Investigating the processes and rate of iodide ion and compound oxidation in subterranean hydrothermal waters

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Abstract. Studies using physico-chemical methods have been conducted to evaluate the oxidative characteristics of various reagents for the technological extraction of iodine from groundwater and sufficient data have been obtained. According to the research results, iodine is predominantly present in the form of molecular iodine (85.6%), iodide ions (3.2%), iodate (9.1%) and iodine chloride (2.1%) were detected. Preserving all forms of iodine in solution at the same time is possible only in an alkaline environment, where the oxidizing properties of iodates are sharply reduced. This information is important for choosing a method for purifying iodine paste using various physical and chemical methods. From experiments in research, the beginning of the release of elemental iodine was noted at a voltage above 0.250 V and a pH of 5-3 or less. In this case, the solution usually becomes dark red with a reddish or brownish tint, which indicates the formation of complex compounds of iodine with other ions in the solution.

1 Introduction

Iodine is utilized globally in the food and pharmaceutical sectors, as well as in medicine, veterinary medicine, the manufacture of mineral fertilizers, and as a catalyst in the chemical industry [1]. It is also employed in producing ultrapure materials, special glass, fuel, and synthetic rubber, which are used in industrial and agricultural machinery [2-21]. Additionally, iodine plays a crucial role in preventing endemic goiter and other illnesses. Consequently, a key priority is to develop enhanced technology for commercially extracting iodine from underground hydrothermal waters, which are considered the primary source for meeting the iodine requirements in our republic.

Globally, particular focus is placed on iodine synthesis for medical purposes using iodine-containing resources. In this regard, the development of memory technologies necessary for medicine, food and chemical industries is one of the urgent tasks. When devising a technology for extracting iodine from underground saline waters containing iodine

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compounds, it is essential to justify several scientific considerations. These include identifying the optimal technological parameters for the iodide ion's kinetics and mechanism oxidation in acidic drilling waters, selecting suitable oxidizing agents, establishing the optimal technological conditions for iodine precipitation from iodine concentrate, and developing a process for isolating molecular crystalline iodine [22, 23].

Leading scientific centers and institutions of higher education worldwide conduct scientific research focused on the development and implementation of efficient methods for crystal storage and the equipment necessary for their application, including the National Oceanic and Atmospheric Administration, the National Science Foundation (USA), NOAA (USA), NERC - Deutsche Forschungsgemeinschaft (Germany), Consejo Superior de Investigaciones Científicas, CSIC (Spain), Natural Environment Research Council (UK), National Institute of Environmental Research Yamagata Yoshihiro (Japan), Yomito Motomura National Institute of Advanced Industrial Science and Technology (Japan) , The Sysin-named RTFA is held at the Research Institute of Human Ecology and Environmental Hygiene (Russia), Baku State University (Azerbaijan), Institute of Chemistry of the State Concern "Turkmankimyo" (Turkmenistan), Termez State University (Uzbekistan), National Commission for Scientific and Technological Research of the Republic of Chile, CONICYT (Chile), Department of Geosciences (Canada), National Research Center of Tomsk Polytechnic University (Russia), Perm State National Research University (Russia).

2 Materials and methods

During the extraction of iodine from underground hydrothermal waters using the air-desorption method, the iodine-containing waters are introduced into an acidic environment, and subsequently, the iodine compounds are oxidized using either liquid or gaseous chlorine. However, as liquid chlorine is not manufactured within our republic, this technological process fails to meet environmental and economic standards. To evaluate the oxidative characteristics of several reagents for the technical extraction of iodine from subterranean saline fluids, physicochemical experiments have been carried out. Regarding the oxidation of iodine compounds in waters containing hydrothermal iodine, the following oxidizing agents were chosen: $Na_2S_2O_8$, $NaNO_2$, H_2O_2, $Ca(C1O)_2$. For the entire oxidation of iodine compounds in 50 milliliters of the investigated water, 0.3-0.4 ml of 2% solutions of $Na_2S_2O_8$ and $NaNO_2$ are required, from which it is clear that the latter of the solutions of $Na_2S_2O_8$ and $NaNO_2$ of the same concentration is a stronger oxidizing agent. In this case, for the entire oxidation of iodine compounds in 50 milliliters of the investigated water, 0.2-0.25 ml of a 5% H_2O_2 solution is required. Calcium hypochlorite has also been tested as an iodine oxidizer.

$$3OCl^- + I^- \rightarrow IO3^- + 3Cl^-$$

Diffusion controls the iodide oxidation reaction with calcium hypochlorite, which is slower than the chlorine reaction. Though not as much as when oxidizing iodide with chlorinated water, shortening the oxidation reaction's duration also boosts the production of elemental iodine (from 94 to 97%) and lowers oxidizer use.

