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REPORT

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Highly effective technology of iodine production from hydrothermal mineralized natural brines

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EXECUTIVE SUMMARY

The present annual report covers the period of January 1, 1998 – December 31, 1999 During this period, the following stages of the project were carried out

a) The purchase of suitable software for the investigation of the kinetics of iodide oxidation

b) A spectrophotometric method for the determination of various iodine compound concentrations in mineralized waters was improved

c) The equilibrium and kinetics of iodide oxidation was studied at 25°C as a function of the following parameters

oxidant/iodide molal ratio (0 5 – 1 7),

molality of chloride (1 0 – 5 28 mol/1000 kg H_2O),

initial concentration of iodide (0 0002 – 0 0006 M),

concentrations of oxidazible impurities Br (0 003 – 0 006 M), H_2S (2 – 10 mg/l), Fe^{2+} and Fe^{3+} (14 mg/l), naphthenic acid (50-100 mg/l) for solutions with average mineralization (2 84 mol Cl /1000 kg H_2O) and iodide concentration 0 0004 M

d) A method for calculating the main kinetics parameters (order and rate constant) for stoichiometric ratio of oxidant/iodide was developed

e) The algorithms of the solution for kinetic problems in the first approximation have been developed the direct algorithm (a calculation of reagent concentrations and reaction product concentrations vs time by using known kinetic parameters) and the reverse algorithm (estimation of kinetic parameters by implementing experimental data)

RESEARCH OBJECTIVES

A Introduction

The process of iodide oxidation proceeds through a number of several fast, consecutive-concurrent reactions (Ksenzenko and Stasinevich, 1995) of oxidation, complexation and hydrolysis The system in the equilibrium contains the initial and final substances (I , Cl_2, Cl , I_2,) side-by-side with intermediate compounds (I_2Cl , I_3 , ICl, ICl_2 , IOH, IO , IO_3 , etc) The composition of an equilibrium system depends on the composition of the initial brine, the oxidant content added, the content of oxidizable impurities, on pH and temperature We have recently proposed (Kazantseva et al , 1998) several hypotheses that allowed us to estimate the mechanism of

iodide oxidation by chlorine in mineralized solutions depending on various factors A system that was formed in chloride brines due to iodide oxidation, contains too many components absorbing light at close wavelengths in order to determine the concentrations of all existing substances in a solution by a spectrophotometric analysis Taking into consideration the industrial aspects of the current project, we simplified a system in order to estimate the contents of the main iodine compounds with maximal trustworthiness

Accordingly, with the acceptable conditions of iodide production, the pH≤3 values should be kept for high iodine yielding A preliminary study showed that the hydrolysis of iodine in mineralized solutions was suppressed under these conditions HOI, which is the most significant intermediate in the iodine and iodine monochloride hydrolysis, becomes protonated around pH=2 (Lengyel et al , 1996) The formation of oxygen containing iodine compounds was not observed during iodide oxidation in a natural brine with chloride concentration of 3 5 mol/l and pH=3 (Ernepesova et al , 1988 and Ernepesova, 1990) In order to completely suppress iodide hydrolysis in solutions with chloride concentrations of 0 1-1 0 mol/l, it is enough to keep pH around 1 (Margerum et al , 1986) The hydrolysis path was not observed in the study of ICl_2 reaction with I in solutions containing chloride concentrations of 0 1-1 0 M for pH that equaled either 0 or 1 In solutions with higher chloride concentrations, the iodide hydrolysis has to be suppressed at a lesser solution acidity Therefore, we assume that at conditions close to industrial ones, the first mechanism that excludes the formation of oxygen containing iodide compounds at pH<2 is the main mechanism

In accordance with the third mechanism, at pH >2 the hydrolytic reactions of iodine and chlorine occur, and oxygen-containing compounds are formed The mechanism of iodine hydrolysis in salt free solutions was studied in detail by Palmer and Lietzke (1982), Deane and Marsh (1985) and Wang et al (1989) Since the values of molar extinction coefficients for oxygen containing iodine compounds are significantly smaller than those for halogen containing compounds (Kazantseva et al , 1998, Table 4), it is impossible to determine the concentrations of iodine hydrolysis products HIO и IO in solutions with high chloride content Therefore, the possibility to study a system by the third mechanism using spectrophotometry was not found

Iodine monochloride easily forms dichloroiodate ICl_2, which is very stable in solutions with chloride concentrations of 0 5 M or larger (Cazon and Neumann, 1961) Therefore, amount of monochloride existing in the studied solution is negligible In industrial processes of iodine production, the oxidant excess does not exceed 1 5-1 7 comparatively to stoichiometric amount Cazon and Neumann (1961) found that four times the excess of oxidant is necessary for ICl_4

formation Therefore, we assume that at given conditions the ICl_4 concentrations are negligible Taking into consideration all the above-mentioned, it is necessary for studying the equilibrium and kinetics of iodide oxidation in natural brines and for determination of the optimal technological regime, to determine the influence of various factors on the formation of the following compounds I (initial compound and suboxided iodine form), I_3 (suboxided iodine form), I_2 and I_2Cl (target iodine forms) and ICl_2 (peroxided iodine form) The proposed mechanism of iodide oxidation is described by the following reactions

$$I^- + Cl_2 \Leftrightarrow ICl_2^- \quad (1)$$

$$ICl_2^- \Leftrightarrow ICl + Cl^- \quad (2)$$

$$ICl + I^- \Leftrightarrow I_2Cl^- \quad (3)$$

$$I_2Cl^- \Leftrightarrow I_2 + Cl^- \quad (4)$$

$$I_2 + I^- \Leftrightarrow I_3^- \quad (5)$$

$$I_2Cl^- + Cl^- \Leftrightarrow ICl_2^- + I^- \quad (6)$$

This set of reactions is usually used for the description of the iodide oxidation by various oxidants It was found that iodine monochloride is an essential intermediate compound (Beck and Rabai, 1986, Kumar et al , 1986 and Nagy et al , 1988) at iodide oxidation by various chlorine containing compounds Contributions of high H^+ and Cl concentrations give ICl_2 as the predominant species in solution (Margerum et al, 1986) The reactions with the formation of chloride and iodine compounds in solutions with ionic strength less than 1 0 were studied by the pulsed-accelerated-flow method (Kumar et al , 1986, Margerum et al, 1986 and Nagy et al , 1988) Experimental studies devoted to iodide oxidation by chlorine in solutions with large chloride concentrations are not numerous (Abrosimova et al , 1976, Ernepesova et al , 1988) The equilibrium constants and rate constants for major reactions presented above are summarized in Table 1

Table 1 The equilibrium and rate constants for iodine compounds at 25°C

Reaction [a]	Equilibrium constants	Rate constants	Literature source
$ICl_2^- \xrightarrow{k_2}$ $\xleftarrow[k_{-2}]{} ICl + Cl^-$	K_2=0 0060 M* K_2=0 013 M ***	k_2>>6 6 10^4 s ** 10^8 $M^{-1}s^{-1}$<k_2<6 10^9 $M^{-1}s^{-1}$ (diffusion limit) **	* Cazon and Neumann, 1961 ** Margerum et al , 1986 *** Wang et al , 1989
$ICl + I^- \xrightarrow{k_3}$ $\xleftarrow[k_{-3}]{} I_2Cl^-$	K_3=7 3 10^8 M^{-1}*	k_3=1 1 10^9 $M^{-1}s^{-1}$ * k_{-3}=1 5 s^{-1} * k_3=5 1 10^8 M^{-1} s^{-1} **	* Margerum et al , 1986 ** Wang et al , 1989

		k_{-3}=0 7 s^{-1} **	
$I_2Cl^- \xrightarrow{k_4} \xleftarrow[k_{-4}]{} I_2 + Cl^-$	K_4=0 60 M	k_4=5 10^4 s^{-1}	Margerum et al , 1986
$I_2 + I^- \xrightarrow{k_5} \xleftarrow[k_{-5}]{} I_3^-$	K_5=748 M^{-1} $^{\$}$ K_5=710 M^{-1} $^{\$\$}$	k_5=6 2 10^9 M^{-1} s^{-1} * k_{-5}=7 5 10^6 s^{-1} * k_5=5 6 10^9 M^{-1} s^{-1} ** k_{-5}=7 5 10^6 s^{-1} **	$^{\$}$Ramette & Sandford, 1965, $^{\$\$}$Ksenzenko & Stasinevich, 1995, * Turner et al , 1972 ** Ruasse et al , 1986
$I_2 + Cl^- \xrightarrow{k_6} \xleftarrow[k_{-6}]{} I_2Cl^-$	K_6=1 7 M^{-1} * K_6=1 66 M^{-1} **		* Cazon & Neumann, 1961 ** Ksenzenko & Stasinevich, 1995
$I_2Cl^- + Cl^- \xrightarrow{k_7} \xleftarrow[k_{-7}]{} ICl_2^- + I^-$	K_7=1 12 10^7 K_7=6 9 10^8		Ernepesova et al , 1988

[a] There is no kinetics data for reaction #1 in literature

The rate constants show that the above reactions are extremely fast, so that they cannot be studied by either stopped-flow or relaxation methods Since our equipment allows studying reactions starting with 0 1 s, it was impossible for us to investigate a separate reaction and to determine its kinetics parameters The purpose of the current stage of our project was to determine the mechanism of oxidation processes in solutions with large chloride contents, the optimal conditions of oxidation processes and the calculation of total rate constants depending on process parameters (solution composition, oxidant amount and temperature)

B Experimental section

B1 Reagents

Chlorides of sodium, calcium and magnesium, and potassium iodide of analytical grade have been used to prepare model solutions resembling the underground natural brines of Turkmenistan A basic solution has been prepared with the largest chloride concentration amongst the natural studied brines with the following ionic concentrations (mol (kg $H_2O)^{-1}$) m_{Ca2+}=0 5498, m_{Mg2+}=0 0921, m_{Na+}=4 6462, m_{HCO3} =0 0007, m_{SO42} =0 0013, m_{Cl} =5 9269, I_m=6 5734 (Kazantseva et al , 1998, brine #13, Table 3) Less concentrated solutions were prepared by diluting the basic solution with distilled water 0 1M solution of KI was prepared using a standard KI solution and was used as a basic solution for the preparation of solutions containing iodide ions by their dilution

to the required concentrations with a saline solution Chlorine water used for iodide oxidation was obtained by passing gaseous chlorine through cooled distilled water Gaseous chlorine was obtained by a reaction between HCl and $KMnO_4$ The prepared chlorine water was kept in a refrigerator and its concentration was determined with iodometric titration directly before each oxidation experiment The measured volume of a standard solution of I_2+KI was added to an aliquot of the chlorine water, and the excess of iodine was determined by volumetric titration with 0 01 M $Na_2S_2O_3$ using starch solution as an indicator

