

Dependence of the Yield of Hypochlorite Potassium on the Current Density and on the Position Electrodes in an Electrolysis Installation

Khamidov Abdusamat Ganijanovich, Yakhyayev Umar Abdikhakimovich,
Pardayev Asadbek Parpi ugli

Tashkent Institute of Chemical Technology

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ABSTRACT

The article considers the dependence of the product yield on the concentration of the initial substance and the current density in the process carried out in an electrolytic cell with horizontally and vertically installed graphite electrodes in a closed flow mode. Graphite electrodes are used in the plant to prevent side processes. The article also provides factors affecting the formation of potassium hypochlorite. Natural source materials were used for the experiments.

The Tyubegatan deposit of potassium salts is located in the Dekhkanabad district of the Kashkadarya region, 75 km south of the city of Guzar and is confined to the southwestern spurs of the Gissar Range. The deposit is located on the border of Uzbekistan and Turkmenistan and is separated by the border river Shordarya [1].

In this regard, the problem of processing low-grade sylvinit from the Tyubegatanskoye deposit is relevant for the potash enterprise.

The processing of sylvinit ores for potassium chloride, along with the flotation method, is mainly carried out by the halurgie method. This method of separating the main components of raw materials - KCl and NaCl, is based on the difference in the temperature coefficients of the solubility of these salts in water [2]. The use of the halurgical method allows, in most cases, to significantly increase the efficiency of processing low-grade potash ores [3].

In 1774, the Swedish chemist Carl Wilhelm Scheele obtained gaseous chlorine (Cl₂) as a result of the interaction of manganese (IV) oxide MnO₂ and hydrochloric acid (HCl) [4]. Later, in 1785 (according to other sources - in 1787 [5]), the French chemist Claude Louis Berthollet discovered that an aqueous solution of gaseous chlorine ("chlorine water") containing hypochlorous and hydrochloric acids can bleach linen, and reported on their conclusions of the French Academy of Sciences [6,7]



Knowledge of the bleaching properties of chlorine was immediately put to use by James Watt at a textile factory in Glasgow. Despite the fact that bleaching with chlorine was much more effective than traditional methods of bleaching with sunlight, weak solutions of acids and alkalis, the use of chlorine was limited by its toxicity and destructive effect on tissues. To stabilize the solution of gaseous chlorine in water and the safety of its use, in 1787 at the Paris enterprise *Societe Javel* chlorine steel passed through an aqueous solution of potassium carbonate (potash)



The head of the enterprise, Leonard Alban, called the new product " *Eau de Javel* " ("javel water"), and soon bleaching liquid became popular in France and England due to the ease of its transportation and storage [8].

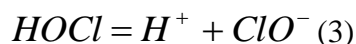
Hypochlorites are salts of hypochlorous acid HClO . The most common of these are sodium hypochlorite, calcium hypochlorite and potassium hypochlorite. Hypochlorites are widely used for drinking water disinfection, bleaching, degassing and disinfection. Hypochlorites are among the most important chemical compounds.

The systematic name is **potassium hypochlorite** . The traditional name is potassium hypochlorous acid , javel water (potassium hypochlorite mixed with potassium chloride), chemical formula KO Cl .

physical properties. Condition yellow-greenish-gray liquid with a strong smell of chlorine. Potassium hypochlorite is quite soluble in water (25%/100 ml at 25°C). Melts at -2 °C, boils with decomposition at 102 °C. Molar mass 90.55 g/mol.

Safety. Toxicity. Corrosive, oxidizer, toxic (in high doses), hazardous to the environment.

Theoretical basis. The acid-base balance between hypochlorous acid and hypochlorite ion is described by a reversible reaction with an equilibrium constant $K_p = 2.63 \times 10^{-8}$ at 20°C.



Using the equilibrium constant K_p , one can calculate the molar fractional distribution of hypochlorous acid and hypochlorite ions depending on pH (Fig. 1).

