

REACTIVITY OF THE SOLID SODIUM CARBONATE TOWARDS THE GASEOUS HYDROGEN CHLORIDE AND THE SULPHUR DIOXIDE

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The rate of reaction of the anhydrous sodium carbonate with the hydrogen chloride and its mixture with sulphur dioxide was measured in an integral fixed-bed reactor. Reactivity of the active sodium carbonate towards the hydrogen chloride is lower as compared with its reactivity towards the sulphur dioxide. A relationship was found between the reactivity of the solid and the way of its preparation. The inactive form of the sodium carbonate is inactive towards both the sulphur dioxide and the hydrogen chloride. The active form of the sodium carbonate exhibits towards the hydrogen chloride a reactivity which is by orders of magnitude higher than that of the inactive form. The variation of the ratio of partial pressures of the hydrogen chloride and the sulphur dioxide in the reaction with the sodium carbonate does not affect significantly the total degree of the solid conversion, which attained a value of 65% in laboratory experiments. The degree of gas purification from the acid components did not fall under a value of 99% up to a solid conversion of about 50% at a mean gas contact time of about 10^{-2} s.

The neutralization of industrial waste gases of acidic nature represents up to now a serious and an open problem in most industrial countries. The methods for removing the acid components can be divided, according to the principles used, into four groups: 1) absorption of acid gas components by aqueous solutions or suspensions of alkaline substances, 2) sorption on carbonaceous materials of various origin, 3) catalytic processes, 4) dry processes using a chemical reaction with solids of basic nature.

An important feature of the dry processes, based on a heterogeneous gas-solid reaction, is the fact that they permit to carry out both the chemical reaction and the separation of products in a single operation. The original czechoslovak method of removing the sulphur dioxide from waste gases AKSO (ref.¹) employs the knowledge that the solid sodium carbonate exists in two forms differing one from another in their reactivity by several orders of magnitude²⁻⁶, and that the conditions of their formation can be well defined. One form reacts with the sulphur dioxide only very slowly and incompletely, whereas the other form of the sodium carbonate, called active soda, exhibits an extremely high reactivity towards the sulphur dioxide. The high reaction rate of the latter form may be demonstrated by the fact that a gas contact time of hundredths of a second is sufficient to remove more than 99% of the



FIG. 3
Character of intergranular corrosion of E1617 alloy in 15% NaNO_3 . Magnification 200 \times ,
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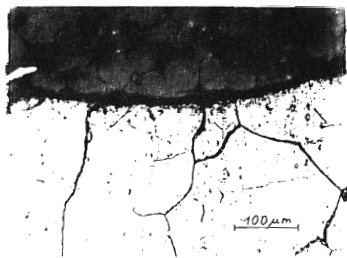


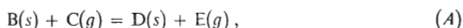
FIG. 4
Character of intergranular corrosion of E1617 alloy in 15% NaNO_3 . Magnification 200 \times ,
etched electrolytically in 10% oxalic acid

sulphur dioxide from the gas stream at temperatures of about 150°C and at concentrations in the range of 10^3 ppm (*i.e.* 0.1 per cent by vol.).

The rate of the heterogeneous reaction of the solid sodium carbonate with the gaseous hydrogen chloride and the simultaneous reaction of sulphur dioxide and hydrogen chloride with the active anhydrous sodium carbonate has been investigated here from both practical and theoretical reasons.

THEORETICAL

A heterogeneous reaction taking place in an integral fixed-bed reactor without any change of the mole number



the kinetics of which is expressed by the rate equation

$$r = kpx^{1/2}(1-x)^{3/2} \quad (1)$$

(x is the degree of solid conversion) can be rationally described in dimensionless terms of Y , M and W defined as follows

$$Y = y_r/y_0, \quad (2)$$

$$M = k'Pn_s/F, \quad (3)$$

$$W = y_0F\tau/n_s = F_g\tau/n_s, \quad (4)$$

where y_r is the mole fraction of the reacting gas component at the reactor outlet, y_0 is its mole fraction in the feed, k' is the effective rate constant in the kinetic equation (1), P is the total pressure of gas in the bed (in kPa), n_s is the amount of the solid substance in the bed (in mol), F is the total feed rate (in mol s^{-1}), F_g is the feed rate of the reacting gas, and τ is the time (in seconds). The solution in terms of the dimensionless variables defined by equations (2), (3) and (4) is conditioned by linear dependence of the rate of reaction (A) on the partial pressure⁷ of the reacting gas component p as expressed by the rate equation (1).