The obtained results indicated that 0.4-0.45 ml of a 0.2% Pa(PlO)2 solution is needed for the full oxidation of iodine compounds in the tested iodine-containing waters. Because iodine changes from its iodide to iodate form, a partial increase in the oxidizing agent's concentration also causes a drop in the concentration of the end product, iodine.

Additionally, the link between the salt content and the oxidizing agent consumption during the release of iodine from mineralized water was researched for the springs Ortabulok, Kokaiti, Khaudag, and Uchkizil. The degree of mineralization of the water determines how much sulfuric acid and oxidizing solutions are needed to completely oxidize the iodine compounds in the iodine-containing waters under study.

Table 1. Relationship between oxidizing agent consumption and salt content while iodine is being extracted from mineralized waters (V=50 ml).

No	Source name	Water mineralization, g/l	Volume of 2 % H_2SO_4, ml	Volume of oxidizers, ml			
				2% $Na_2S_2O_8$	2% $Ca(ClO)_2$	2% $NaNO_2$	5% H_2O_2
1	Ortabulok	113	0.132	0.20	0.154	0.120	0.074
2	Kokaiti	142	0.166	0.29	0.225	0.175	0.124
3	Khaudag	210	0.245	0.37	0.287	0.223	0.138
4	Uchkizil	283	0.330	0.55	0.450	0.350	0.225

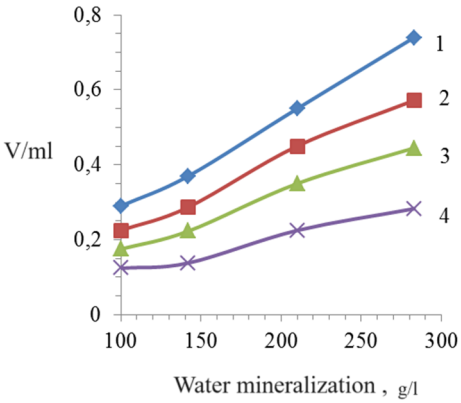

Fig. 1. The impact of salt quantity in mineralized water on the utilization of oxidizing agents in iodine absorption: 1- 2% $Na_2S_2O_8$; 2- 2% $Ca(ClO)_2$; 3- 2% $NaNO_2$; 4- 5 % H_2O_2.

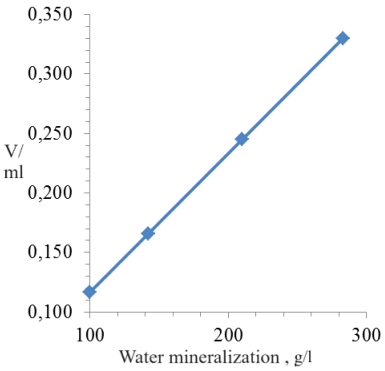

Fig. 2. Iodine is subjected to mineralization with 2% sulfuric acid, taking into account the impact of salt quantity in the water.

The findings from the research are detailed in Table 1 and illustrated in Figures 1-2. Additionally, the usage of the oxidizing solutions correlates with the consumption of sulfuric acid in stoichiometric proportions as outlined below:

1. 2% $Na_2S_2O_8$ - 0,20 ml; 2% $Ca(C1O)_2$ - 0,154 ml; 2% $NaNO_2$ - 0,120 ml; 5% H_2O_2 - 0,074 ml.
2. 2% $Na_2S_2O_8$ - 0,29 ml; 2% $Ca(C1O)_2$ - 0,225 ml; 2% $NaNO_2$ - 0,175 ml; 5% H_2O_2 - 0,124 ml.

3. 2% $Na_2S_2O_8$ - 0,370 ml; 2% $Ca(C1O)_2$ - 0,287 ml; 2% $NaNO_2$ - 0,223 ml; 5% H_2O_2 - 0,138 ml.
4. 2% $Na_2S_2O_8$ - 0,550 ml; 2% $Ca(C1O)_2$ - 0,450 ml; 2% $NaNO_2$ - 0,350 ml; 5% H_2O_2 - 0,225 ml.

It was thus demonstrated that the consumption of sulfuric acid and oxidizing solutions, which increases by 1.5 times and 2.5 times, respectively, is proportionately related to the mineralization of underground hydrothermal waters, which increased from 113 g/l to 283 g/l in the studied sources.

