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Intensification of the Dealkalization Process of Silicate Glasses with Acid Gases

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Abstract—The results of studies on the intensification of the dealkalization process of alkaline silicate industrial and synthesized glasses with acid gases are analyzed and summarized. The composition of the reaction products of glasses with gaseous reagents is identified using X-ray phase analysis, X-ray spectral electron probe microanalysis, thermal analysis, flame photometry, and quantitative chemical analysis. The physicochemical properties of industrial glassware modified with gaseous reagents are determined in laboratory and factory experiments. Ways of intensifying the dealkalization process of silicate glasses with acid gases are discussed.

INTRODUCTION

For many centuries, dealkalization of the glass surface by furnace gases was an accompanying and uncontrolled process during annealing of various types of glassware. For example, M.A. Bezborodov noted that in those days, when glass factories did not have any measuring equipment in their furnaces and much was determined by eye, glassmakers noticed that well-annealed glassware were covered with a white coating with a bluish tint [1]. In the 1930s, it was found that bloom on the surface of flat glass [2] and bottles [3] contains sodium sulfate. It follows that sulfur dioxide dealkalizes glass.

For the first time, the effect of temperature on the mass of Na_2SO_4 formed on the surface of sheet glass was explained in [2]. Experiments have also shown that dealkalization of glassware SO_2 increases the chemical resistance of glass by several times, while its mechanical strength and thermal stability increase [1–3]. Unique studies were carried out to determine the resistance to internal hydrostatic pressure (RIHP) of bottles annealed in a lehr with furnace gases [4]. Having tested more than 130 000 bottles, the author came to the conclusion that furnace gases increase their strength by 20–30%.

In subsequent studies, increased attention was paid to the mechanism of dealkalization of industrial and model glasses by acid gases. The works [5–7] are of interest. In total, more than 400 publications have been devoted to the problem of dealkalization of silicate glasses with acid gases, and a single monograph [8] has also been published.

The main disadvantage of the acid gas dealkalization method is the small thickness of the dealkalized glass layer. Depending on the chemical composition of the samples and the conditions of thermochemical treatment, the thickness of the densified layer in industrial glasses varies from fractions of a micrometer to 1 μm. During the transportation and operation of glassware, the dealkalized layer is easily damaged, as a result of which their physicochemical properties deteriorate [8].

The aim of this study is to analyze and generalize the results of studies on the intensification of the dealkalization process of silicate glasses with acid gases.

EXPERIMENTAL

The objects of research are industrial glassware for various purposes and synthesized two- and three-component glasses. The following objects were used in the experiments: sheet glass; glass containers (bottles, jars, flasks) made of transparent decolorized glass; dark green glass bottles; assorted glassware made from

Table 1. The chemical composition of industrial glasses according to factory analyses

Glass type	Content of oxides (mass fraction, %)								
	SiO_2	Al_2O_3	Fe_2O_3	CaO	MgO	Na_2O	K_2O	SO_3	Other
Sheet of vertical stretching	72.65	1.55	0.11	7.60	3.71	13.62	0.35	0.31	–
Container colorless	71.81	2.53	0.07	6.54	4.60	13.72	0.25	0.43	–
Bottle dark green	69.68	4.83	0.69	9.68	0.35	14.37	0.21	0.34	–
Assorted colorless	71.95	4.22	0.04	6.52	0.20	17.15	0.10	0.12	–
Assorted blue	71.49	1.72	0.05	8.01	0.15	8.08	10.09	0.38	0.08CoO
Illuminating rosaline	71.48	2.74	0.04	7.32	0.22	17.30	0.36	0.31	0.02 Se, 0.14Sb
Illuminating milky	65.03	7.03	0.04	3.84	0.11	19.53	0.16	0.10	$4.88F^-$
Medical colorless	72.81	4.52	0.05	6.05	0.82	8.15	1.64	–	$6.11B_2O_3$
Insulating colorless	72.31	2.44	0.10	7.67	3.61	9.73	3.86	0.21	–
Insulating low alkaline	63.41	15.34	0.10	12.81	3.97	2.02	–	0.25	$2.04F^-$

Table 2. Dealkalization rate of Na^+ from glasses of the $Na_2O-R_2O_3-SiO_2$ system by difluorochloromethane (temperature 550°C; amount of reagent substance for processing, 0.67 mol; time, 15 min)