The preparation of natural solutions with oxidizable compounds was carried out as follows

a) 0 1M solution of KBr was prepared using a standard KBr solution and was used as a basic solution for the preparation of solutions containing bromide ion by their dilution to the required concentrations with a saline solution,

b) H_2S solutions were prepared by the following procedure a calculated amount of Na_2S was added to a mineralized solution After adding acid to the solution up to pH=2, the formation of H_2S took place H_2S content in the solutions was determined by adding an excess of I_2 + KI solution with a known concentration to a sample and then by back titration with 0 1M $Na_2S_2O_3$ (Reznikov et al , 1963)

c) Solutions containing 1 g Fe^{2+} and Fe^{3+} per liter have been prepared using $FeSO_4$ and $FeCl_3$ of analytical grade, respectively, and were used as basic solutions for the preparation of solutions containing ferric ions by their dilution to required concentrations with a saline solution Fe^{2+} concentration was determined by colorimetric analysis with using 1,10-fenantroline (Lurie and Rybnikov, 1974) Fe^{3+} concentration was determined by complexonometry analysis with sulphosalicyl acid as an indicator (Reznikov et al , 1963)

Modeling the composition of natural brine of Cheleken oil field (Nijazov, 1962) was attempted using low molecular fractions of natural naphthenic acids obtained from Turkmenistan oil However, the introduction of such acids in a mineralized solution leads to the formation of a colloidal cloudy solution that cannot be subjected to spectral analysis Therefore, we used sodium salt of cyclohexanecarbonic acid $C_6H_{11}COONa$ instead of naphthenic acid for the preparation of model solutions 1 g/l solution of $C_6H_{11}COONa$ was prepared and used as a basic solution for preparing solutions containing naphthenic acid by their dilution to the required concentrations with a saline solution The above naphthenic acids were supplied by Prof A Nijazov (Head of the Laboratory of Organic Synthesis at the Institute of Chemistry)

During the kinetic experiments, solutions containing iodide and chlorine water were mixed in a mixing cell In order to prevent changes in the solution composition (undergoing mixing during

kinetic experiments) the mixed iodide containing solution and chlorine water had the identical ionic matrix and pH values

B2 Spectrophotometric Measurements

UV/visible measurements were conducted with a Hewlett Packard diode array spectrophotometer (8453 UV-Visible Spectrophotometer) interfaced with a HP Vectra XA 5/133 computer All scans were performed at 25±1°C Spectral data were obtained from 200 to 600 nm for all compounds In all UV/visible region, slit width of the instrument has a default set of 2 nm To compensate for absorbency of chloride and other active optical compounds, solutions having the same composition with the exception of iodine compounds, were measured as blank solutions

B3 Kinetic measurements

Kinetic measurements were carried out using a SFA-20 Rapid Kinetics Stopped-Flow Accessory of Hi-Tech Scientific combined with a spectrophotometer This model comprises a drive unit, a constant temperature supply tube and an observation cell with an integral mixer Solution reservoirs, drive syringes, a mixing cell and solutions used for kinetic experiments were kept at 25±1°C The dead-time of the stopped-flow apparatus was approximately 20 ms, and the minimum collection time of spectrophotometer was 0 1 s The time required for thorough mixing of the solutions entering in a mixing cell was determined by the change of absorbency at 225 nm while mixing the solutions with or without iodide The time for mineralized solutions was found less than 0 1 sec Every reaction was measured at wavelengths of 225, 248, 350 and 474 nm Three to seven replicate runs were conducted in order to obtain concentrations of the main iodine compounds and the experimental rate constant was calculated with high precision

B4 Spectrophotometric procedure for kinetic studies of iodide oxidation

In order to calculate concentrations of the main iodine compounds I , I_3 , I_2+I_2Cl , ICl_2, the spectra of the reaction mixtures were analyzed by a method developed especially for such brines (Kazantseva et al , 1998) During kinetic calculations, it was concluded that the use of the average extinction coefficient of SumI_2 at a wavelength 350 nm accepted by us earlier (Kazantseva et al , 1998), resulted in considerable errors Therefore, this extinction coefficient was recalculated taking into account the influence of the chloride concentration On the basis of the absorbance spectra of solutions with a constant iodine concentration and variable chloride

concentrations (Kazantseva et al, 1998, chapter B3b) the dependence of the extinction coefficient ε(SumI_2 350) on the chloride molality m_{Cl^-} has been estimated as

$$\varepsilon(\text{Sum}I_2\ 350)=180\ 2+0\ 63\ (m_{Cl^-})^3 \quad (7)$$

The value of the extinction coefficient of I_3 was checked once more at a wavelength of 350 nm At the studied I_3 concentration range (1 5 10 ^{6}-2 5 10 ^{4}) the value of ε(I_3 350) was found to be equal to 25,000 These findings coincide with literature data from Palmer et al (1984) The concentration of I_2Cl was calculated with the use of values of optical density at a wavelength of 248 nm and the extinction coefficient ε(I_2Cl, 248) equal to 39,600 (Abrosimova et al, 1976) The spectral parameters obtained (Table 2) have been used to improve the calculations of iodine compound concentrations at their common presence

Table 2 The main spectral characteristics needed for calculating concentrations of iodine compounds

Iodine compound	Analytical band length, nm	Error of absorption measuring, %	Extinction coefficient, $dm^3\ mol^{-1}\ cm^{1}$
Γ	225	0 20	12,875±30
	248	5 42	1,012–66 1 m_{Cl^-}
SumI_2	225	2 17	8,400+4,276 log m_{Cl^-}
	248	0 36	20,923+14,255 log m_{Cl^-}
	350	3 12	180 2+0 63 $(m_{Cl^-})^3$
	474	1 35	610 2±19 4
ICl_2	225	0 21	47,100±360
	248	0 40	7,040±274
	350	2 82	217 6±6 0
	474	15 83	10 3±3 1
I_3	350	0 62	25,000±400

B4a An improved algorithm for calculating iodide compound concentrations

1 Calculation of extinction coefficients dependence on m_{Cl^-}
ε(SumI_2 225), ε(SumI_2 248), ε(SumI_2 350), ε(I 248)

2 Calculation of SumI_2 concentrations for absorption in 474 nm {A(474)}, where A is the absorption at a wavelength given in brackets
(SumI_2 474)=A(474)/ε(SumI_2 474) lv
where lv=1 cm is the path length in visible region,
ε(SumI_2 474)=610 2

3 Light absorption calculation of SumI_2 in 225, 248 and 350 nm
A(SumI_2 225)=(SumI_2 225) ε(SumI_2 225) lu
A(SumI_2 248)=(SumI_2 248) ε(SumI_2 248) lu,
A(SumI_2 350)=(SumI_2 350) ε(SumI_2 350) lu,

where lu is the path length in ultraviolet region
where lu=0 2 cm

4 Calculation of difference of light absorption at wavelengths of 225, 248 and 350 nm and that of $SumI_2$ at the same wavelengths

$\Delta A(225)=A(225)-A(SumI_2\ 225)$

$\Delta A(248)=A(248)-A(SumI_2\ 248)$

$\Delta A(350)=A(350)-A(SumI_2\ 350)$

5 Selection of a calculation path

Calculation of $K1=\Delta A(225)/\Delta A(350)$

If K1<20 then go to steps 6–11,17 (either deficiency of the oxidant or the stoichiometric amount of the oxidant),

If K1>20 then go to steps 12–17 (excess of oxidant compared to stoichiometric amount of oxidant)

6 Calculation of concentration of I_3

$I_3 = \Delta A(350)/(\varepsilon(I_3\ 350)\ lv)$

$\varepsilon(I_3\ 350)=25{,}000$

7 Calculation of residual concentration of I

$I_R=\Delta A(225)/(\varepsilon(I\ 225)\ lu)$

$\varepsilon(I\ 225)=12{,}875$

8 Calculation of absorbance of I at 248 nm

$A(I_R, 248)=I_R\ \varepsilon(I\ 248)\ lv$

9 Calculation of concentration of I_2Cl

$A(I_2Cl, 248)=A(248)-A(I_R, 248)$

$I_2Cl=A(I_2Cl, 248)/(\varepsilon(I_2Cl, 248)\ lu)$,

$\varepsilon(I_2Cl, 248)=39{,}600$

10 Calculation of concentration of I_2

$I_2=Sum\ I_2 - I_2Cl$

11 Mass balance

$Sum1=2\ SumI_2+I_R+3\ I_3$ (recalculated in moles of I)

12 Calculation of concentration of ICl_2

$ICl_2 = \Delta A(225)/\varepsilon(ICl_2\ 225)\ lu$

$\varepsilon(ICl_2\ 225)=47{,}100$

13 Calculation of absorbance of ICl_2 in 248 nm

$A(ICl_2^-, 248)=ICl_2^-\ (\varepsilon ICl_2^-, 248)\ lu)$,

$\varepsilon\ (ICl_2^-, 248)=7{,}040$

14 Calculation of concentration of I_2Cl

$A(I_2Cl, 248)= A(248)-A(ICl_2, 248)$

$I_2Cl=A(I_2Cl, 248)/(\varepsilon(I_2Cl, 248)\ lu)$,

$\varepsilon(I_2Cl, 248)=39{,}600$

15 Calculation of concentration of I_2

$I_2 = Sum\ I_2 - I_2Cl$

16 Mass balance

$Sum2=2\ SumI_2+ ICl_2$ (recalculated in moles of I)

17 Error calculation, %

$error=(I_{init}-Sum)\ 100/I_{init}$, where I_{init} is the initial concentration of iodide

B4b Precision of measurement and calculation procedures

The precision for the experimental determination of absorption was determined by conducting several parallel measurements (n=3–7, Table 2) The largest mistakes observed were due to the absorption of ICl_2 at 474 nm (15 8%) and I at 248 nm (5 42%) However, these values were not significant for our calculations The extinction coefficient of ICl_2 at 474 nm is negligible compared to that of $SumI_2$ at the same wavelength and therefore was ignored in our calculations The extinction coefficient of I at 248 nm is used for the calculation of I_2Cl concentration, which does not play significant role in the current study The total precision of the developed method for the calculation of iodide compounds in solutions with oxidant excess (Cl_2/2I molal ratio < 2) was less than 5 2% Such a precision is considered as quite acceptable while conducting kinetic studies even in solutions containing the only iodide compound ICl_2 (Wang et al , 1989) In technological processes of iodine production, the Cl_2/2I molal ratio is kept less than 1 7 in order to obtain high outputs of a target product Therefore, the method developed is acceptable for studying the problem in the current project

B5 Examples of concentration calculations of various iodine compounds

The developed method was checked out on solutions with various chloride concentrations and additions of microcomponents of natural solutions Favorable results with rare exceptions (as listed below) were observed (Table 3)

