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Highly effective technology of iodine production from hydrothermal mineralized natural brines

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EXECUTIVE SUMMARY

The present final report covers the period of January 1, 1997 to December 31, 2001. The results obtained here are discussed below. Turkmenistan is the fourth-largest producer of iodine in the world after Japan, Chile and the U.S. The raw material for iodine production is underground-mineralized natural waters. Turkmenistan's natural mineralized waters are characterized by a considerably higher mineralization and lower iodide content than those of Japan and the U.S. The development of curtain aspects of a new, rather inexpensive and ecologically safe process of the recovery of iodine from Turkmenistan natural brines with a low iodide content by an air-desorption method was conducted in the current project. One of the main ways to intensify iodine production from natural brines is to search for the optimal regime of iodide oxidation by chlorine. The process of iodide oxidation by chlorine proceeds through a number of several fast, consecutive-concurrent reactions and leads to the formation of equilibrium system contains the initial and final substances side-by-side with intermediate compounds. The composition of these systems depends on many factors, amongst them the initial composition of the brine, the amount of oxidant, pH, temperature, etc.

The overall aim of the project was in the development of a scientific basis for a very effective technology of iodine extraction by the air-desorption method from natural chloride brines characterized by a very low content of iodide ions. The basis for this method is the complex process of the oxidation of I^- ion to iodine. The following major problems have been studied during fulfilling the current project:

a). The study of kinetics of I^- oxidation in natural brines and in their modeling solutions as a function of mineralization degree, content of I^-, Br^- and micro-impurities, pH, temperature and the amount of the added oxidant.

b). The development of mathematical models (equilibrium and kinetic) of the I^- oxidation process in order to forecast the yield of the various iodide forms as a function of brine composition and oxidation conditions.

c). The verification of developed models on natural brines in order to forecast an optimal regime of the technology of iodine production.

The most suitable method for determining the composition of iodine-containing solutions is a spectrophotometric method that allows the examination of solutions without disturbing their equilibrium. We developed the usage of this method for the study of iodide oxidation reaction. During the investigation, the following results were obtained which are very important for chemical industry of Turkmenistan:

a). A spectrophotometric method for determining the concentrations of various iodine compounds (I^- - initial compound, I_3^- - suboxided iodine form, I_2 and I_2Cl^- - target iodine forms and ICl_2^- - peroxided iodine form) at their joint presence has been developed especially for solutions with high chloride content.

b). The equilibrium and kinetics of iodine oxidation reaction were investigated. It was found that the optimal quantity of oxidant required for the highest yield of target product (which is iodine) depends on the concentrations of chloride, bromide, phenols and hydrogen sulfide acid. Ferric ions and saturated naphtenic acids do not influence the iodide oxidation process. In the presence of chloride, bromide and phenols, almost 100% oxidation of iodide to iodine can be provided by well-matched dose of chlorine. In the presence of hydrogen sulfide acid and its salts the iodide oxidation reaction is not effective (it takes a great amount of oxidant, therefore, a high yield of iodine cannot be provided in any case). The regularities obtained for model solutions are quite suitable for natural underground waters. Thus, knowing the composition of natural brine, we can predict the optimal regime for the iodide oxidation process.

RESEARCH OBJECTIVES

At present, iodine is one of the important export products of Turkmenistan after oil and gas. A new approach to the solution of the problem of iodine production in Turkmenistan consists of the construction of small units (modules) for iodine extraction close to the wells in order to save expenses of pipeline construction (for brine supply from oil and gas fields) to a plant. The development of such small units will allow the creation of a modern production of iodine compounds without large investments. The use of highly effective technology will allow an increase in the degree of iodine extraction to 90%, and the elimination of hazardous chlorine blowouts in the atmosphere. The brines used will be pumped underground in order to keep formation pressure as high as possible. At present, the brines used are disposed of in desert areas with accompanying pollution effects on local environment. The development of an effective and ecologically safe technology of iodide extraction from natural brines requires knowledge of the mechanism of the main technological stage: the oxidation of I^- into I_2.

The current investigation was devoted to the study of the mechanism, equilibrium and kinetics of iodide oxidation by chlorine in solutions with high chloride concentration and additives of organic and inorganic compounds that can be oxidized by chlorine and to the determination of optimal conditions for the formation of the final product, iodine. The obtained regularities were checked for natural brines. The study was carried out for natural underground waters and model solutions.

For the determination of iodine compound concentrations, we used spectrophotometric analysis. The reaction rate calculations are based on the changes of optical absorbance at a spectral wavelength that is specific for either one of initial substances or for one of the reaction products. In order to avoid overlapping the spectrum of any of the selected substances with any of its by-products, it is necessary to create reaction conditions that will suppress the formation of by-products (Palmer et al., 1982, Margerum et al., 1986, Lengyel et al., 1996, and Nagy et al., 1988, Wang et al., 1989). A universal spectrophotometric technique for determining various iodine forms at their mutual presence in natural brines with different mineralization degrees was developed during this investigation.

A. Introduction

Turkmenistan is the fourth-largest producer of iodine in the world after Japan, Chile and the U.S. Raw material for iodine production is gas-oil accompanying underground-mineralized natural waters. Turkmenistan's mineralized natural waters are characterized by considerably higher mineralization and lower iodide content than those of Japan and the U.S.

One of the main ways to intensify iodine production from natural brines using the air-desorption method is to search for the most optimal regime of iodide oxidation by chlorine. It is known ((Ksenzenko and Stasinevich, 1995) that the process of iodide oxidation by chlorine proceeds through a number of several fast consecutive-concurrent reactions 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, H_2OI^+, etc.). Recently, Kazantseva et al. (2002) found that at conditions similar to industrial ones (pH<3, $Cl_2/2I^-$ molar ratio < 2), the main iodine forms are the follows: I^- (initial compound), I_3^- (suboxided iodine form), I_2 и I_2Cl^- (target iodine forms) and ICl_2^- (peroxided iodine form). The proposed mechanism of the reaction of iodide oxidation by chlorine in conditions under study is reactions (1)-(7):

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

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

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

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

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

$$Cl_2 + Cl^- \Leftrightarrow Cl_3^- \quad (6)$$

A reaction of iodide disproportionation occurs in solutions with high chloride concentrations (Cason & Neumann, 1961):

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

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	Equilibrium constants	Rate constants
$ICl_2^- \xrightarrow{k_2}$ $\xleftarrow[k_{-2}]{} ICl + Cl^-$	K_2=0.0060 M [a] K_2=0.013 M [c]	k_2>>6.6·10^4 s^{-1} [b] $M^{-1}s^{-1}$ (diffusion limit) [b]
$ICl + I^- \xrightarrow{k_3}$ $\xleftarrow[k_{-3}]{} I_2Cl^-$	K_3=7.3·10^8 M^{-1} [b]	k_3=1.1·10^9 M^{-1}s^{-1} [b] k_{-3}=1.5 s^{-1} [b] k_3=5.1·10^8 M^{-1} s^{-1} [c] k_{-3}=0.7 s^{-1} [c]
$I_2Cl^- \xrightarrow{k_4}$ $\xleftarrow[k_{-4}]{} I_2 + Cl^-$	K_4=0.60 M [b] K_4=0.59 M [a] K_4=0.68 M [d]	k_4>5·10^4 s^{-1} [b] Value k_{-4} was not found in literature.
$I_2 + I^- \xrightarrow{k_5}$ $\xleftarrow[k_{-5}]{} I_3^-$	K_5=748 M^{-1} [e] K_5=710 M^{-1} [f]	k_5=6.2·10^9 M^{-1} s^{-1} [g] k_{-5}=7.5·10^6 s^{-1} [g] k_5=5.6·10^9 M^{-1} s^{-1} [h] k_{-5}=7.5·10^6 s^{-1} [h]
$Cl_2 + Cl^- \xrightarrow{k_6}$ $\xleftarrow[k_{-6}]{} Cl_3^-$	K_6=0.19 M^{-1} [i] 0.11 & 0.13 M^{-1} (at I=1.14 and I=4.0, respectively) [j] K_6=0.18 M^{-1} [k]	Values k_6 and k_{-6} were not found in literature.
$I_2Cl^- + Cl^- \xrightarrow{k_7}$ $\xleftarrow[k_{-7}]{} ICl_2^- + I^-$	K_7=1.12·10^{-7} [l] K_7=1.12·10^{-7} [m] (at [Cl$^-$]=3.2 M) K_7=6.9·10^{-8} [m] (at [Cl$^-$]=5.2 M)	Values k_7 and k_{-7} were not found in literature.

[a] Cason and Neumann, 1961; [b] Margerum et al., 1986; [c] Wang et al., 1989; [d] Abrosimova et al., 1976; [e] Ramette & Sandford, 1965; [f] Ksenzenko & Stasinevich, 1995; [g] Turner et al., 1972; [h] Ruasse et al., 1986; [i] Zimmerman et al., 1957; [j] Artamonov & Gergert, 1977; [k] Wang et al., 1994; [l] Latimer, 1952; [m] Ernepesova et al., 1988.

Recently, reactions #2, 3, 4 and 5 with the formation of iodine compounds have been studied in weak-mineralized solutions (solutions with ionic strength less than 1.0) by a pulsed-accelerated-flow method (Kumar et al., 1986; Margerum et al, 1986 and Nagy et al., 1988). The studies concerning the iodine compounds formation in solutions with high chloride concentrations are few and are mostly devoted to calculate the equilibrium constant either for reaction #5 (Cason & Neumann, 1961, Abrosimova et al., 1976) or for a reaction #7 (Cason & Neumann, 1961, Ernepesova et al., 1988). The current investigation was devoted to the study of mechanism, equilibrium and kinetics of iodide oxidation by chlorine in solutions with high chloride concentrations and additives of organic and inorganic compounds that can be oxidized by chlorine, and to determine optimal conditions for the formation of the final product, iodine. The regularities obtained were checked for natural brines.

B. EXPERIMENTAL SECTION

B1. Reagents used in the experimental section

In order to examine the influence of each parameter on the kinetics of iodide oxidation, we conducted our study on model solutions resembling the underground natural brines of Turkmenistan. The compositions and physico-chemical properties of underground brines of Turkmenistan were given in Table 3 of Annual Report (1997). The solutions were prepared from chlorides of sodium, calcium and magnesium, sulfate and bicarbonate sodium and potassium iodide. We prepared a basic solution with an ionic strength of 5.8716 in molarity units, which resembles the highest chloride concentration amongst the natural brines studied with the following molar ionic concentration of Na^+, Mg^{2+}, Ca^{2+}, Cl^-, HCO_3^- and SO_4^{2-} as 4.1502, 0.0823, 0.4911, 5.2942, 0.0006, and 0.0012 in mol/l, respectively. Less concentrated solutions were prepared by volumetric dilution of the basic solution with distilled water. Solutions with chloride molarity equal to 5.1936, 4.2830, 2.6927 and 0.9806 were used.

Concentrated iodine solutions were prepared by dissolving weighed portions of crystalline iodine in saline solutions acidified to pH=1 in order to avoid hydrolysis of iodine. Sulfuric acid was used for acidification of solutions based on KI while hydrochloric acid was used for those containing calcium. An iodine concentration in the solutions was analyzed directly before conducting each experiment by volumetric titration with 0.01 mol/l $Na_2S_2O_3$ using a starch solution as an indicator. Less concentrated iodine solutions were obtained by diluting the main solution with a saline solution, described above, or with distilled water, while keeping the constant pH. The solutions obtained were immediately subjected to spectrophotometric study.

0.1 mol/l solutions of KI were prepared using standard KI solutions and used as a basic solution for the preparation of solutions containing iodide ions. This was carried out by diluting them to the required concentration using a saline solution. The solutions with the following iodide concentrations were prepared for experimental studies: $2.0 \cdot 10^{-4}$, $4.0 \cdot 10^{-4}$, $6.0 \cdot 10^{-4}$ and $12.0 \cdot 10^{-4}$ M, respectively.

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 at low temperatures and its concentration was determined with iodometric titration directly before each oxidation experiment. The measured volume of the standard solution of I_2+KI was added to an aliquot of chlorine water, and the iodine excess was determined by volumetric titration with 0.01 mol/l $Na_2S_2O_3$ using a starch solution as an indicator.

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

a) 0.1 M solution of KBr was prepared using standard KBr solution and used as a basic solution for the preparation of solutions containing bromide ion by their dilution to 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 the 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). The concentration of H_2S solution used was less then 3 mg/l. The higher concentration leads to the formation of a colloidal cloudy solution that cannot be subjected to spectral analysis;
c) solution containing 1 g/l Fe^{2+} was prepared using $FeSO_4$ of an analytical grade and used as a basic solution for the preparation of solutions containing ferric ion by their dilution to required concentrations with a saline solution. Fe^{2+} concentration was determined by colorimetric analysis using 1,10-fenantroline (Lurie and Rybnikov, 1974);
d) Modeling the composition of natural brine from the Cheleken oil field (Nijazov, 1962) was attempted using low molecular fractions of natural naphthenic acids obtained from Turkmenistan oil. However, the introduction of these types of 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 $C_6H_{11}COONa$ 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.