Number of glass	Molar ratio in glass				Dealkalization rate, $\mu mol\ Na^+/(dm^2\ min)$
	Na_2O	Al_2O_3	B_2O_3	SiO_2	
1	1	–	–	2	19.7*
2	1	–	–	3	15.1
3	1	0.05	–	2	37.6*
4	1	0.15	–	2	54.0*
5	1	0.05	–	3	28.1
6	1	–	0.05	2	11.7
7	1	–	0.15	2	7.5

* The bloom was not completely washed off with water.

transparent colorless and blue glasses; diffusers made from rosaline and milky glass; glassware made from transparent colorless medical glass; and insulators made of transparent colorless and low alkali glass. The chemical compositions of industrial glasses, the conditions for melting the glass, the methods for molding glassware for various purposes, and their physicochemical properties differ significantly from each other. The chemical compositions of the glasses are presented in Table 1.

Synthesized glasses of the $Na_2O-R_2O_3-SiO_2$ system, where $R_2O_3-Al_2O_3$ and B_2O_3 were used to determine the effect of some glass components on their chemical interaction with gaseous reagents. Table 2 lists the chemical compositions of the model glasses.

For the synthesis of glasses, finely ground anhydrous pure-grade silicon dioxide and chemically pure alumina, boric acid, and soda were used. Tiles were formed from the welded glass mass, and then they were annealed, ground, and polished. The deviation of the glass components from the specified composition did not exceed 1 mol %.

Sulfur and nitrogen dioxide, difluorodichloromethane, difluorochloromethane, and gas mixtures of fluorochlorine derivatives of hydrocarbons and sulfur dioxide were used for the thermochemical treatment of the glass samples. Solutions of HF, HCl, and HBr acids were used as sources of fluoride, chloride, and hydrogen bromide. The experiments were carried out in laboratory and factory conditions.

Laboratory regimes of thermochemical treatment of glass samples with gaseous reagents: the temperature was changed in the range of 300 to 600°C, the amount of the reagent substance per treatment was 0.05–1.50 mol, and the duration was 1–120 min. The following properties of glass were established in the experiments: water and acid resistance, strength in centrally symmetrical bending, impact strength, microhardness, and thermal resistance. The method for determining water and acid resistance was developed taking into account the chemical composition of industrial glassware and their operating conditions. The strength of sheet glass in the case of centrally symmetrical bending was determined according to the

procedure [9]. Recommendations [10] were taken into account to determine the impact strength of sheet glass. The microhardness of the samples was measured on a PMT-3M microhardness tester at different loads on the diamond pyramid indenter. To determine the maximum thermal stability of glass, the temperature difference was increased until all samples were completely destroyed.

The thermochemical treatment regimes of hollow glassware with gaseous reagents at glass factories were as follows: the temperature was changed in the range of 450 to 600°C, the volume of the gaseous reagent per unit of glassware was 0.05−100.0 mL, and the duration was 1 s−80 min. Glass containers (bottles, jars, and flasks) were dealkalized by the reagents at the stage of the final blowing of glassware, on the cooling tables of glass-forming machines, on the conveyor when transporting glassware to the lehr, and during annealing. Glassware were tested for RIHP, microhardness, heat resistance, and water resistance. For jars, the resistance to the compression force was additionally determined in the direction perpendicular to the walls of the body. For samples, the maximum values of RIHP and resistance to the compression force in the direction perpendicular to the walls of the case were set; i.e., the load was increased to a value at which the glassware was destroyed. The maximum thermal stability of industrial glassware was determined by a method similar to that for samples under laboratory conditions.

Thermochemical treatment of industrial and synthesized glasses with gaseous reagents in laboratory and factory conditions is accompanied by the formation of chemical reaction products on the surface of samples. The composition of the dealkalization bloom was identified using X-ray phase analysis, X-ray spectral electron probe microanalysis, thermal analysis, flame photometry, and quantitative chemical analysis.