The data indicate that acidification of hypochlorite solutions increases the proportion of unstable hypochlorous acid. At $pH < 7.58$, the solution contains mainly hypochlorous acid, and at $pH > 7.58$ there are predominantly hypochlorite ions.

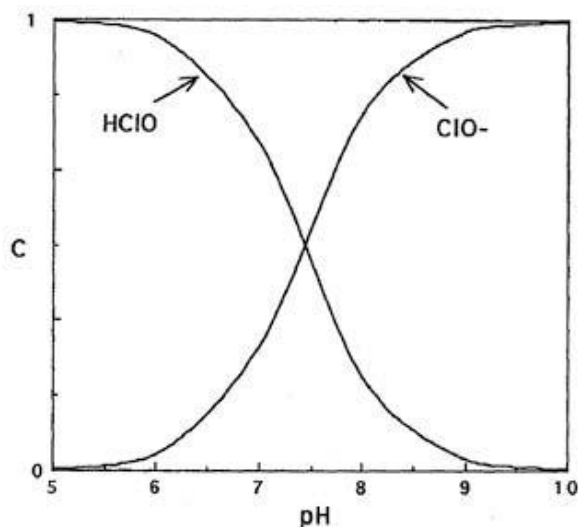


Fig. 1. Molar share distribution of hypochlorous acid and hypochlorite ions depending on the acidity of the medium.

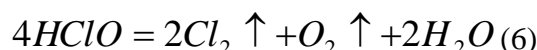
Chemical properties. Hypochlorites are unstable compounds that easily decompose with the release of oxygen. *The decomposition of solid potassium hypochlorite* can be represented by the equation



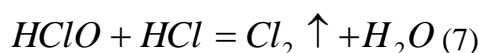
Processes at room temperature are slow, and when heated, they can proceed with an explosion. In parallel with the reactions accompanied by the formation of chlorides and free oxygen, the disproportionation reaction can proceed [9].



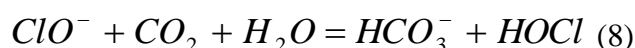
The decomposition of hypochlorites in aqueous solutions depends on the acidity of the solution and its temperature. In strongly acidic media at $pH \leq 3$, hypochlorous acid decomposes to chlorine and oxygen at room temperature



If hydrochloric acid is used during acidification or if chlorides are present in the solution, no oxygen is formed.



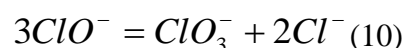
Hypochlorous acid is very weak, so it can be displaced from the solution of its salts by the action of carbon dioxide.



In slightly acidic and neutral media at $3 < pH < 7.5$, the following redox reaction occurs

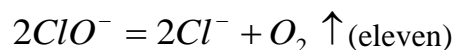


In neutral and alkaline solutions, a competing reaction of the formation of chlorides and chlorates takes place

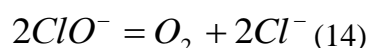
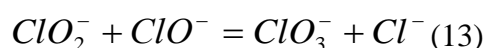


At room temperature, the disproportionation reaction proceeds slowly, but at temperatures above 70 °C, this reaction becomes predominant.

In alkaline media at $pH > 7.5$, hypochlorite ions predominate in solutions, decomposing as follows:



Stabilization of hypochlorites in aqueous solutions. Salts of hypochlorous acid are much more stable than the acid itself. With an increase in pH, the mole fraction of hypochlorous acid in the solution decreases and, thereby, the stability of hypochlorite increases (Fig. 1). At $pH > 11$, the content of hypochlorous acid is extremely low, however, even at this acidity, slow decomposition of chlorine (I) compounds is observed. The ongoing reactions can be written as:

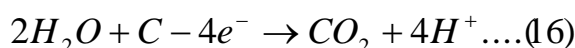
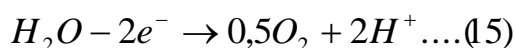


About 95% of the total amount of hypochlorite ions decompose as a result of successive reactions (1) and (2), with reaction (1) being the slowest (limiting) one and determining the overall rate of the process. Reaction (3) is not the main one, but is responsible for the release of oxygen, the amount of which can be significant.