Saline solutions and chlorine water were acidified to pH≤2 in order to avoid iodine hydrolysis. Hydrochloric acid was used for this purpose.

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 chlorine water, and iodine excess was determined by a volumetric titration with 0.01 M $Na_2S_2O_3$ using a starch solution as an indicator.

The equilibrium study for oxidation reactions was conducted by mixing an iodide containing solution with chlorine water and by diluting the obtained mixture by twice-distilled water to the proper volume. The solutions obtained were immediately subjected to spectrophotometric measurements.

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 regions, a slit width of the instrument has a default set of 2 nm. To compensate for the absorbency of 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. 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 minimum collection time of the spectrophotometer was 0.1 s. The time required for thorough mixing of the solutions entering a mixing cell was determined less than 0.1 sec.

In order to prevent the influence of changes in a solution ionic matrix for the kinetic measurements, mixed iodide solutions and chlorine water were adjusted to a similar salt composition and pH. During investigation of model solutions, syringes of equal volumes were used for mixing iodide solutions and chlorine water. During investigation of natural brines, syringes of different volumes were used; volume ratio of brine/(chlorine water) was equal to 10. The changes regarding iodine compound concentration after mixing were taken into account.

Every reaction was measured at wavelengths of 225, 350 and 474 nm. Three to seven replicate runs were conducted in order to obtain concentrations of main iodine compounds and the experimental rate constant was calculated with high precision.

B4. Calculation of iodine compounds concentrations

All investigated iodine compounds absorb light in UV and visible ranges. Their main spectral characteristics are presented in **Table 2**. As a rule, the reaction rate calculations are based on changes of optical absorbance at a spectral wavelength that is specific for either one of the initial substances or for one of the reaction products. In order to avoid overlapping, the spectrum of any of the selected substances with any of its byproducts, it is necessary to create reaction conditions that will suppress the formation of by-products. The optimum wavelength for spectral studies of the kinetics for reactions #2-#5 is 350 nm corresponding to the maximum absorbance of I_3^- (Palmer et al., 1982, Margerum et al., 1986, Lengyel et al., 1996, and Nagy et al., 1988) which is formed at the end of a series of these reactions, whereas the other species have much less intense absorbance in the visible region (Table 2). A required condition for the formation of I_3^- is the excess of I^-. However, since the formation of I_3^- is suppressed in solutions with large chloride concentrations (Kazantseva et al., 2002), we could not use a wavelength of 350 nm for our measurements in highly mineralized solutions. Therefore, if one of the compounds formed was ICl_2^-, the changes of its absorbance at 230 nm (Wang et al., 1989) could be used as an indicator for the reaction. The absorbance changes at wavelengths of 225-250 nm for oxidation process studied were conditioned both by a decrease of iodide content and an increase in the concentrations of I_2Cl^- and ICl_2^- compounds. This fact can lead to large errors in kinetic parameter calculations. Therefore, we decided using the changes of main component concentrations with time but not absorbance changes at one selected wavelength for studying the reaction kinetics of the iodide oxidation process.

Concentrations of the main iodine compounds (I^-, I_3^-, I_2, I_2Cl^- and ICl_2^-) were calculated by a method of determination for the equilibrium iodine compound concentrations at their joint presence developed specifically for solutions with high chloride concentrations (Kazantseva et al., 2002). A short description of the algorithm of the calculation is given below. The method was based on the fact that the spectra of solutions with constant iodide concentrations and variable chloride concentrations have an isobestic point with a molar extinction coefficient of I_2 and I_2Cl^- equal to 610.2 $dm^3 \cdot mole^{-1} \cdot cm^{-1}$ at a wavelength of 474 nm, while absorbance of other iodine forms at this

wavelength is negligible. This thus allows us to use light absorbance at 474 nm for calculating the iodine concentration in solutions with variable chloride concentrations.

Table 2. The main spectral characteristics of iodine compound

Iodine compound	Our data (Kazantseva et al., 2001)		Literature data		
	Analytical band length, nm	Extinction coefficient, $dm^3 \cdot mol^{-1} \cdot cm^{-1}$	Analytical band length, nm	Extinction coefficient, $dm^3 \cdot mol^{-1} \cdot cm^{-1}$	Literature source
I^-	225	12,875±30	226	12,600	Drago, 1967
			226	12,580	Ernepesova, 1990
	248	$1{,}021-75.25 \cdot M_{Cl^-}$			
$I_2+I_2Cl^-$	225	$8{,}457+1{,}936 \cdot \ln(M_{Cl^-})$			
	350	$184.2-13.71 \cdot (M_{Cl^-}) + 6.855 \cdot (M_{Cl^-})^2$			
	474	610.2±19.4	440	557	Ernepesova, 1990
			460	728	Cazon and Neumann, 1961
			460	731	Palmer et al., 1984
I_2Cl^-	248	39,500±400	250	39,600	Abrosimova et al., 1976
ICl_2^-	225	47,100±360	224	47,000	Cazon and Neumann, 1961
			230	42,000	Wang et al., 1989
	248	7,040±274			
	350	217.6±6.0	343	243	Cazon and Neumann, 1961
			343	274	Wang et al., 1989
	474	10.3±3.1			
I_3^-	350	25,000±400	350	25,000	Gottardi, 1982
				25,750	Palmer et al., 1984

An extinction coefficient of total iodine is a non-linear function of chloride contents at all other wavelengths. In order to calculate the concentrations of other iodine compounds, light absorbances for the following wavelengths were used: 225 nm (I^- and ICl_2^-), 248 nm (I_2Cl^-) and 350 nm (I_3^-). The dependence equations for the extinction coefficient of total iodine and iodide on chloride molality and extinction coefficient values of ICl_2^- and I_3^- at particular wavelengths obtained by us are presented in **Table 2**. The light absorbance of iodine compounds at selected wavelengths was observed to obey to Beer's law. Therefore, linear equation can be used for the calculation of optically active compounds at their joint presence in the systems being studied. The criteria for the accuracy of concentration calculation were estimated as the difference between the initial

iodide concentration and the sum of all determined iodine compounds. One limitation of the method developed is the impossibility to calculate low concentrations of I^- and ICl_2^- at their joint presence. These low concentrations are observed in brines with high chloride contents at oxidant/iodide ratios close to a stoichiometric one. The reason for the above is that both UV and visible fields cannot be used to distinguish the I^- and ICl_2^- since their wavelengths of maximum absorbance ICl_2^- are practically identical to the wavelengths of maximum absorbance of two suboxided iodine forms: I^- (225 nm) and I_3^- (350 nm). Since we could not determine the concentrations of I^- and ICl_2^- at their mutual presence, we assumed that solutions with different oxidation degrees contain various iodine compounds. We accepted that compounds I^-, I_2, I_2Cl^- and I_3^- exist in solutions at conditions of $Cl_2/2I^- \leq 1$, while the compounds I_2, I_2Cl^- and ICl_2^- are dominant at condition $Cl_2/2I^- > 1$. Total precision for the method developed to calculate iodine compounds was better than 5.2% for solutions with $Cl_2/2I^-$ molar ratio less then 2. This type of precision is considered to be quite acceptable while conducting kinetic studies even in solutions containing the only iodine compound ICl_2^- (Wang et al., 1989). Total precision for the method was better than 15.0% for natural underground waters with $Cl_2/2I^-$ molar ratio less then 2. In technological processes of iodine production, the $Cl_2/2I^-$ molar ratio is kept at less than 1.7 in order to obtain high outputs of a target product. Therefore, the method developed is acceptable for equilibrium and kinetic studies of iodine oxidation under various conditions.

C. IODIDE OXIDATION IN HIGHLY MINERALIZED CHLORIDE SOLUTIONS

C1. Equilibrium of iodide oxidation in highly mineralized chloride solutions

The study of the iodide oxidation mechanism allows us to solve a very important technological problem: what amount of oxidant should be added to a solution under processing in order to reach the maximum yielding of the desired products? Both incompletely oxidized (I^-) and peroxidized (ICl_2^-) iodine compounds, on the contrary, with iodine and its complex compound with chloride (I_2Cl^-) are not blown off by air during the technological process of iodine production. This leads to the loss of valuable components in the forms of I^- and ICl_2^-.

The total reaction of iodide oxidation by chlorine is given as:

$$2I^- + Cl_2 \Leftrightarrow I_2 + 2Cl^- \qquad (8)$$

The equilibrium constant of summary reaction of iodide oxidation by chlorine is very large: $K_8 = 8.3 \cdot 10^{25}$ (Ksenzenko & Stasinevich, 1995). Therefore, the iodide oxidation process is irreversible in either salt-free solutions or solutions with low chloride concentrations. For instance, according to Yavorsky and Zalkind (1965), oxidation of I^- to I_2 in salt-free solutions reaches 100%, an oxidant consumption of 1.03 from the stoichiometric value. However, this reaction is reversible in solutions where chloride concentrations exceed iodide concentration by thousands of times. 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^-). The composition of an equilibrium system depends on many factors, including the composition of the initial brine (the concentration of iodide and chloride) and an oxidant. With the rise of chloride concentration, the amount of oxidant corresponding to the maximum of iodine yield monotonically increases (Zalkind and Yavorsky, 1962). We found experimentally that the iodine yield in chloride solutions at pH=2.0 and a temperature of 25°C also reaches 100%. However, the oxidant amount required to reach a maximum iodine yield depends on solution mineralization. The

maximum iodine yield was observed in solutions with chloride concentrations less than 3.5 M at $Cl_2/2I^-$ molar ratios 1.0-1.05, i.e., at an oxidant amount that is close to a stoichiometric one (**Fig. 1a**). In solutions with a chloride concentration of 4.28 M, the maximum iodine yield is observed at $Cl_2/2I^-$ molar ratio 1.1-1.2 (**Fig. 1c**). Thus, oxidant excess is required for shifting the equilibrium for iodine formation only at a chloride concentration corresponding the disproportion reaction #7. Ernepesova (1988) proved that reaction #7 occurred in solutions with iodide concentration $(0.19\text{-}2.75)\cdot 10^{-4}$ M and chloride concentrations of 3.5-5.0 M.

The experimental data obtained allowed us to develop a model describing iodide oxidation in brines with various mineralization. Schcherbakova et al. (1978) and Ernepesova et al., (1989) tried to create an equilibrium model for iodine distribution between liquid and air phases. The system describing the oxidation of iodide by equations #1-#6, is the system of linear-independent equations, since each compound is formed only on one stage. Knowing the initial concentrations of iodide, chloride and chlorine, we calculated equilibrium concentrations of all iodine containing compounds. Thus, we determined the equilibrium constants for reaction #1-#6 (see below) which give the best agreement between experimental and calculated values.

The mass action law (Eqns. 9-14) and the equations of material balance (Eqns. 15-17) were used for treatment of experimental data by a non-linear least-square method. Expressing concentrations of all iodine forms while using concentrations of the initial substances $[I^-]$, $[Cl_2]$ and $[Cl^-]$, and equilibrium constants of reactions #1-#6, we received the law of mass action in the following forms:

$$[ICl_2^-] = K_1 \cdot [I^-] \cdot [Cl_2] \tag{9}$$

$$[ICl] = \frac{K_1 \cdot K_2 \cdot [I^-] \cdot [Cl_2]}{[Cl^-]} \tag{10}$$

$$[I_2Cl^-] = \frac{K_1 \cdot K_2 \cdot K_3 \cdot [I^-]^2 \cdot [Cl_2]}{[Cl^-]} \tag{11}$$

$$[I_2] = \frac{K_1 \cdot K_2 \cdot K_3 \cdot K_4 \cdot [I^-]^2 \cdot [Cl_2]}{[Cl^-]^2} \tag{12}$$

$$[I_3^-] = \frac{K_1 \cdot K_2 \cdot K_3 \cdot K_4 \cdot K_5 \cdot [I^-]^3 \cdot [Cl_2]}{[Cl^-]^2} \tag{13}$$

$$[Cl_3^-] = K_6 \cdot [Cl_2] \cdot [Cl^-] \tag{14}$$

The equations of material balance for initial substances were developed based on the following assumptions:

a) I^- is consumed for the formation of all other iodine containing compounds:

$$[I^-]_0 = [I^-] + [ICl_2^-] + [ICl] + 2[I_2Cl^-] + 2[I_2] + 3[I_3^-] \tag{15}$$

b) Cl_2, being an oxidant, is consumed for the formation of all oxidized iodine forms:

$$[Cl_2]_0 = [Cl_2] + [ICl_2^-] + [ICl] + [I_2Cl^-] + [I_2] + [I_3^-] + [Cl_3^-] \tag{16}$$

c) Cl^- plays several roles such as a medium ion, a product of oxidation reaction and a complexing agent:

$$\begin{aligned}[Cl^-]_0 &= [Cl^-] - [ICl_2^-] - [ICl] - 2[I_2Cl^-] - 2[I_2] - 2[I_3^-] + [ICl_2^-] + [I_2Cl^-] + [Cl_3^-] = \\ &= [Cl^-] - [ICl] - [I_2Cl^-] - 2[I_2] - 2[I_3^-] + [Cl_3^-]\end{aligned} \tag{17}$$

By substituting the Eqns. 9-14 for Eqns. 15-17, a system of equations of material balance was obtained. The system obtained contains only the concentrations of initial substances and equilibrium constants of the reactions #1-#6. The equations of material

balance and the mass action law can be expressed by using the component stoichiometric matrix A:

$$A^T \cdot X = B \tag{18}$$

where A^T is the transposed matrix of the system studied via concentrations of initial substances and equilibrium constants for reactions #1-#6 presented in **Table 3**, and B is the vector of the initial data.

