

Původní práce

THE EFFECT OF ATMOSPHERE ON THE RATE
AND MECHANISM OF REACTIONS IN THE SYSTEM $\text{CaCO}_3\text{—SiO}_2$
AT LOW TEMPERATURES

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Transition of CaO and SiO_2 into a silicate bond in the system calcite-quartz (molar ratio 1 : 1) at 700—1000 °C in air, hydrogen, CO_2 , H_2O and in $\text{H}_2\text{O}/\text{CO}_2$ mixtures can be described by the exponential equation $\alpha_i = 1 - \exp(-Bt^z)$, in which the value z is constant and indicative of a diffusion mechanism of the controlling process. Constant B is a function of the firing atmosphere composition. Water vapour likewise accelerates the combination of the components into silicate bonds in the temperature region below 1000 °C which has not so far been investigated experimentally. In CO_2 -containing atmosphere, the silicates are produced by direct reaction of calcium carbonate with quartz. The reaction mechanism is based on surface diffusion of Ca^{2+} ions through the polycrystalline layer of the products, namely C_2S and CS .

INTRODUCTION

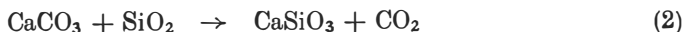
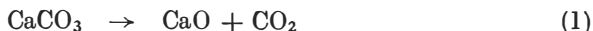
Synthesis of calcium silicates is a subject of continuing interest owing to their significance in the chemistry of cement and ceramics (wollastonite).

The problems of their synthesis from pure initial components have been investigated since 1910 [1]. The effect of firing atmosphere on the rate of transition of CaO into the silicate bond was noticed α by Balarew [2, 3], also by Jander and Stamm [4], Jander and Hoffman [5], Hedvall et al. [6], [7], [8] and more recently by Wagner [9] and others [10], [18], [20], [21]. In all the studies mentioned the reaction was investigated at temperatures above 900 °C where transition of the components into a silicate bond follows decomposition of calcite.

The rate of combining of the components into a silicate bond was found to be influenced by the neutral components of gaseous atmosphere at temperatures from 1000 to 1300 °C. The most distinct influence on the rate of the processes was established on firing in hydrogen and in water vapour, whereas CO_2 had a retarding effect compared to dry air.

The present study was aimed at investigating the effect of some firing atmosphere components on the rate and quality of reactions in the system $\text{CaCO}_3\text{—SiO}_2$ at lower temperatures.

The equilibrium CO_2 pressures for the reactions



calculated on the basis of thermodynamic data [11] for the initial reaction mixture $\text{CaCO}_3/\text{SiO}_2 = 1 : 1$ are plotted in Fig. 1.

Since the region of CO_2 partial pressures within which wollastonite can arise as the sole product is very narrow, formation of both thermodynamically possible products is observed in the course of the synthesis, quite in agreement with the respective thermodynamic data. The synthesis takes place at higher temperatures under laboratory conditions (under a pressure of about 100 kPa) in region III

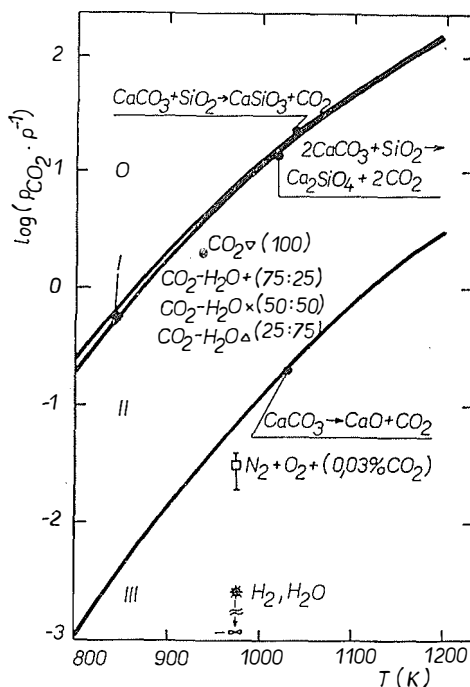


Fig. 1. Equilibrium pressure of CO_2 for reactions 1 through 3; I — region of CaSiO_3 formation, II — CaSiO_3 and Ca_2SiO_4 , III — CaSiO_3 , Ca_2SiO_4 and CaO . The marking indicates the furnace atmosphere compositions including the ratio of its components.

