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Highly effective technology of iodine production from hydrothermal mineralized natural brines

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Principal Investigator: Prof. Boris Krumgalz
Grantee Institution: National Institute of Oceanography, Israel
Collaborator: Prof. A.M. Khodjamamedov and Dr. N.N. Kazantseva
Institution: Institute of Chemistry, Turkmenistan

Israel Oceanographic & Limnological Research, National Institute of Oceanography,
Ministry of Energy and Infrastructure
State of Israel

Institute of Chemistry,
Turkmenistan Academy of Science,
Ashgabat, Turkmenistan

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EXECUTIVE SUMMARY

The present annual report covers the period of January 1, 2000 – December 31, 2000. During this period, the authors have been involved in the development of 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. The method was used to study the process of iodine processing from underground brines in Turkmenistan. These brines are characterized by considerably higher mineralization and lower iodide content compared with those of Japan and the US. It was found that solutions with constant iodine concentrations and variable chloride concentrations have an isobestic point at 474 nm wavelength with an extinction coefficient of I_2 and I_2Cl^- equal to 610.2, while the absorbance of other iodine forms at this wavelength is negligible. This allows us to use the light absorbance at 474 nm for calculating of the iodine concentration in solutions with variable chloride concentration. For calculating concentrations of other iodine

compounds, light absorbances on other wavelengths were used: 225 nm (I^- and ICl_2^-), 248 nm (I_2Cl^-) and 350 nm (I_3^-). The validity of the Beer Law was observed for all iodine compounds in solutions with constant salt concentrations at all wavelengths. The authors have also developed detailed algorithm for calculating various iodine forms at their joint presence. The method developed was applied to solutions with various chloride concentrations and additions of microcomponents of natural solutions (bromide and iron ions, naphthenic acid and hydrogen sulfide). The total precision of our method for calculating iodine compounds was better than 5% for solutions with oxidant excess of less then 2, and with chloride concentrations of less than 5 mol/kg H_2O.

During reported period the dependence of iodine yield under natural brine oxidation from solution acidity and from the molal ratio of oxidant/iodide was also studied.

EXPERIMENTAL SECTION

Turkmenistan is in fourth place in the world after Japan, Chile and the US renowned for iodine production. In addition to numerous thermal iodide underground brines with outlet temperatures from wells ranging from 40 to 70°C, there are large amounts of mineralized natural waters, enriched by iodide, in various parts of Turkmenistan. These waters are used for keeping excess pressure during oil production and may also be used for iodine production. Turkmenistan natural mineralized waters are characterized by considerably higher mineralization and lower iodide content compared to those of Japan and the US. The various aspects of the development of a new, rather inexpensive and ecologically safe process of recovery of iodine from Turkmenistan natural brines with a low iodide content by an air-desorption method are under investigation in the current study.

One of the main ways to intensify iodide production by the air-desorption method is to search for the most optimal regime of iodide oxidation by chlorine: $2I^- + Cl_2 = I_2 + 2Cl^-$. This process goes through a number of several fast, consecutively concurrent reactions of oxidation, complexation and hydrolysis. The system in equilibrium contains the initial and final substances (I^-, Cl_2, Cl^-, I_2,) side-by-side with intermediate compounds (I_2Cl^-, I_3^-, ICl, ICl_2^-, IOH, IO^-, IO_3^-, etc.). The composition of an equilibrium system is

influenced by the composition of the initial brine, the oxidant amount, the amount of oxidizable components, pH and temperature.

A new spectrophotometric method was developed to study the oxidation process. The method allows the concentration determination of I^-, $I_2+I_2Cl^-$, I_3^- and ICl_2^- compounds under their common presence in mineralized brines. The concentration of end product considerably increases with the increase of brine acidity to pH≈2, while further acidification leads to the increase of oxidation degrees only on 1.0÷1.5%. The study of iodide oxidation at pH=2 in natural waters and in model solutions resembling them showed that the predominance of various iodide compounds is determined by oxidant amount.