Table 3. Component stoichiometric matrix A for modeling the system I^-, Cl_2 and Cl^-.

Molecular matrix	I^-	Cl_2	Cl^-	$\ln(K_i)$
I^-	1	0	0	0
Cl_2	0	1	0	0
Cl^-	0	0	1	0
ICl_2^-	1	1	0	$\ln(K_1)$
ICl	1	1	-1	$\ln(K_1 \cdot K_2)$
I_2Cl^-	2	1	-1	$\ln(K_1 \cdot K_2 \cdot K_3)$
I_2	2	1	-2	$\ln(K_1 \cdot K_2 \cdot K_3 \cdot K_4)$
I_3^-	3	1	-2	$\ln(K_1 \cdot K_2 \cdot K_3 \cdot K_4 \cdot K_5)$
Cl_3^-	0	1	1	$\ln(K_6)$

The solution of the system of the three nonlinear equations of material balance (15-17) for each experimental point was conducted by the modified Newton-Raphson method (Albert et al., 1965; Evseev and Nikolaeva, 1988). The purpose of the calculation is to determine the minimum of nonlinear function by the least-square method:

$$F = \sum_{i-1}^{N} w_i \cdot ([c]_{exp} - [c]_{calc}) \tag{19}$$

where $[c]_{exp}$ is the experimental equilibrium component concentration, $[c]_{calc}$ are the calculated equilibrium component concentrations, and w_i is the weight coefficient that was accepted to be equal to 1. The Newton-Raphson method requires good quality approximation of equilibrium component concentrations. As the first approximation in the Newton-Raphson procedure, we used the values $[c]=0.1[c]_0$, where the $[c]_0$ are the initial concentrations of the substances. For each step of iteration, the values obtained at each previous step of calculation were used as initial approaches. Minimization of the nonlinear function F was carried out by method of "ravines" (Evseev and Nikolaeva, 1988) using equilibrium constants expressed in logarithmic form. We conducted statistical analysis using Fisher criteria in order to check the reliability of the results. The degree of the probability for the chosen scheme of reaction and the equilibrium constants obtained is more than 0.95 if:

$$\frac{F_{min}}{(2\sigma_{exp})^2 \cdot (N-2n)} \langle 1 \tag{20}$$

where σ_{exp} is the experimental error in determining equilibrium constants, N is the amount of experimental points, and n is the amount of determined parameters. The programs for calculation of parameters were developed on PASCAL FOR WINDOWS and FORTRAN FOR WINDOWS.

The best set of calculated equilibrium constants is presented in **Table 4**. We would like to emphasize here that the equilibrium constant for the reaction #1 was calculated for

the first time. Since component concentrations but not activities were used for calculations, the calculated equilibrium constants are not thermodynamic ones, therefore, they are dependent on solution ionic compositions, and in our case, mainly on chloride concentrations. Most of the equilibrium constants obtained (**Table 4**) are in accord with the literature quoted (**Table 1**). A large discrepancy between the calculated and literature values was observed only for K_5 values. The reason, to our mind, is that literature equilibrium constants were determined in chloride-free solutions. The low K_5 values found for chloride containing solutions as compared with the literature data, are supported by the observations of Lipatova and Stasinevich (1976). These authors observed that the equilibrium constant for the formation of I_3^- ion in aqueous solutions decreased significantly with chloride addition to solutions.

Table 4. Equilibrium constants for reactions (1-6) at various chloride concentrations

Equilibrium constant	Calculated equilibrium constants at various chloride concentrations, mol/l		
	0.98	2.69	4.28
K_1, M^{-1}	$(1.08\pm0.04)\cdot10^7$	$(2.24\pm0.05)\cdot10^7$	$(3.98\pm0.08)\cdot10^7$
K_2, M	$(3.41\pm0.22)\cdot10^{-3}$	$(4.28\pm0.35)\cdot10^{-3}$	$(1.76\pm0.08)\cdot10^{-2}$
K_3, M^{-1}	$(5.31\pm0.07)\cdot10^8$	$(8.01\pm0.08)\cdot10^8$	$(2.40\pm0.15)\cdot10^9$
K_4, M	0.74±0.02	0.81±0.03	1.10±0.03
K_5, M^{-1}	575±31	379±17	185±11
K_6, M^{-1}	0.11±0.02	0.12±0.02	0.12±0.03

C2. Factors influencing the rate of oxidation process

The experimental study of the kinetics of iodide oxidation by chlorine by a stopped-flow method at 25°C demonstrated that the main factor influencing the rate of iodide oxidation is chlorine/iodide ratio. Even at relatively law oxidant excess ($Cl_2/2I^- \geq 1.25$), the oxidation process takes less than 0.1 sec (**Fig. 2**). At oxidant excess, the I_2, I_2Cl^- and ICl_2^- compounds are formed (**Fig. 3**). However, if the oxidant amount is equal to or less than the stoichiometric one ($Cl_2/2I^- \leq 1$) I_2, I_2Cl^- and I_3^- are then formed and there is some residual of I^- in the solution (**Fig. 4**). If there is an oxidant shortage ($Cl_2/2I^- \leq 0.5$) the oxidation process then takes also less than 0.1-0.2 sec (**Fig. 2**). It is possible that at oxidant efficiency, the mechanism of iodide oxidation is analogous to the process of extremely rapid reactions by ICl_2^- and I^- at iodide excess studied by Margerum et al. (1986). Thus, if there are large excesses or a large shortage of oxidant (chlorine) in the systems studied, the equilibrium of the reaction is reached very quickly. Only at a $Cl_2/2I^-$ ratio close to 1, the oxidation reaction runs relatively slowly (**Fig. 2, 4**). This fact will be explained further during the discussion of the mechanism of iodide oxidation process. We also observed chloride concentration influence on oxidation rates under these conditions. If the amount of oxidant is close to the stoichiometric one, the reaction rate then depends on chloride concentration and increases with its increase from 0.98 to 4.28 M (**Fig. 5**). Thus, provided that all other parameters of the process are kept constant ($[I^-]_{initial}=4\cdot10^{-4}$ M, $Cl_2:2I^-=1.0$ and pH=2), the time required for complete oxidation process reduces from 4-5 s at chloride molarity 0.98 to 1-2 s at chloride molarity 2.69 mol/l, then to 0.5 s at chloride molarity 4.28 mol/l and less then 0.1 s

at chloride molarity 4.71 mol/l. The equilibrium time is inversely proportional to chloride concentration (**Fig. 6**).

In solutions with chloride concentrations larger than 3.5 M, the reaction of iodide disproportionation #7 continues for a long time (up to 24 hours) after quick reactions #1-#5. The reaction of iodide disproportionation can be observed by the decrease of absorbance at 248 nm, corresponding to a concentration decrease of I_2Cl^-. It can be observed an increase of absorbance at 225 nm, corresponding to a concentration increase of ICl_2^- and I^- (**Fig. 7**). Since the rate of reaction #7 is negligible as compared with those of reactions #1-#5, the changes in iodine concentrations are then due to reaction #7 for 30 s (the time of our experiments) are approximately $8 \cdot 10^{-7}$ M. This value is smaller than the errors of iodine concentration calculations and we, therefore, neglected its contribution to the iodide concentration changes in the studied time interval of 0.1-5.0 s.

The above-mentioned facts prove that the mechanism of iodide oxidation process is dependent on oxidant/iodide ratio. Previously, only the mechanism of iodide oxidation by reaction #2-#5 at large excesses of iodide and with an ionic strength of a solution less than 1.0 was investigated (Kumar et al., 1986; Margerum et al., 1986; and Nagy et al., 1988). The large excess of iodide leads to pseudo first-order dependence for the constant of process rate on iodide. Under these conditions, all reactions are extremely rapid and all literature kinematics parameters for reactions #2-#5 presented in Table 1 were determined at large iodide excesses. Since reaction #5 takes place only during the presence of iodide, we presume that when an iodide will be completely oxidized due to reaction #3 at an oxidant excess, the mechanism of oxidation process is described by equations #1-#4. Our experiments at various oxidant/iodide ratios demonstrated that the changes in oxidation process occur at reagent concentrations that correspond to a maximal yield of iodine. It is obvious that the rate of iodide oxidation at the excess of any reagent is very large. Under these conditions, kinetic parameters of the oxidation process cannot be determined by a stopped-flow method since the reactions are completed within the dead time of a stopped-flow instrument. However, this method allowed us to estimate the rate of process for component ranges of various stoichiometric ratios. It should be emphasized that reliable values of maximal yield for target products of I_2+I_2Cl^- were obtained under these conditions.

C3. Calculating method for kinetic parameters.

The method used to calculate the reaction order and apparent rate constant of oxidation reaction was described in detail in the Annual Report (1999, Chapter C3a). A short description of the method developed for calculation is given below. The rate of this reaction is given as:

$$-d[A]/dt = k \cdot [A]^n \qquad (21)$$

where A is the experimental iodide concentration, n is the total order of oxidation reaction, and k is the apparent rate constant of the oxidation reaction that summarizes the rates of reactions #1-#7. For estimation of the reaction order, we used the classic graphic method. A dependence of $1/[A]^{n-1} = f(t)$ was fitted for different "n" ($n \neq 1$) values by using the experimental concentration data. For instance, for n=2, linear dependence should be observed in the coordinates $1/[A] = f(t)$; for n=3, linear dependence should be observed in the coordinates $1/[A]^2 = f(t)$, and so forth. For n=1, linear dependence in coordinates $\ln[A] = f(t)$ should be observed. The reaction constant at $n \neq 1$ was calculated by the equation:

$$k = \sum_{i=1,N} \frac{\left(\frac{1}{[A]_i^{n-1}} - \frac{1}{[A]_0^{n-1}}\right)}{[(n-1)\cdot t_i \cdot N]} \tag{22}$$

where N is the number of experimental points.

The calculated value of reagent "A" concentration for $n \neq 1$ is calculated by the following equation:

$$[A]_i = k \cdot [A]_o \Big/ \left[(n-1)\cdot t \cdot [A]_o^{n-1} + 1\right]^{1/(n-1)} \tag{23}$$

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

$$k = \sum_{i=1,N} \frac{\ln [A]_o / [A]_i}{N \cdot t_i} \tag{24}$$

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

$$[A]_i = [A]_o \cdot \exp(-k \cdot t) \tag{25}$$

The function correlation is estimated by correlation coefficient (R). The most probable n corresponds to the function with the largest R-value.

C4. Kinetic parameters for process of iodide oxidation

According to the calculations of Eqns. 22-25 at a stoichiometric ratio of reagents in the entire range of iodide and chloride concentrations studied and at time intervals from 0 to equilibrium time, the second order dependence on the I^- concentrations for iodide oxidation reaction was observed. The average rate constant of the second order for iodide oxidation reaction considerably increases with chloride concentration: rate constants increase from $(1.24\pm0.28)\cdot10^4$ to $(5.04\pm0.43)\cdot10^4$ $M^{-1}s^{-1}$ as chloride molarity increases from 0.98 to 2.69 and is independent on initial iodide concentration (**Table 5**).