EXPERIMENTAL

The quantities Y , M and W can be easily determined from experimental data. The conductance sensor with recycle³ indicated at each time the amounts of the unreacted acid component in the reactor. From the feed rate and from the reading of the conductance sensor the quantity Y has been obtained by a numerical differentiation according to time. This quantity represents the rela-

tive outlet concentration of the reacting acid gas component and the value of $(1 - Y)$ denotes the degree of gas purification. The dimensionless quantity W is directly accessible by experiment, experiment, and it can be characterized as a degree of the stoichiometric loading of the bed. At a value of $W = 1$, a stoichiometric amount of the reacting acid gas components passed the bed with regard to the amount of the present solid. The quantity M/k' is a characteristic parameter indicating the operating mode at which the measurement has been carried out.

The description in the above mentioned terms is a rigorous one under isobaric-isothermic conditions only. These conditions have been well fulfilled owing to a small pressure drop along the bed and to an efficient temperature control of the reactor which has been enhanced by a high dilution of acidic gas reactants. The results of measurements are given graphically in Y vs W coordinates. The mentioned way of evaluation of the experimental data and presentation of results proved to be suitable already in a detailed kinetic study of the reaction between the sulphur dioxide and the solid anhydrous sodium carbonate^{3,4} and, therefore, it has been applied even in this paper. In this way it is possible to compare the kinetic properties of the sulphur dioxide with those of the hydrogen chloride in their reaction with the active and inactive form of the solid anhydrous sodium carbonate in both the isolated reactions and in the reaction with their mixture.

Experimental investigation of the rate of the reaction between the gaseous hydrogen chloride or its mixtures with the sulphur dioxide and the solid sodium carbonate has been carried out in a modified apparatus³. The measurements have been carried out with a sodium carbonate prepared by thermal decomposition of the sodium hydrogen carbonate in situ prior to the reaction with acid gas reactants. In this way samples of the active form of the sodium carbonate have been prepared. The inactive form has been prepared by dehydrating the sodium carbonate decahydrate. In all the measurements the same particle size from 0.25 to 0.33 mm has been used.

RESULTS AND DISCUSSION

Reaction of Gaseous Hydrogen Chloride with Solid Sodium Carbonate

Effects of the following factors have been studied: presence of the water vapour in the gas phase, effect of variation of the parameter of M/k' , effect of the method of solid preparation, degree of the solid conversion, and effect of the partial pressure of hydrogen chloride. All the measurements have been carried out at a temperature of 150°C with nitrogen as the carrier gas.

The catalytic effect of the presence of water vapour in the gas phase on the rate of reaction of the hydrogen chloride with the active sodium carbonate does not appear so significant (Fig. 1) as in the reaction with the sulphur dioxide⁴. The average degree of the solid conversion in the experiments with a dry and humid hydrogen chloride was in the range from 44 to 49%. The effect of varying the parameter of M/k' under otherwise identical conditions is shown in the Fig. 2. A 2.7-fold increase of the parameter (*i.e.* a longer contact time) resulted in an increase of the average degree of the solid conversion from 49 to 60%. The nature of the Y vs W dependence did not change significantly, however, a shift of the breakthrough time of hydrogen chloride through the bed has been observed. Similar behaviour has been already found in the kinetic study of the reaction between the sulphur dioxide with the active

sodium carbonate³. In the Fig. 3, the reaction course is visualized between the gaseous hydrogen chloride and both the inactive and the active form of the solid sodium carbonate under otherwise identical conditions. The reactivity of both forms of the sodium carbonate towards the sulphur dioxide is apparent from the Fig. 4. The differences in the reactivity of the active sodium carbonate towards the hydrogen chloride and the sulphur dioxide are apparent by comparing the curves 2 in the Fig. 3 and 4. The average degree of the solid conversion amounted to 49% in the reaction with the hydrogen chloride, and to 98.5% in the reaction with the sulphur dioxide.