The results obtained have formed the foundation for devising a technological process for acquiring iodine from hydrothermal groundwater through the air-desorption method.

To gather data on the kinetics of iodide ion oxidation when sodium nitrite, calcium hypochlorite, and hydrogen peroxide are present, 50 milliliters of simulated aqueous solutions with a starting concentration of iodide ions of 21.32 mg/l at 20°C were subjected to oxidation at various ratios of oxidizing agents.

By extracting the resulting molecular iodine into the chloroform phase and titrating with sodium thiosulfate, according to a particular protocol, the amount of oxidized iodide ions was measured. The data obtained from this process are illustrated in Figures 3-4.

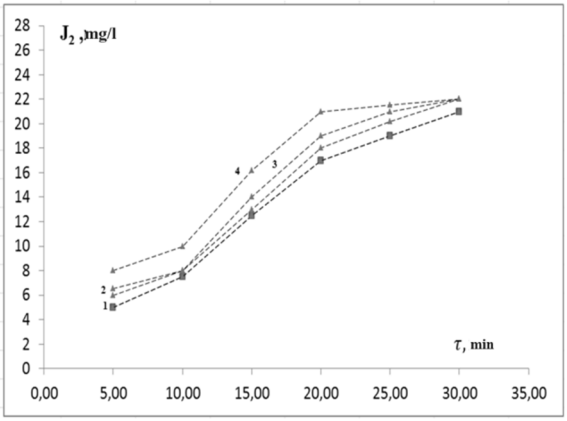

Fig. 3. The kinetics of iodide ion oxidation in the presence of a 2% $NaNO_2$ aqueous solution. Volume of $NaNO_2$ in ml: 1-0,6; 2-0,8; 3-1,0; 4-1,2.

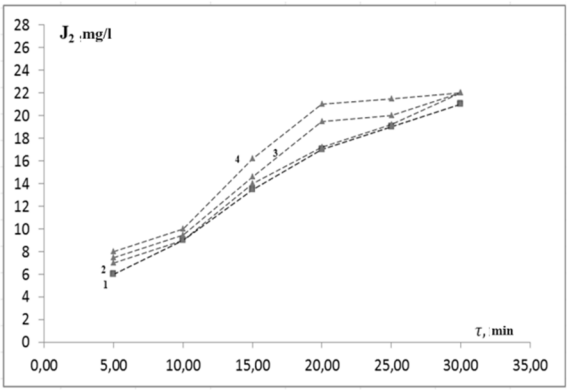

Fig. 4. The kinetics of iodide ion oxidation in the presence of a 2% $Ca(ClO)_2$ aqueous solution. Volume of $Ca(ClO)_2$ in ml: 1-1; 2-2; 3-3; 4-4.

The most rapid oxidation rate of iodide ions was seen with hydrogen peroxide (15–20 min), followed by sodium nitrite (20–25 min) and calcium hypochlorite (25–30 min), according to data analysis.

In this instance, the rate of the oxidation reaction is not significantly affected by changes in the oxidizing agent concentrations. The oxidation process in the upper section of the desorption column takes place in 0.5-0.8 minutes at 70°C, which is the temperature of the raw material water used. This is because the reaction rate increases by 2-4 times for every 10°C increase in temperature.

The data obtained indicates that the oxidation reaction rate of iodide ions is considerably higher than the rate of molecular iodine oxidation to iodate, leading to a thorough desorption of molecular iodine into the air phase, achieving a level of completeness up to 94%.

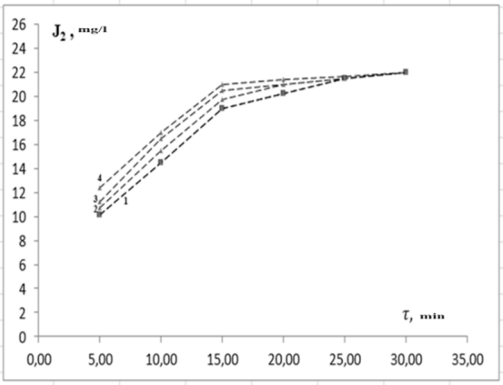

Fig. 5. The kinetics of iodide ion oxidation in the presence of a 5 % H_2O_2 aqueous solution. Volume of H_2O_2 ml: 1-0,2; 2-0,4; 3-0,6; 4-0,8

To explore alternative conditions for depositing iodine from absorbent solutions, this process was examined using potentiometric and spectral methods. Among various approaches such as spectrophotometric and sorption methods, the potentiometric research method enables the determination of the mechanisms involved in oxidation-reduction processes between iodine ions and oxidants during the separation of iodine from aqueous mediums using air desorption, extraction, and precipitation methods.