1 Solutions containing H_2S Hydrogen sulfide is oxidized simultaneously with iodide Therefore, its addition into initial solution used as a blank cannot compensate its contribution in the total spectra and distorts the results obtained
2 Solutions with mineralization higher than 5 0 mol Cl /kg H_2O The error of concentration determination in these types solutions exceed 6% of that determined by the existence of small concentrations of I and ICl_2 simultaneously in a solution These two compounds have similar spectrums in ultraviolet range Since I does not absorb light in visible range, we tried to calculate ICl_2 concentrations using the difference between absorption at 350 nm and that of $SumI_2$ However, the error of these calculations considerably exceeded both relative errors of determination for concentrations of other compounds and possible ICl_2 concentrations Therefore, it was recommended to use only the changes of concentrations comprising total iodide content in order to study the regularity of iodide oxidation in brines with chloride concentrations larger than 5 mol/kg H_2O

Table 3 Calculated concentrations of iodine compounds in solutions with various compositions at different ratios of iodide and chlorine

Example	Molal ratio, $Cl_2/2I$	Concentration, mol/l 10^4				Sum I, mol I	Error, %
		I	Sum I_2	I_3	ICl_2		
Example 1	0 44	1 907	1 018	0 006	0	4 12	0 9
4 088 10^{-4} mol I /l,	0 99	0 220	2 047	0	0	4 29	4 8
1 0 m Cl , pH = 1	1 09	0	1 850	0	0 365	4 06	0 6
	1 53	0	1 586	0	0 797	3 969	2 9
	1 97	0	1 053	0	1 246	3 35	10 1
Example 2	0 5	1 691	1 007	0 034	0	3 81	4 8
$[I]_{init}$ =4 000 10^{-4} mol/l,	1 0	0 100	1 915	0 002	0	3 94	1 7
3 28 m Cl , pH = 1	1 2	0	1 954	0	0 230	4 14	3 5
	2 0	0	0 490	0	2 486	3 47	13 4
Example 3	0 5	1 680	0 991	0 012	0	3 90	2 5
$[I]_{init}$ =4 030 10^{-4} mol/l,	0 9	0 366	1 730	0 002	0	3 83	4 3
4 68 m Cl , pH = 1	1 05	0 187	1 830	0 001	0	3 85	3 8
	1 2	0	1 930	0	0 053	3 91	1 9
	1 6	0	1 440	0	1 250	4 13	3 2
Example 4	0 5	2 476	0 777	0 024	0	4 10	0 1
$[I]_{init}$ =4 100 10^{-4} mol/l,	1 0	0 327	1 825	0 009	0	4 01	2 4
2 84 m Cl , pH = 1	1 3	0 071	1 968	0 001	0	4 01	2 4
3 0 10^{-3} mol Br /l	1 6	0	2 027	0	0 014	4 07	0 9
	2 0	0	1 472	0	1 143	4 09	0 4
Example 5	0 5	1 408	1 292	0	0	3 992	2 2
$[I]_{init}$ =4 080 10^{-4} mol/l,	1 0	0	2 006	0	0 110	4 122	1 0
2 84 m Cl , pH = 1	1 4	0	1 482	0	1 058	4 022	1 4
14 mg Fe^{2+}/l	1 6	0	1 291	0	1 357	3 939	3 5
Example 6	0 5	1 665	1 183	0 017	0	4 08	2 0
$[I^-]_{init}$ =4 000 10^{-4} mol/l,	1 0	0	1 954	0	0 114	4 023	0 6
2 84 m Cl , pH = 1	1 3	0	1 480	0	1 256	4 151	3 9
50 mg/l organic acid	1 6	0	0 924	0	2 364	4 212	5 3
Example 7	1 0	3 434	0 287	0 010	0	4 037	1 1
$[I]_{init}$ =4 080 10^{-4} mol/l,	2 0	1 882	0 952	0 018	0	3 839	5 1
2 84 m Cl , pH = 1	3 0	0 929	1 388	0 013	0	3 031	8 2
2 mg H_2S/l							

C Results and discussion

C1 Mechanism of iodide oxidation in highly mineralized chloride solutions

Investigation of iodide oxidation by chlorine in artificial salt solution (i e without the addition of oxidizable substances) at 25°C shows that the mechanism of the process is controlled by the oxidant/iodide molal ratio and by a degree of mineralization of the solution The typical spectrums, which demonstrate the composition changes of the iodide containing solution with

time changes while introducing the oxidant are presented in Fig 1 (oxidant/iodide stoichiometric ratio) Fig 2 (deficiency of oxidant) and Fig 3 (excess of oxidant)

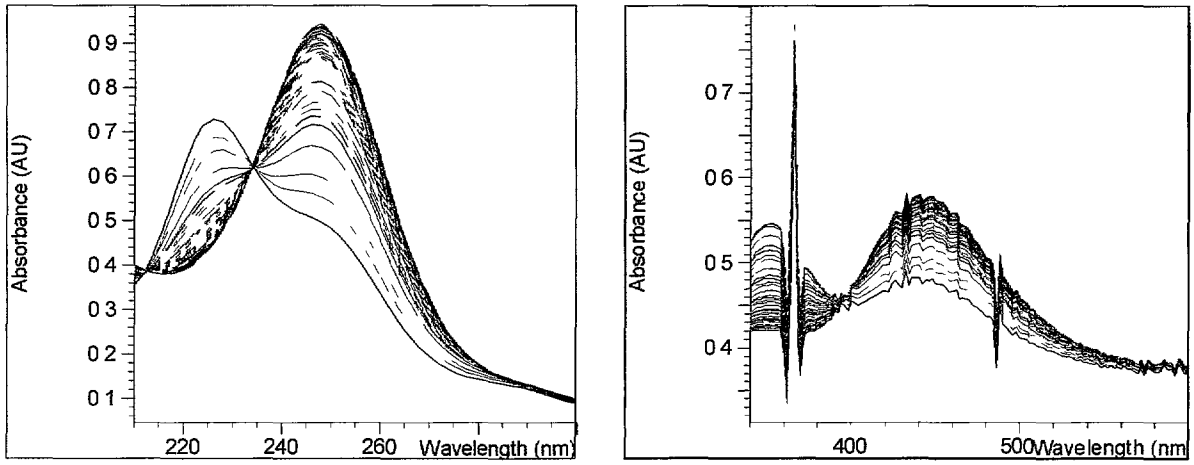

Fig 1 Absorption spectra at temperature of 25°C for a solution with I initial concentration of 0 0004 M, chloride molality of 1 0, Cl_2/2I molal ratio of 1 0, pH=2 and reaction time of 5 second (The black continuous curve corresponds to time 0 1 s, and the lilac interrupted curve corresponds to 4 7 s)

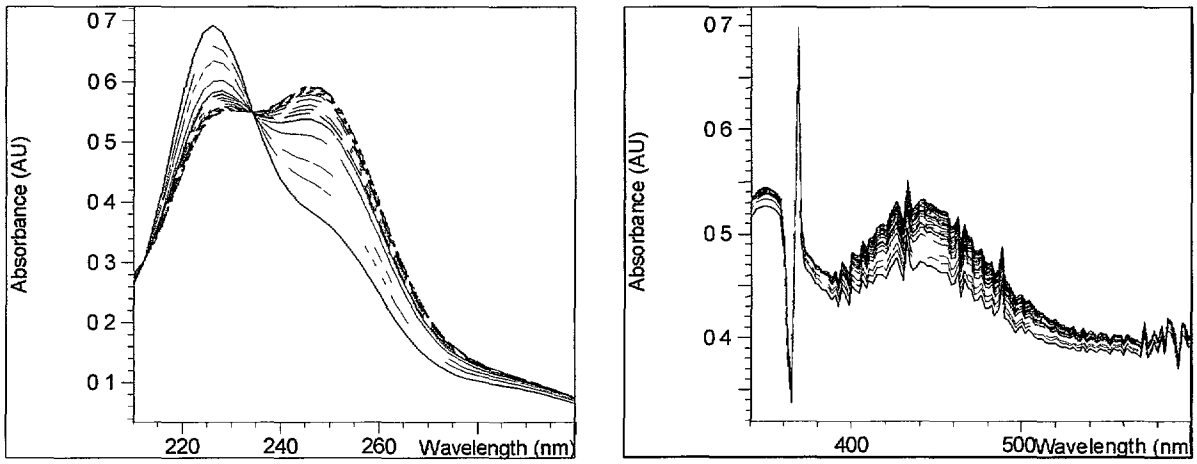

Fig 2 Absorption spectra at temperature of 25°C for a solution with I initial concentration of 0 0004 M, chloride molality of 1 0, Cl_2/2I molal ratio of 0 75, pH=2 and reaction time of 5 second (The black continuous curve corresponds to 0 1 s, and the lilac interrupted curve corresponds to 4 7 s)

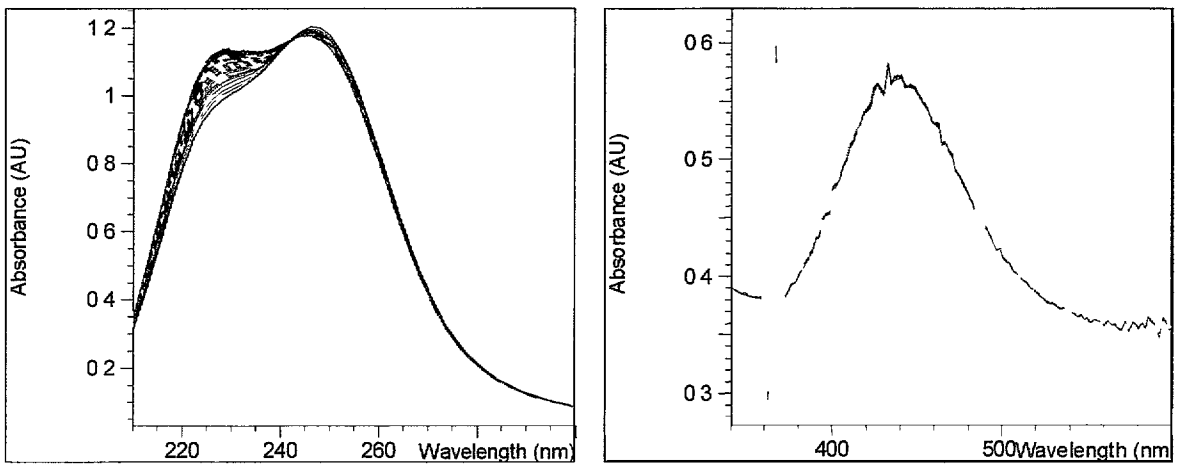

Fig 3 Absorption spectra at temperature of 25°C for solution with I initial concentration of 0 0004 M chloride molality of 2 84, $Cl_2/2I$ molal ratio of 1 7, pH=2 and reaction time of 5 second (The black continuous curve corresponds to 0 1 s, and the green interrupted curve corresponds to 4 8 s)