One of the main ways to intensify iodide production by the air-desorption method is to search for the most optimal regime of iodide oxidation by chlorine:

$$2I^- + Cl_2 = I_2 + 2Cl^- \quad (1)$$

This process goes through a number of several fast, consecutively concurrent oxidation and complexation reactions (2-11) and hydrolysis reactions (12-16):

$$I^- + Cl_2 = ICl_2^- \quad (2)$$
$$ICl_2^- = ICl + Cl^- \quad (3)$$
$$I^- + ICl = I_2Cl^- \quad (4)$$
$$I_2Cl^- = I_2 + Cl^- \quad (5)$$
$$I_2 + I^- = I_3^- \quad (6)$$
$$I_2Cl^- + Cl^- = ICl_2^- + I^- \quad (7)$$
$$ICl_2^- + Cl_2 = ICl_4^- \quad (8)$$
$$Cl_2 + Cl^- = Cl_3^- \quad (9)$$
$$I_2 + Br^- = I_2Br^- \quad (10)$$
$$ICl_2^- + Br^- = IBrCl^- + Cl^- \quad (11)$$
$$I_2 + H_2O = I^- + H^+ + HIO \quad (12)$$
$$HIO = H^+ + IO^- \quad (13)$$
$$HOI + H_2O = I^+H_2O + OH^- \quad (14)$$
$$3HIO = IO_3^- + 2I^- + 3H^+ \quad (15)$$
$$Cl_2 + H_2O = Cl^- + H^+ + HClO \quad (16)$$

The spectrophotometric methods are the most effective ones for determining the composition of a solution containing various iodide compounds. These methods allow the study of such a solution without disturbing reaction equilibrium. Practically all iodide compounds participating in the oxidation process absorb light in ultraviolet and visible spectra (Table 1).

Table 1. The optical characteristics of iodine compounds

Compound	Analytical band length, nm	Molar extinction coefficient
I^-	226	12600
I_2 in H_2O	460	746
I_3^-	350 460	25000 975
IO^-	365	310
IO_3^-	194	
I_2Cl^-	248	39600
ICl_2^-	343 224	243 47000
I_2Br^-	280	
$IBrCl^-$	255	

RESULTS AND DISCUSSION.

a. Spectrophotometric method development.

A spectrophotometric method in UV and visible spectrum was developed to study kinetics of iodide oxidation reactions without disturbing the system equilibrium in the process of the oxidation of natural mineralized brines. The method allows the concentration determination of I^-, I_2+I_2Cl^-, I_3^- and ICl_2^- compounds under their common presence in mineralized brines with better than 6% precision. The developed method was

verified at pH from 1 to 7 on model solutions resembling natural brines with variable iodide and chloride concentrations: $[I^-]=(1\div4)\cdot10^{-4}$ M and $[Cl^-]=0.4\div5.6$ mole/(kg H_2O). It was found that at pH<2, the following compounds prevailed in studied brines depending on chlorine/iodide ratio:

I^-, I_2, I_2Cl^-, I_3^-	at	$[Cl_2]$: $2[I^-]<1$;
I^-, ICl_2^-, I_2, I_2Cl^-	at	$[Cl_2]$: $2[I^-]\approx1$;
I_2, I_2Cl^-, ICl_2^-	at	$[Cl_2]$: $2[I^-]>1$;
ICl_2^-, ICl_4^-	at	$[Cl_2]$: $2[I^-]>2$.

At higher pH values, the contributions of hydrolysis and iodide disproportion were observed to become more noticeable in iodide oxidation process.

The quantitative determination of oxygen containing iodide compounds by the developed spectrophotometric method was found to be impossible due to lower values of their extinction coefficients compared to those of inter-halogen compounds. The estimation of the total content of iodide compounds by using optical density at a wavelength of 474 nm shows that the loss of the end product considerably increases with an increase of pH. This loss can reach approximately 12% at pH changes from 1 to 5.

b. Influence of brine pH on iodine yield.

The dependence of iodine yield under natural brine oxidation from the pH values is presented in Fig. 1. As can be seen, the considerable increase yield of the end product (I_2 and I_2Cl^-) is observed with increase of solution acidity of up to pH=2. Further acidification leads to considerable consumption of an acid but increases the oxidation of iodide ions only for an additional 1.5-2.0%. Therefore, pH=2 was chosen as the optimal value for the process of iodide oxidation. The results obtained demonstrate that the iodine yield at any particular brine acidity depends on the following factors: solution mineralization, initial iodide concentration, the nature and amount of oxidizable components.

c. Influence of iodide/oxidant ratio on iodine yield.

The maximal yield of the end product (I_2+I_2Cl^-) under iodide oxidation in model brines was found to be reached at the molal ratio of oxidant/iodide equal to 1.06-1.20. The maximal yield of the end product in natural solutions was reached under 12 to 69% of oxidant surplus as compared to its stoichiometric ratio. The well waters without H_2S and iron ions require 12-20% chlorine surplus for the oxidation of organic acids. Approximately 60% of the required oxidant are spent on H_2S oxidation in stratal waters. Air blowing H_2S from natural brines allows the decrease of oxidant expenditure. However, in this case, the iodine yield decreases on approximately 10% due to aeration. It was also found that in the case of natural waters containing iron ions, the oxidant surplus could reach 60%. The influence of oxidant/iodide ratio on iodine yield for various natural brines at various conditions is presented in Fig. 2.