Potentiometric titration of absorbent solutions enables the determination of iodine precipitation conditions, including pH levels and the oxidant utilized. The experiment involved using model solutions of potassium iodide and iodate with concentrations of 4, 8, 12, and 16 g/l, their combinations, as well as factory absorbent acidified with H_2SO_4 solutions to varied pH levels. Sodium nitrite was used as the oxidant. The results revealed that iodide ions are not oxidized by nitrate or iodate up to a pH of 4 and above. Decreasing the pH value of the solutions below 3.5 had minimal impact on the complete separation of iodine, as indicated by the residual iodine content in the absorbent and model solutions, which ranged from 318 mg/l to 326 mg/l in absorbent solutions and from 279 mg/l to 388 mg/l in model solutions. The residual iodine content in the solutions was assessed based on the solubility limit of iodine in saline waters with the studied composition and pH values.

3 Results and discussion

The results of the spectrophotometric analysis of oxidation-reduction processes involved in the separation of iodine from absorbent solutions are depicted in Figure 6, with measurements

conducted within the range of the optical density's limiting values. As illustrated in Figure 6, the maxima of the optical densities of iodide (I-) and polyiodide (I-3) solutions align with a wavelength value of 225 nm, which can be leveraged for the calibration of these solutions. A 5% NaOH solution containing 12 g/l of iodine was utilized as a model absorbent solution, diluted 100 and 1000 times. Oxidation-reduction reactions during the separation of molecular iodine were examined using the spectrophotometric method in the ultraviolet range, employing an SF-26 spectrophotometer. Absorption spectra were recorded within the 215-340 nm range using a cuvette with a thickness of 1 cm. Model samples comprised solutions of standard reagents with the "kt" brand purity: KI (0.25 mg/l) solution for iodide ions, KIO_3 (0.22 mg/l) solution for iodate ions, $KI+I_2$ (1.42 mg/l) for iodide and molecular iodine, and a 0.28 mg/l solution of crystalline iodine in water. Distilled water served as the reference solution. The obtained absorbent solutions were studied after acidification with H_2SO_4 (dilution 1:4). The UV absorption data for these solutions are presented in Figures 6-7.

Curve 1 in Figure 6 is the absorbance in a model solution of an absorbent with a 1000-fold dilution and a cuvette thickness of 1 cm.

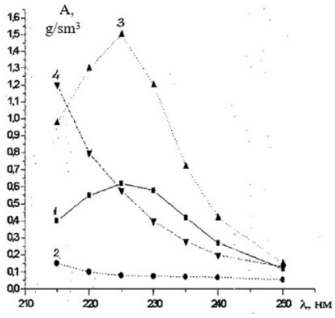

Fig. 6. Solutions containing iodide, iodate polyiodide ions, and UV absorption spectra of molecular iodine.

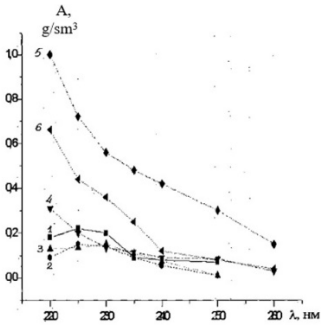

Fig. 7. Absorptoin spectra of the absorbent in the UV region without sulfuric acid (curve 1) and in its presence (curves 2-6).

The standard solution consists of a 5% NaOH solution diluted by a factor of 1000, with a cuvette thickness of 1 cm. Curve 2 represents the optical density in a simulated absorbent solution diluted by a factor of 1000, to which 0.1 ml of H_2SO_4 (diluted 1:4) is added per 100 ml of solution, also with a cuvette thickness of 1 cm. The reference solution mirrors the standard solution, consisting of the 5% NaOH solution diluted by 1000 times and with a 1 cm cuvette thickness, with the addition of 0.1 ml H_2SO_4 (1:4) per 100 ml of solution. Curve 3 depicts the optical density in a simulated absorbent solution diluted by 1000 times, supplemented with 0.1 ml of H_2SO_4 per 100 ml of solution, and using a 1 cm cuvette thickness. The reference solution corresponds to an analogous composition to references 1