of Fig. 1, where decomposition of calcite is the primary process. The rate of decomposition is accelerated by water vapour and hydrogen as a result of an adsorption-catalytical mechanism [12]. The mechanism by which the actual synthesis is affected by the atmospheric components has not so far been explicitly explained; however, one may generally assume influencing of structural defects in the initial components, intermediate products and reaction products [13], transport of the Si component through gaseous phase in the form of SiO [11] and $\text{Si}(\text{OH}_4)$ [14], effects exerted by the atmosphere on the transport of the Ca^{2+} component through gaseous phase [15], and finally surface diffusion.

EXPERIMENTAL

The following materials were employed for the synthesis of wollastonite:

- quartz, low-temperature, of hydrothermal origin from the locality Mníšek nad Hnilcom, ground so as to pass through sieve 004 (ČSN) and to a specific surface of $0.42 \text{ m}^2 \text{ g}^{-1}$ (Blaine), Fe_2O_3 content = $2 \times 10^{-3} \%$;
- calcite, precipitated, complying with ČsL-2 (Lachema Brno), undersize of sieve 004 (ČSN). Specific surface area $0.34 \text{ m}^2 \text{ g}^{-1}$. Content of impurities lower than 0.1 %.

The molar ratio of the initial substances, $\text{CaO}/\text{SiO}_2 = 1$, which corresponds to the composition of the initial mixture 35.02 % CaO, 37.51 % SiO_2 and 27.47 % CO_2 . The homogenized and dried mixture was weighed in amounts by 1.5 g for the preparation of pellets (compressed at 75 MPa) for the experimental work. The pelletized specimens of the mixtures were tempered on the Netzsch type 409 thermobalance, which allows work in defined atmospheres. The types of atmospheres included water vapour, air, hydrogen, carbon dioxide and mixtures $\text{H}_2\text{O} + \text{CO}_2$, $\text{H}_2 + \text{CO}_2$ at a flow rate of $0.150 \text{ dm}^3 \text{ min}^{-1}$ (calculated for 0°C and 101 kPa; this corresponds to a linear rate of 0.64 cm s^{-1}). The temperature interval was 700—1000 °C.

In the fired and ground specimens the non-reacted CaO was determined by the glycolate method [16], the non-reacted SiO_2 by the gravimetric method (ČSN 72 2111). The weight loss due to carbon dioxide (ΔCO_2) was established by evaluating the thermograms and the conversions α_C , α_S and α_{CO_2} were calculated as a ratio of the reacted proportion of component to its total amount in mixture.

The accuracy of the experiments was calculated from a series of double firing and analyses, and the standard deviation (s_a) of one determination was smaller than ± 0.018 . The phase composition was verified by X-ray phase analysis.

The results for the individual temperatures and the constant time of 120 minutes are listed in Table I and for various atmospheres at 700 °C and the constant time of 120 minutes are given in Table II.

Table I

Conversion of components in terms of firing temperature in air and water vapour atmospheres. Time of firing 120 minutes. Mixture $\text{CaCO}_3 + \text{SiO}_2$ (1 : 1, molar)

T [°C]	Air			Water vapour		
	α_{CO_2}	α_{CaO}	α_{SiO_2}	α_{CO_2}	α_{CaO}	α_{SiO_2}
700	0.767	0.484	0.257	0.808	0.627	0.350
800	0.858	0.565	0.352	0.890	0.745	0.472
900	0.939	0.655	0.385	1.000	0.882	0.566
1000	1.000	0.740	0.423	1.000	1.000	0.664

Notice

C = CaO

S = SiO_2

CS = CaSiO_3

C_2S = Ca_2SiO_4

Table II

Degree of CaCO_3 decomposition (α_{CO_2}) and conversion of CaO and SiO_2 into silicate bond in the mixture of CaCO_3 with SiO_2 (1 : 1, molar). Firing temperature 700 °C

