
**SORPTION
AND ION EXCHANGE PROCESSES**

Effect of Gas Environment Parameters on Operation Efficiency of Chemical Absorbents of Carbon Dioxide

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Abstract—Effect of main characteristics of the gas medium on the absorbing properties of alkaline chemical absorbents is demonstrated. The following gas flow parameters were examined as variables: carbon dioxide content of the gas flow within the range 0.2–5.0 vol %, gas humidity of 25–90 rel %, and pressure in the zone of the chemisorption process in the range from 2 to 6 MPa. As objects of study served mixed chemical absorbents based on calcium, sodium, and lithium hydroxides.

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The problem of purification of gas environments is exceedingly important for such human activity fields as development of collective and individual life-support systems, purification of technological gases in industries, and production of breathing mixtures. At present, this problem is solved by using sorption methods with nonregenerative alkaline absorbents [1].

Most of materials belonging to this class are based on oxides and hydroxides of alkali metals owing to their chemical properties [2]. These compounds enter into the reaction with carbon dioxide to form metal carbonates. The characteristic features of the majority of reactions of this kind are the strong exothermic effect and the significant influence exerted by the content of water on the reaction rate [3].

The composition and application method of an absorbent are chosen in accordance with the conditions in which a gas purification process is to be performed. By the conditions are primarily meant the initial and maximum admissible (breakthrough) concentrations of carbon dioxide after the absorber layer and the humidity and temperature of the gas at the adsorber inlet [2].

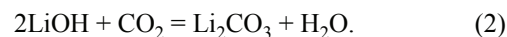
When considering the specificity of processes in which a mixed chemical absorbent interacts with carbon dioxide, we should note that there exist certain differences in the nature of reaction between active components and carbon dioxide.

Calcium hydroxide interacts with carbon dioxide by the following overall reaction:



This reaction occurs in a liquid film in the interaction of carbonate ions with calcium ions, and its rate is correlated with the concentration of Ca^{2+} , CO_3^{2-} , and HCO_3^- ions. There is no published evidence on whether the formation of hydroxo complexes can affect the mechanism and extent of the reaction. The total heat effect of the reaction is 73.2 kJ mol^{-1} , and the stoichiometric capacity of calcium hydroxide for CO_2 reaches a value of 0.59 g g^{-1} .

The interaction of lithium hydroxide with carbon dioxide can be described in the general form by the stoichiometric formula



Here, the change in the Gibbs free energy, which characterizes the reaction, is $\Delta G = -90.8 \text{ kJ mol}^{-1}$, and the stoichiometric capacity for CO_2 , 0.91 g g^{-1} .

This interaction may occur by two main mechanisms, directly or via formation of a crystal hydrate. The interaction of lithium hydroxide with carbon dioxide is described by the stoichiometric equation



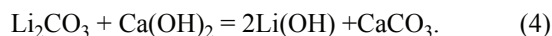
It was shown in [4] that the carbonization rate of the anhydrous hydroxide is tens of times that of the crystal hydrate, being nearly temperature-independent and increasing in proportion to the CO₂ pressure raised to the power of 0.3. The carbonization rate of the monohydrate is nearly independent of the pressure of the gaseous reagent and varies with temperature in a complex way. If LiOH·H₂O is involved in the reaction, the carbonization course is limited by the dehydration of the crystal hydrate. For this reaction, the apparent activation energy of carbonization is 52.5 kJ mol⁻¹ in the temperature range 30–60°C, which is close to the enthalpy of dehydration (61.2 kJ mol⁻¹).

It was also noted that the carbonization of lithium hydroxide monohydrate at 0–30°C is accompanied by the formation of a humidified caked product. The processing of the results of kinetic measurements in [4] demonstrated that the process rate is independent of the CO₂ pressure, remains nearly unchanged at 0–30°C, steeply grows as the temperature is raised from 50 to 60°C, and then weakly decreases as the temperature increases further.

Apparently, the process mechanism suffered a significant change due to the increase in temperature in this case. In the low-temperature range, the course of the reaction can be represented by Eq. (3).

