

# Research into the Possibility of Converting HCl to Molecular Chlorine with the Use of a Nanosecond Electron Beam

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**Abstract** – Numerous methods for processing of hydrogen chloride to chlorine are known. A traditional method is electrolysis of an aqueous solution of hydrochloric acid. Chemical methods include oxidation of hydrogen chloride by nitrogen oxides or air oxygen (with heating in the presence of catalysts). Physical methods are ultraviolet irradiation and the electrical pulse discharge.

The present work deals with the possibility of converting HCl to molecular chlorine with the use of a nanosecond electron beam in liquid and gas phases and as an aerosol. The experiments were realized on a radiochemical installation based on a URT-0.5 accelerator (400 keV, 50 ns, 1 kW).

It is shown that the highest conversion (up to 25%) is achieved in aqueous solutions of hydrochloric acid. The conversion in the irradiated gas phase is a maximum at the minimum pressure of the water vapor: not over 1%. Irradiation of aerosols practically does not initiate the desired process. In the experiments, the adsorbed dose was 0.16 to 1.6 MGy.

The use of hydrochloric acid more than 1% strong does not increase the amount of chlorine and, therefore, for adaptation of this process to industrial requirements it is expedient to separate chlorine as crystalline hydrate. The process is realizable in a continuous regime and can be aimed at recycling of hydrochloric acid waste and production of chlorine-containing oxidizers and whiteners.

The proposed process can also be used to disinfect water. The exposure of ~0.02% hydrochloric acid to an electron beam can provide a “chlorinating agent”. The addition of this “chlorinating agent” to potable water will have an effect similar to chlorination. An advantage of this scheme is the elimination of poisonous molecular chlorine.

Generally, the process can be referred to processes of “green chemistry” as it does not require the use of high temperatures, dangerous reagents and solvents. The relevant equipment meets the same requirements.

## 1. Introduction

One of significant problems facing the national economy is the disposal of hydrogen chloride, which is a

by-product of many production processes. More than half of chlorine, which is used for production of chlorine-containing solvents, is spent to the formation of hydrogen chloride. It is formed also in large amounts during hydrolysis of inorganic chlorides. Therefore, an efficient production process and subsequent recycling of incidental hydrogen chloride not only have the economic significance, but also prevent the environmental pollution. An extremely promising task is the conversion of hydrogen to molecular chlorine for development of safe processing cycles.

Methods for the conversion of hydrogen chloride to chlorine are numerous [1–9]. A traditional method is electrolysis of an aqueous solution of hydrochloric acid. Chemical methods include oxidation of hydrogen chloride by nitrogen oxides or air oxygen (with heating in the presence of catalysts). The use of UV radiation and the method of electrical pulse discharges may be referred to physical methods.

The available chemical and electrochemical methods have considerable drawbacks, primarily as regards the power consumption (up to 5 kW · h/kg). This was an impetus to development of physical methods, including the use of electrical pulse discharges [10–16] (the conversion of up to 74%) and UV radiation, which provided encouraging results (the conversion of up to 100% [15, 16]). However, the use of UV radiation is limited by a low energy efficiency of UV sources and the requirement that their casing be transparent in the UV range in a corrosive medium.

These limitations of UV radiation led to the use of electron beams, which already were used for initiation of the reverse reaction, namely the synthesis of HCl [17]. The specific energy loss of electrons is high, making it possible to release energy in small volumes and stimulate various chemical reactions.

A relatively low energy (up to 1 MeV) of nanosecond electron beams (NEBs) ensures their efficient use for irradiation in gas and liquid phases. At the same time, this limitation results in a low radiation hazard from NEBs and simplicity of radiation protection means. The last circumstance is very important for the direct introduction of radiation technologies into chemical processing schemes.

The frequency operating regime of nanosecond accelerators makes it possible, on the one hand, to real-

ize reactions in thin mass layers with quick replacement of the material or the reagents under the beam and, on the other hand, to exactly proportion the energy injection to the process by the proper choice of the operating frequency of the accelerator.

## 2. Experimental technique

The experiments were performed on a radiochemical installation based on a URT-0.5 accelerator (400 keV, 50 ns, 1 kW [18]), which consisted of an accelerator and a radiochemical reactor whose design and the irradiation pattern depended on the phase of materials to be irradiated.

In the case of the liquid phase (in a closed vessel, Fig. 1), 5 ml of 0.025% HCl saturated with O<sub>2</sub> (a stoichiometric  $\mu\text{HCl}/\mu\text{O}_2$  ratio) were irradiated. The experimental results are given in Table 1.

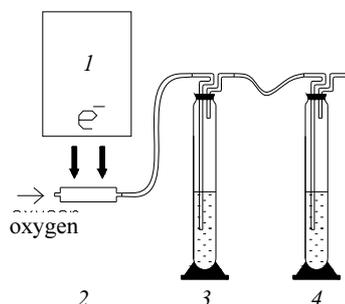


Fig. 1. The scheme of the experiment in the liquid phase: 1 – electron accelerator; 2 – plasma chemical reactor; 3, 4 – absorption vessels with alkali

Table 1. Results of the experiments on irradiation in the liquid phase

Time-frequency, min/Hz	3/3	3/10	10/3	3/30	10/10
Absorbed dose, kGy	162	540	540	1620	1800
Conversion, %	9.5	13	20	24	25

Thus, the level of the HCl conversion under irradiation in the liquid phase flattened out at sufficiently moderate absorbed doses.

In the case of the full conversion to chlorine (the HCl concentration of 0.025%), the chlorine concentration will be  $\sim 200$  mg/l.