Table 5. Calculated kinetic parameters for the reaction of iodide oxidation by chlorine at their stoichiometric molar ratio

Initial composition of solution		Reaction time, s	Kinetics parameters			
$[I^-]$, M	$[Cl^-]$, M		Reaction order	Rate constant		Correlation coefficient
				$M^{-1}s^{-1}$	s^{-1}	
Time period: $0<\tau<\tau_{eqiulibrium}$						
0.0002	0.98	4.1	2	$1.56\cdot10^4$		0.912
0.0004	0.98	4.7	2	$1.14\cdot10^4$		0.994
0.0006	0.98	4.7	2	$1.01\cdot10^4$		0.959
0.0002	2.69	1.5	2	$5.14\cdot10^4$		0.953
0.0004	2.69	1.5	2	$4.63\cdot10^4$		0.960
0.0006	2.69	1.5	2	$5.36\cdot10^4$		0.938
Time period: $\tau\leq0.1$ s						
0.0002	0.98	0-0.1	1		15.43	0.990
0.0004	0.98	0-0.1	1		14.69	0.999
0.0006	0.98	0-0.1	1		16.18	0.994
0.0002	2.69	0-0.05	1		18.82	0.999
0.0004	2.69	0-0.05	1		19.07	0.999
0.0006	2.69	0-0.05	1		19.83	0.985

The kinetic curves (**Fig. 4**) show that the rate of iodide oxidation during the initial time period ($\tau<0.1$ s) is considerably higher than the average rate. During this time period, more than 50% of the initial amount of iodide is in effect oxidized. The equipment used in the current study did not allow us to quantitatively measure the changes of iodide concentrations for a time period of less than 0.1 s. Such changes for the time range of $0<\tau<0.1$ s were calculated by interpolation using the spline-functions method (Albert et al., 1972; Anselon and Laurent, 1968; and Marchuk, 1980). The use of cubical spline-functions produces favorable agreement between calculated and experimental data at a time reaction of more than 0.1 s. Therefore, we assume that this method could also be used for a time reaction of less than 0.1 s. To verify this suggestion, we tested the method for model reaction between iodine and β-phenyl-propionic acid (Spiridonov and Lopatkin, 1970). Like the reaction under discussion, this reaction has the second order dependence on concentration of initial compound (iodine). We excluded three points of experimental data in which form 0 to 50% of the initial amount of iodine reacted. We then calculated the excluded concentrations by the spline-functions method using concentrations for points remained. The calculation method did not distort the view of kinetic curves in different coordinates: $[I^-]=f(\tau)$, $\ln[I^-]=f(\tau)$ and $1/[I^-]=f(\tau)$ (**Fig. 8**). The value of the rate constant calculated using the concentrations obtained is equal to $6.294\cdot10^{-2}$ $dm^3\cdot mol^{-1}\cdot min^{-1}$, the reported value is $6.14\cdot10^{-2}$ $dm^3\cdot mol^{-1}\cdot min^{-1}$, and the difference between these values is less then 1%. In this manner, we suggested that the method of spline-functions produces favorable results for calculating the missing points of a kinetic curve.

The iodide concentration changes obtained by the above method for a time reaction of less than 0.1 s were then used for building kinetic curves and calculating kinetic parameters (**Table 5**). In order to determine an order of the studied reaction, we presented iodide concentration changes vs. time in different coordinates: $\ln[I^-]=f(\tau)$ and $1/[I^-]=f(\tau)$ (**Fig. 9**). The kinetic curves in these coordinates may be separated on two groups: time less than 0.1 s and time from 0.1 s to equilibrium time (**Fig. 9**). This type of dependence indicates that the mechanism of the reaction changes during the observed time intervals. The kinetic curve in coordinate $1/[I^-]=f(\tau)$ is not linear for the time intervals less than 0.1 s (**Fig. 9c**), therefore, for initial time interval the iodide oxidation reaction is not described by the second order of dependence on I^- concentrations. The kinetic curve in coordinate – $\ln[I^-]=f(\tau)$ demonstrated that for time intervals less than 0.1 s, linear dependence is observed (**Fig. 9b**). We propose that the iodide oxidation reaction on the whole has the second order dependence on I^- concentrations, but during initial time intervals, the first order dependence of the rate constant on I^- concentration occurs. Calculations by Eqn. 24 produce an average initial first-order rate constant equal to 17.3 ± 2.2 s^{-1} (**Table 5**).

C5. Mechanism of iodide oxidation by chlorine in chloride solutions at the stoichiometric ratio of reagents

It was demonstrated above that the rate of iodide oxidation by chlorine is very high at the excess of one of the initial substances, i.e., at either $Cl_2/2I^- \ll 1$ or $Cl_2/2I^- \gg 1$. However, at the reagent ratio ($Cl_2/2I^-$) close to 1, the rate of iodide oxidation by chlorine was observed to be relatively small and sharply decreased when than more half of the iodide was oxidized. In order to study the mechanism of oxidation process we suggest several hypotheses of this mechanism which we checked using our experimental data. The proposed hypotheses are:

Hypothesis 1. The process of iodide oxidation is limited by reaction (1).

Hypothesis 2. The process of iodide oxidation by chlorine in chloride solutions at $Cl_2/2I^-$ close to 1 runs through reactions #2-#5 and its kinetic is probably similar to the reactions between iodide and chlorine containing compounds with iodide excess studied by Kumar et al. (1986), Margerum et al. (1986) and Nagy et al. (1988).

Hypothesis 3. The process of iodide oxidation by chlorine in chloride solutions at ($Cl_2/2I^-$)=1 has another mechanism with the formation of other intermediate compounds.

Hypothesis 4. The process of iodide oxidation by chlorine in chloride solutions at $Cl_2/2I^-$ close to 1 runs through the reactions #2-#5 but a limiting reaction which determines the process rate differs from that of the process described by Hypothesis 2 (with iodide excess).

Let us consider Hypothesis 1. The rate constant for reaction #1 was not studied previously. Margerum et al. (1986) studied the rate of reaction between ICl_2^- and I^- using pre-prepared ICl_2^- solution. It is known that the optimal ratio of $Cl_2/2I^-$ for ICl_2^- formation is approximately $Cl_2/2I^-=2.0\div2.3$ which corresponds to the stoichiometric amount of an oxidant required to oxidize I^- to ICl (Kazantseva et al., 2002). Therefore, in all ranges of the ratio $Cl_2/2I^-<2.0$ studied, there is an iodide excess in reaction #1. Since at $Cl_2/2I^-<0.5$ and $Cl_2/2I>1.2$ the process rate is high, it is illogical to assume that at $Cl_2/2I^-$ closed to 1.0 at an excess of iodide in reaction #1 is sharply braked and then accelerated. Therefore, we assume that reaction #1 is not a limiting one.

Let us discuss the correspondence between Hypothesis 2 and our experimental data. It was found that the rate of reaction between ICl_2^- and I^- at iodide excess passing via reactions #2-#5 was limited by reaction #3 with $k_3=1.1\cdot10^9$ $M^{-1}s^{-1}$ (Margerum et al., 1986). The average initial first-order rate constant для нашей системы was found to be equal to 17.3 ± 2.2 s^{-1}. This first-order rate constant is two magnitude of orders less than the pseudo-first-order rate constant of reaction #3 with a large excess of iodide. Let us assume that the observed process deceleration was conditioned by very low concentrations of initial substances under conditions closed to the equilibrium. Using this rate constant for the estimation of the reaction rate for the process of iodide oxidation at a stoichiometric ratio, we found that the experimentally observed rate is considerably smaller than a calculated one. Therefore, the decrease of iodide concentration at our experimental conditions cannot be described by rate constants of reactions determined at iodide excess.

Let us consider Hypothesis 3. The analysis of literature data shows that the rates and mechanisms of oxidation processes are strongly dependent on reagent ratios and reaction conditions. We assumed that deceleration of the oxidation process observed in solutions with relatively low chloride content is conditioned by the hydrolysis of chlorine at pH≥2 with further interactions between HOCl and I_2. Reactions HOCl + I_2 and I^- + ClO_2 are relatively slow autocatalytic reactions (Beck and Rabai, 1986; Rabai and Beck, 1987; Lengyel et al., 1996) depending on reagent ratios. The kinetic parameters of this complex process are comparable with those determined by us. Thus, a) the time for a complete reaction is varied from several seconds to several minutes; b) chloride decreases induction time, and consequently accelerates the oxidation process. However, we did not found any proof of an autocatalytic process in our experiments. The concentration of iodine smoothly increases in the oxidation process without extremes and without an induction period (**Fig. 2-5**). Therefore, there is no proof that there is another reaction with the exception of reactions #1-#5 and the formation of another intermediate compound.

Let us consider Hypothesis 4. The data obtained demonstrated a strong influence of chloride concentration on the kinetic. Thus, the rate of oxidation process at chloride absence is very high (**Fig. 5**). At a chloride concentration of 0.98 M, the process rate is considerably lower than at chloride absence. This is in accord with the findings of Margerum et al. (1986) that the pseudo-first-order rate constant reaction of ICl with I^- at an iodide excess ($[I^-]=0.96\cdot10^{-3}$ M, $[ICl]=3.0\cdot10^{-5}$ M) and at pH=1 decreases from $36\cdot10^3$ s^{-1} till $18\cdot10^3$ s^{-1} at the increase of a chloride concentration from 0.26 to 1.0 M. However, the

increase of chloride concentration from 0.98 to 4.71 M led to the increase of a solution rate (**Fig. 5, Table 5**). It is possible that chloride anions, starting from a particular concentration, accelerate any of reactions #1-#5. Let us find which of these reactions is accelerated.

It should be noted that the absorption spectra of the solution with chloride molarity 0.98 M has a specific peculiarity: the intensity of the absorption with a maximum of 350 nm increases during 0.1-0.3 s and then decreases (**Fig. 10 a,b,c**). In solution spectra with a chloride concentration of 2.69 M, the absorption at 350 nm is small and constant, while in solutions with larger chloride concentrations the absorption at 350 nm is completely missing (**Fig. 11**). Simultaneously, with the decrease of absorption at 350 nm, we observed the increase of absorption at 248, 440 and 474 nm conditioned by the formation of I_2 and I_2Cl^-, and a decrease of absorption at 225 nm due to a decrease of an iodide concentration.

What is the reason for the decrease of absorption at 350 nm? The absorption at 350 nm is known to correspond with three compounds: I_3^-, ICl_2^- and Cl_3^-. Therefore, it is possible to suggest that its decrease is conditioned by the decrease of a concentration of one of these substances:

1). Let us assume that the absorption decrease at 350 nm is conditioned by the decrease of Cl_3^- concentration due to oxidant consumption. The calculations using the equilibrium constants of reaction #6 and the molar extinction coefficient of Cl_3^- (K_6=0.18, ε_{355} =100 $dm^3 \cdot mol^{-1} \cdot cm^{-1}$, Wang et al., 1989) demonstrate that the absorption obtained at 350 nm corresponds to $Cl_2 + Cl_3^-$ concentration equal to $3.64 \cdot 10^{-2}$ M. This concentration is approximately 200 times larger than the initial oxidant amount ($2.0 \cdot 10^{-4}$ M). Therefore, the decrease of Cl_3^- concentration due to oxidant consumption cannot be a reason for the absorption decrease at 350 nm.

2) Let us now assume that the absorption decrease at 350 nm is conditioned by the decrease of the ICl_2^- concentration that is formed according to reaction #1 and participates in reaction #2. Calculations using Beer's law together with the molar extinction coefficient of ICl_2^- (ε_{350} =217 $dm^3 \cdot mol^{-1} \cdot cm^{-1}$, Kazantseva et al., 2002) demonstrated that in this case, the decrease of ICl_2^- concentration is $\Delta[ICl_2^-]=\Delta A/(\varepsilon_{350} \cdot l)=(0.546-0.434)/(217 \cdot 1)=0.00052$ M, i.e., 2.5 times larger than the concentration of initial substances. Therefore, absorption decrease at 350 nm was not conditioned by the decrease of ICl_2^- concentration in the reaction. In addition, in both cases, concentrations Cl_3^- and ICl_2^- and, therefore, absorption at 350 nm have to be larger in solutions with higher chloride concentrations. We observed the opposite phenomenon.

3) We, therefore, assume that the time decreasing absorption at 350 nm together with a stoichiometric reagent ratio, or close to it, was determined by I_3^-. Maximum absorption was observed for solutions with an I^- initial concentration of $6 \cdot 10^{-4}$ M, chloride molarity of 0.98, $Cl_2/2I^-$=1.0 and pH=2 and corresponded to an I_3^- concentration of 4.3% of the initial iodide concentration at a time reaction of 0.1 s and 2.5% under equilibrium conditions. The I_3^- concentration calculated from absorption values at 350 nm decreases with the increase of chloride concentrations. Thus, in a solution with only different chloride (chloride molarity of 2.69), the maximum I_3^- concentration consists of less than 1.0% of the initial iodide concentration. These values of I_3^- concentrations favorably agree with the calculations for the equilibrium system conducted both by us and other researchers (Ksenzenko & Stasinevich, 1995; Margerum et al., 1986). The molar ratio $I_3^-/SumI_2$ calculated each time decreases with time and increases with the increase of the molar ratio I^-/Cl^- in a starting solution. The ratio $I_3^-/Sum\ I_2$ in solutions with chloride molarity of 0.98 decreases from 0.04 at a reaction time of 0.1 sec to 0.001 at a reaction time of 4.0 sec. For solutions with chloride molarity of 2.69 and initial iodide concentration of $6 \cdot 10^{-4}$ M, the above ratio decreases by 60 times for 1.0 sec.

Thus, we could conclude that the spectrum peculiarities discussed are conditioned by the decrease of an I_3^- concentration and by an increase of Sum I_2 in time intervals of 0.2-

0.3 sec until equilibrium. The reasons which conditioned these changes of concentrations might trace a limiting reaction. We present here several hypotheses related to the problem of determining limiting reactions: Hypothesis A (the process rate is determined by the rates of reactions #4-#5) and Hypothesis B (the process rate is determined by the rate of reaction #3).