The calculations based on the spectrum obtained demonstrate that the mechanism of this process is mainly controlled by the amount of the oxidant added At high degrees of iodide oxidation, i e at $Cl_2/2I$ molal ratio is more than stoichiometric one, the reaction rate is large and therefore equilibrium time equals to approximately 0 1 sec and less for all ranges of chloride concentrations (Fig 4) If the oxidant is added in an amount less than its stoichiometric one or close to this value the reaction rate is then small and the reaction system reaches equilibrium much slower (Fig 5-7) In low mineralized brines with a chloride molality of 1 0 mol/ kg H_2O equilibrium time is equal to approximately 5 sec (Fig 5) The rate of increase for iodine concentration under these conditions is approximately proportional to the rate of iodide concentration decrease These facts point out different mechanisms of investigated processes for the oxidant amount less than its stoichiometric one or close to the value, and more than stoichiometric one The change of the reaction mechanism occurs at iodide/oxidant ratio optimal for the formation of iodine

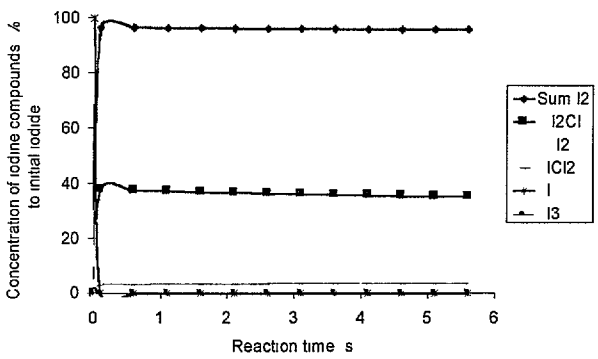

Fig 4 Concentration changes for iodine compounds with time changes at temperature of 25°C for a solution with I initial concentration of 0 0004 M, chloride molality of 1 0, $Cl_2/2I$ molal ratio of 1 25 and pH=2

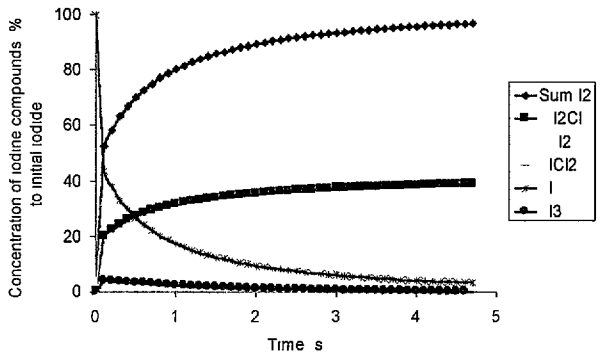

Fig 5 Concentration changes of iodine compounds with time changes at temperature of 25°C for the solution with I initial concentration of 0 0004 M, chloride molality of 1 0, $Cl_2/2I$ molal ratio of 1 0 and pH=2

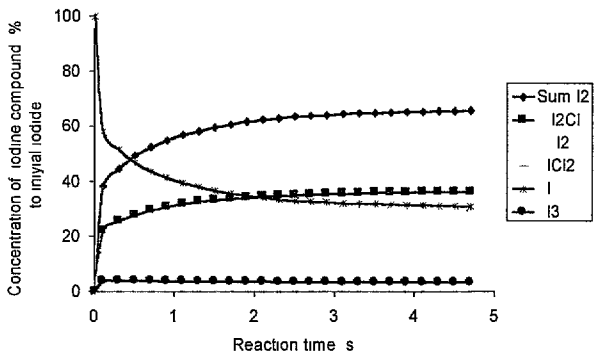

Fig 6 Concentration changes of iodine compounds with time changes at temperature of 25°C for the solution with I initial concentration of 0 0004 M, chloride molality of 1 0, $Cl_2/2I$ molal ratio of 0 75 and pH=2

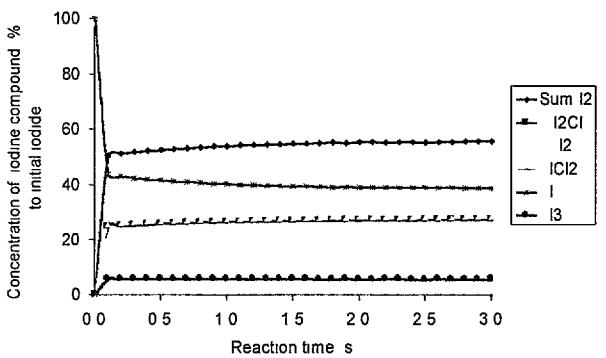

Fig 7 Concentration changes of iodine compounds with time changes at temperature of 25°C for the solution with I initial concentration of 0 0004 M, chloride molality of 1 0, $Cl_2/2I$ molal ratio of 0 6 and pH=2

Under the oxidant excess the formation of I_2, I_2Cl, ICl_2 compounds take place while the existence of I_3 and I was not observed (Fig 4) It is obvious that the process goes according to the reactions (1-4) All these reactions are extremely rapid as can be seen from Table 1 The rate constant for the reaction (1) was not found in literature, although while due to large total rate of the process under these conditions, reaction (1) is not limiting one If the oxidant is added in an amount less than its stoichiometric one or close to this value the formation of I_2 I_2Cl I_3 occurs in the solution and some residual amounts of I exist in the solution (Fig 5-7) Obviously, the process is determined by reactions (1-5) The higher the oxidant amount close to the stoichiometric one the longer the equilibrium time is At time equaling 0 1 s (the minimum experimental time accessible for us to study the kinetics of the process), we observed a

maximum concentration of I_3 and then its concentration decreases This fact is explained by an extremely large equilibrium and rate constants for the reaction of the I_3 formation (Table 1) The formation of I_3 in accord to the reaction (5) at the initial stage of the process (at the excess of I) is preferable than the formation of I_2Cl according to the reaction (6) due to larger values of equilibrium constant of the reaction (5) $K_5 >> K_6$, K_6 = 1 7 M (Cazon and Neumann, 1961) When the system reaches the equilibrium, the I concentration decreases that leads to the destruction of I_3 and the formation of I_2 and I_2Cl occur (k_{-5}=7 5 10^6, Ruasse et al , 1986) The reaction (5) moves directly and reverse very quickly, therefore, this reaction cannot limit the process rate under oxidant deficiency

The other factor that determines oxidation mechanism of iodide is chloride concentration The rate of oxidation grows with the increase of chloride concentration Thus provided that all other parameters of the process are kept constant, the equilibrium time in solutions with oxidant/iodide stoichiometric ratio is reduced from 4-5 s at chloride molality 1 0 mol/kg H_2O (Fig 5) to 1-2 s at chloride molality 2 84 mol/kg H_2O (Fig 8), then to 0 5 s at chloride molality 4 68 mol/kg H_2O (Fig 9) and less then 0 1 s at chloride molality 5 2 mol/kg H_2O The equilibrium time is inversely proportional to chloride molality (Fig 10)

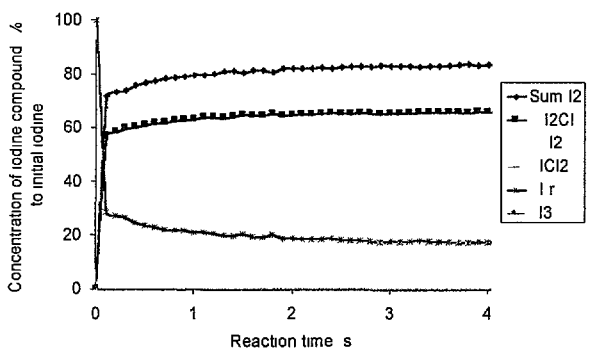

Fig 8 Concentration changes of iodine compounds with time changes at temperature of 25°C for the solution with I initial concentration of 0 0004 M, chloride molality of 2 84, Cl_2/2I molal ratio of 1 0 and pH=2

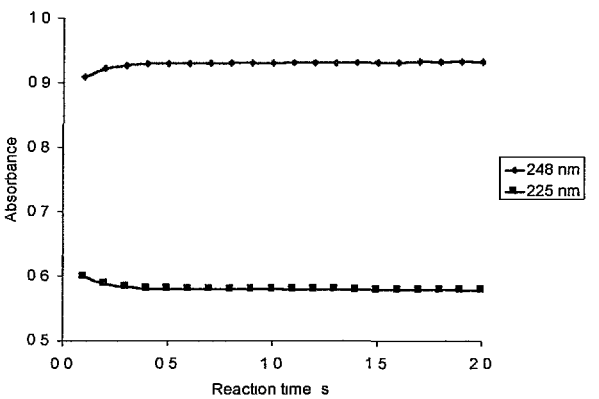

Fig 9 Absorbance time dependence at temperature of 25°C for the solution with I initial concentration of 0 0004 M, chloride molality of 4 68, Cl_2/2I molal ratio of 1 0 and pH=2 {the black curve corresponds to wavelength 225 nm (ICl_2 and I) and the red curve corresponds to wavelength 248 nm (I_2Cl)}

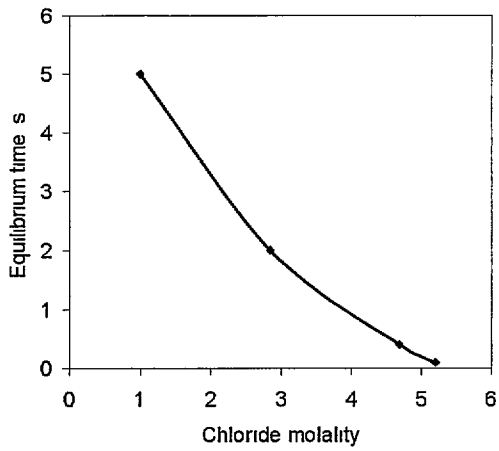

Fig 10 The dependence of equilibrium time at temperature of 25°C with chloride molality for the solutions with I initial concentration of 0 0004 M, $Cl_2/2I$ molal ratio of 1 0 and pH=2