Atmosphere composition	Conversion of component α	Time of isothermal heating (min)			
		30	80	120	180
H_2O	CO_2	0.439	0.664	0.808	0.914
	C	0.418	0.554	0.627	0.695
	S	0.214	0.278	0.350	0.349
$\text{CO}_2 + \text{H}_2\text{O}$ (0.25 + 0.75)	CO_2	0.292	0.384	0.418	0.477
	C	0.292	0.385	0.418	0.477
	S	0.156	0.217	0.224	0.256
$\text{CO}_2 + \text{H}_2\text{O}$ (0.50 + 0.50)	CO_2	0.232	0.309	0.349	0.381
	C	0.232	0.309	0.349	0.381
	S	0.118	0.182	0.204	0.235
$\text{CO}_2 + \text{H}_2\text{O}$ (0.75 + 0.25)	CO_2	0.137	0.176	0.206	0.229
	C	0.137	0.176	0.206	0.229
	S	0.069	0.094	0.104	0.120
CO_2	CO_2	within the measurement dispersion the values were determined at level 0			
	C				
	S				
H_2	CO_2	0.521	0.984	0.987	1.000
	C	0.222	0.391	0.409	0.424
	S	0.113	0.197	0.207	0.213
$\text{H}_2 + \text{CO}_2$ (0.50 + 0.50)	CO_2	0.050	0.070	0.088	0.103
	C	0.050	0.070	0.089	0.103
	S	0.026	0.036	0.045	0.052
Air	CO_2	0.408	0.630	0.767	0.865
	C	0.324	0.425	0.484	0.516
	S	0.184	0.245	0.257	0.265

DISCUSSION

The following rational kinetic relationship has been chosen for mathematical description of the relationship between the conversion of calcite and quartz respectively and the time of isothermal heating at 700 °C:

$$\alpha_i = 1 - \exp(-Bt^z) \tag{4}$$

where α_i is conversion of the respective component (C or S),
 t is the time of isothermal holding in the course of firing,
 B, z are coefficients of the equation related to the initial state of the system and to the firing conditions (B) and to the mechanism of the processes involved (z).

Because the initial state and the temperature schedule were identical for all the specimens listed in Table III, the relationship between the coefficients and the

furnace atmosphere composition was assumed to be the single variable in the series of isothermic firing.

Having linearized relationship (4) by double logarithming, the values of coefficients B and z were determined by the least square deviations method (Table III). According to literary data [17] the values of exponent z vary within the interval of 0.54—3.0 in dependence on the control mechanism. For diffusion-controlled processes the interval is given as 0.54—0.62 in the system of monodisperse particles dispersed throughout a homogeneous medium of the other component. The lower values established in our experiments can be explained, in agreement with theory, by polydispersity of the reaction mixture so that the assumption that diffusion controlled the reactions is quite acceptable. Since the values of z for the individual

Table III

The values of exponents in equation (4) for firing temperature 700 °C
Conversion of component CaO

Composition of atmosphere in furnace	$z \pm s_z$	$\ln B \pm s_{\ln B}$	B_{corr}
H ₂ O	0.43 ± 0.01	-2.12 ± 0.05	0.18
H ₂ O + CO ₂ (0.75 + 0.25)	0.34 ± 0.01	-2.30 ± 0.07	0.10
H ₂ O + CO ₂ (0.50 + 0.50)	0.33 ± 0.01	-2.52 ± 0.04	0.08
H ₂ O + CO ₂ (0.25 + 0.75)	0.31 ± 0.01	-3.21 ± 0.08	0.04
CO ₂	—	—	0
$\Phi z_c \pm s_z$	0.35 ± 0.05		
Conversion of component SiO ₂			
H ₂ O	0.32 ± 0.01	-2.65 ± 0.05	0.08
H ₂ O + CO ₂ (0.75 + 0.25)	0.30 ± 0.03	-2.81 ± 0.15	0.05
H ₂ O + CO ₂ (0.50 + 0.50)	0.42 ± 0.02	-3.50 ± 0.10	0.05
H ₂ O + CO ₂ (0.25 + 0.75)	0.32 ± 0.01	-3.91 ± 0.04	0.02
CO ₂	—	—	0
$\Phi z_s \pm s_z$	0.34 ± 0.05		
$\Phi z \pm s_z$	0.346 ± 0.05		