The phase composition of the reaction products of glass with gaseous reagents was determined on a DRON-3.0 diffractometer during CuK_α-radiation. Glass plates subjected to thermochemical treatment with gaseous reagents and powders of reaction products were used for analysis. The elemental composition of the dealkalization bloom and the nature of its distribution on the glass surface were studied using an EMMA-2 electron microscope with a MAP attachment for X-ray microanalysis. The presence of the following elements was analyzed in the reaction products: Si, Al, Fe, Ca, Mg, K, F, and Cl (Na was not determined). Thermal analysis was performed on an OD-102 derivatograph. The presence of Na^+, K^+, and Ca^{2+} was detected using a Flapho-4 flame photometer. The ionic composition of the bloom was determined based on the quantitative chemical analysis.

The HF sectioning method was used to analyze the composition and structure of the surface layers of industrial and model synthesized glasses. The core of this method lies in the sequential layer-by-layer dissolution of the surface layers of model two- and three-component glasses with a low-concentration HF solution and analysis of the resulting extracts [11]. We have developed a technique for sectioning industrial glasses of various compositions with an HF solution [12]. The maximum relative error in determining the thickness of the dissolved layer was ±5%, and the etching rates ±4%. In the extracts after glass etching, the concentrations of Na^+, K^+ and Ca^{2+} were determined by flame photometry.

RESULTS AND DISCUSSION

In the laboratory experiments, the thermochemical treatment of samples of all types of industrial glass with gaseous reagents in the temperature range of 300 to 600°C leads to the formation of bloom of varying intensity. The higher the treatment temperature and the higher the content of alkaline oxides in the glass composition, the more intense the coating that is formed on the surface of the samples. The phase, elemental, and ionic compositions of the reaction products of all types of industrial and synthesized glasses with gaseous reagents were identified using complex analysis. First, the phase composition of the bloom was determined, and then it was compared with the data on the elemental and ionic compositions. We note that the results of different methods of bloom analysis completely coincided.

The thermochemical treatment of industrial SO_2 glasses is accompanied by the formation of bloom, consisting of various modifications of Na_2SO_4 and a small amount of K_2SO_4, with the molar ratio between Na_2SO_4 and K_2SO_4 in the reaction products corresponding to their content in the glass composition. The surface of low-alkali insulating glass under the influence of sulfur dioxide is covered with a light coating of $CaSO_4$. Na_2SO_4 was detected in the reaction products of the synthesized glasses with SO_2. In the reaction of NO_2 with industrial glasses, a weak coating appears containing $NaNO_3$.

In the thermochemical treatment of CF_2Cl_2, CHF_2Cl, and HCl industrial glasses, their surface is covered with bloom, which includes NaCl and a small amount of KCl. Fluorine compounds were not found in the bloom. Low-alkali insulating glass reacts weakly with difluorodichloromethane, forming a bloom of $CaCl_2$ and NaCl. On the surface of synthesized glasses dealkalized with CF_2Cl_2, only NaCl was detected. The reaction of CF_2Cl_2 with glasses of the Na_2O-SiO_2 system proceeds very vigorously, as a result of which not only NaCl but also the α-form of $Na_2Si_2O_5$ was identified on the surface of the samples. Therefore, despite the significant difference between the compositions of both industrial and synthesized glasses, and different regimes of thermochemical treatment in laboratory and production conditions, as a result of the reaction

of the samples with CF_2Cl_2, CHF_2Cl, and HCl products of the same composition are formed.

The presence of NaF, KF, and CaF_2 was found on the surface of industrial glasses exposed to hydrogen fluoride. Hydrogen bromide dealkalizes industrial glasses to form NaBr containing bloom.

The composition of the reaction products of industrial glasses with a mixture of CF_2Cl_2 and SO_2 in a volume ratio of 1 : 1 includes mainly different modifications of Na_2SO_4 and contains a smaller amount of NaCl and K_2SO_4. The results obtained mean that when using gas mixtures, the glass dealkalization process is intensified due to the catalytic effect of the fluorochlorine-containing reagent on sulfur dioxide.

Thus, the formation of bloom on the surface of glassware, which is a thin film of the reaction products, is a characteristic sign of glass dealkalization by acid gases.

In the literature, the intensity of dealkalization of industrial and model glasses with acid gases is characterized by the mass of the reaction products formed per unit area of the sample [2, 3, 5, 13]. This method has significant drawbacks. First, it is impossible to compare the reactivity of different acid gases even with respect to glass of the same composition, since the reaction products have different chemical compositions. Second, it is impossible to compare the data obtained with different durations of thermochemical treatment. There are no other criteria for estimating the intensity of dealkalization of inorganic glasses by acid gases in the literature.