Simultaneous Reaction of Hydrogen Chloride and Sulphur Dioxide with the Active Sodium Carbonate

Studies of the simultaneous reaction with the active sodium carbonate have been aimed at an investigation of the following variables: effect of the ratio of partial pressures $p_{\text{HCl}}/p_{\text{SO}_2}$ on the reaction course, effect of varying the parameter of M/k' , degree of the solid conversion, reaction course of the sulphur dioxide with the active sodium carbonate when mixed with the hydrogen chloride, and the time of incipient breakthrough of acid components through the bed of the active sodium carbonate, *i.e.* the instant when $Y \cong 0.05$.

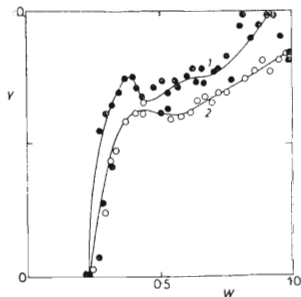


FIG. 1

Reaction course of the hydrogen chloride with active sodium carbonate. $M/k' = 306.6$ kPa s, $\tau_s = 0.03$ s; 2 humid hydrogen chloride ($p_{\text{H}_2\text{O}} = 0.84$ kPa), 1 dry hydrogen chloride

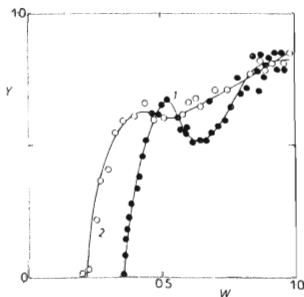


FIG. 2

Effect of the parameter of M/k' on the reaction course of humid hydrogen chloride with the active sodium carbonate; 2 $M/k' = 306.6$ kPa s, $\tau_s = 0.03$ s; 1 $M/k' = 826.6$ kPa s, $\tau_s = 0.10$ s

The effect of the ratio of partial pressures of $p_{\text{HCl}}/p_{\text{SO}_2}$ on the reaction course with the active sodium carbonate at roughly the same parameter of M/k' and the same temperature is given in Table I. The symbol of W_f denotes the final degree of the stoichiometric loading of the bed. The symbol \bar{x} denotes the total average degree of conversion of the sodium carbonate, x_{HCl} is the degree of conversion of the sodium carbonate in the reaction with gaseous hydrogen chloride, and x_{SO_2} is the degree of conversion of the sodium carbonate in the reaction with sulphur dioxide gas. The mean contact time of the gas with the solid is denoted as τ_s (in seconds). Table I shows that with increasing of the ratio $p_{\text{HCl}}/p_{\text{SO}_2}$ the value of W_f decreases, the value of x_{HCl} increases, and the value of x_{SO_2} decreases. The total average degree of conversion, \bar{x} , is not very altered and is kept within the limits from 45 to 64%.

The quantity of W_f has been determined from the indication of the conductance sensor. In experiments, where the sensor was put out of operation and was replaced by absorbers with an iodine solution, the value of W_f has not been determined. In some experiments the complete analysis of the solid at the end of the reaction

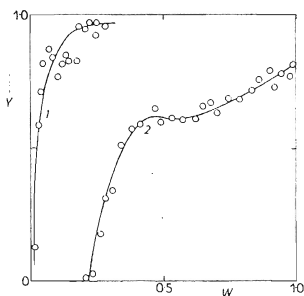


FIG. 3

Effect of the way of solid preparation on reaction course of humid hydrogen chloride with solid sodium carbonate; 1 inactive form of the sodium carbonate, $M/k' = 626.6$ kPa s, $p_{\text{H}_2\text{O}} = 0.84$ kPa, $\tau_s = 0.013$ s; 2 active sodium carbonate, $M/k' = 306.6$ kPa s, $p_{\text{H}_2\text{O}} = 0.84$ kPa, $\tau_s = 0.03$ s