atmospheres are all within a narrow interval (0.30 to 0.43) the mean value z_0 was calculated for the purposes of the further discussion. By means of this value it was possible to determine the corrected values of rate constant B_{corr} which may obviously be correlated with the composition of the atmosphere (Table III).

The only phases identified in the reaction mixtures by X-ray diffraction analysis

were those of calcite, quartz, CaO, β -wollastonite, β and γ -dicalcium silicate. The presence of spurrite ($2\text{C}_2\text{S} \cdot \text{CaCO}_3$) was not established. The experimentally determined α_i values served for calculating the proportions of the individual phases in the reaction mixtures according to the relationships:

$$n_{\text{C}_2\text{S}} = \alpha_{\text{C}} - \alpha_{\text{S}} \quad n_{\text{SiO}_2\text{free}} = 1 - \alpha_{\text{S}} \quad (5, 6)$$

$$n_{\text{CS}} = 2\alpha_{\text{S}} - \alpha_{\text{C}} \quad n_{\text{CaOfree}} = \alpha_{\text{CO}_2} - \alpha_{\text{C}} \quad (7, 8)$$

$$n_{\text{CaCO}_3} \equiv n_{\text{CO}_2} = 1 - \alpha_{\text{CO}_2} \quad (9)$$

$$x_i = \frac{n_i M_i}{\sum n_i M_i} \cdot 100 \quad (10)$$

where

x_i is the content of the component in product in % by wt.,

n_i is the molar amount of substance i ($i = \text{C}_2\text{S}, \text{CS}, \text{CaO}_{\text{free}}, \text{CaCO}_3, \text{SiO}_2\text{free}$),

M_i is the molar weight of substance i .

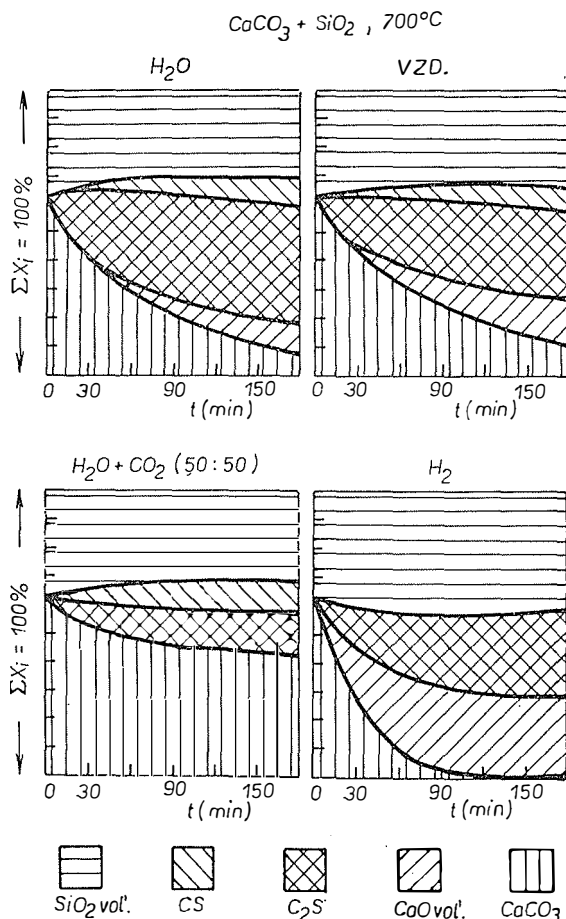


Fig. 2. Development of phase composition in the mixture $\text{CaCO}_3 + \text{SiO}_2$ at 700°C .

The development of phase composition calculated according to (5 through 10) is plotted in Figs. 2 and 3.