Margerum et al (1986) assumed that chloride ion suppressed the I reaction with ICl much more than it suppressed the I reaction with I_2 due to the fact that $K_3 << K_5$ and ICl reacted 5 6 times slower than I_2 with I (the rate constant k_3 for iodide transfer to ICl is 1 1 10^9 $M^{-1}s^{-1}$, whereas the rate constant k_5 for the reaction iodide with I_2 is 6 2 10^9 $M^{-1}s^{-1}$) In this case, I_3 formation at earlier stages of the process should be observed for brines with any ionic matrix Our results do not support this suggestion We observed that higher chloride concentration is the smaller role of reaction (5) for the I_3 formation plays Our experimental data demonstrates that at the oxidation of a solution with an I initial concentration of 0 0006 M, chloride molality of 1 0, $Cl_2/2I$ molal ratio of 1 0 and pH=2 at temperature 25°C at time 0 1 s the maximum I_3 concentration is 4 3%, while the maximum equilibrium I_3 concentration is 2 5% For a solution with an I initial concentration of 0 0006 M, chloride molality of 2 84, maximum equilibrium I_3 concentration is ca 1 0%, while at a chloride molality larger than 2 84 the formation of I_3 was not observed This experimental data agrees satisfactorily with the results of the calculation of equilibrium concentrations of iodide containing compounds counted from equilibrium constants in Eqns (5) and (6) (Margerum et al, 1986) The calculations were carried out for solutions with H^+ concentration of 1 0 M, an iodide ion concentration of 10^{-3} M and chloride ion concentrations of 0 10-1 00 M For acidic solutions containing I_2 and Cl, the ratios of the main products of reaction (I_2, I_2Cl, I_3) are dictated by the initial I and Cl concentrations The product distribution varies from 9 to 42% of I_3, 9 to 55% of I_2Cl, and 26 to 77% of I_2(aq)

An extremely important peculiarity of the process of iodide oxidation in brines with large chloride concentrations is the occurrence of disproportionation reaction

$$I_2Cl^- + Cl^- \Leftrightarrow ICl_2^- + I^- \qquad (7)$$

Ernepesova et al (1988) proved that the reaction (7) occurred in solutions with an iodide concentration (0 19-2 75) 10^{-4} M and chloride concentration large than 5 M During a spectrophotometric investigation of the I_2 brine system, a sharp isobestic point at a wavelength of 474 nm was observed (Kazantseva et al , 1998, Chapter B3b, Fig 8) in the absorption spectra for solutions with constant iodine concentrations and variable chloride concentrations from 0 to 3 0 molal This isobestic point demonstrates the existence of two main substances in the solution I_2 and I_2Cl With a further increase of chloride concentration, the solution spectrum does not go through an isobestic point due to the appearance of ICl_2

The following experiments proved the formation of ICl_2 under iodide oxidation in solutions with chloride molarity larger than 3 For a solution with a chloride concentration of 4 68 mol/ (kg H2O) the added amount of the oxidant (Cl_2/2I molal ratio 1 2) was insufficient for complete oxidation of iodide to iodine (Fig 11) This observation was based on the absorbance value at a wavelength of 225 nm for a reaction time of 0 1 s However, the value of absorbance at a wavelength of 225 nm increased later due to the increase of ICl_2 and I concentrations (Fig 12) Simultaneously, the absorbance value at a wavelength of 248 nm determined by on I_2Cl concentration decreases In the solutions with chloride concentration of 5 80 mole/(kg H_2O), the influence of the disproportionation is even more considerable despite of the large content of incompletely oxidized iodide (Fig 13) Since the rate of disproportionation is small, the changes of the spectra are observed during several hours (up to 24 hours) Our study regarding a disproportionation reaction is only qualitative one, since we could not develop a method for the determination of each ICl_2 and I concentrations in their joint presence in the system The mechanism of oxidation processes at a chloride concentration larger than 3 0 is described by reactions (1-4, 7)

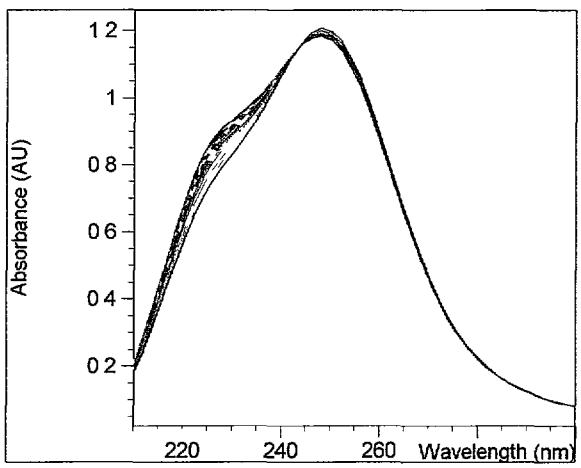

Fig 11 Absorption spectra at temperature of 25°C for a solution with an initial I concentration of 0 0004 M, chloride molality of 4 68, Cl_2/2I molal ratio of 1 20, pH=2 and time of reaction 5 s (The black continuous curve corresponds to 0 1 s, and the green interrupted curve corresponds to 4 8 s)

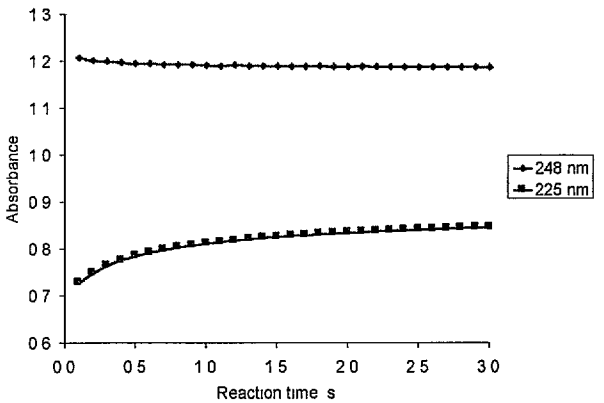

Fig 12 Time dependence of absorbance at temperature of 25°C for a solution with an initial iodide concentration of 0 0004 M, chloride molality of 4 68, $Cl_2/2I$ molal ratio of 1 20 and pH=2 {the black curve corresponds to 225 nm (ICl_2 and I), and the red curve corresponds to 248 nm (I_2Cl)}

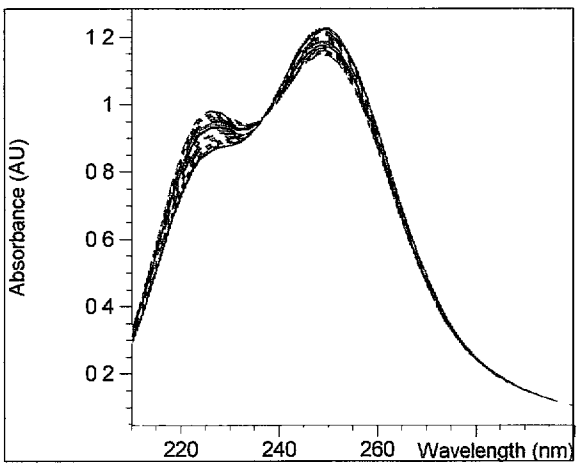

Fig 13 Absorption spectra at temperature of 25°C of a solution with an initial iodide concentration of 6 10^{-4} M, chloride molality of 5 80 mole/(kg H_2O), $Cl_2/2I$ molal ratio of 1 0, pH=1 and time of reaction 30 min {The spectrum with maximum absorbance at a wavelength of 225 nm and maximum one at a wavelength of 248 nm corresponds to the reaction time of 0 1 s The spectrum with maximum absorbance at a wavelength of 225 nm and maximum one at a wavelength of 248 nm corresponds to reaction time 1800 s }

According to (Margerum et al , 1986) the reaction

$$ICl + I^- = I_2 + Cl^- \tag{8}$$

is irreversible because k_3 is very large (more that 5 10^4 s^{-1}) Thus, the dissociation of I_2Cl to I_2 and Cl is many orders of magnitude faster than its dissociation to ICl and I The reaction of I with ICl has a second-order rate constant of 1 1 10^9 $M^{-1}s^{-1}$, whereas the rate constant for the reaction of I with ICl_2 is at least 1,000 times smaller The value of k_7 obtained by them is uncertain (k_7=(1±3) 10^6 $M^{-1}s^{-1}$), therefore a path for the direct reaction between I and ICl_2 to produce I_2Cl and Cl was omitted from the mechanism due to the uncertainty of the k_7 value for this second-order rate constant Thus, a disproportionation reaction (7) does not occur The above-mentioned conclusions are applicable to the brines studied by the above authors The reaction of ICl_2 solutions with iodide was studied in aqueous media with H^+ concentrations of 1 0 or 0 1 M, iodine ion concentration 0,001 M and chloride ion concentrations between 0 10 and 1 00 M with a Cl /I ratio less than 10^3 The ratio of Cl /I for the brines investigated in the current study reached 25 10^3 The fact that the reaction of disproportionation occurred in the studied solutions

proves that in such conditions, the reaction $ICl+I = I_2+Cl$ is reversible even its rate is considerably less than those of other reactions occurring in the oxidation process Therefore, under such conditions, the reaction rate is determined by the dissociation of I_2Cl for ICl and I ($k_{-3} = 0\ 7\ s^{-1}$)

It is interesting to find why the oxidation rates differ so significantly for the process taking place either with an excess of oxidant or with oxidant deficiency All reactions occurring in the iodide oxidation process are extremely rapid as it can be seen from Table 1 The value of the rate constant for the reaction (1) was not found in literature, while due to a large total rate of the oxidation process at oxidant excess, this reaction is not the rate-determining step To our opinion, the reaction between ICl_2 and I has a diffusion-controlled rate constant Margerum et al (1986) and Wang et al (1989) showed that ICl_2 and I react via ICl(aq) and the formation of I_3 was observed too Thus, the reaction (3) of I_2Cl is the rate determining step The results of our experiments do not contradict this opinion Based on our experimental data, we have come to the following conclusions

1) The rate of the oxidation process is maximal at conditions where either I_3 formation is impossible ($Cl_2/2I > 1\ 0$, Fig 4) or the solution conditions such as large chloride concentration depress its formation (Fig 9)
2) The rate of the oxidation process is large if the conditions are favorable for I_3 formation large concentration of I residual and low salt background (Fig 7)
3) The rate of the oxidation process is minimal if there are conditions at which the I_3 formation is possible but difficult a combination of low salt background and oxidants amounting close to the stoichiometric one leads to a low I residual concentration (Fig 5)

Therefore, the I_3 formation reaction (5) plays a very important role in the kinetics of iodide oxidation We were the first who demonstrated that partial decomposition of I_3 and the I_2Cl formation takes place under iodide oxidation Since the rate of I_3 formation is about one order higher than that of I_2Cl ($k_5=6\ 2\ 10^9\ M^{-1}\ s^{-1}$, Turner et al , 1972, $k_3=5\ 1\ 10^8\ M^{-1}\ s^{-1}$, Wang et al , 1989), then the I_3 formation in the beginning period is preferable Therefore, this is the reason why the ratio of the formed iodine compounds I_2, I_2Cl and I_3 in the starting period differ from those under equilibrium conditions However, equilibrium concentrations of these compounds are determined by the concentrations of initial products, therefore, the disproportionation of iodine takes place accordingly with the equilibrium constants of the proper reactions The observed decrease of I_3 concentration is less than the increase of I_2 and I_2Cl concentrations This is determined by the fact that I_2 и I_2Cl are formed due to I_3 dissociation which goes by one of two ways either by I_2 formation due to I_3 dissociation (k_{-5} step) or by