Based on the data on the composition of bloom and its geometric parameters (thickness, size, shape of crystals, etc.) and characteristics of the composition and structure of the dealkalized glass layer, we developed five criteria for assessing the intensity of dealkalization of alkali silicate glasses by acid gases: (1) the rate of extraction of alkali metal cations from the surface layer of glass; (2) thickness of the dealkalization bloom on the glass surface; (3) thickness and degree of dealkalization of the surface layer of glass; (4) change in the chemical composition and structure of the glass surface layer; and (5) increase in microhardness in the dealkalized glass layer. The advantages and disadvantages of the criteria are given in [14].

An analysis of our and the published data has shown that when alkaline silicate glasses are treated with acid gases, a bloom is formed, which always contains Me^+ (Na^+, K^+, etc.). An important conclusion follows from this: it is advisable to characterize the kinetics of the interaction of glass with acid gases by the dealkalization rate of Me^+ [8]. In this case, it is possible to evaluate the ability of glass to dealkalize, regardless of the composition of the reaction products, and at different processing times. In addition, determining the extraction rate of Me^+, it becomes possible to compare the intensity of dealkalization of silicate glasses when they are exposed to different kinds of reagents: acid gases, water, acid solutions, etc. To calculate the extraction rate of Me^+ from glass with acid gases, the following formula was used:

$$\upsilon_{Me^+} = C_{Me^+} V S^{-1} \tau^{-1},$$

where υ_{Me^+} is the Me^+ extraction rate from the surface layer of glass, $\mu mol\ Me^+/(dm^2$ glass surface $\cdot$ min); C_{Me^+} is the concentration of Me^+ in the solution obtained after washing off the reaction products with distilled water, $\mu mol\ Me^+/dm^3$; V is the solution volume, dm^3; S is the sample surface area, dm^2; and τ is the duration of thermochemical treatment, min.

The following ways of intensifying the dealkalization process of silicate glasses with acid gases are proposed.

(1) Optimization of the regimes of thermochemical treatment of glass with acid gases.

The influence of various factors on the rate of dealkalization of silicate glasses by gaseous reagents was studied: temperature, chemical composition of the glass and gaseous medium, duration of thermochemical treatment, concentration and humidity of the gaseous reagent, additional heat treatment, and state of the surface of the samples.

The effect of temperature and composition of some gaseous reagents on the dealkalization process of illuminating rosaline glass is shown in Fig. 1.

The dealkalization rate of glass at temperatures below 300°C was 0.09 $\mu mol\ Na^+/(dm^2$ min) and did not differ from the dealkalization rate of samples washed with distilled water. At a temperature of 300°C and above, a dealkalization bloom forms on the surface of glass treated with all gaseous reagents. Figure 1 shows CHF_2Cl dealkalizes glass more intensively than sulfur dioxide. Fluorochlorine derivatives of hydrocarbons actively react with samples at temperatures above 400°C, when they are pyrolyzed to form hydrogen fluoride and chloride. CHF_2Cl mixed with SO_2 interacts most actively with glass.

Increasing the temperature from 300 to 600°C increases the dealkalization rate of Na^+ from glass with gaseous reagents repeatedly (Fig. 1). Thus, the higher the temperature the more intensively the glass is dealkalized by the gaseous reagents. A favorable increase in temperature for the intensification of the dealkalization process was established using industrial and synthesized glasses and gaseous reagents of different compositions.