In this case, a barrier film of a saturated solution of lithium hydroxide and carbonate in water is formed on the active surface of LiOH·H₂O, which leads to a slow conversion of the hydroxide into a carbonate. The process rate is limited in this stage either by the dissolution followed by the diffusion of the carbonate ion to the surface of the solid reagent, or by the dissolution of LiOH and diffusion of the metal ion toward the interface with the gas phase.

It should also be noted that the following reaction between lithium carbonate and calcium hydroxide is possible in the liquid film in operation of a mixed chemical absorbent:



The change in the Gibbs free energy for this reaction is 24 kJ mol⁻¹.

It follows from the aforesaid that the following specific effects will be observed in operation of a mixed chemical absorbent:

– strong dependence of the rate and completeness of the processes in which active components are car-

bonized on the carbon dioxide concentration in the gas mixture;

– dependence of the completeness and specific features of the process on the moisture content of the chemical absorbent and, similarly, on the humidity of the gas flow;

– effect of the gas flow pressure on the absorption of carbon dioxide by alkaline chemical absorbents;

– strong influence exerted on the degree of utilization of the stoichiometric capacity of the absorbent by the occurrence side processes, such as the decomposition or formation of hydroxo complexes, change in the pH of a film, and change in the temperature of the liquid film.

In the present study, we consider the influence exerted by gas medium parameters on the course of the process in which carbon dioxide is absorbed from the gas flow by the mixed alkaline absorbent. The humidity of the gas flow, initial carbon dioxide concentration, and pressure in the reaction zone were taken as the variable parameters of the medium. The chemical absorbents are represented by mixed sorbents based on calcium, sodium, and lithium hydroxides. A significant number of experiments were performed at low initial contents of carbon dioxide in the gas-air flow (GAF) due to the lack of data on the operation of alkaline absorbent in this concentration range and to the necessity to use gas environments nearly fully free of carbon dioxide in various fields of technology, such as analytics, hydrogen power engineering (for certain kinds of fuel cells, e.g., AFC), etc.

EXPERIMENTAL

A moldable paste was prepared by the procedure described in [5], according to which sodium hydroxide in the form of a 20% solution or lithium hydroxide in the form of a concentrated solution (or water suspension) was added to Ca(OH)₂ under permanent agitation to a humidity of the moldable paste not exceeding 36%, with the subsequent molding of the paste by forcing (to preclude the squashing of the porous structure of the absorbent in accordance with the commonly accepted industrial technology for manufacture of a chemical lime absorbent, CLA) through dies and by thermal treatment of grains at 120°C for 2 h.

The abrasion strength *P* (%) of the chemical absorbent (CA) was determined in conformity with GOST (State Standard) 6755–88 [2].

The dynamic capacity *Ad* of CAs for CO₂ was determined under various experimental conditions.

Table 1. Effect of GAF humidity on characteristics of chemical absorbents^a

LiOH, % (mass fraction)	<i>P</i> upon an experiment, %, at indicated ϕ				A_d , cm ³ g ⁻¹ , at indicated ϕ				$\omega_{CA.res}$, wt %, at indicated ϕ			
	25	45	60	90	25	45	60	90	25	45	60	90
0	70	65	62	62	8.9	12	14	16	2.1	15	18	18
25	35	12	7	0	29	28	26	25	3.2	10	28	32
30	35	0	0	0	38	32	31	30	3.3	15	35	37

^a ϕ is the relative humidity of inflowing air; $\omega_{CA.res}$, residual humidity of CA; *P*, CA abrasion strength; and A_d dynamic activity of CA with respect to CO₂.

(1) Humidity ϕ of the gas flow varied at a constant fixed initial carbon dioxide concentration in the gas and its pressure. Air temperature 20–25°C; relative input air humidity 25, 45, 60, and 90%; CA moisture content $18 \pm 0.5\%$; sorbent bed height 8 cm; specific GAF rate 0.3 L min⁻¹ cm²; CO₂ content of the input gas flow 0.2 vol %, CO₂ content behind the layer (breakthrough concentration) ≤ 0.2 vol %; atmospheric pressure.