Let us discuss Hypothesis A. The decrease of I_3^- concentration and molar ratio I_3^- /Sum I_2 during the oxidation process are conditioned by the differences between the equilibrium and the kinetic parameters of the formation reactions of two complex iodide compounds: I_3^- and I_2Cl^-. The equilibrium constant and reaction rates for the reaction of I_3^- formation are very large: K_5=738 M^{-1} (Ramette & Sandford, 1965) and $k_5 = 6.2 \cdot 10^9$ $M^{-1} \cdot s^{-1}$ and $k_{-5} = 7.5 \cdot 10^6$ s^{-1} (Ruasse et al., 1986). Therefore, the formation of I_3^- begins when an excess of iodide presents itself in the solution. However, under equilibrium conditions, the compound concentrations are determined by the concentrations of initial substances and by equilibrium constants of the proper reactions. Therefore, the dissociation of I_3^- and the formation of I_2Cl^- occur when the system reaches the equilibrium and iodide is consumed. The formation reaction of I_2Cl^- from I_2 and Cl^- is the reverse reaction of reaction (4). Therefore, we can accept that the equilibrium constant of the formation of this complex ion is equal to $(K_4)^{-1}$=1.7 M^{-1} (Cason and Neumann, 1961). The constant k_{-4} is missing in literature but can be roughly estimated by the equation $K_4=k_4/k_{-4}$, where $k_4>5 \cdot 10^4$ s^{-1} (Margerum et al., 1986). The value obtained is $k_{-4}>2.9 \cdot 10^4$ $M^{-1} \cdot s^{-1}$. This value is several magnitudes of order less than k_5, therefore, the dissociation of I_3^- and the formation of I_2Cl^- can be observed with time. The presence of two isobestic points in the solution spectra (**Fig. 20**) supports the coexistence of the above mentioned iodine compounds and their redistribution with time: an isobestic point at 234 nm corresponds to a pair of I^- and I_2Cl^- and an isobestic point at 396 nm corresponds to a pair of I_2Cl^- and I_3^-. In order to prove that the difference in the equilibrium constants of two complex iodine forms is a reason for inhibition of the oxidation process at a stoichiometric component ratio, we conducted an additional experiment by changing the order of component mixing. Ksenzenko & Stasinevich (1995) assumed that it was possible to obtain identical solutions by adding the stoichiometric chlorine amount to chloride solution with iodide and by the dissolution of iodine in the chloride solution. We studied the reaction rate by mixing a solution containing I_2 and I^- and a solution containing Cl^-. The concentration of initial substances were chosen so that a final solution corresponded to a solution obtained by mixing iodide solution and chlorine water and containing I^- initial concentration equal to 0.0004 M, $Cl_2/2I^-$=0.75 and pH=2. Spectrums of these two solutions at equilibrium are identical, but the kinetics of the processes is different. While mixing a solution containing I_2 and I^- with a solution containing Cl^-, the oxidation process passes through reactions #4 and #5. Disproportionation of iodine forms and the formation of the equilibrium system containing I_2(aq), I_2Cl^- and I_3^- was very quick, approximately 0.2-0.3 s. Therefore, the reactions of complex formation (4) and (5) are not limiting factors of the oxidation process.

Let us now discuss Hypothesis B. Another explanation of I_3^- diminution can be the fact that iodide reacts with iodine much faster than with ICl (see Table 1). At the initial stage of the process, I_3^- formation is preferable. At a stoichiometric component ratio the I^- shortage for reaction #3 takes place and as a result, dissociation of I_3^- occurs. It is known that reactions of I^- with ICl_2^- (Margerum et al., 1986) and HClO (Nagy et al., 1988) plus hydrolysis of iodine chloride (Wang et al., 1989), which are limited by reaction #3, are accelerated with the increase of iodide concentration. We observed, that with an iodide excess ($Cl_2/2I^-<1$), the rate of iodide oxidation is also increased (the less is the molar ratio $Cl_2/2I^-$, the more is the rate) (**Fig. 2**) It is possible that inhibition of the oxidation process is conditioned by decreasing the rate of reaction #3 at low iodide concentrations of $Cl_2/2I^-=1$.

Thus, on the basis of all results obtained, we conclude that the process of iodide oxidation by chlorine both at a stoichiometric component ratio ($Cl_2/2I^-=1$) and at an excess

of iodide is limited by reaction #3. However, the rates of the processes are different. We suggest that a reaction of interaction between ICl and I^- at $Cl_2/2I^-=1$ is accelerated with the increase of a chloride concentration higher than 1 M. However, the last suggestion can be defined only by other methods applied to very quick reactions.

D. IODIDE OXIDATION IN CHLORIDE SOLUTIONS CONTAINING OXIDIZABLE ADDITIVES.

According to the general accepted point of view (Ksenzenko and Stasinevich, 1995), natural brines contain organic and inorganic compounds which can be oxidized by chlorine (Br^-, H_2S and its sodium salt, sodium salts of naphthenic acids, iron ions). Their nature and amount affect both the excess of the oxidant needed to obtain a high degree of oxidation, and the kinetics of the oxidation process. The purpose of this investigation was to study the influence of each additive on the equilibrium and the kinetics of the iodide oxidation reaction and to test obtained peculiarities on natural brines. The study was carried out for solutions with average values of initial I^- concentration of 0.0004 M, chloride concentrations of 2.69 and 0.98 M and pH 2 at a temperature of 25°C. The chosen chloride concentrations were dictated by technical possibilities of using equipment.

D1. Bromide ion.

Zalkind and Yavorsky (1962) showed that when bromide content in brine increases, the optimal oxidant consumption increases. They believed that iodine-yielding decrease was caused by complex formation of compounds containing iodine and bromine. Eyal and Treinin (1964) observed the formation of I_2Br^- and IBr_2^- in iodine and bromide containing solutions due to the following reactions:

$$I_2 + Br^- \Leftrightarrow I_2Br^- \qquad K_9=10.5 \qquad (26)$$

$$IBr + Br^- \Leftrightarrow IBr_2^- \qquad K_{10}=480 \qquad (27)$$

In chloride containing solutions, the formation of $IBrCl^-$ is preferable by use of the following reaction (Mokhnach, 1963):

$$IBr + Cl^- \Leftrightarrow IBrCl^- \qquad K_{11}=45.5 \qquad (28)$$

All the above-mentioned compounds absorb light (**Table 6**), and we expected an absorption increase in 25-280 and 360-370 nm at $Cl_2/2I^-$ molar ratio≥1.0 due to their formation. Ernepesova (1990) observed significant absorption increases at 220-230 nm and $Cl_2/2I^-$ molar ratios >1.2 during iodine oxidation by chlorine in bromide and chloride containing solutions. This phenomenon was explained by the $IBrCl^-$ formation although we did not observe any difference of spectra at 250-280 and 360-370 nm for solutions with and without bromide (**Fig. 12,13**). The only difference observed was absorption at far UV-ranges with the maximum at 206-207 nm corresponding to bromide. If solutions with the same concentrations of bromide are used as a blank, the spectra of solutions with and without bromide are identical in all ranges of $Cl_2/2I^-$ molar ratios investigated. In any event, we did not see any spectral evidence of iodine-bromine compounds for the solutions under study. Nevertheless, our experimental results show that oxidant consumption increases when bromide concentration increases (**Fig. 14**). The highest yield of $SumI_2$ reaches 99.5-100% and is observed at the following $Cl_2/2I^-$ molar ratios:

1.2-1.3 at bromide concentration 0.003 M;
1.3-1.6 at bromide concentration 0.006 M.

Table 6. Optical characteristics of complex compounds of iodine and bromine

Compound	Solution composition	Optical characteristics		Literature source
		Band length, nm	Extinction coefficient, $dm^3 \cdot mol^{-1} \cdot cm^{-1}$	
I_2Br^-	0.003 M I_2, 0.1 M Br^-	270 360	No data	Savko and Fraerman, 1966
	$1.1 \cdot 10^{-3}$ M IBr, 1.0 M $HClO_4$	273 350 428 440	61,000 13,000 3,000 2,700	Troy et.al., 1991
IBr_2^-	0.005 M IBr, 0.1 M Br^-	256 370	No data	Mokhnach, 1963
	$1.0 \cdot 10^{-5}$ M I_2, 0.20 M Br^-, $1.0 \cdot 10^{-3}$ M I^-	253 375 428 440	55,000 580 140 97	Troy et.al., 1991
$IBrCl^-$	0.0005 M solution $[RbI(ClBr)] \cdot H_2O$ in 0.1 M RbCl aqueous solution	228 255 445	6,825 1,419 113	St'epin and Pl'uschev, 1961

During the presence of bromide, time when the equilibrium of iodide oxidation reaction is reached is approximately 2 times less (**Fig. 15**). Kinetics of the reaction is dependent on bromide concentration. The following values of kinetic parameters for solutions with initial I^- concentration of 0.0004 M, chloride concentration of 0.98 M, $Cl_2/2I^-$ molar ratio = 1.3-1.4 and pH=2 at a temperature of 25°C have been obtained: reaction order n = 2, rate constant $k = 3.20 \cdot 10^4$ $M^{-1}s^{-1}$ and $4.47 \cdot 10^4$ $M^{-1}s^{-1}$ for 0.003 and 0.006 M solutions of Br^- accordingly. The rate of iodide oxidation with the same concentrations of iodide and chloride is 2.8-3.9 times slower ($k = 1.14 \cdot 10^4$ $M^{-1}s^{-1}$) when bromide is not present in the solution (**Table 8**). For solutions with the same concentrations of iodine and chlorine, and chloride concentration of 2.69 M the following values of kinetic parameters been obtained: reaction order n = 2, rate constant $k = 5.80 \cdot 10^4$ $M^{-1}s^{-1}$ and $7.78 \cdot 10^4$ $M^{-1}s^{-1}$ for 0.003 and 0.006 M solutions of Br^- accordingly, and $k=4.63 \cdot 10^4$ $M^{-1}s^{-1}$ without bromide. For this chloride content the bromide addition leads to an increase of the rate of iodide oxidation by 1.3-1.7 times. Our results support the data of Zalkind and Yavorsky (1962).

Table 8. Calculated kinetic parameters for the reaction of iodide oxidation by chlorine for model solutions at 25°C and pH=2 ($Cl_2/2I^-$ molar ratios corresponding to the highest yield of $SumI_2$).

Initial composition of solution			$Cl_2/2I^-$ molar ratio	Reaction time, s	Rate constant, $M^{-1}s^{-1}$
$[I^-]$, M	$[Cl^-]$, M	Additives			
0.0004	0.98		1.0	4.7	$1.14 \cdot 10^4$
0.0004	2.69		1.0	1.5	$4.63 \cdot 10^4$
0.00037	0.98	0.003 M Br^-	1.3	2.0	$3.20 \cdot 10^4$
0.0004	0.98	0.006 M Br^-	1.4	1.5	$4.47 \cdot 10^4$
0.0004	2.69	0.003 M Br^-	1.3	1.3	$5.80 \cdot 10^4$
0.0004	2.69	0.006 M Br^-	1.4	1.2	$7.78 \cdot 10^4$
0.0004	0.98	50 mg/l $C_6H_{11}COOH$	1.0	1.1	$8.48 \cdot 10^4$

0.0004	2.69	50 mg/l $C_6H_{11}COOH$	1.0	1.0	$1.08 \cdot 10^5$
0.0004	0.98	50 mg/l C_6H_5OH	1.7	4.0	$2.11 \cdot 10^4$
0.0004	2.69	50 mg/l C_6H_5OH	1.7	2.0	$4.31 \cdot 10^4$
0.0004	0.98	28 mg/l Fe^{2+}	1.0	0.9	$1.02 \cdot 10^5$
0.0004	2.69	28 mg/l Fe^{2+}	1.0	0.6	$1.30 \cdot 10^5$

D2. H_2S

The consequence of using of sulfur containing brines for iodine production is very important for Turkmenistan as there are great stocks of strata and gas-oil accompanying underground waters with relatively high iodide and sulfur compound concentrations (brines #18, 22, 23, Gaurdak and Boya-Dag deposits (Annual Report, 1997, Table 3).

There are a few sulfur compounds that are reduced during the oxidation reaction of iodine to iodide: H_2S, HS^-, S_2^{2-}, $S_2O_3^{2-}$ and SO_3^{2-}. The content of last three ones is too small and may be negligible (Reznikov et al., 1970). The main reason for the difficulty of iodide oxidation reaction is the reduction of iodine due to the following reactions:

$$H_2S + I_2 \rightarrow S + 2H^+ + 2I^- \quad (29)$$
$$HS^- + I_2 \rightarrow S + H^+ + 2I^- \quad (30)$$

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 3 mg H_2S/l high yields of iodine even at a 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. 14**) under these conditions. The kinetics study of iodide oxidation showed that a hydrogen sulfide presence in the brine after the stage of quick iodide oxidation (the time reaction is less than 0.1 s), brought about the long reverse process of iodine reduction to iodide (**Fig. 15-16**). With respect to the aforementioned, it is impossible to obtain a large iodine yield from brines containing hydrogen sulfide.

D3. Organic compounds

The underground waters of west Turkmenistan are characterized by a poor content of organic compounds. This can be explained by weak leaching of organic compounds from rocks by highly mineralized Cl-Na-Ca waters (Kiryukhin and Shvets, 1980).

