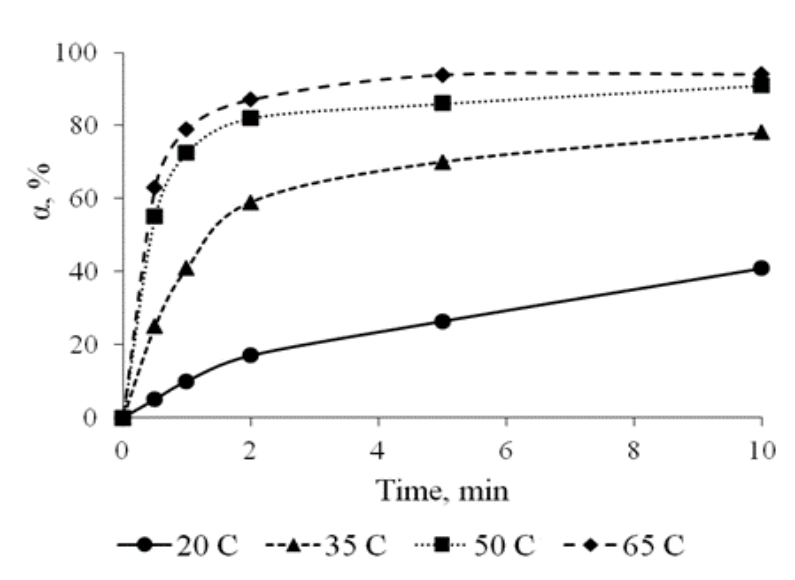
t, ^{0}C	1/T, K^{-1}	$k_{эф}$, c^{-1}	ln $k_{эф}$
20	0,0034	0,0025	-5,9915
35	0,0032	0,0072	-4,9337
50	0,0031	0,0201	-3,9070
65	0,0030	0,0328	-3,4173

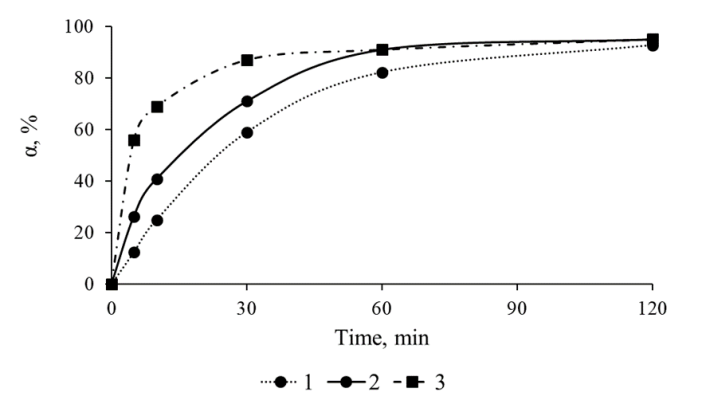
For the first stage ($\tau < 120$ s)

Ea = 47 kJ/moL

Oxidation of iron (II) ions in distilled water with organic substances







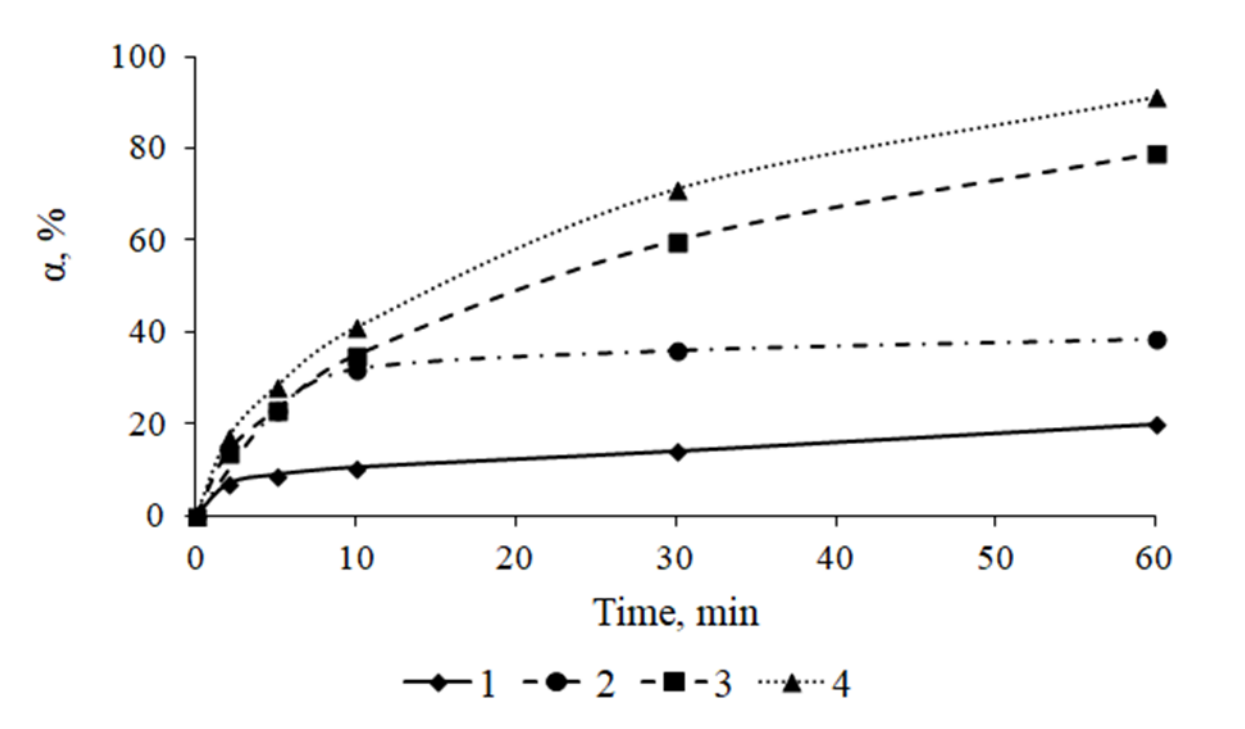
t, ^{0}C	1/T, K^{-1}	$k_{эф}$, c^{-1}	ln $k_{эф}$
20	0,0034	0,0018	-6,3200
35	0,0032	0,0092	-4,6885
50	0,0031	0,0241	-3,7255
65	0,0030	0,0296	-3,5200