(2) Carbon dioxide concentration varied at a fixed gas humidity and pressure. Air temperature 20–25°C; relative humidity of input air 23%; CA humidity $18 \pm 0.5\%$; sorbent bed height 8 cm; GAF rate 0.3 L min⁻¹ cm²; CO₂ content 0.2, 0.48, 2.0, and 5.0 vol %; CO₂ content behind the layer ≤ 0.2 vol %; atmospheric pressure.

(3) Gas mixture pressure varied at the equilibrium carbon dioxide concentration of 0.2 vol % and relative air humidity of 60%. It should be noted the capacity of the materials was determined in this case under static conditions for a unit CA grain.

The dynamic activity was calculated as the product of time until appearance of 0.02 vol % carbon dioxide after the layer by the volumetric flow rate of GAF and initial content of carbon dioxide in the GAF, divided by the mass of the weighed portion.

In the first stage of the study, we determined the effect of the gas flow humidity on the sorption characteristics of both the conventional CLA (96 wt % calcium hydroxide and 4 wt % sodium hydroxide) and those containing lithium hydroxide in addition to the classical formula at low CO₂ content in the GAF. The results we obtained are listed in Table 1. It can be seen that an increase in the gas flow humidity from 25 to 90 rel % not only failed to lead to a higher dynamic capacity of materials containing lithium hydroxide, but, by contrast, favored its certain decrease. Also noteworthy is the inverse relationship

between the final humidity of a material and its dynamic capacity. It can also be seen that raising the GAF humidity at a high content of lithium hydroxide in the absorbent leads to a stronger fall of the dynamic capacity of the material. In particular, raising the GAF humidity from 25 to 90 rel % at a lithium hydroxide content of 30 wt % leads to a 11.2-fold increase in the residual moisture content of a sample (from 3.3 to 37 wt %), which results in that the dynamic capacity decreases by 21%. A similar increase in the GAF humidity at a lithium hydroxide content of the material equal to 25% leads to 10.0-fold humidification of the absorbent to 32 wt % (the optimal moisture content of the absorbents of the given type is about 20 wt %, which is determined by the specificity of their porous structure and, in particular, by the linear size of their pores. In this case, a 1.5 times smaller decrease in the dynamic capacity is observed (by 14%), which is due to the lower hygroscopicity of the absorbent. When carbon dioxide absorption processes are performed with absorbents of classical CLA formula without lithium hydroxide, no excessive moistening of the sample is observed because of the lower hygroscopicity of the base material of the absorbent at approximately the same exothermicity of the occurring process, as shown above. In this case, the absolute moisture content of the material substantially increases, compared with the absorption at GAF humidity of 25 rel %, to be 18 wt % in the given case, which is the optimal moisture content for the absorbent of a similar structure. The residual moisture content $\omega_{CA.res}$ of the material is 1.8–2.1 times lower than the residual moisture content of materials containing 25–30 wt % lithium hydroxide. At a low GAF humidity (25 rel %), the absorption capacity of the chemical absorbent containing 30 wt % lithium hydroxide exceeds the CLA capacity by a factor of 4.3,

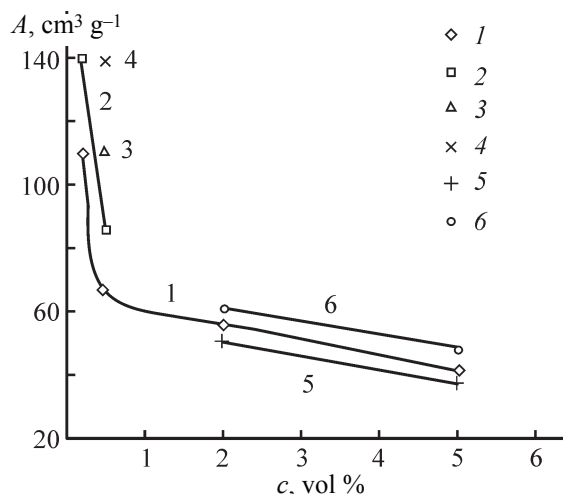


Fig. 1. Effect of the carbon dioxide content c of the starting GAF (breakthrough concentration 0.02 vol %) on the the dynamic sorption capacity A of CA. (1) Standard CLA, (2) CLA (LiOH = 4%), (3) CLA (LiOH = 15%), (4) CLA (LiOH = 22%), (5) CLA ($F = 0.01\%$), (6) CLA ($F = 0.02\%$).