I_2Cl formation due to I and ICl interaction (k_3 step) This type of behavior of the system studied confirms that the reaction (3) is a rate-determining step However, the large value of k_3 disagrees with the oxidation time observed According to Margerum et al (1986), rapid equilibrium occurs between I_2(aq), I_2Cl and I_3 It should be noted that the conclusions related to high rates of formation of major iodide compounds have been drawn for systems with specific conditions favorable for the formation of some of these compounds It is possible that there are specific conditions for the slow reversible reaction in brines of the composition studied By analogy, the disproportionation reaction (7) is extremely slow even the kinetics parameters of the formation of all participating compounds are extremely large We assume that under certain conditions, the rate-determining step is a reaction

$$I_3^- + Cl^- \Leftrightarrow I_2Cl^- + I^- \qquad (9)$$

Probably, sometimes there are peculiar conditions in brines that lead to a slow destruction of I_3 and I_2Cl formation The study of the reaction (8) will be an object for a separate study in the near future

C2 Equilibrium of iodide oxidation in highly mineralized chloride solutions

It is generally accepted that oxidation of I to I_2 in salt-free solutions reaches 100% at an oxidant consumption of 103% from stoichiometric value (Yavorsky and Zalkind, 1965) The amount of oxidant that is necessary to reach a maximum oxidation degree increases with the rise of Cl concentration (Zalkind and Yavorsky, 1962) It was necessary to estimate the amount of oxidant required for a maximum yield of iodine depending on brine composition both for the determination of the optimal regime of oxidation and for the estimation of kinetic parameters It was shown in a previous chapter at what $Cl_2/2I$ molal ratio the change of oxidation mechanism occurred It was found (Fig 14-16) that the maximal yield of iodine depending on brine mineralization the higher chloride concentration was the larger amount of the oxidant was required for reaching the most favorable conditions Thus, at pH=2 0 and a temperature of 25°C, the highest yield of $SumI_2$ was observed at the following $Cl_2/2I$ molal ratios

1 0-1 05 at a chloride molality of 1 0 mole/(kg H_2O) (Fig 14),

1 0-1 1 at a chloride molality of 2 84 mole/(kg H_2O) (Fig 15),

1 1-1 2 at a chloride molality of 4 68 mole/(kg H_2O) (Fig 16)

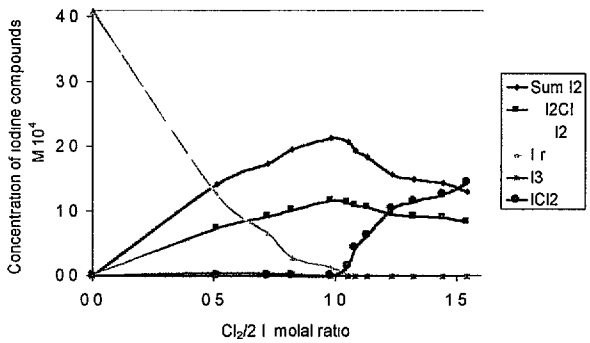

Fig 14 Concentration changes of iodine compounds at temperature of 25°C with a $Cl_2/2I$ molal ratio of solution with an initial iodide concentration of 0 0004 M, chloride molality of 1 0 mole/(kg H_2O) and pH=2

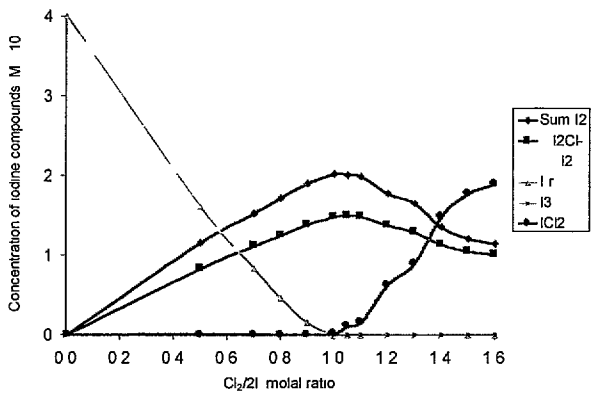

Fig 15 Concentration changes of iodine compounds at temperature of 25°C with a $Cl_2/2I$ molal ratio of a solution with initial iodide concentration of 0 0004 M, chloride molality of 2 84 mole/(kg H_2O) and pH=2

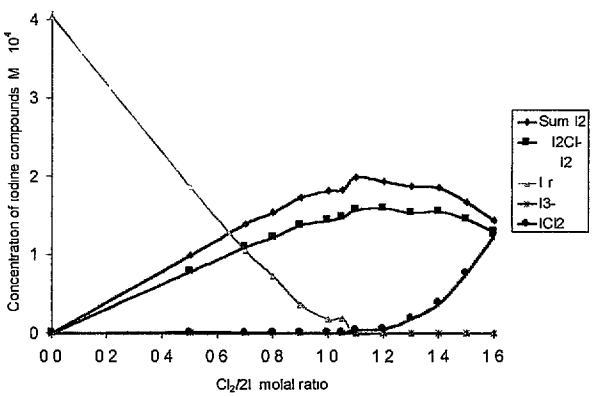

Fig 16 Concentration changes of iodine compounds at temperature of 25°C with a $Cl_2/2I$ molal ratio of solution with initial iodide concentration of 0 0004 M, chloride molality of 4 68 mole/(kg H_2O) and pH=2

At present, we are involved in developing the mathematical model of iodide oxidation in various brines This model will allow us to calculate concentrations of various compounds containing iodide depending on the initial concentrations of chloride, iodide and oxidant

C3 Kinetics of iodide oxidation in highly mineralized chloride solutions

The results of the experimental study of the kinetics in oxidation processes depending on brine mineralization and oxidant/iodide molal ratios are presented in section C1 It was found that the oxidation process is extremely rapid for brines with a chloride molality of more then 3 mole/(kg H_2O) and for brines with oxidant excesses with respect to stoichiometry (oxidant/iodide molal ratio > 1 0) Therefore, the kinetics of this process at given conditions cannot be studied by

using the equipment in our laboratory From a technological point of view, such a high rate of the process means that this process is not limited by kinetic aspects at given conditions The minimal rate of the process was observed for brines with oxidant/iodide molal ratio close to a stoichiometric one, when the highest yield of iodine is provided This field is a most important one for technology, therefore, the main kinetic parameters have been calculated for this field

C3a Method for calculating the kinetic parameters

In order to estimate the kinetics of iodide oxidation by chlorine we determined the major kinetics parameters general order of a reaction and an apparent rate constant ("observed rate constant" according to Margerum et al , (1986) definition) Let us consider the following reaction

$$I + Cl_2 \rightarrow \text{products}$$

The initial substances (I and Cl_2) will be designated as A and B The rate of this reaction is given as

$$-d[A]/dt = k\ [A]^a\ [B]^b \tag{10}$$

At a stoichiometric ratio of reacting substances, i e , at conditions that are close to optimal ones for the studied iodide oxidation by chlorine, the Eqn (10) can be expressed in the form of

$$-d[A]/dt = k\ [A]^{a+b} \tag{11}$$

or

$$-d[A]/dt = k\ [A]^n \tag{12}$$

For the estimation of a rate constant (k) of the reaction and reaction order (n), we developed a method consisting of the following using the experimental data a dependence of $1/[A]^{n-1} = f(t)$ is designed for different "n" ($n \neq 1$) values by a fitting method For instance, for n=2 linear dependence should be observed in the coordinates $1/[A] = f(t)$ and so on For n=1 the linear dependence in the coordinates $\ln[A] = f(t)$ should be observed The function correlation is estimated by correlation coefficient (R) The most probable n corresponds to the function with the largest R-value The reaction constant at $n \neq 1$ is calculated by the equation

$$k = \sum_{i=1\ N} \frac{\left(\frac{1}{[A]_i^{n-1}} - \frac{1}{[A]_0^{n-1}} \right)}{[(n-1)\ t_i\ N]} \tag{13}$$

where N is the number of experimental points

The calculated value of reagent A concentration for n ≠1 is calculated by the following equation

$$A = [A]_o \Big/ \left[(n-1)\ t\ [A]_o^{n-1} + 1\right]^{1/(n-1)} \tag{14}$$

If n=1, the reaction constant is calculated by the equation

$$k = \sum_{i=1\ N} \frac{\ln {[A]_o}/{[A]_i}}{N\ t_i} \tag{15}$$

then the calculated value of reagent A concentration is calculated by the following equation

$$A = [A]_o\ \exp(-k\ t) \tag{16}$$

A program for the calculation of the parameters n and k was developed on TURBO PASCAL FOR WINDOWS The method developed demonstrated high accuracy when calculating a model example for a reaction of iodination of β-phenylpropyl acid (Table 4) with a known reaction order of n=1 and a constant of rate reaction k=0 1 c^{1} (Table 5)

C_6H_5-C≡C-COOH+I_2→C_6H_5-CI=CI–COOH

The known kinetic parameters of this reaction were taken from Emanuel and Knorre (1974) and Spiridonov and Lopatkin (1970)

Table 4 Kinetics of the interaction of I_2 with β-phenylpropyl acid

Experimental data		Calculated data ($[I]_{calc}$)		
Time, min	$[I]_{exp}$	Method of Ross (Ross, 1982)	Method of Wilkinson, (1961)	**Our method**
0	0 0251	0 0251	0 0251	0 0251
114 0	0 0213	0 02295	0 021335	0 021393
273 0	0 0177	0 02026	0 017635	0 017712
405 0	0 0155	0 001827	0 01540	0 015483
662 0	0 0124	0 01493	0 001236	0 012413
1,388 0	0 0079	0 00844	0 007916	0 007907
1,780 0	0 0066	0 00621	0 00623	0 006594
2,790 0	0 0046	0 00281	0 004655	0 004600
S		0 00212	5 583E-05	3 934E-05
n	2	1	1 98	2 0
k, $dm^3\ mol^{1}\ min^{1}$	0 0614	0 000785	0 05778	0 06215

Table 5 Results of the calculation of order and rate constant for model reaction

Kinetics parameters	Known values	Method of Ross (1982)	Method of Wilkinson, (1961)	**Our method**
N	1 0	1 0	1 173	1 0
K	0 1	0 101	0 0702	0 10
S (standard deviation)		2 97 10^{2}	6 64 10^{2}	3 70 10^{2}