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 and therefore decrease iodine yield. It is therefore recommended to conduct oxidation process with an excess of oxidants. There are volatile organic compounds (mostly phenols) aside from organic acids in natural waters. The only study dealing with the investigation of 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 with respect to iodide oxidation by either chlorine or hypochlorite and showed that in cases of a simultaneous presence of iodide ions and organic acids in brine, iodide ions are oxidized first irrespective of acid concentration; then formed iodine interacts with naphthenic acids.

Studying the influence of naphthenic acids on iodide oxidation, we found that the presence of 50-100 mg/l (0.0004-0.0008 M) of cyclohexanecarbonic acid did not influence iodide oxidation. 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. 14**). The addition of naphtenic acid changes the kinetics of the iodide oxidation reaction (**Fig. 15**). In the presence of 50 mg/l $C_6H_{11}COOH$, the rate of iodide oxidation is $8.48 \cdot 10^4$ $M^{-1}s^{-1}$ and $1.08 \cdot 10^5$ $M^{-1}s^{-1}$ for solutions with chloride concentration of 0.98 and 2.69 M accordingly, so the rate constants are 7 and 4 times higher. 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 reduce iodine.

In our minds, for iodine reduction it is necessary to add unsaturated organic acids. We propose that they may be phenols. This hypothesis was experimentally checked. In the presence of 0.001 M phenol C_6H_5OH, maximum yielding of iodine decreased to 89% at $Cl_2/2I^-$ molar ratio 1.4 (**Fig. 14**), so that the equilibrium of iodide oxidation reaction changed. We did not observe any influence of phenol addition to kinetics during the process (**Fig. 15, Table 8**).

Consequently, the necessity of oxidant excess for high iodine yielding is caused by the presence of phenols not naphtenic acids in natural brines. The presence of more complex unsaturated organic compounds could possibly help in reducing iodine. However, we could not study this phenomena as adding 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) since this leads to the formation of cloudy solutions.

D4. 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 approximately 100% at a $Cl_2/2I^-$ molal ratio of 1.0-1.05 (**Fig. 15**). In the presence of 28 mg/l Fe^{2+} the rate of iodide oxidation is $1.02 \cdot 10^5$ $M^{-1}s^{-1}$ and $1.30 \cdot 10^5$ $M^{-1}s^{-1}$ for solutions with chloride concentrations of 0.98 and 2.69 M accordingly, so the rate constants are 9 and 3 times higher (**Table 8**). Iodide oxidation is possibly accelerated by the presence of Fe^{2+} ions.

As a generalization of the above, we conceive that the following oxidizable impurities of natural brines have real influence on iodide oxidation process: bromide, hydrogen sulfide acid and phenol. In the presence of bromide and phenol, high iodine yield can be achieved by adding an excess of oxidant (required $Cl_2/2I^-$ molal ratio of 1.2-1.4). The most negative influence is hydrogen sulfide acid. The presence of 2-3 mg/l H_2S leads to a few folds of an oxidant excess and the reduction of formed iodine occurs over a long period of time. The regularities obtained were tested for natural brines.

E. IODIDE OXIDATION IN NATURAL BRINES

The natural underground waters from different regions of Turkmenistan with various compositions were used as objects for the next study.

E1. Influence of pH on iodine yielding

We found which pH values should use for the highest iodine yielding. The dependence of iodine yield under natural brine oxidation from the pH values is presented in **Fig. 17**. As can be seen, a considerable increase in yield of the end product (I_2 and I_2Cl^-) is observed with increase of solution acidity of up to pH=2. The iodine yielding increases on

13-23% with a decrease of pH value from 3 to 2. Further acidification leads to a considerable consumption of an acid but increases the formation of iodine only for an additional 1.5-2.0%. Therefore, pH=1.9-2.1 was chosen as the optimal value for the process of iodide oxidation.

E2. Underground water of Cheleken deposit (brine # 4, Annual Report, 1997, Table 3)

This brine has high concentrations of chloride, bromide and ferric ion and low iodide content: $[Cl^-]=4.4176$ M, $[Br^-]=6.6\cdot10^{-3}$ M, $[Fe^{2+}]=7.1\cdot10^{-4}$ M (20 mg/l), $[I^-]=2.164\cdot10^{-4}$ M. For this natural brine, the maximum iodine yield of 92.5-94.2% is observed at $Cl_2/2I^-$ molar ratio 1.1-1.4 (**Fig. 18**). We can suggest that for a solution with such a high content of chloride and bromide, the highest iodine yield should be at $Cl_2/2I^-$ molar ratio approximately equal to 1.6-1.7, but due to the presence of ferric ions the optimum $Cl_2/2I^-$ ratio is less. According to our expectation, the reaction of iodide oxidation is extremely fast for solution with this composition and cannot be measured by a stopped-flow method (**Fig. 19**).

E3. Underground water of Nebit-Dag region, Vyshka deposit (brine # 16, Annual Report, 1997, Table 3)

This brine has a close to average concentration of chloride and bromide, a low content of iodide and ferric ion: $[Cl^-]=1.9456$ M, $[Br^-]=2.0\cdot10^{-3}$ M, $[Cl^-]=1.9456$ M, $[I^-]=2.640\cdot10^{-4}$ M, $[Fe^{2+}]=2.1\cdot10^{-4}$ M. For this natural brine the maximum iodine yield 97.6% is observed at $Cl_2/2I^-$ molar ratio 1.15 (**Fig. 18**). The iodine compound distribution is mach with this one for iodide oxidation of model solution 4, **Fig. 14**. The rate constant of the reaction ($k = 4.80\cdot10^4\ M^{-1}s^{-1}$) corresponds to iodide oxidation for solution with average chloride and bromide contents.

E4. Underground water of Nebit-Dag region, Boya-Dag deposit (brine # 18, Annual Report, 1997, Table 3)

This brine has a high chloride concentration, an average bromide content, relatively low iodide concentration and contains hydrogen sulfide acid and it's salts: $[Cl^-]=3.1894$ M, $[Br^-]=4.8\cdot10^{-3}$ M, $[I^-]=2.576\cdot10^{-4}$ M, $[H_2S]=37$ mg/l. The reaction of iodide oxidation for this brine corresponds to the oxidation process in model hydrogen sulfide acid containing solution. For high iodine yield, there is a great excess of oxidants, the yield of iodine equals 96% of the initial iodide content observed at $Cl_2/2I^-$ molar ratio 2.0 (**Fig. 18**). During the process, iodine formation takes place and it's destruction then occurs (**Fig. 19**).

E5. Underground water of the Nebit-Dag region, Ordekly deposit (brine # 21, Annual Report, 1997, Table 3)

This brine has less than average chloride concentration, average bromide content, high iodide concentration ($[Cl^-]=1.5717$ M, $[Br^-]=3.0\cdot10^{-3}$ M, $[I^-]=5.730\cdot10^{-4}$ M) and does not contain oxidizable impurities. The process of iodide oxidation corresponds to the reaction for model solutions with a concentration of chloride 0.98 M, bromide 0.003 M (**Fig. 14, 15**): an iodine yield equal to 99.9% at $Cl_2/2I^-$ molar ratio 1.0 (**Fig. 18**), the rate constant $k=2.90\cdot10^4\ M^{-1}s^{-1}$.

E6. Underground water of Dovletobad deposit (brine # 24, Annual Report, 1997, Table 3)

This brine has low concentrations of chloride and bromide, average iodide concentration and contains organic acids ([Cl^-]=0.5653 M, [Br-]=$1.4\cdot10^{-3}$ M, [I^-]=$3.403\cdot10^{-4}$ M, [organic acids]=53 mg/l). For this natural brine, the maximum iodine yield of 96.5% is observed at $Cl_2/2I^-$ molar ratio 1.0 (**Fig. 18**). The rate of iodide oxidation reaction is low (rate constant k=$1.08\cdot10^4$ $M^{-1}s^{-1}$) and corresponds to the oxidation rate for model solutions with chloride content of 0.98 M.

IMPACT RELEVANCE AND TECHNOLOGY TRANSFER

The results obtained in the current study are used in industry by the State Company "Turkmendokunkhimiya" and were taken into consideration during the design of units for iodine extraction on the Davletabad and Ordekli deposits. The optimal regimes of iodide oxidation recommended by us were applied in the Balkanabad iodine plant, Vyshka deposit, Cheleken Chemical plant and Boya-Dag unit for iodine extraction. The results obtained allow us to forecast oxidation process of natural brine based upon its chemical composition and to estimate the effectiveness of the use of a given deposit.

The most important practical result of this investigation is the development of the spectrophotometric method to determine equilibrium iodine compound concentrations at their joint presence developed specifically for solutions with high chloride concentrations (Kazantseva et al., 2002). This method is now successfully used in Scientific & Production Cooperation "Sun" (former Institute of Chemistry, Turkmenistan Academy of Science) for the determination of an optimal regime of iodide oxidation for different iodine producing plants.

It was found that an optimal quantity of oxidant required for the highest yield of a target product (which is iodine) depends on the concentration of chloride, bromide, phenols and hydrogen sulfide acid. Ferric ions and saturated naphtenic acids do not have any influence on the iodide oxidation process. In the presence of chloride, bromide and phenols almost 100% oxidation of iodide to iodine can be provided by a well-matched dose of chlorine. In the presence of hydrogen sulfide acid and its salts, the iodide oxidation reaction is not effective (it takes a great amount of oxidant; a high yield of iodine cannot be provided in any case). The regularities obtained for model solutions are quite suitable for natural underground waters. So after knowing the composition of the natural brine, we can predict the optimal regime of iodide oxidation process.

As to kinetics of iodide oxidation reaction, we summarize the following: it was found that the process of iodine extraction from natural brines occurs in the diffusion-kinetics regime and the rate of chemical reaction is close to the rate of iodine exchange between liquid and gas phases (Reutskii et al., 1976; Ishankuliev et al., 1990). There is no literature data that enable us to directly compare these rates. Dubik et al. (1982) investigated the kinetics of iodine exchange between liquid and gas phases during its air desorption from salts solutions and drill waters. They found that rate of reaction #4 is much higher then the exchange rate; the last one decreased when salt concentration increased. Therefore, iodine diffusion is difficult in solutions with high mineralization. It is possible that in solutions with high salt concentrations, the rate-controlling step is reaction of iodide oxidation. We showed that rate of the chemical process for solutions with chloride concentrations higher than 3 M is extremely rapid and cannot create difficulties for technology.

The results obtained by us showed that for most of natural and model waters, the time of chemical reaction is much less than the time of contact of oxidizable natural brine with air in the industrial plant for iodine production. Therefore, the rate of iodide oxidation reaction may be neglected excluding two cases:

- For a solution with low chloride concentration (for example, the water of the Dovletobad deposit) the reaction time is approximately 3-5 s. For these solutions, it is impossible to note the rate constant of iodine oxidation reaction while constructing the plants for iodine extraction.
- For solutions containing hydrogen sulfide acid and its salts, the reduction of formed iodine takes place during the entire time of air desorption. For a working plant (Boya-Dag deposit) we recommend to remove H_2S by air desorption before the oxidation reaction which will decrease the time of the process maximally.

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PROJECT ACTIVITIES/OUTPUTS

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.

Prof. B. Krumgalz (Israel) visited Institute of Chemistry, Turkmenistan Academy of Science in 1997.

In 1998, 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" held on 29 June – 2 July, 1998 in Ivanovo (Russia) with talks on "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.

In 1999, Dr. O. Geldyev spent two weeks of training in the M.I. Mendeleev Russian Chemical Technological University (Moscow). The purpose of his training was to assimilate modern methods for processing experimental kinetic data to work out equilibrium and kinetic models for oxidation of iodide by chlorine. Dr. Kazantseva N.N. discussed with Prof. V.I. Ksenzenko mechanism of iodide oxidation reactions (1999, Moscow).

Prof. B.S. Krumgalz and Dr. Kazantseva N.N. 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 (2001, Moscow).

Three manuscripts were prepared on the basis of the results obtained:

1. N. N. Kazantseva, A. Ernepesova, A. Khodjamamedov, O. A.Geldyev and B. S. Krumgalz. 2002. "Spectrophotometric Analysis of Iodide Oxidation by Chlorine in Highly Mineralized Solutions", in press, Anal. Chim. Acta.
2. N. N. Kazantseva, A. Khodjamamedov, O. A.Geldyev, A. Ernepesova and B. S. Krumgalz "Mechanism and Kinetics of the Reaction of Iodide Oxidation by Chlorine in High Mineralized Solutions", prepared for submission in Inorg. Chem.
3. N. N. Kazantseva, A. Khodjamamedov, A. S. Ernepesova, O. A.Geldyev, and B. S. Krumgalz. "Equilibrium and Kinetics of the Reaction of Iodide Oxidation by Chlorine in Natural High Mineralized Solutions", prepared for submission in Inorg. Chem.

PROJECT PRODUCTIVITY

In general, the current project accomplished almost all the proposed goals. However the limitations of the equipment purchased did not allow us to study the kinetics of very fast reaction steps.