CONCLUSIONS.

1. The process of oxidation of iodide containing natural solutions in various formations in Turkmenistan is under investigation.
2. The optimal value of acidity for iodide oxidation in natural brines was found to be at pH=2 and does not depend on solution mineralization, initial iodide concentration and the amount of oxidizable components.
3. It was demonstrated that the optimal amount of oxidant depends on solution mineralization, nature and amounts of oxidizable ingredients.

MANAGEMENT

During the reported period, we met with a problem of a serious illness of Israeli partner. This problem created some delay in the fulfillment of the project.

COLLABORATION

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.

Two 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 "Spectrophotometric Analysis of Iodide Oxidation by Chlorine in Highly Mineralized Solutions" (submitted in 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 submition in Inorg. Chem.).

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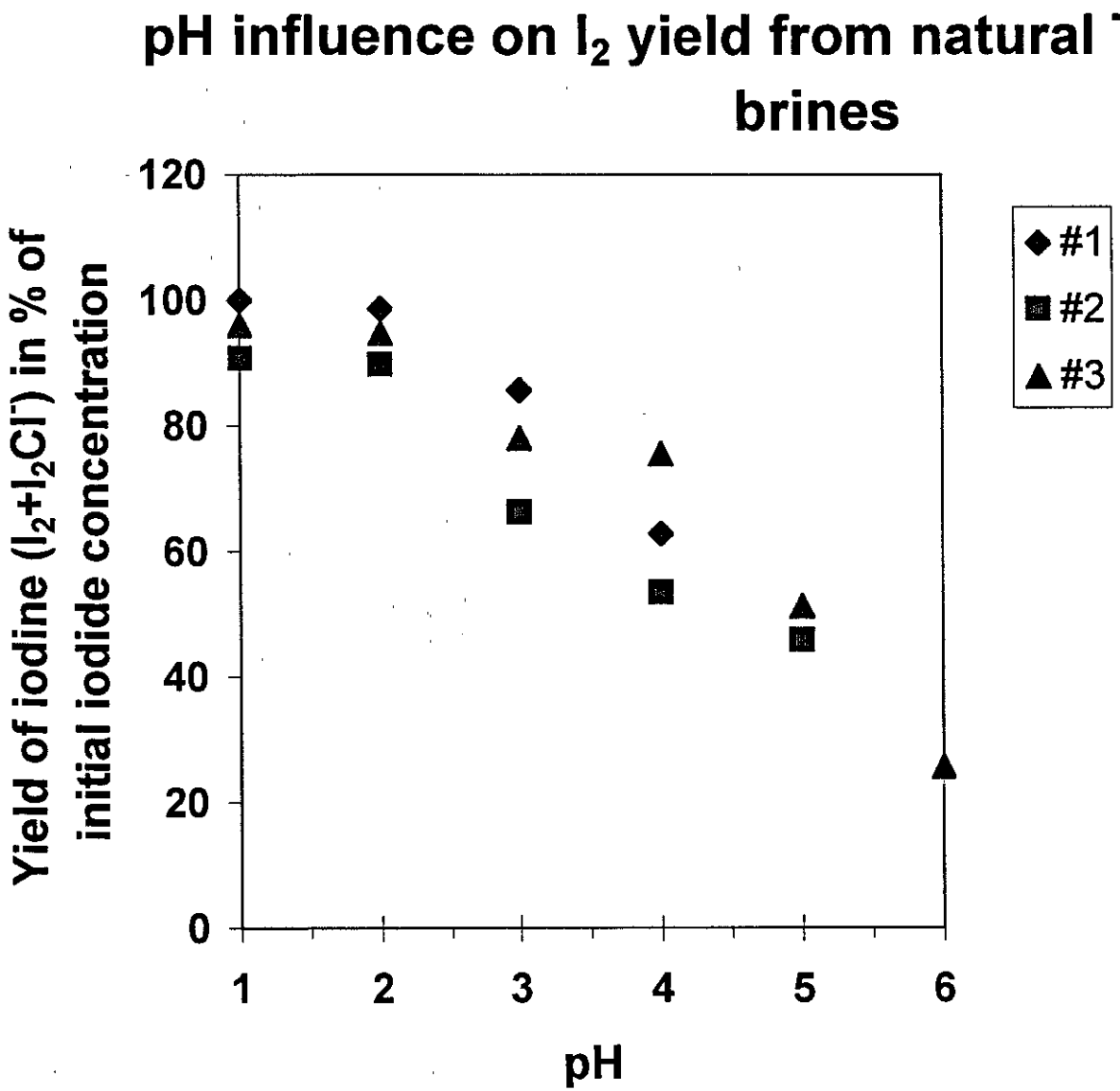
We would like specifically to acknowledge the assistance that we constantly receive from Mr. Boaz Ayalon from the American Embassy, Tel Aviv (Israel).