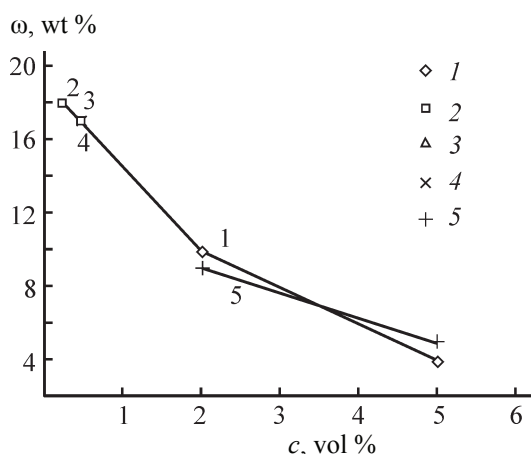


Fig. 2. Effect of the carbon dioxide content c of the residual moisture content ω of the spent chemical absorbent. (1) Standard CLA, (2) CLA (LiOH = 4%), (3) CLA (LiOH = 15%), (4) CLA (LiOH = 22%), (5) CLA ($F = 0.01\%$); the same for Figs. 3 and 4.

whereas at a GAF humidity of 90 rel %, this factor is only 1.9. Analysis of the data in Table 1 also shows that an increase in the GAF humidity strongly impairs the mechanical strength of the absorbent containing lithium hydroxide. In this case, a slight decrease in strength is observed for a sample of the classical CLA formula within the acceptable range of values (from 70 to 62 wt %). As already noted previously [4], the reason for the fall of the strength of mixed absorbents containing lithium hydroxide is the change of the crystal structure of the substances contained in the absorbents because lithium hydroxide has a tetragonal lattice, and lithium carbonate belongs to the monoclinic crystal system, whereas both calcium hydroxide and calcium carbonate crystallize in the hexagonal crystal lattice. The increase in the content of lithium compounds in a material makes its structure more disordered and, as a consequence, leads to a dramatic decrease in the strength of the chemical absorbent. Thus, it follows from an integrated analysis of the main characteristics of a chemical absorbent produced by the procedure of molding via forcing through dies (industrial technology for CLA molding), such as the dynamic capacity and mechanical strength that, at a low GAF humidity, the chemical absorbent containing lithium hydroxide is advantageous in dynamic capacity. At a high GAF humidity, the strength of the chemical absorbent containing lithium hydroxide falls to zero in the course of operation, with the advantage in protective capacity

exhibited by the classical CLA whose abrasion resistance is in this case no less than 62 wt %.

The next stage of the study was devoted to determining the influence exerted by the content of carbon dioxide in GAF on the dynamic capacity of the absorbent. This was necessary because gases with low carbon dioxide content became needed in, e.g., analytical chromatography and fuel power generation, when hydrogen delivered to fuel cells of certain designs should contain very low admixtures of carbon dioxide. A study in a wide range of carbon dioxide contents in the GAF revealed the following fundamental aspects that cardinaly differ from those in processes based on the physical adsorption phenomenon, even those complicated by heat effects significant for the given mechanism.

The generalization of the data obtained in the study, made in Fig. 1, shows that the decrease in the carbon dioxide content of the GAF in the order 5–2–0.48–0.2 vol % leads to an increase in the dynamic activity for all the chemical lime absorbents under study, including those subjected to modification. As objects of study served in this case chemical lime absorbents with addition of lithium hydroxide (LiOH) and fullerenes (F). The use of fullerenes for the given purpose is substantiated by the assumption of their possible positive effect on the hydration of limes, with their strength increased [6].