FUTURE WORK

The results obtained in the current proposal demonstrated that some aspects of iodide oxidation process, specifically fast reactions, should be studied in future work. Future study can be carried out if the proper equipment can be purchased.

ACKNOWLEDGMENT.

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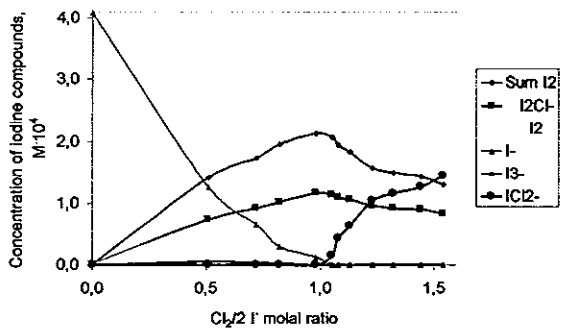
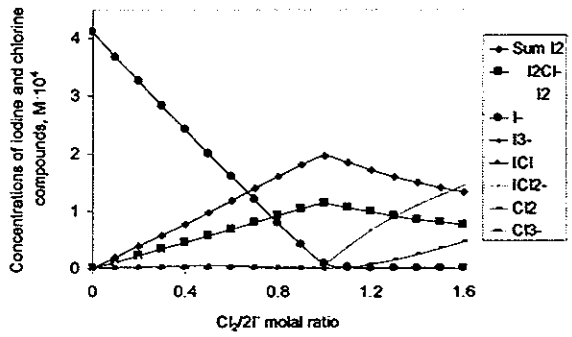
The authors would like to acknowledge Dr. O. Geldyev and Dr. A.S. Ernepesova for their participation and valuable contributions at various stages of project fulfillment, including the experimental part, treatment of experimental data and the writing of the report. We would like to specifically acknowledge the assistance that we constantly receive from Mr. Boaz Ayalon from the American Embassy, Tel Aviv (Israel).

FIGURES



a)



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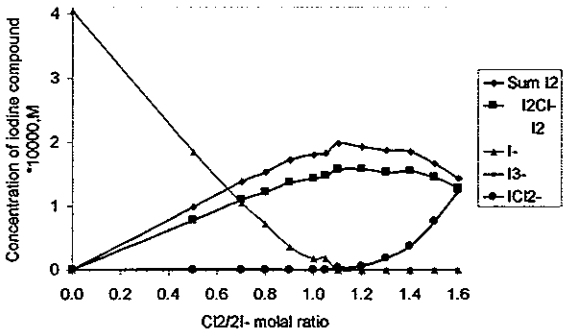


c)

Fig. 1. Concentration changes of iodine compounds on a $Cl_2/2I^-$ molar ratio of a solution with $[I^-]_{initial}=4\cdot10^{-4}$ M at temperature of 25°C and pH=2: $[Cl^-]=0.98$ M (a – experimental data, b – calculated data) and 4.28 M (c – experimental data).

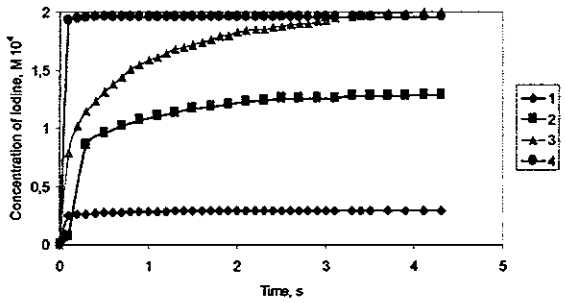


Fig. 2. Kinetics curves of iodine in the oxidation process at t=25°C and pH=2 for solutions with $[I^-]_{initial}=4\cdot10^{-4}$ M, $[Cl^-]=0.98$ M and various $Cl_2:2I^-$ molar ratios: 1- 0.2, 2 - 0.75, 3 - 1.0, 4 - 1.25.

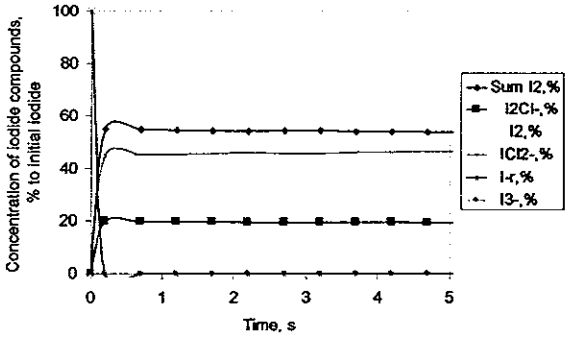


Fig. 3. Concentration changes of iodine compounds with time at t=25°C and pH=2 for a solution with the following component concentrations: $Cl_2/2I^-=1.5$, $[I^-]_{initial}=4\cdot10^{-4}$ M, $[Cl^-]=0.98$ M.

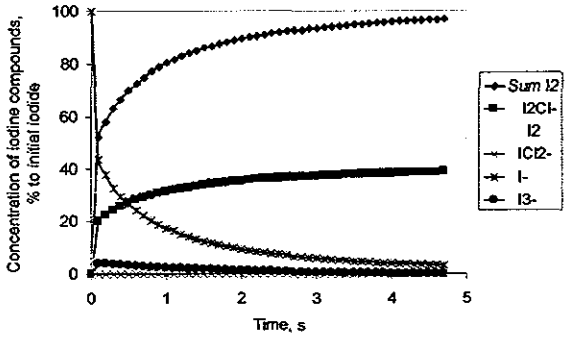


Fig. 4. Concentration changes of iodine compounds with time at t=25°C and pH=2 for a solution with the following component concentrations: $[I^-]_{initial}=4\cdot10^{-4}$ M, $[Cl^-]=0.98$ M, and $Cl_2:2I^-=1.0$.

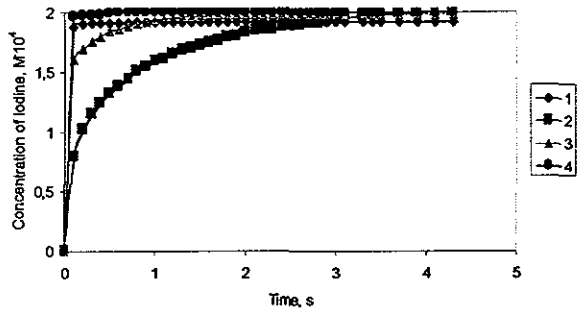


Fig. 5. Kinetics curves of iodine in the oxidation process at t=25°C and pH=2 for solutions with $[I^-]_{initial}=4\cdot10^{-4}$ M, $[Cl^-]=0.98$ M and various chloride concentrations: 1- 0, 2 – 0.98 M, 3 - 2.69 M, and 4 - 4.28.

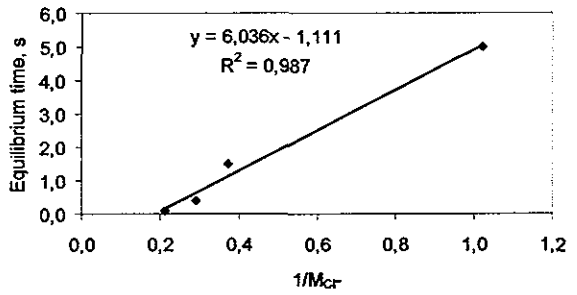


Fig. 6. Dependence of equilibrium time on chloride concentration at t=25°C and pH=2 for solutions with $[I^-]_{initial}=4\cdot10^{-4}$ M and $Cl_2:2I^-=1.0$.

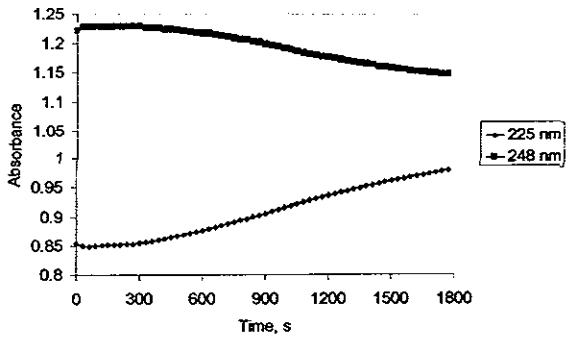
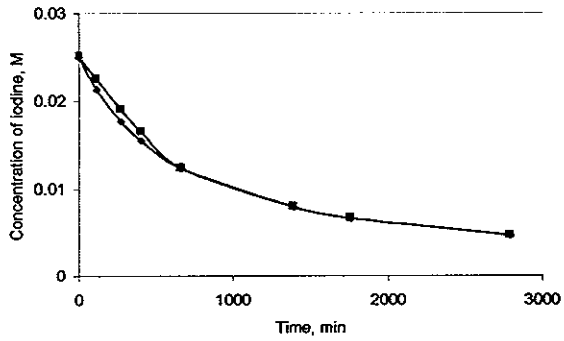
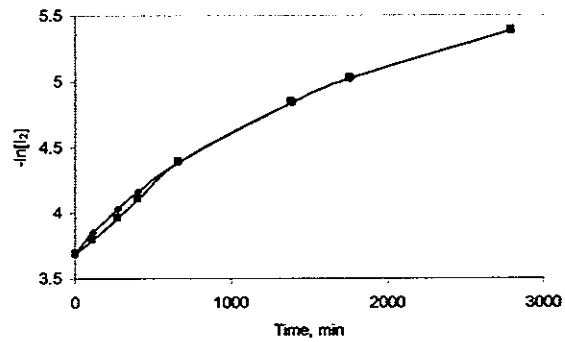


Fig. 7. Absorbance changes with reaction time at 225 nm and 248 nm at t=25°C and pH=1 for a solution with $[I^-]_{initial}=6\cdot10^{-4}$ M, $[Cl^-]=5.19$ M and $Cl_2:2I^-=1.0$.



a



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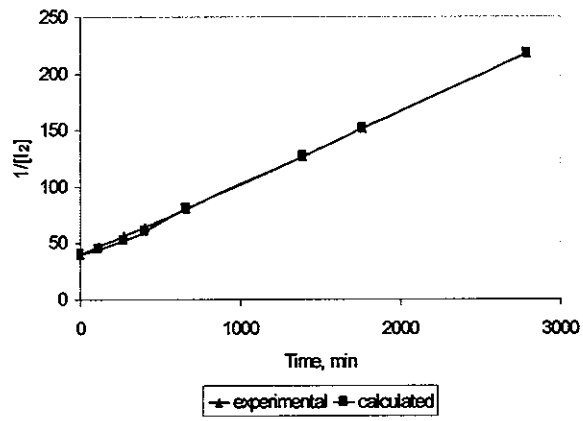
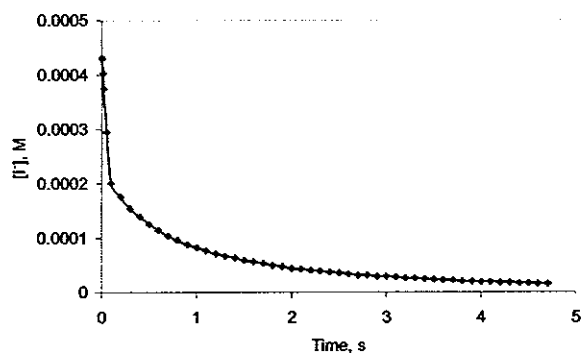
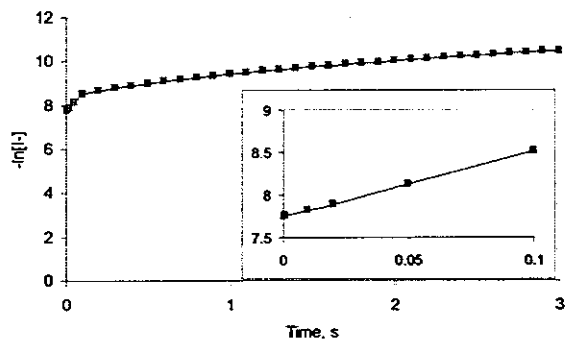


c

Fig. 8. Kinetics curves of iodine with time for a model reaction between iodine and β-phenyl-propionic acid in different coordinates:
a – $[I_2]$=f(time),
b – $-\ln[I_2]$=f(time),
c – $1/[I_2]$=f(time).