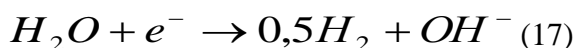
In the presence of some metal ions, for example, copper, nickel, cobalt, catalytic decomposition of hypochlorite ions is observed. Iron ions have a weak catalytic effect and are cocatalysts in combination with other metal ions. In the simplest case, when the content of copper (II) ions in the solution at a concentration of 1 mg/kg, the orders of the homogeneous reaction with respect to hypochlorite and copper (II) are equal to unity.

Heterogeneous catalysis by metals and their insoluble compounds is complex and poorly reproducible. The insoluble catalysts, nickel and its oxides have the greatest interfering effect on the hypochlorite solutions at contact with alloyed nickel steels used for the manufacture of pipelines and tanks.

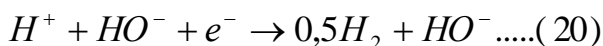
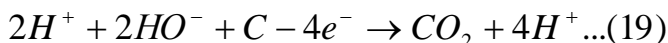
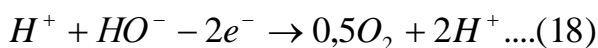
The authors of some sources write erroneously that a side reaction occurs at the anode with the discharge of a water molecule, forming molecular oxygen on metal and carbon dioxide on graphite anodes:



At the cathode, gaseous hydrogen is released, which is removed from the cathode space, hydroxide ions are regenerated, which form alkali metal hydroxide with sodium ions [10]:



water molecules that are discharged, but their already dissociated ions, and the reactions should be depicted in the following form:



Experimental part

For the purpose of more efficient use of the mineral fertilizer of the Dekhkanabad potash plant, the dependence of the potassium hypochlorite yield on the current density and on the position of the electrodes in the installation was studied. For this, an electrolyte was prepared with a content of 74.55 g / dm³ (1N) potassium chloride from a crude mineral fertilizer by dissolving it in the city tap water of Tashkent. The calculated number of samples was stirred for 5 minutes with a magnetic stirrer at a temperature of 15 °C and filtered through a paper filter. The concentration of the obtained saturated solutions was determined by volumetric titration with a solution of silver nitrate, and by diluting a solution of the desired concentration of 74.55 g/dm³ (1N) of potassium chloride was obtained.

The studied fertilizer was taken from Dekhkanabad potash plant containing 90% potassium chloride (45 % K and 45% C) with composition is shown in table 1). Analysis of the original mineral fertilizer composition was carried out on the device " High-performance energy dispersive X-ray fluorescence spectrometer - Japan, Rigaku NEX CG EDXRF Analyzer with Polarization in set - 9022 19 000 0". The process temperature was measured using glass laboratory thermometers manufactured in accordance with GOST 215-73. The GUNT Geratebau GmbH instrument (CE – 105, Germany) was used as a DC power source. Hydrogen parameters

of the resulting hypochlorite products were measured on a Bante 210 pH meter. The mineralogical composition of the feedstock is below.

Table 1, Elemental composition of the initial mineral fertilizer, %]

No.	1	2	3	4	5	6	7	8
Elements	Cl	Br	S	K	Ca	Ti	Fe	Cu
Result	45.0	0.058	0.34	45.0	0.5	0.0023	0.0257	0.0016
No.	9	10	eleven	12	13	14	15	16
Elements	Rb	Sr	Y	Zr	sn	Te	Fr	Dy
Result	0.009	0.0014	0.0005	0.175	0.003	0.0017	0.0074	0.0037