In the case of irradiation in the gas phase (in a closed vessel, Fig. 2), the HCl gas was generated from a mixture of strong hydrochloric and sulfuric (H<sub>2</sub>SO<sub>4</sub>) acids (the HCl gas is liberated when these acids are mixed) with bubbling of oxygen. The mixture was irradiated for 3 min at a frequency of 10 Hz (the absorbed dose of 540 kGy). The experimental results are given in Table 2.

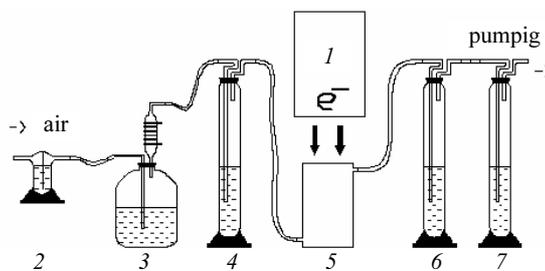


Fig. 2. The experimental scheme: 1 – accelerator; 2 – carbonic acid neutralizer; 3 – Tishchenko vessel with hydrochloric acid; 4 – dehumidifier; 5 – plasma chemical reactor; 6, 7 – absorbers

Thus, the maximum amount of chlorine and the maximum conversion were achieved at  $\mu\text{HCl}/\mu\text{O}_2 = 1:1$  (4-fold excess oxygen). This ratio was used in the later experiments at different partial pressures of water. The experimental results are given in Table 3.

Thus, it was found that the conversion in the gas phase was a maximum when HCl was the driest. The conversion decreased with growing humidity.

However, the amount of generated chlorine was smaller than in any solution starting from the concentration of 1%. In other words, irradiation in the gas phase was less favorable.

The saturation with oxygen (by achieving its dissolution limit) in the liquid phase was impossible and, for this reason, it was thought reasonable to adopt irradiation of the HCl aerosol in an oxygen flow. The use of the aerosol was rather problematic. On the one hand, it did not provide dry HCl and, on the other hand, it could lead to a specific interaction on the interface.

The experimental scheme included bubbling of air through 20-% hydrochloric acid and irradiation of the gas mixture (3 min at a frequency of 30 Hz; the

Table 2. Results of the experiments on irradiation in the gas phase

№	VH <sub>2</sub> SO <sub>4</sub> , ml	VHCl, ml	$\mu\text{HCl}/\mu\text{O}_2$	pHCl, mm Hg	Cl <sub>2</sub> formed, $\mu\text{mole/kGy}$	Conversion, %
1	35	7	8.7	1392	$36 \cdot 10^{-3}$	0.05
2	16	3.2	4	640	$63 \cdot 10^{-3}$	0.19
3	4	0.8	1	160	$75 \cdot 10^{-3}$	0.90
4	0.25	0.05	$\sim 0.1$	$\sim 10$	$5 \cdot 10^{-3}$	0.50

Table 3. Results of the experiments on irradiation in the gas phase at different partial pressures of water

pH <sub>2</sub> O, mm Hg	0.005	0.04	0.31	3.1	7.2	12.2
Cl <sub>2</sub> formed, $\mu\text{mole/kGy}$	$75 \cdot 10^{-3}$	$47 \cdot 10^{-3}$	$41 \cdot 10^{-3}$	$37 \cdot 10^{-3}$	$23 \cdot 10^{-3}$	$9.2 \cdot 10^{-3}$
Conversion, %	0.90	0.53	0.40	0.45	0.26	0.09

absorbed dose of 1620 kGy). Chlorine was not detected in the reaction products.

Nevertheless, chlorine was formed with the conversion of up to 10% during oxygen bubbling, which corresponded to  $22 \cdot 10^{-3}$   $\mu\text{mole/kGy}$ . Thus, the comparison of these results with the data obtained for the gas phase ( $9.2 \cdot 10^{-3}$  and  $23 \cdot 10^{-3}$ , Table 3) showed that this was the anticipated value, i.e. the gas phase was irradiated and the aerosol was not formed during bubbling.

Therefore experiments, in which the aerosol was formed using a compressor and an ultrasonic nebulizer, were performed. A zero conversion was observed in the experiments.

### 3. Conclusion

It is shown that the highest conversion (up to 25%) is achieved in aqueous solutions of hydrochloric acid. If the gas phase is irradiated, the maximum conversion is realized at a minimum pressure of the water vapor, but it is not over 1%. The desired process is initiated little if at all during irradiation of aerosols.

Since the use of hydrochloric acid more than 1% strong does not increase the amount of generated chlorine, it is reasonable to separate chlorine as crystalline hydrate in industrial processes. The process can be realized in a continuous regime and can be used for recycling of hydrochloric acid waste and production of chlorine-containing oxidizers and whiteners.

The proposed process can also be used for disinfection of water. The exposure of hydrochloric acid  $\sim 0.02\%$  strong to an electron beam can give a "chlorinating agent". The addition of this agent to potable water has an effect similar to chlorination. An advantage of this scheme is that it does not require the supply of poisonous molecular chlorine. The capacity of the installation with an URT-0.5 accelerator is not

over 0.017 mmole  $\text{Cl}_2/\text{min}$  (79 mg/h) at a frequency of 30 Hz and can be increased by nearly 6 times if the installation runs at a maximum frequency (up to 200 Hz).

Generally, the process can be referred to processes of "green chemistry" as it does not require high temperatures, hazardous reagents and solvents. The relevant equipment meets the same requirements.

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