and 2. Curve 4 illustrates absorption in a simulated absorbent solution diluted by 100 times, with the addition of 2 ml of H_2SO_4 solution (1:4) per 100 ml of solution. The reference solution matches a 100-fold dilution, with 2 ml of H_2SO_4 (1:4) per 100 ml of solution, and follows the same specifications as solutions 1 and 2, with a 1 cm cuvette thickness. Curve 5 represents the optical density in the absorbent solution, where 4 + 2 ml H_2SO_4 (1:4) is added per 100 ml of solution, with a 1 cm cuvette thickness. The reference solution corresponds to a counterpart of point 4, with an additional 2 ml of H_2SO_4. Curve 6 depicts the optical density in the absorbent solution, where 5 + 2 ml H_2SO_4 (1:4) is added per 100 ml of solution, with a 1 cm cuvette thickness. The reference solution is akin to point 5, with an extra 2 ml of H_2SO_4 (1:4).

The data obtained indicate that the original absorbent solution primarily contained iodide ions, as evidenced by curve 1. Upon the initial addition of sulfuric acid, there is no significant alteration in the solution's initial state, as the sulfuric acid serves solely for neutralization purposes, as depicted by curve 2. Subsequent additions of sulfuric acid result in the generation of elemental iodine, which then forms polyhalides such as I3-, establishing an equilibrium with iodide ions, as illustrated by curve 3. Evidently, the reaction leading to the formation of molecular iodine can only occur through the reduction of sulfate ions:

$$2I^- + 2H^+ + SO_4^{2-} = I_2 + SO_3^{2-} + H_2O$$

Continued addition of sulfuric acid facilitates the equilibrium between iodide ions and polyhalides, represented by the equation $I_2 + I^- = [I_3]^-$, resulting in an augmented yield of elemental iodine, as observed in curves 4, 5, and 6. The evaporation of solution 5 can be elucidated by the reduction of sulfate ions to sulfite ions, prompting the crystallization of the respective salt:

$$2I^- + 4H^+ + 2SO_4^{2-} = I_2 + 2SO_3^{2-} + 2H_2O$$

A subsequent reduction in the optical density of the solution suggests the reoxidation of iodide ions to iodate ions:

$$I^- + 3SO_4^{2-} = IO_3^- + 3SO_3^{2-}$$

These findings align with earlier results obtained when using 2 ml of 2% sodium nitrite to assess the impact of solution acidity on achieving complete iodine precipitation. To explore the oxidizing capabilities of sodium nitrite (2% $NaNO_2$), previously recommended for iodine separation, absorption spectra of absorbent solutions were examined, with varying dilutions of $NaNO_2$ added, akin to previous experiments. These data hold potential for use in technological oversight of the oxidation process and in the extraction of iodine from iodide ions through continuous monitoring of changes in wastewater optical density. This approach facilitates the automation of iodine production processes. The potentiometric titration method was used to analyze the quantity and availability of iodine within the absorbent. The research was conducted subsequent to the precipitation of elemental iodine from the absorbent, which possessed a concentration of 0.354 g/l. The concentration of free iodine was determined by subtracting the concentration of its bound forms from its total concentration:

$$X_{I2} = X_{tot} + X_{I^-} + X_{IO3^-} + X_{I^+}$$

Table 2. The quantity of distinct iodine configurations within absorbent materials subsequent to the precipitation of elemental iodine from operational solutions.

No	Forms of iodine	Average of forms of iodine amount (%)
1	Molecular Iodine Iodide (I-) Iodine (IO_3-) Iodine	85.6
2	Iodide (I^-)	3.2
3	Iodine (IO_3^-)	9.1
4	Iodine chloride (I^{+1})	2.1

Table 4 shows that the predominant form of iodine is molecular iodine (85.6%), with iodide ions (3.2%), iodate (9.1%), and iodine chloride (2.1%) observed when the pH is maintained at 3 in the investigated working solutions. Maintaining all iodine forms in solution simultaneously is feasible only in an alkaline setting, where the oxidizing capabilities of iodates are significantly diminished. This data holds significance for selecting an appropriate physicochemical method for purifying iodine paste.

4 Conclusion

In the experiments, it was observed that elemental iodine separation commenced when the voltage exceeded 0.250 V and the pH was between 5 and 3, or lower. Under these conditions, the solution typically assumes a dark-red hue with reddish or brown undertones, suggesting complexation of iodine with other ions present in the solution.

Hence, the potentiometric titration method of alkaline iodine-containing solutions demonstrated the generation of diverse iodine ion forms in the presence of oxidants across different pH levels of the solution. The proportional makeup of these forms is influenced by the pH level, as well as the type and concentration of oxidant present. Through this approach, it was illustrated that distinct iodine forms can be generated at specific voltages.

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