C3b Kinetics parameters for process of iodide oxidation

The results of the kinetic parameter calculations (Table 6) demonstrate that the rate of iodide decrease at the initial step of iodide oxidation (reaction time 0-0 5 s) is characterized by a first-order for iodide, the rate constant k is equal 1 6-2 2 s^{1} for a solution with a chloride molality of 1 0 and 5 5-6 5 s^{1} for a solution with chloride molality of 2 84 In general, this reaction is characterized by a third order The third-order rate constants for the loss of iodide increase from (1 3-7 0) 10^{7} to (3 0-3 6) 10^{8} $M^{-2}s^{1}$ as the chloride molality increases from 1 0 to 2 84 The values of rate constants increase approximately on an order when chloride concentration increases from 1 0 to 2 84 molality and only slightly rises when the initial iodide concentration is increased from 0 0002 to 0 0006 M

Table 6 Calculated kinetic parameters for iodide loss during iodide oxidation

Initial composition of solution			Reaction time, sec	Kinetics parameters		
[I], M	Cl , mol/(kg H_2O)	$Cl_2/2I$		Reaction order	Rate constant	Standard deviation
0 0002	1 0	1 0	0-1 1	1	1 608	6 5 10^{5}
0 0002	1 0	1 0	0-0 5	1	2 188	6 8 10^{5}
0 0004	1 0	1 0	0-0 3	1	2 072	8 7 10^{5}
0 00061	1 0	1 0	0-0 2	1	2 08	1 24 10^{4}
0 0002	1 0	1 0	0-2 3	3	1 31 10^{7}	8 5 10^{3}
0 0004	1 0	1 0	0-0 5	3	2 74 10^{7}	5 2 10^{5}
0 0004	1 0	1 0	0-1 1	3	1 88 10^{7}	4 7 10^{5}
0 0006	1 0	1 0	0-1 5	3	6 96 10^{7}	4 4 10^{5}
0 0006	1 0	1 0	0-2 8	3	5 58 10^{7}	4 4 10^{5}
0 0002	2 84	1 0	0-0 5	1	5 84	4 5 10^{5}
0 0002	2 84	1 0	0-0 7	1	5 45	4 7 10^{5}
0 0004	2 84	1 0	0-0 7	1	6 10	8 8 10^{5}
0 0006	2 84	1 0	0-0 5	1	6 47	11 0 10^{5}
0 0002	2 84	1 0	0-1 1	3	29 50 10^{7}	1 9 10^{5}
0 0002	2 84	1 0	0-0 9	3	33 52 10^{7}	4 7 10^{5}
0 0004	2 84	1 0	0-1 1	3	29 70 10^{7}	5 3 10^{5}
0 0006	2 84	1 0	0-1 1	3	35 67 10^{7}	2 1 10^{5}

The reaction is a first-order one regarding total iodine The rate of iodine formation increases with an increase of initial concentrations of iodide and chloride The rate constant k for

total iodine is equal to approximately 3 5 10^{2} s^{1} for solutions with chloride molality 1 0 and (8 1-12 5) 10^{2} s^{1} for solutions with chloride molality 2 84 (Table 7)

Table 7 Calculated kinetics parameters for total iodine during iodide oxidation

Initial composition of solution			Reaction time, s	Kinetics parameters		
[I], M	Cl, mol/(kg H_2O)	Cl_2/2I		Reaction order	Rate constant	Standard deviation
0 0002	1 0	1 0	0-1 0	1	4 16 10^{2}	4 4 10^{7}
0 0002	1 0	1 0	0-1 7	1	2 53 10^{2}	4 4 10^{7}
0 0004	1 0	1 0	0-1 7	1	3 60 10^{2}	1 8 10^{7}
0 0006	1 0	1 0	0-1 0	1	3 45 10^{2}	5 49 10^{7}
0 0002	2 84	1 0	0-1 4	1	8 12 10^{2}	9 3 10^{7}
0 0004	2 84	1 0	0-1 0	1	10 73 10^{2}	1 1 10^{6}
0 0006	2 84	1 0	0-0 5	1	12 48 10^{2}	9 0 10^{7}

The reaction is a first-order one regarding to I_3 The rate constant k for I_3 is equal (5±1) s^{1} for solutions with chloride molality 1 0

C4 Influence of oxidizable components in natural brines on iodide oxidation

Natural brines contain organic and inorganic compounds (Br, H_2S, sodium salts of naphthenic acids, iron ions) which can also be oxidized by chlorine (Ksenzenko and Stasinevich, 1995) Their nature and amount affect both the excess of the oxidant required in order to obtain a high degree of oxidation, and the kinetic of the oxidation process We determined the influence of each of these substances on the equilibrium and kinetics of oxidation processes in solutions with average values of initial iodide and chloride concentrations, for the solution with an I initial concentration of 0 0004 M, chloride molality of 2 84 and pH=2 at temperature 25°C

C4a Bromide ion

Bromide as other halides decreases the iodine yielding due to its complex formation When the bromide content in brine increases, the optimal oxidant consumption increases too Zalkind and Yavorsky (1962) observed that the rate of iodide oxidation increases in bromide solutions Our experimental results show that at a chloride molality of 2 84 mole/(kg H_2O), pH=2 0 and a temperature of 25°C, the highest yield of $SumI_2$ was observed at the following Cl_2/2I molal ratios 1 2-1 3 at a bromide concentration of 0 003 M (Fig 17) and 1 3-1 6 at a bromide concentration of 0 006 M (Fig 18) The equilibrium in a system with an I initial concentration of 0 0004 M, a bromide concentration of 0 006 M, chloride molality of 2 84,

$Cl_2/2I$ molal ratio of 1 2 and pH=2 reaches 0 1-0 2 s at a temperature of 25°C (Fig 19) The following values of kinetic parameters for the loss of iodide have been obtained reaction order n=3 rate constant k=5 09 10^8 $M^{-2}s^{-1}$ S=2 90 10^{-5} The rate of iodide oxidation with the same concentrations of iodide and chloride is 1 7 times slower (k=2 97 10^8 $M^{-2}s^{-1}$) when bromide is not present in the solution

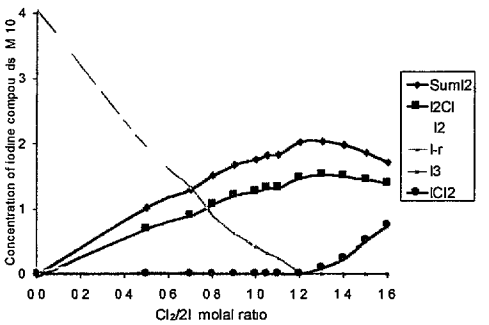

Fig 17 Concentration changes of iodine compounds at temperature of 25°C with $Cl_2/2I$ molal ratio of a solution with an initial iodide concentration of 0 0004 M, a bromide concentration of 0 003 M, chloride molality of 2 84 mole/(kg H_2O) and pH=2

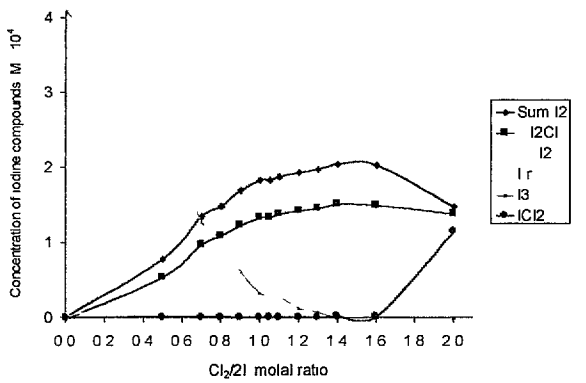

Fig 18 Concentration changes of iodine compounds at temperature of 25°C with $Cl_2/2I$ molal ratio of a solution with an initial iodide concentration of 0 0004 M, bromide concentration of 0 006 M, chloride molality of 2 84 mole/(kg H_2O) and pH=2

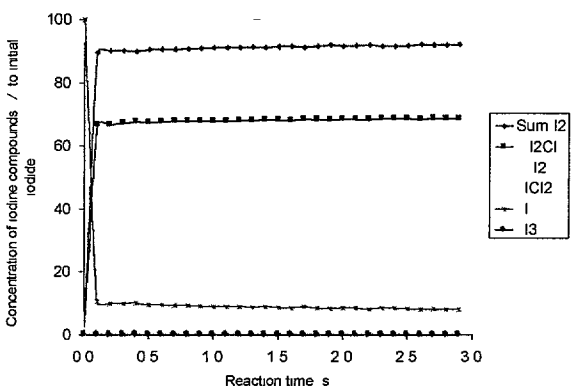

Fig 19 Concentration changes of iodine compounds at temperature of 25°C with time changes for the a solution with an I initial concentration of 0 0004 M, bromide concentration of 0 006 M, chloride molality of 2 84, $Cl_2/2I$ molal ratio of 1 2 and pH=2

C4b H_2S

The use of brines containing hydrogen sulfide for iodine production is very important for the Turkmenistan economy since there are large stocks of stratal waters with relatively high

iodide content and low mineralization (Kazantseva et al , 1998, brines # 22-33 in Table 3) The process of iodide oxidation was found to be very difficult even with a minimal amount of hydrogen sulfide in the brine For instance despite the presence of 2 mg H_2S/l high yields of iodine even at 3 5-multiple excess of oxidant compared with the stoichiometric amount cannot be obtained The yield of iodine did not exceed 42% of the initial iodide (Fig 20) under these conditions The kinetics study of iodide oxidation showed that at a hydrogen sulfide presence in brine after the stage of quick iodide oxidation (the time reaction is less than 0 1 s) the long reverse process of iodine reduction to iodide occurred (Fig 21)

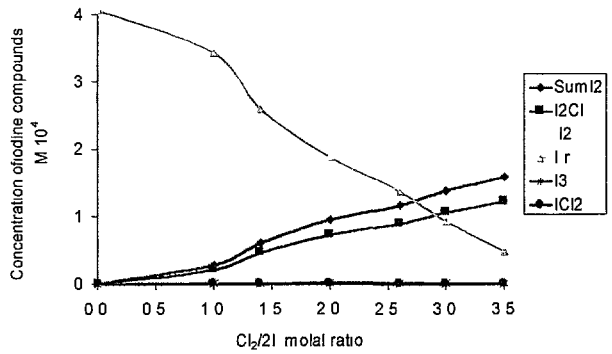

Fig 20 Concentration changes of iodine compounds at temperature of 25°C with Cl_2/2I molal ratio of the solution with an initial iodide concentration of 0 0004 M, chloride molality of 2 84 mole/(kg H_2O), H_2S concentration of 2 mg/l and pH=2