In some studies, for example [15, 16], it is noted that repeated heat treatment of products can change the state of the glass surface and its properties. Additional heat treatment of glass was carried out according to regimes similar to thermochemical treatment, but without gas reagents. The data in chart 4 in Fig. 1 illustrate that repeated heat treatment slightly
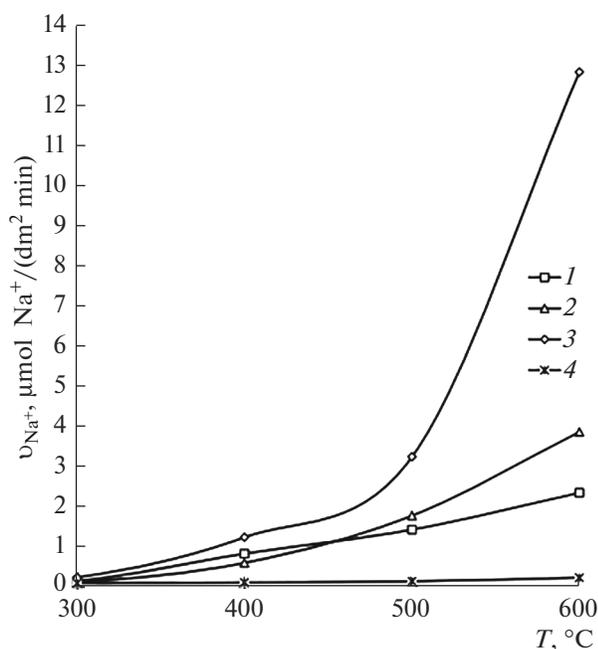
Fig. 1. Dependences of dealkalization rate υ_{Na^+} from illuminating rosaline glass treated with SO_2 (*1*), CHF_2Cl (*2*), CHF_2Cl mixture with SO_2 in a volume ratio of 1 : 1 (*3*) and after additional heat treatment (*4*) on temperature.

Fig. 2. Dependences of the dealkalization rate of assorted colorless glass by difluorochloromethane (*1*) and sulfur dioxide (*2*) on the duration of treatment.

increases the dealkalization rate of glass. This indicates that an increase in the dealkalization rate of Na^+ during the thermochemical treatment of samples completely depends on the course of the chemical reaction between the alkaline components of the glass and gaseous reagents and is not related to the effect of temperature on the mobility of Na^+.

The most complex and least studied factor is the influence of glass components on the process of its dealkalization. It is well known that glasses containing aluminum oxide are most intensively dealkalized by sulfur oxides [5]. It was also of interest to find out the effect of boron oxide on the process of dealkalization model glasses with gaseous reagents, since this oxide reduces the mobility of alkali cations in the glass structural network. For this reason, we studied the dealkalization of glasses of the $Na_2O-R_2O_3-SiO_2$ system containing $R_2O_3-Al_2O_3$ and B_2O_3. Table 2 shows the values of the dealkalization rate of Na^+ from synthesized glasses treated with CHF_2Cl.

The experimental results show that at a higher content of Na_2O in glasses of the Na_2O-SiO_2 system more intense dealkalization of CHF_2Cl occurs. The dealkalization rate of soda silicate glasses with CHF_2Cl was several times higher than the dealkalization rate of industrial glasses treated with the same reagent in a similar regime. This is due, firstly, to the higher content of Na_2O in the model glasses (by times of two to three), and secondly, in two-component glasses, the
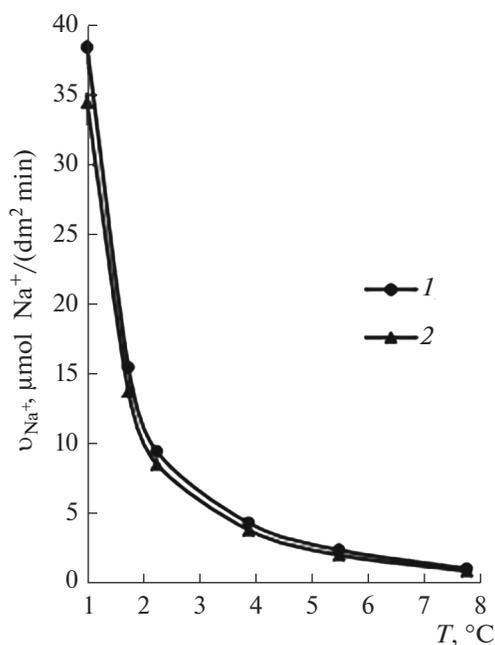
mobility of Na^+ from deep layers to the surface is higher.

The addition of Al_2O_3 into two-component glasses significantly increases the extraction rate of Na^+ CHF_2Cl, while the introduction of the same amount of B_2O_3 reduces the rate of dealkalization. The increase in the Al_2O_3 content in glass up to 0.15 mole fractions sharply enhances the dealkalization of Na^+ CHF_2Cl, as a result of which the bloom "burns" to the surface of the samples. In these experiments, the bloom was not completely washed off with water; therefore, in Table 2 for glass nos. 1, 3, and 4, the dealkalization rates of Na^+ are not accurate.