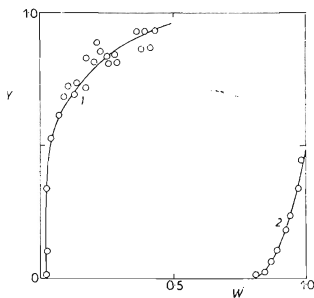


FIG. 4

Effect of the way of solid preparation on reaction course of humid sulphur dioxide with solid sodium carbonate; 1 inactive form of the solid sodium carbonate, $M/k' = 546.6$ kPa s, $p_{\text{SO}_2} = 0.20$ kPa, $p_{\text{H}_2\text{O}} = 2.06$ kPa, $\tau_s = 0.010$ s; 2 active sodium carbonate, $M/k' = 324.0$ kPa s, $p_{\text{SO}_2} = 0.11$ kPa, $p_{\text{H}_2\text{O}} = 1.03$ kPa, $\tau_s = 0.03$ s

has not been carried out, and hence it was not possible to evaluate the quantities of x_{HCl} and x_{SO_2} .

It follows from the Table I that at a twofold value of the parameter of M/k' , the value of W_i decreases with increasing of the ratio of $p_{\text{HCl}}/p_{\text{SC}_2}$, the total average degree of the solid conversion being constant. At higher values of the ratio of $p_{\text{HCl}}/p_{\text{SO}_2}$, the reaction of the active sodium carbonate with the hydrogen chloride prevails, and, consequently, the value of x_{HCl} increases and that of x_{SO_2} decreases.

The dependence of the reaction course of the sulphur dioxide and hydrogen chloride with the active sodium carbonate on the value of the ratio of $p_{\text{HCl}}/p_{\text{SO}_2}$ at approximately the same parameter of M/k' is illustrated in the Fig. 5. The quantity \bar{Y}_{SO_2} denotes the mean relative outlet concentration of the sulphur dioxide in mixture and \bar{W} is the mean stoichiometric loading of the with both acid components of the gas mixture. The effect of the parameter of M/k' on the reaction course of sulphur dioxide in mixture with hydrogen chloride, approximately at the same ratio of $p_{\text{HCl}}/p_{\text{SO}_2}$, is given in the Fig. 6. From Figs 5 and 6 an approximate value of W_i can be read off for the breakthrough of sulphur dioxide through the bed at a selected degree of gas purification from the sulphur dioxide.

From the results of rate studies of the heterogeneous reaction of the anhydrous sodium carbonate with hydrogen chloride and of the simultaneous reaction with the sulphur dioxide, the following may be concluded. The reactivity of the sodium carbonate towards the hydrogen chloride is lower as compared with that towards the sulphur dioxide. This fact is shown by a lower final degree of conversion of the solid and by an outstanding shift of curves of the Y vs W dependence in the direction

TABLE I

Effect of the ratio of partial pressures of $p_{\text{HCl}}/p_{\text{SO}_2}$ and of the parameter of M/k' on the reaction course with active sodium carbonate