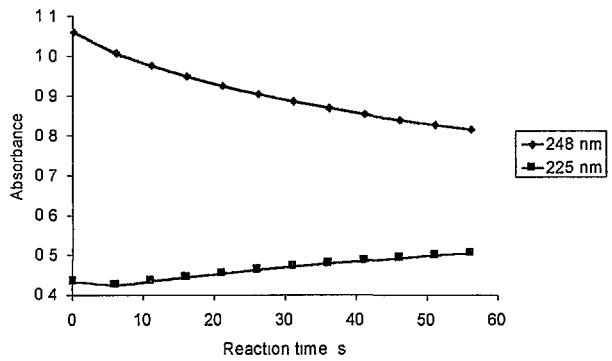

Fig 21 Absorbance – time dependence at temperature of 25°C for a solution with an initial iodide concentration of 0 0004 M, chloride molality of 2 84, H_2S concentration of 2 mg/l, Cl_2/2I molal ratio of 2 5 and pH=2 {the red curve corresponds to a wavelength of 225 nm (ICl_2 and I) and the black curve corresponds to a wavelength of 248 nm (I_2Cl)}

With respect to the aforementioned, it is impossible to obtain a large iodine yield from brines containing hydrogen sulfide The preliminary removal of hydrogen sulfide by either aeration or absorption should be proposed as the technological solution of this problem

C4c Naphthenic acids

It is generally accepted (Ksenzenko and Stasinevich 1995) that organic acids as ingredients of natural waters interact with chlorine and iodine These organic acids are naphthenic ones which are oxidized very slowly and during the desorption process they react with iodine decreasing its yield Therefore it is recommended to the conduct oxidation process

with an excess of oxidants The only study dealing with the investigation of the kinetics of iodide oxidation in natural brines was conducted by Zalkind and Yavorsky (1963) They studied the influence of organic acids extracted from the natural waters of the Cheleken plant on the iodide oxidation by either chlorine or hypochlorite Earlier, Niyazov (1962) found the presence of terephthalic acid (p-benzenedicarboxylic acid n-$C_6H_4(COOH)_2$) in Cheleken well water Zalkind and Yavorsky (1962) studying the oxidation-reduction potential of the Pt/Hg_2Cl_2 electrode pair showed that in the case of a simultaneous presence of iodide ions and organic acids in brine iodide, ions are oxidized first irrespective of acid concentration The iodine formed interacts with naphthenic acids from 8 to 20% of formed iodine are reduced for 30 min at 20°C and the concentration of naphthenic acids from 0 25 to 2 0 mg-eqv/l The iodine reduction increases with increase of naphthenic acids content in the brine, pH and temperature The interaction of acids with chlorine is accelerated with the increase of acid concentration, pH and temperature

Studying the influence of naphthenic acids on iodide oxidation, we first attempted to create artificial natural brine similar to the Chelecken formation The attempt was made to use mixtures of sodium salts of natural naphthenic acids (low-molecular, water soluble fractions of R-COONa, where R = C_6H_{11}, C_5H_9 with various side substitutes) obtained from oil by multistage distillation and extraction (Niyazov et al , 1992) It was found that the introduction of aqueous solutions of the given mixture in mineralized solutions and their acidification to pH=2 leads to the formation of cloudy solutions which cannot be investigated by a spectrophotometric method We also could not use a solution of terephthalic acid, since it is insoluble in water Therefore, in order to study the influence of naphthenic acids on iodide oxidation we used synthetic sodium salt of cyclohexanecarbonic acid ($C_6H_{11}COONa$) which was synthesized by Niyazov et al (1992) with a further solution acidification to pH=2 It was found that the presence of 50-100 mg/l of cyclohexanecarbonic acid did not influence the iodide oxidation The maximum iodine yield (approximately 100% of the initial iodide content) was reached at a $Cl_2/2I$ molal ratio equal to 1 0-1 1 (Fig 22) The change of iodine compounds with time changes was independent to the presence of the naphthenic acid (Fig 8 and 23) During a 30-minute observation, the changes of solution spectra, which could be the evidence of the reduction of iodine, were not observed Thus, pure naphthenic acids, as saturated hydrocarbon, do not influence iodide oxidation and iodine reduction

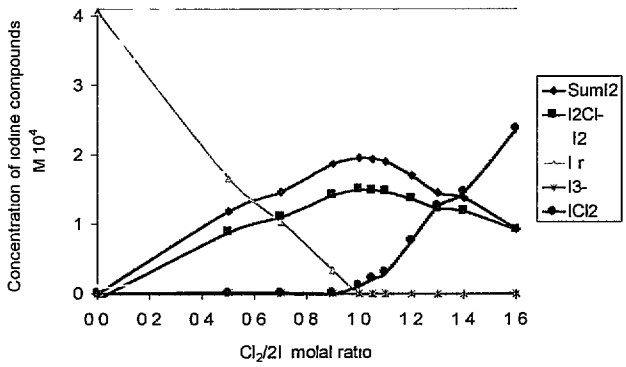

Fig 22 Concentration changes of iodine compounds at temperature of 25°C with $Cl_2/2I$ molal ratio of a solution with an initial iodide concentration of 0 0004 M, chloride molality of 2 84 mole/(kg H_2O), organic acid concentration of 100 mg/l and pH=2

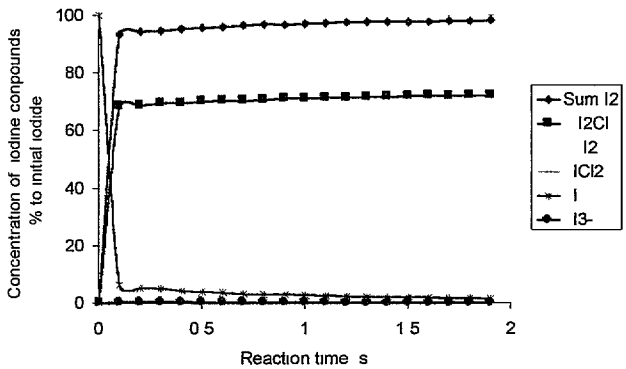

Fig 23 Concentration changes of iodine compounds at temperature of 25°C with time changes for the a solution with an I initial concentration of 0 0004 M, organic acid concentration of 100 mg/l, chloride molality of 2 84, $Cl_2/2I$ molal ratio of 1 0 and pH=2

Our findings are supported by the results of Shenker and Koifman (1965) who did not observe the formation of iodide at the long contact of iodine with pure naphthenic acids (carboxyl derivatives of cyclopentane hydrocarbon of the general formula $C_nH_{2n\ 2}O_2$) in a sodium chloride solution at a pH ranging from 2 to 3 in a sealed ampoule The observed discrepancy with the data of Yavorsky and Zalkind (1963) can be explained bv insufficient purification of naphthenic acids In our opinion, organic unsaturated compounds are probably required for the iodine reduction The underground waters of west Turkmenistan are characterized by a poor content of organic compounds This can be explained bv weak leaching of organic compounds from rocks by highly mineralized Cl-Na-Ca waters (Kiryukhin and Shvets, 1980) There are volatile organic compounds (mostly phenols) besides organic acids in natural waters It is possible that these volatile organic compounds influence on iodide oxidation This hypothesis will be further investigated

C4d Iron ions

The presence of iron ions in natural waters explains the corrosion of pipes for brine supply We could not find any data in literature regarding the influence of iron ions on iodide oxidation It was found through experiments that the presence of Fe^{2+} ions does not affect the equilibrium of iodide oxidation the iodine yield reaches about 100% at a $Cl_2/2I$ molal ratio of

1 0-1 05 (Fig 24) The oxidation takes less than 0 1 s, i e, iodide oxidation is possibly accelerated by the presence of Fe^{2+} ions

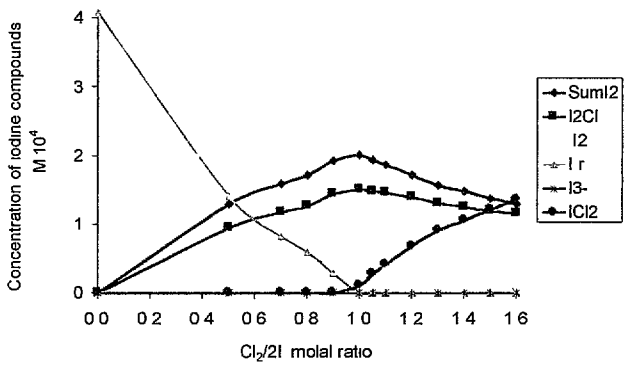

Fig 24 Concentration changes of iodine compounds at temperature of 25°C with a $Cl_2/2I$ molal ratio of a solution with an initial iodide concentration of 0 0004 M, chloride molality of 2 84 mole/(kg H_2O), Fe^{2+} concentration of 14 mg/l and pH=2

CONCLUSIONS

1 It was proven that only bromide and hydrogen sulfide amongst discussed oxidizable natural ingredients of natural brines influenced on iodide oxidation

2 The influence of organic compounds requires further investigation

3 In order to calculate kinetic parameters of iodide oxidation in the presence of oxidizable ingredients the solutions with 1 0 molal chloride concentration will be studied henceforth The oxidation rate in such solutions is one order magnitude less than that in studied solutions in the current investigation

4 The major features of the oxidation process at 50°C will also be studied Due to equipment limitations, this study will be carried out only at chloride concentrations less than 1 0 molality

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MANAGEMENT

During the reported period, we met with a serious budgetary problem This problem was related to the delay in money transfer for work fulfilled by the Turkmenistan partners

COLLABORATION AND TRAVEL

Prof B S Krumgalz, Dr Kazantseva N N , Prof Khodjamamedov A M and Dr Ernepesova A S participated in XVI Mendeleev Congress, which took place in Saint Petersburg and in VII International Conference "The problems of solvation and complex formation in solutions" which took place in Ivanovo with talks "PECULIARITIES OF IODIDE OXIDATION IN NATURAL MINERALIZED WATERS OF TURKMENISTAN" and "COMPLEXING AND HYDRATION PHENOMENA IN THE PROCESS OF IODIDE OXIDATION IN CHLORIDE SOLUTIONS", respectively Participation in these conferences helped in the re-establishment of scientific connections between Turkmenistan scientists and their colleagues in Ivanovo, Moscow and Saint Petersburg

Dr N N Kazantseva visited Prof V I Ksenzenko in Moscow (1999) in order to discuss the experimental results related to various aspects of the kinetic aspects of iodide oxidation

Dr O Geldyev spent two weeks of training in the M I Mendeleev's Russian Chemical Technological University (Moscow) The purpose of his training was to assimilate modern methods for the processing of kinetic experimental data to work out the equilibrium and kinetic models for oxidation of iodide by chlorine

Both sides discussed, in detail, the scientific plans for fulfillment of the project, details of financial and scientific reports, the results of experimental work and necessary future steps for successful fulfillment of the project

ACKNOWLEDGEMENT

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The authors would like to acknowledge Dr O Geldyev and Dr A S Ernepesova for their participation and valuable contributions on various stages of the project fulfillment, including the experimental part, treatment of experimental data and the writing of the report We are also thankful to Prof Niyazov A for organic acids, which he supplied us

We would like specifically to acknowledge the assistance that we constantly receive from Mr Boaz Ayalon from the American Embassy, Tel Aviv (Israel)