The duration of the treatment is an important factor in the interaction of glass with gaseous reagents. Considering that the fastest dealkalization rate of glass was observed at a temperature of 600°C, the experiments were carried out at this temperature and the amount of the gas reagent per treatment was 0.67 mol. The test results for the assorted colorless glass are presented in Fig. 2.

It can be seen from the given data that the maximum dealkalization rate of glass by gaseous reagents was observed during the first 3 min. With a treatment time of more than 15 min, the dealkalization rate of Na^+ glass is greatly reduced. The same result was obtained during the thermochemical treatment of other industrial glasses with different reagents. Dependences of a similar nature were obtained when determining the effect of the concentration and

Table 3. The relationship of the physicochemical properties of sheet glass with the regimes of thermochemical treatment, the dealkalization rate of Na^+ by gaseous reagents and characteristics of the dealkalized layer

Treatment regime		Dealkalization rate, $\dfrac{\mu mol\ Na^+}{dm^2\ min}$	Glass properties				Characteristics of dealkalized glass	
gaseous reagent	temperature, °C		resistance to water, mg Na_2O/dm^2	impact strength, kJ/m^2	micro-hardness, GPa	thermal stability, °C	thickness of dealkalized layer, μm	relative concentration of Na^+, C_{min}/C_0
CF_2Cl_2	300	0.22	0.50	2.9	4.23	111	0.3	0.8
	400	0.55	0.40	3.0	4.45	112	0.4	0.7
	500	1.44	0.22	3.7	4.62	115	0.6	0.5
	600	3.48	0.14	4.4	4.97	122	0.8	0.4
SO_2	600	2.23	0.18	4.7	4.83	125	0.8	0.4
CF_2Cl_2 with SO_2 (1 : 1)	600	9.87	0.06	4.3	5.03	120	1.0	0.2
—	20	0.09	0.52	2.8	4.22	110	—	—

C_0 is the concentration of Na^+ in the bulk of the glass.

humidity of the gaseous reagent on the dealkalization rate of glass. Under industrial conditions, freshly produced hot glassware are more actively dealkalized by reagents than glassware that were in storage and in operation.

Based on the experiments performed, the following optimal regime of thermochemical treatment of industrial glasses was determined under laboratory conditions: temperature, 600°C; amount of reagent per treatment, 0.67 mol; and duration, 15 min. Under production conditions, the optimal regime of glass treatment with gaseous reagents was established only experimentally.

Thermochemical treatment of industrial glasses with gaseous reagents under laboratory conditions increases their water and acid resistance by several times, strength under static and dynamic loads by 50–70%, microhardness by 10–20%, and thermal resistance by 10–15%. The results of production experiments are presented in [17].

A close relationship has been established between the dealkalization rate of Me^+ cations with acid gases, which are extracted from the surface layer of glass, its composition, structure, and physicochemical properties of the glassware. Table 3 presents the results taken from [17] and supplemented with the data on the mechanical strength and thermal stability of sheet glass dealkalized with various gaseous reagents.

From Table 3 it follows that the maximum increase in the thermomechanical properties and chemical resistance of glass is achieved at the greatest depth of the dealkalized layer and the degree of its dealkalization. The thermochemical treatment of industrial glasses with gaseous reagents does not lead to the complete removal of Na^+ from the dealkalized layer (Table 3).

In our studies, model two- and three-component glasses were dealkalized with gas reagents to a depth of 30 μm or more.

(2) Application of effective gaseous reagents for glass dealkalization based on thermodynamic analysis.

The search for new gas reagents that react with alkaline oxides was carried out based on thermodynamic analysis. Calculations were performed both for reactions between alkali oxides and individual acid gases, and for reactions involving gas mixtures of different compositions. The change in the Gibbs energy for the equations of the most probable chemical reactions in the temperature range from 298 to 1000 K was calculated according to the procedure [18]. Table 4 shows the calculation of the change in the Gibbs energy for reactions between sodium oxide and gaseous reagents at temperatures of 298 and 1000 K.