M/k'	$p_{\text{HCl}}/p_{\text{SO}_2}$	W_f	W_i	\bar{x}	x_{HCl}	x_{SO_2}	τ_s
321.4	1.08	1.114	—	0.532	0.254	0.278	0.030
271.8	2.00	1.058	0.50	0.639	—	—	0.028
296.1	2.47	1.132	0.33	0.529	—	—	0.029
286.9	2.51	1.250	—	0.559	0.342	0.217	0.028
282.8	2.66	1.107	0.31	0.447	—	—	0.027
575.6	0.874	1.147	0.53	0.632	0.254	0.378	0.053
600.1	1.033	1.107	—	0.679	0.293	0.386	0.055
573.5	1.098	1.019	0.45	0.661	0.275	0.386	0.055
605.4	2.389	1.248	—	0.669	0.413	0.256	0.055
552.9	2.407	1.109	0.40	0.639	0.431	0.208	0.053

of lower values of W . The lower final degree of the solid conversion could be explained in a simple way by a more pronounced increase of volume of the solid product in the reaction with hydrogen chloride (by 28%), whereas in the reaction with the sulphur dioxide a markedly minor volume change of the solid phase takes place (by 11.4%). However, a major role may be played here by the structure of the activated complex, for the formation of which the active form of the sodium carbonate will not be preformed in such a favourable way as in the case of the sulphur dioxide.

An impressive relationship has been found between the reactivity and the way of preparation of the solid. This dependence is of the same nature as in the reaction with sulphur dioxide⁴. The inactive form of the sodium carbonate towards the sulphur dioxide is inactive even with respect to the hydrogen chloride. The active form of the sodium carbonate exhibits a reactivity which is by orders of magnitude higher with regard to the hydrogen chloride than the inactive form.

The catalytic effect of water vapour on the rate of reaction of the hydrogen chloride with the active sodium carbonate was not found so important as in the reaction with sulphur dioxide. Even this fact may be explained by a different structure of the activated complex.

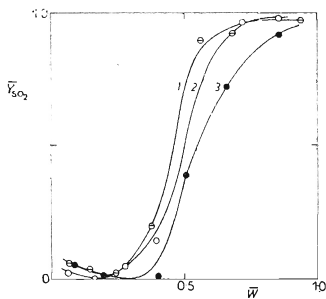


FIG. 5

Dependence of the reaction course of gas mixture of the sulphur dioxide and hydrogen chloride with active sodium carbonate on the value of the ratio of $p_{\text{HCl}}/p_{\text{SO}_2}$; $M/k' = 600.0$ kPa s, $\tau_s = 0.055$ s, 1 $p_{\text{HCl}}/p_{\text{SO}_2} = 1.76$, 2 $p_{\text{HCl}}/p_{\text{SO}_2} = 1.03$, 3 $p_{\text{HCl}}/p_{\text{SO}_2} = 0.84$

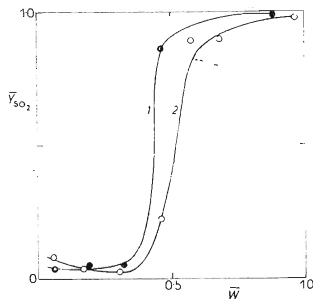


FIG. 6

Effect of the parameter of M/k' on reaction course of the gas mixture of sulphur dioxide and hydrogen chloride with active sodium carbonate; 1 $M/k' = 285.3$ kPa s, $p_{\text{HCl}}/p_{\text{SO}_2} = 1.51$, $p_{\text{H}_2\text{O}} = 0.85$ kPa, $\tau_s = 0.03$ s; 2 $M/k' = 600.0$ kPa s, $p_{\text{HCl}}/p_{\text{SO}_2} = 1.76$, $p_{\text{H}_2\text{O}} = 0.57$ kPa, $\tau_s = 0.06$ s

The increasing ratio of partial pressures of the hydrogen chloride to that of the sulphur dioxide in the simultaneous reaction with the active sodium carbonate does not affect the total final degree of conversion of the solid in a significant manner. The value of W_i corresponding to a breakthrough of acid gas components through the bed decreases with increasing x_{HCl} and decreasing x_{SO_2} . Under conditions investigated in this paper, a final degree of conversion of the solid of about 65% has been obtained approximately in 50 minutes with a mixture of sulphur dioxide and hydrogen chloride. A degree of conversion of the solid of about 50% together with a simultaneous gas purification of acid components higher than 90% is reached at a mean residence time of the gas in the bed of $\tau_s = 0.05$ s.

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