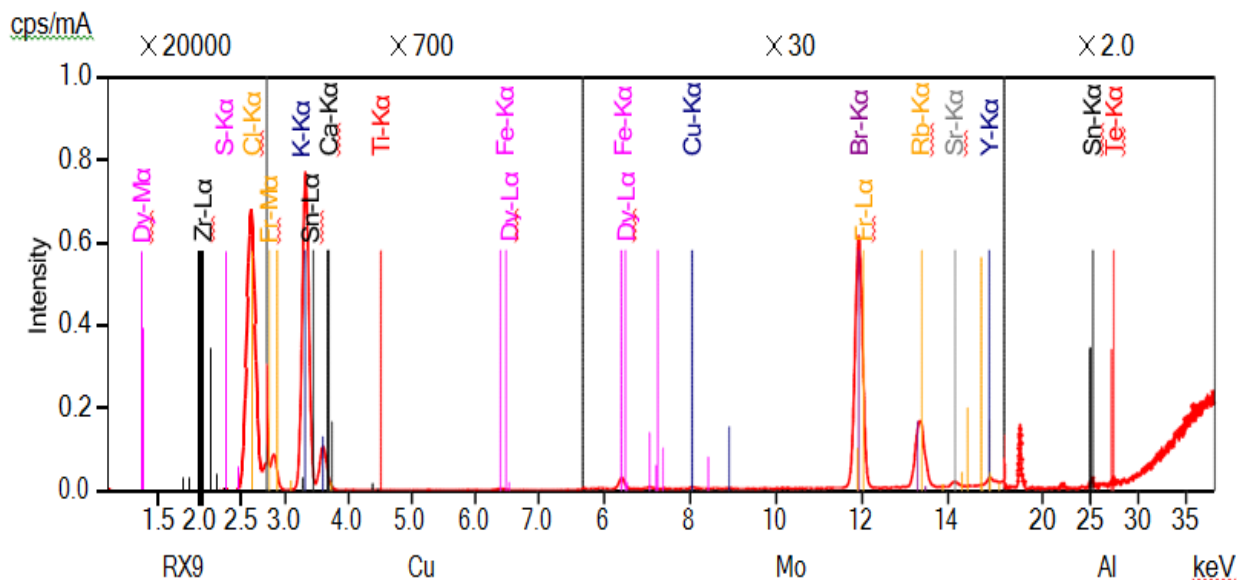


Fig. 1 XRF data of initial fertilizer

The first series of experiments. Graphite electrodes are installed vertically, with an area of 0.14 dm², the distance between the electrodes is 11 mm. The concentration of potassium chloride in the electrolyte is 74.55 g / dm³ (1N) . pH of distilled water 5.02, electrolyte pH before electrolysis 5.80. The movement of liquid in flow mode at a speed (70 ml / min) 13 - 14 min / l. The temperature of the electrolyte is 14⁰ C. Conditions for the analysis of active chlorine in the product: the concentration of sodium thiosulfate 0.05N, potassium iodide 5 cm³ . 10%, starch solution 1 cm³ . 1%, product sample volume 10 cm³ . The calculation of active chlorine is made according to the following formula:

$$X_{z/n} = \frac{V_{TCH} \cdot 0,003545 \cdot 1000}{10 \cdot 2} = V \cdot 0,17725 =$$

The results obtained are summarized in Table 2.

Table 2. Experimental results of 1st series

No.	Current strength, A	Voltage, V	Current density, A / dm ²	V _{Na₂S₂O₃} , CM ³	Active chlorine, g / dm ³	medium pH
1	0.28	3.15	2	0.4	0.07	8.45
2	0.5 6	3.70	4	0.8	0.14	8.31
3	0.84 _	4.10	6	1.4	0.25	8.54

4	1, 1 2	4.15	8	2.2	0.39	8.63
5	1, 4	4.33	10	3.0	0.53	8.71

Second series of experiments. Graphite electrodes are installed horizontally, with an area of 0.14 dm^2 , the distance between the electrodes is 11 mm. The concentration of potassium chloride in the electrolyte is 74.55 g / dm^3 (1N). pH of distilled water is 5.02, pH of the electrolyte before electrolysis is 5.80. The movement of liquid in flow mode at a speed ($70 \text{ cm}^3 / \text{min}$) 13 - 14 min / l. Electrolyte temperature 15°C . Conditions for the analysis of active chlorine in the product: concentration of sodium thiosulfate 0.05N, potassium iodide 5 cm^3 . 10%, product sample volume 10 cm^3 , starch solution 1 ml. 1%. The results are shown in table 3