It can be seen from the graphical dependence that lowering the content of carbon dioxide in the GAF

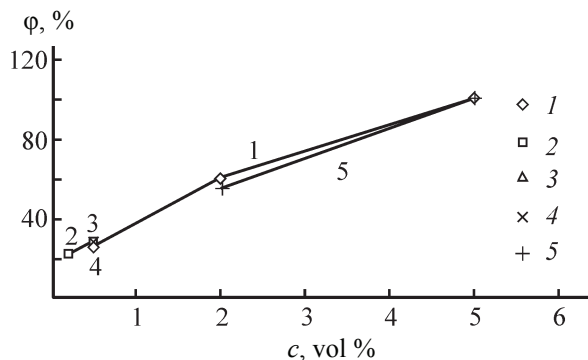


Fig. 3. Dependence of the relative humidity ϕ of GAF after the CA on the content c of carbon dioxide in GAF.

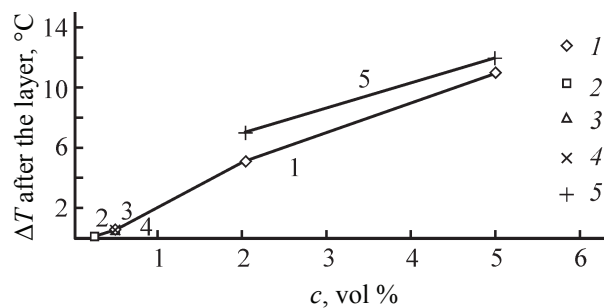


Fig. 4. Effect of the carbon dioxide content c of GAF on the change (increase) ΔT in the temperature of the effluent gas.

from 5 to 1 vol % leads to a certain increase in the dynamic sorption capacity of the materials in terms of gaseous carbon dioxide from 40 to 60 cm³ g⁻¹. However, further decrease in the GAF content of carbon dioxide to 0.48 vol % and then to 0.2 vol % lead to a more significant increase in the absorption capacity up to 140 cm³ g⁻¹. This tendency is accounted for by the fact that, at carbon dioxide concentrations of 1 vol % and more, the interaction of the acid gas with the alkaline chemical absorbent is characterized by a high exothermic effect, which leads to dehydration of the material, with the process decaying. The decrease in the carbon dioxide concentrate eliminates this exothermic effect to nearly zero, which makes it possible to preserve the optimal moisture content of the material and provide its high absorption capacity. Introduction of fullerenes into the CAs leads to an insignificant decrease in the dynamic sorption capacity of the materials. In this case, the mechanical strength of the samples differed only slightly from that of chemical lime absorbents.

The specific nature of the dependence of the sorption capacity (Fig. 1), the dynamic capacity in the given case, on the content of the component being sorbed

Table 2. Effect of gas pressure on the chemisorption characteristics of the chemical absorbent

Operation duration of absorbent, h	Degree of utilization, %, at indicated pressure, MPa		
	2	4	6
2	8	4	2
4	14	8	5
6	18	10	5.5

in the gas phase is untypical of sorption processes in which the sorption capacity must grow with increasing content of the sorbate in the gaseous medium. This classical dependence is represented by the adsorption isotherm, i.e., by the dependence of the equilibrium sorption capacity on the sorbate concentration. The dynamic capacity differs from the equilibrium static capacity by the correction coefficient named “utilization coefficient of the equilibrium (dynamic) capacity.” For low sorbate concentrations, it is somewhat lower due to the lower diffusion in this case, compared with the processes occurring at high sorbate concentrations in the gas medium. However, this difference is not so striking as that illustrated by Fig. 1. The reason is that the chemical absorption of carbon dioxide by alkaline chemical absorbents is, first, characterized by a significant exothermic effect and, second, is accompanied by the dehydration of the absorbent the absorption in which occurs via a water film of the alkali solution.

It is well seen in Fig. 2 to what extent the content of carbon dioxide in GAF determines the loss of water by the chemical absorbent. At a carbon dioxide content of 5 vol % in the gas-air flow, the residual moisture content is 4–5 wt %, whereas a decrease in the carbon dioxide concentration to 0.2 and 0.48 vol % results in that the moisture content of the spent chemical absorbent increases to 17 and 18 wt %, which is in fact the initial moisture content of the material. Thus, in all probability, this insignificant content of carbon dioxide in the GAF does not cause a noticeable heat effect and does not lead to loss of moisture by the alkaline chemical absorbent.