a



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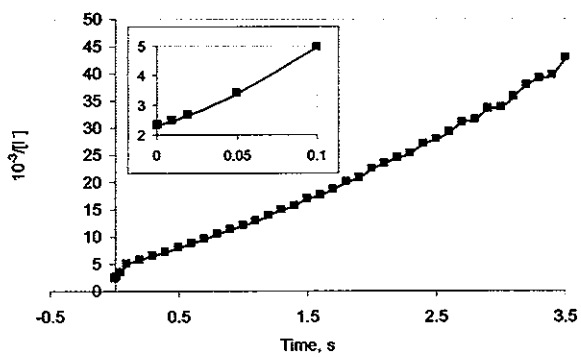
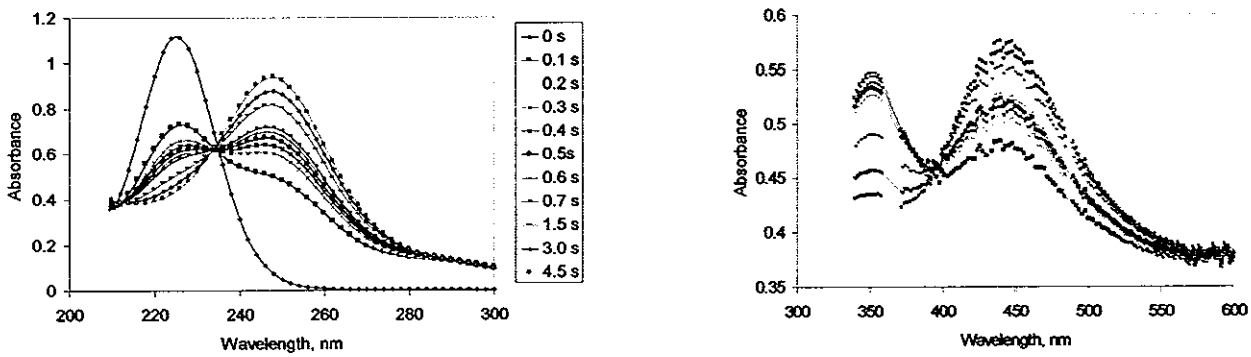


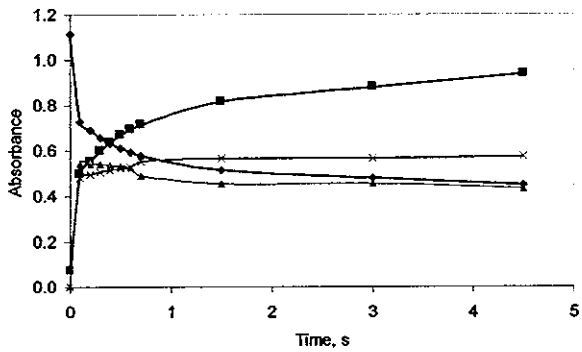
c

Fig. 9. Kinetics curve of iodide with time at t=25÷C and pH=2 for a solution with $[I^-]_{initial}=4\cdot10^{-4}$ M, $[Cl^-]$=0.98 M, $Cl_2/2I^-$=1.0 in different coordinates:
a - $[I^-]$=f(time),
b - $-\ln[I^-]$=f(time),
c - $1/[I^-]$=f(time).



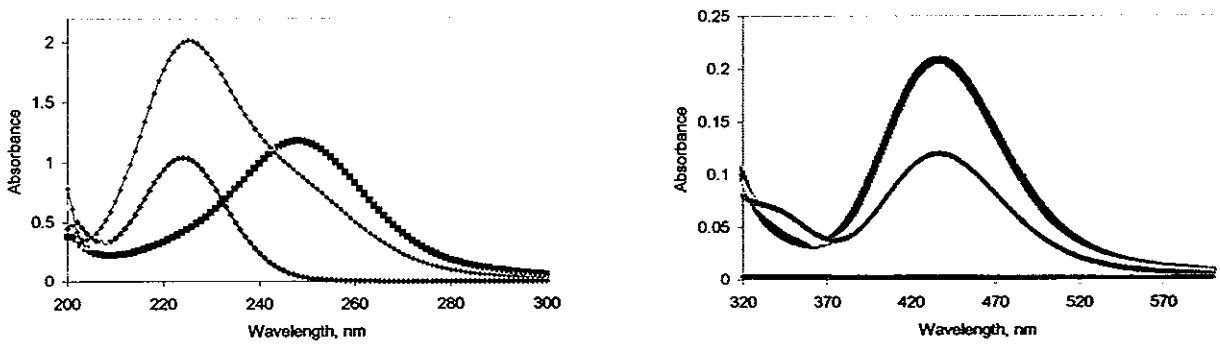
a b

Fig. 10. Absorption spectra at t=25°C and pH=2 for a solution with $[I^-]_{initial}=4\cdot10^{-4}$ M, $[Cl^-]=0.98$ M, $Cl_2:2I^-=1.0$ and a reaction time of 5 second: a – ultraviolet region; b – visible region.



a

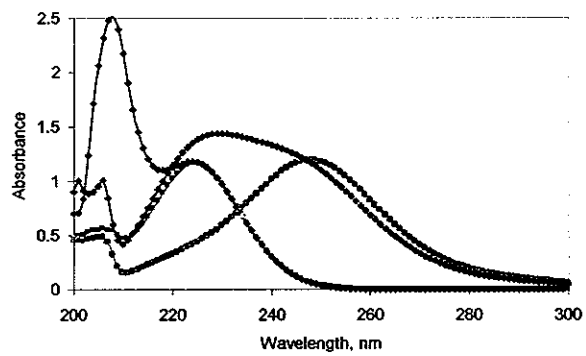
Fig. 11. Absorption spectra at t=25°C and pH=2 for a solution with $[I^-]_{initial}=4\cdot10^{-4}$ M, $Cl_2:2I^-=1.0$ and $[Cl^-]=0.98$ M (a) and 2.69 M (b) at various wavelength vs. reaction time.



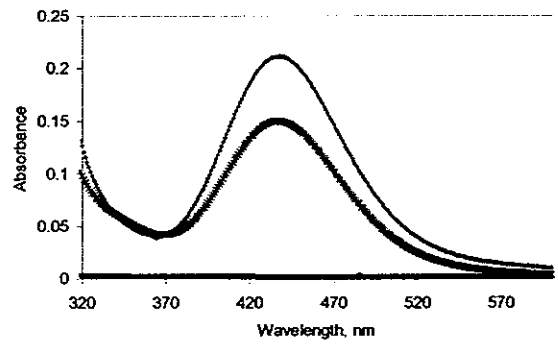
a b

Fig. 12. Absorption spectra at temperature of 25°C for a solution with I^- initial concentration of 0.0004 M, chloride concentration of 2.69 M, pH=2.0 and $Cl_2/2I^-$ molar ratios: 0 – blue curve, 1.0 – rose curve, 1.3 – yellow curve, 1.6 – green curve.

a – ultraviolet region, b – visible region.



a



b

Fig. 13. Absorption spectra at temperature of 25°C for a solution with I^- initial concentration of 0.0004 M, bromide concentration of 0.003 M, chloride concentration of 2.69 M, pH=2.0 and $Cl_2/2I^-$ molar ratios: 0 (without compensation of bromide absorption) – blue curve, 0 (with compensation of bromide absorption) – rose curve, 1.0 – yellow curve, 1.3 – green curve, 1.6 – violet curve.

a – ultraviolet region, b – visible region.

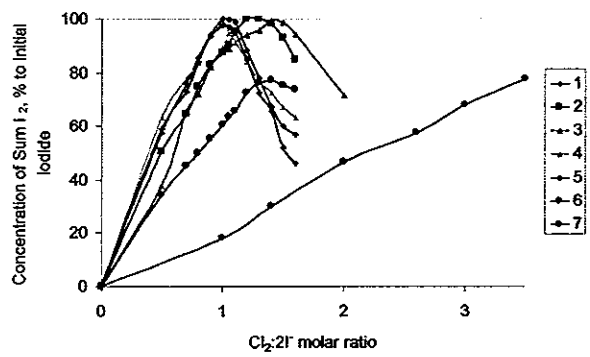


Fig. 14. Iodine yielding at temperature of 25°C and pH=2.0 as function of $Cl_2/2I^-$ molar ratio. The composition of initial solution: iodide concentration 0.0004 M, chloride concentration 2.69. 1 – without additives, 2 - 0.003 M Br^-, 3 - 0.006 M Br^-, 4 - 0.00025 M Fe^{2+}, 5 - 0.0008 M naphtenic acid, 6 - 0.001 M phenol, 7 - 3 mg/l H_2S.

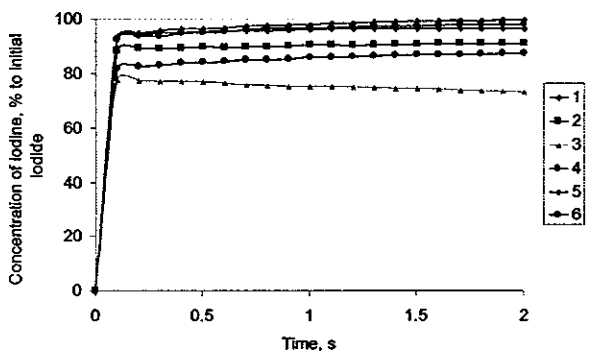


Fig. 15. Concentration changes of total iodine with time at temperature of 25°C for the solutions with I^- initial concentration of 0.0004 M, chloride concentration of 2.69 M and pH=2. 1 – without additives at $Cl_2/2I^-$ molar ratio of 1.0, 2 - 0.006 M Br^- at $Cl_2/2I^-$ =1.3, 3 - 3 mg/l H_2S at $Cl_2/2I^-$=2.5, 4 - 0.0008 M naphtenic acid at $Cl_2/2I^-$=1.0, 5 - 0.00025 M Fe^{2+} at $Cl_2/2I^-$=1.0, 6 - 0.001 M phenol at $Cl_2/2I^-$=1.4.

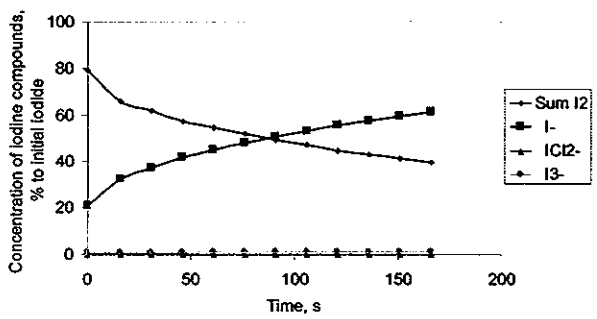


Fig. 16. Concentration of iodine compounds – time dependence for the solution with initial concentration $[I^-]$=0.0004 M, $[Cl^-]$=2.69 M, $[H_2S]$=3 mg/l, $Cl_2/2I^-$ molar ratio 2.5 and pH 2 at a temperature of 25°C.

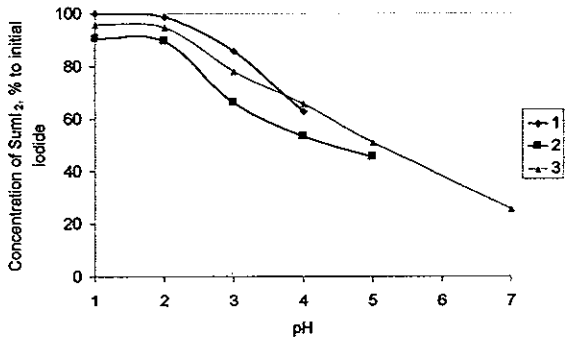


Fig. 17. The dependence of iodine yielding under natural brine oxidation from pH values at temperature of 25°C:
1 – Boya-Dag deposit,
2 – Gaurdak deposit,
3 – Cheleken deposit.

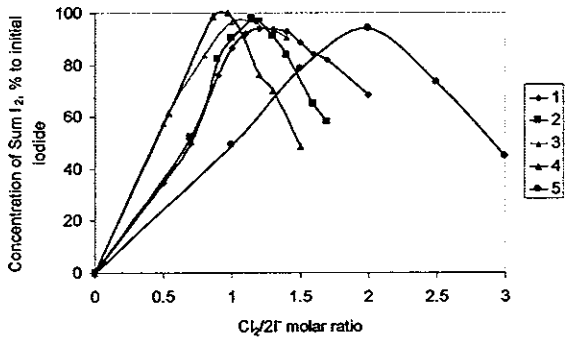


Fig. 18. The dependence of iodine yielding at a temperature of 25°C and pH=2.0 from the $Cl_2/2I^-$ molar ratio the for natural brines: 1– Cheleken deposit, 2 – Vyshka deposit, 3 – Dovletobad deposit, 4 –Ordekli deposit, 5 – Boya-Dag deposit.

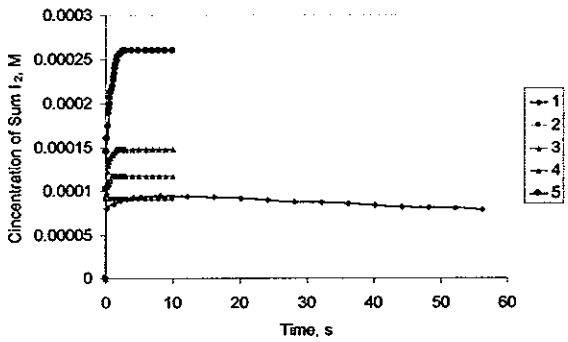


Fig. 19. Concentration changes of total iodine with time at a temperature of 25°C and pH=2 for the natural brines: 1 – Boya-Dag deposit, at $Cl_2/2I^-$ molar ratio of 2.0, 2 – Cheleken deposit, at $Cl_2/2I^-$=1.4, 3 – Vyshka deposit, at $Cl_2/2I^-$=1.15, 4 – Dovletobad deposit, at $Cl_2/2I^-$=1.2, 5 – Ordekli deposit, at $Cl_2/2I^-$=1.0.