Table 3. Experimental results of 2nd series

No.	Current strength, A	Voltage, V	Current density, A / dm^2	$V_{\text{Na}_2\text{S}_2\text{O}_3}, \text{cm}^3$	Active chlorine, g / dm^3	medium pH
1	0.28	3.27	2	0.6	0.106	8.32
2	0.5 6	3.90	4	1.1	0.195	8.64
3	0.84 _	4.20	6	1.8	0.319	9.13
4	1, 1 2	4.55	8	2.8	0.496	9.81
5	1, 4	5.16	10	3.9	0.691	10.62

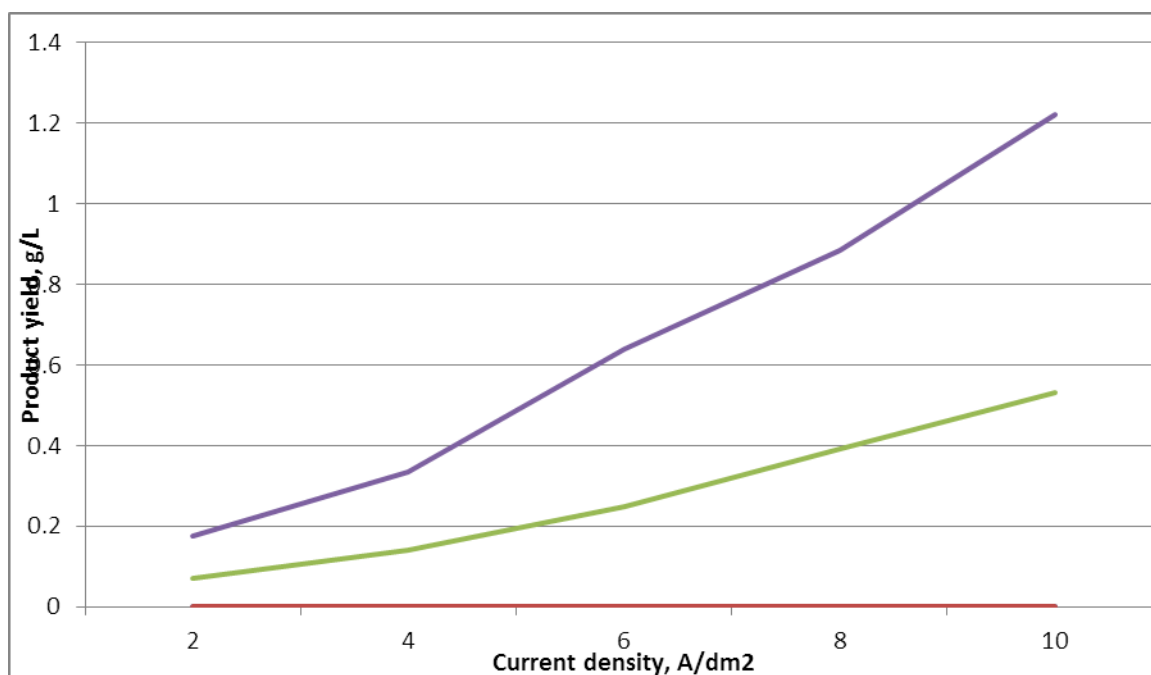


Fig.2 Dependence of the product yield vs current density

Conclusions

1. If the current density increases, the product yield also increases.
2. The pH of the medium is in the range of 8 and 11, and the the of the product yield greater with the higher pH value.
3. Based on the results, at the same uniform conditions the installation of electrodes with a horizontal cathode on top and an anode on the bottom can increase the product yield by $0.691/0.53=1.3$ times.

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