The data in Table 4 indicate that, in the standard conditions, sodium oxide should react with all gaseous reagents, with the exception of hydrogen fluoride. At a temperature of 1000 K, the negative values of the change in the Gibbs energy increase sharply for all reactions, and only hydrogen bromide should not react with sodium oxide. It also follows from the presented results that, from the thermodynamic point of view, sodium oxide should most actively interact with gas mixtures. The experiments confirmed that mixtures of gaseous reagents dealkalize silicate glasses more intensively than individual reagents.

The graphic dependences of the change in the Gibbs energy on temperature for chemical reactions between the components of industrial glasses and gaseous reagents are obtained. Figure 3 shows the effect of temperature on the Gibbs energy change value for the

Table 4. Change in the Gibbs energy for the equations of the most probable reactions of sodium oxide with gaseous reagents at temperatures of 298 and 1000 K

Equations for reactions of sodium oxide with gaseous reagents	ΔrG^0 (298K) kJ/mol	ΔrG (1000 K), kJ/mol
$Na_2O + 2HF = 2NaF + H_2O$	163	−17 102
$Na_2O + 2HCl = 2NaCl + H_2O$	−428	−4917
$Na_2O + 2HBr = 2NaBr + H_2O$	−452	51 616
$Na_2O + CO_2 = Na_2CO_3$	−274	−5759
$Na_2O + SO_2 = Na_2SO_3$	−376	−5159
$Na_2O + SO_3 = Na_2SO_4$	−519	−11 681
$2Na_2O + 2SO_2 + O_2 = 2Na_2SO_4$	−1177	−25 780
$2Na_2O + 4NO_2 + O_2 = 4NaNO_3$	−919	−94 358
$Na_2O + 2NH_3 + 4O_2 = 2NaNO_3 + 3H_2O$	−1036	−105 027
$3Na_2O + 2SO_2 + O_2 + 2HCl = 2Na_2SO_4 + 2NaCl + H_2O$	−1605	−30 926

chemical reaction of hydrogen chloride with alkaline oxides.

The data in Fig. 3 indicate the directly proportional dependence of the value of the change in the Gibbs energy on temperature for the reaction of hydrogen chloride with oxides of sodium and potassium.

(3) The use of electric and magnetic fields to intensify the process of glass dealkalization with acid gases.

The course of chemical processes is greatly influenced by the magnetic, electric, and acoustic fields [19]. There is no information in the literature about the effect of physical fields on glass dealkalization by acid gases. We have studied the dealkalization process industrial glasses with gaseous reagents under the influence of electromagnetic fields. An example of the influence of a constant electric field on the intensity of dealkalization of illuminating rosaline CHF_2Cl is shown in Fig. 4.
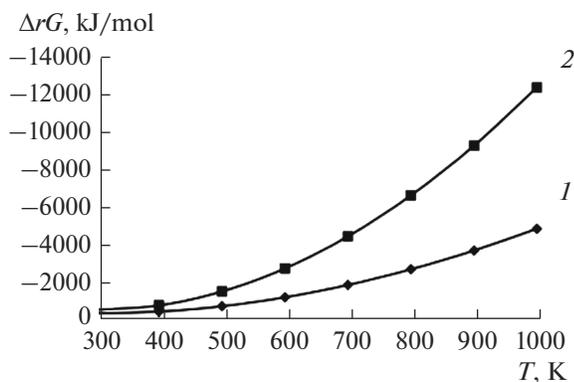
The presented data clearly demonstrate that a constant electric field significantly intensifies the dealkalization of CHF_2Cl glass. This can be explained by the ionization of the gaseous medium, which facilitates the exchange of alkali metal cations for hydrogen cations. The rate of glass dealkalization by gases in an electric field is affected by the voltage value, the size and shape of the electrodes, the distance between the electrodes, the material of the electrodes, and other factors.