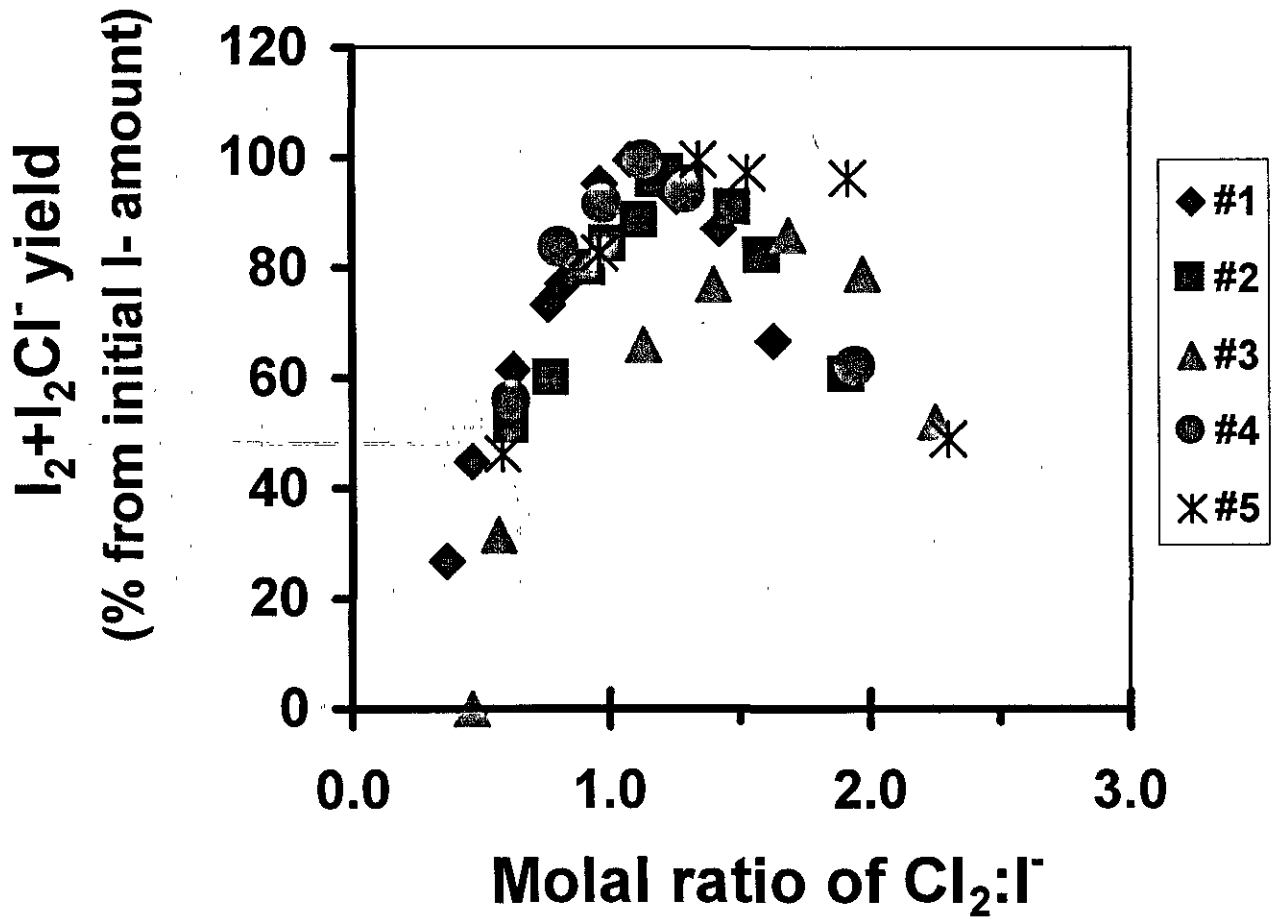
#1 - Borehole water of Boya-Dag formation

#2 - Stratal water of Gaurdak formation

#3 - Evaporated water of Gaurdak formation

Fig. 1

Dependence of I_2 yield from oxidant amount



#1 - Model solution

#2 - Borehole water of Boya-Dag formation

#3 - Stratal water of Gaurdak formation

#4 - Stratal water of Gaurdak formation after H_2S removal

#5 - Borehole water of Cheleken formation

Fig. 2