Analysis of GAF characteristics (Fig. 3) confirms the above conclusion. It is well seen that, at a low content of carbon dioxide in the GAF (0.2 and 0.48 vol %), the humidity of the GAF outflowing from an operating

chemical absorbent is 23–26 rel %, which is nearly equal to the initial humidity of the GAF and is due to the zero loss of moisture by the chemical absorbent. In this case, the high carbon dioxide content of the GAF leads to a stronger heat effect in the interaction of carbon dioxide with the alkaline absorbent, which is reflected in the more pronounced loss of moisture by the chemical absorbent and, accordingly, in a higher humidity of the outflowing GAF.

Determining the temperature of the outflowing GAF (Fig. 4) reflects the rise in the temperature of the operating chemical absorbent with increasing carbon dioxide content of the GAF due to the heat effect of the reaction. It can be seen in Fig. 4 that, at the carbon dioxide content of GAF equal to 0.2 and 0.48 vol %, the temperature of the effluent gas remains nearly unchanged, increasing by 0.0–0.6°C. At the same time, at the carbon dioxide content of 2 and 5 vol %, the GAF temperature increases at the measurement point by, respectively, 5–7 and 11–12°C.

Thus, the chemisorption process that is accompanied by a strong exothermic effect and occurs by the mechanism of the main mass-exchange process in a water film of the alkaline agent is characterized by a higher dynamic sorption capacity at low sorbate concentrations in the GAF. These processes fundamentally differ in this regard from the sorption processes that occur by the classical dispersion interaction mechanism, are not accompanied by a strong exothermic effect, and are not complicated by the necessary presence of water films on the active surface of an absorbent.

In the final stage, we determined the effect of the GAF pressure on the sorption properties of chemical absorbents. The study also demonstrated a significant difference of the chemical absorption processes from those occurring by the physical adsorption (dispersion interaction) mechanism. It can be seen in Table 2 that the capacity characteristics of the chemical absorbent are markedly impaired with increasing pressure. We used as a sorbent a chemical lime absorbent humidified to 18 wt %.

In contrast to chemisorption processes, this is not characteristic of adsorption processes occurring by the physical adsorption mechanism because an increase in pressure leads to a more pronounced tendency of adsorbates toward condensation and to a higher adsorption capacity. This effect is employed, for instance, when performing adsorption drying processes or those of air separation in the pressure-swing adsorption (PSA) mode

at pressures of up to 1 MPa. An increase in pressure (up to 6 MPa) leads to a higher sorption capacity of the adsorbents. However, raising the pressure even further results in that the diffusion hindrance starts to prevail over the rise in the adsorption capacity and the amount of adsorption decreases [7]. At the same time, in the case of a chemisorption process the diffusion hindrance is manifested immediately and the chemisorption capacity of the material falls. For example, it follows from the data in Table 2 that, as the gas pressure is raised from 2 to 6 MPa, the degree of material processing with respect to carbon dioxide decreases by a factor of 3.3–4.0. Thus, performing the processes at high pressures introduces corrections into their occurrence conditions, which is due to the fact that diffusion processes in the chemisorption become slower with increasing pressure in the reaction zone.

CONCLUSIONS

(1) It was shown that the composition of mixed chemical absorbents exerts key influence on their operation at various gas-air flow humidities. An increase in the humidity of the gas flow leads to a lower (by 15–20%) protective capacity of a mixed chemical absorbent containing lithium hydroxide, which is also accompanied by a decrease in the mechanical strength. At the same time, chemical absorbents containing no lithium hydroxide retain a mechanical strength up to 62 wt % at gas flow humidity of 90 rel %.

(2) Raising the concentration of carbon dioxide in the gas leads to warming-up of the working layer of the chemisorption for all kinds of alkaline chemical absorbents, with its dehydration thereby enhanced and its absorption capacity decreasing. The content of carbon dioxide in the gas flow lower than 0.5 vol % hardly causes any noticeable exothermic effect in the chemisorption process.

(3) Raising the pressure of the gas mixture from 2 to 6 MPa leads to a significant (by a factor of 3.3–4.0) decrease in the absorption characteristics of alkaline chemical absorbents, which is determined by the slower diffusion of the target component to the material of the absorbent.

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