Experiments have shown that alternating and pulsed electric fields, as well as constant, alternating, and pulsed magnetic fields, also enhance the process
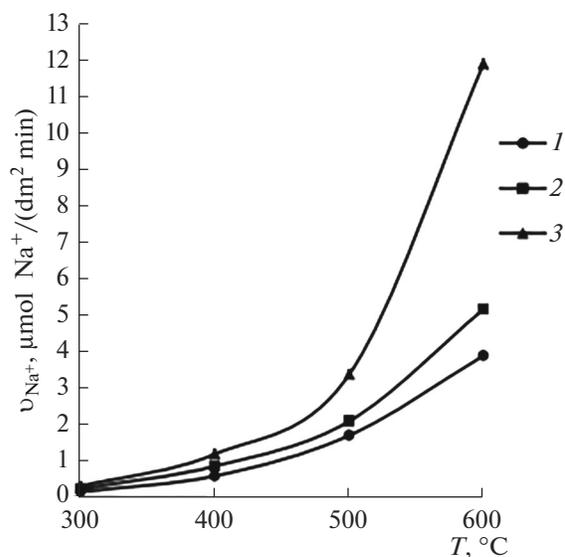
Fig. 3. Dependences of change in Gibbs energy on temperature for the chemical reaction of hydrogen chloride with oxides of sodium and potassium. (*1*) $Na_2O + 2HCl = 2NaCl + H_2O$; (*2*) $K_2O + 2HCl = 2KCl + H_2O$.

Fig. 4. Effect of temperature on dealkalization rate υ_{Na^+} of illuminating rosaline glass with difluorochloromethane in a constant electric field (duration 15 min; CHF_2Cl volume, 15 L). (*1*) $U = 0$; (*2*) $U = 0.5$ kV; (*3*) $U = 1.5$ kV.

Table 5. Influence of treatment of juice bottles with a capacity of 0.5 L with gaseous reagents and a magnetic field on their properties

Treatment regime	Glass condition	RIHP, MPa	Water resistance of glass, mg Na_2O
1	Without treatment	1.34	0.092
2	Thermomagnetic treatment (constant magnetic field, 0.20 T; temperature, 600°C)	1.67	0.092
3	Thermochemical treatment of SO_2 (temperature, 600°C; consumption, 0.5 μmol/m^2)	1.40	0.056
4	Thermochemical treatment of CF_2Cl_2 (temperature, 600°C; consumption, 0.5 μmol/m^2)	1.47	0.009
5	Treatment regime 2 and then 3	1.58	0.006
6	Treatment regime 2 and then 4	1.89	0.000

of glass dealkalization by gaseous reagents. The effect of bottle treatment with gaseous reagents and a constant magnetic field on their properties is given in Table 5.

The data in Table 5 show that thermomagnetic treatment increases mechanical strength by 25%, which is consistent with the published data [20]. Our experiments have shown that the effect of hardening products depends on the value of the modulus of the magnetic induction vector, the glass temperature, and the duration of treatment. The water resistance of glass under the influence of a magnetic field does not change [21].

The thermochemical treatment of SO_2 and CF_2Cl_2 sharply increases the water resistance of glass, while also increasing its mechanical strength, but to a lesser extent than with thermomagnetic treatment. The combination of thermochemical and thermomagnetic treatments leads to the greatest increase in the mechanical strength and water resistance of bottles (Table 5), microhardness, and thermal resistance.

CONCLUSIONS

The thermochemical treatment of industrial and synthesized glasses with SO_2, NO_2, HF, HCl, HBr, CF_2Cl_2, and CHF_2Cl and mixtures of gaseous reagents leads to the formation of reaction products containing Na^+ and K^+.

The main criteria for estimating the intensity of dealkalization of alkali silicate glasses by acid gases are the thickness and degree of dealkalization of the glass surface layer and the extraction rate of Me^+ from the samples. The strongest effect on the intensity of dealkalization of silicate glasses by gaseous reagents is exerted by temperature, as well as the chemical composition of the glass and the gaseous medium.

A close relationship has been established between the physicochemical properties of glass and the conditions of thermochemical treatment, as well as the deal-

kalization rate of Na^+ by acid gases, composition, and the structure of its surface layer. An analysis of the results obtained allows us to conclude that in order to obtain the maximum effect in increasing the mechanical properties and chemical stability of the glassware, thermochemical treatment with gaseous reagents must be carried out according to a regime that provides the largest thickness of the dealkalized glass layer and the degree of its dealkalization.

The process of dealkalization of silicate glasses with acid gases is intensified by optimizing the regimes of thermochemical treatment and using effective gaseous reagents and electromagnetic fields.

CONFLICT OF INTEREST

The authors declare that they have no conflicts of interest.

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