For the first stage ($\tau < 120$ s)

Ea = 50 kJ/moL

Organic substances (mgO/L): 1 – 3.4; 2 – 6.7; 3 – 13.4

Influence of several factors on the iron (II) ions oxidation rate



1 – H_2O; 2 – NH_4^+ (4.8 mg/L); 3 – Hardness (9.0 ^0H); 4 – Organic substances (6.7mg/L)

Oxidation process

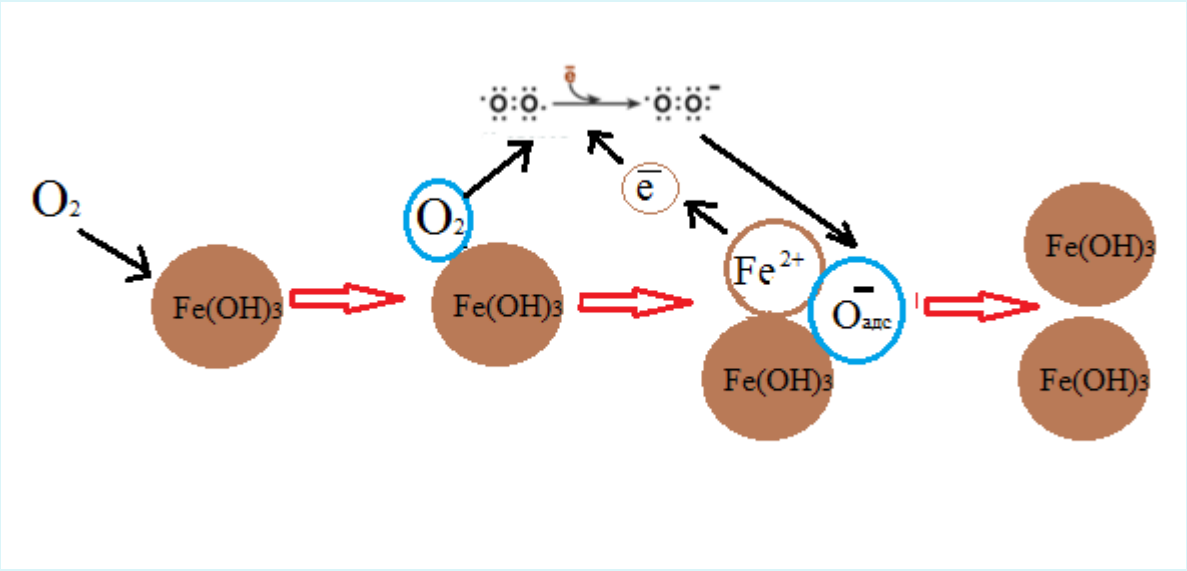
Stage 1 (up to 5 minutes): hydrolysis of iron (II) ions:

$$Fe^{2+} + H_2O = Fe(OH)^+ + H^+$$

$$Fe(OH)^+ + H_2O = Fe(OH)_2 + H^+$$

Stage 2 (5 to 120 minutes)

$$2Fe(OH)_2 + ½\ O_{2(g)} + H_2O = 2Fe(OH)_3.$$



Summary

1. The oxidation rate of iron (II) ions is primarily determined by the pH value. The oxidation rate decreases with decreasing pH. The oxidation process does not occur at pH less than 6.
2. The content of ammonium ions in water at the beginning of the process (up to 5 minutes) reduces the rate of pH change. As a result, the degree of conversion of iron (II) ions in the first stage increases.
3. The rate of oxidation of iron (II) ions is determined by the temperature at pH in the range from 7.1 to 7.7.
4. The presence of hardness salts practically does not affect the rate of oxidation of iron (II) ions.
5. The presence of organic substances (sodium humate) increases the rate of oxidation of iron (II) ions, which is associated with an increase in the pH of the solution.
6. The process of oxidation of iron (II) ions in distilled water in the presence of ammonium ions and without ammonium ions occurs in the diffusion region. The speed is determined by the development of the interface. The limiting stage is the mass transfer between phases.
7. The process of oxidation of iron (II) ions in water in the presence of hardness salts or organic substances at an unchanged pH occurs in the kinetic region. The speed increases with increasing temperature. The limiting stage is the chemical reaction.

Thank you for your attention