The results indicate that at 700 °C in air and water vapour atmosphere, CS and C₂S are formed simultaneously with a great excess of C₂S (Fig. 2). On consumption of component CaO, the last stage of the synthesis (Fig. 3) is represented by the very slow reaction

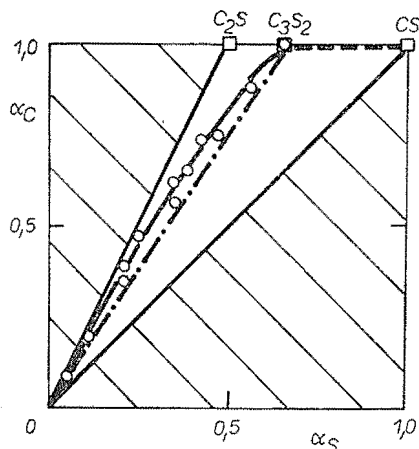


Fig. 3. Dependence of $\alpha_C - \alpha_S$ in the mixture $\text{CaCO}_3 + \text{SiO}_2$. The points indicate experimental conversion values after 120-minute firing.

Water vapour even at 700 °C speeds up the entry of the components into the silicate bond as compared to dry air. However, in contrast to its effect at high temperatures [10], [18] it does not influence distinctly the development of the phase composition of the system.

The CO₂ content in atmosphere is responsible for direct formation of calcium silicates from calcite according to reactions (2 and 3) in agreement with thermodynamic considerations. Combination of the components into silicates is slowed down as a result of a decrease in the driving force of the reaction. In an atmosphere of pure CO₂ the rates of the reactions were so low that none of them could be observed to take place. At the same time it should be acknowledged that the calculated lines of equilibril pressures (Fig. 1) may be shifted in view of the inaccuracy of the thermodynamic data and that the actual state of the reactants may differ from the standard state.

Compared to the results of studies carried out in the temperature region above 1000 °C [9], [10], a retarding effect of hydrogen on the formation of silicates is observed at 700 °C and results in a marked suppression of the formation of wollastonite (Fig. 2) while simultaneously speeding up dissociation of calcite. No sufficient data are so far available for an explicit explanation of the slowing down of the reaction according to equation (11).

On the basis of thermodynamic data [11] one cannot consider transport of the Si component through the gaseous phase at 700 °C which has been established to

take place in the form of SiO in a reducing atmosphere [15] neither in the form of Si(OH)₄ in a water vapour atmosphere [14]. Study [19] indicates that the value of the Ca²⁺ lattice diffusion coefficient in C₂S is of the order of 10⁻¹⁸ m² s⁻¹ at 1200 °C, amounting to a value lower by about 4 orders of magnitude for the diffusion of Ca²⁺ in wollastonite. This is why the participation of lattice diffusion of Ca²⁺ ions through the solid reaction product (CS and C₂S) at 700 °C can also be ruled out.

The above considerations indicate that the single assumed mechanism controlling the synthesis process in the system in question at 700 °C is the surface diffusion of Ca²⁺ ions through the polycrystalline layer of wollastonite and C₂S. The condition of structural electroneutrality and stoichiometry of the products requires the simultaneous transport of O²⁻, the mechanism of which has not so far been explained.

CONCLUSION

[[In the system CaCO₃—SiO₂ at low temperature (700 °C) water vapour was found to have an accelerating effect on the combination of components into silicates without influencing in any distinct way the development of the phase composition in the system as compared to the reaction taking place in air atmosphere.

Hydrogen slows down the rate of the formation of silicates in contrast to its effect at temperatures above 1000 °C. At the same time it suppresses formation of wollastonite.

The kinetics of the reactions and an analysis of thermodynamic data on the possible volatile intermediate products and on the temperature dependence of the lattice diffusion coefficients of Ca²⁺ in calcium silicates allow to formulate an assumption of surface diffusion of calcium ions through a layer of polycrystalline products as the prevailing mechanism involved in the synthesis.

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VPLYV ZLOŽENIA ATMOSFÉRY NA RÝCHLOSŤ
A MECHANIZMUS REAKCIÍ V SÚSTAVE CaCO_3 -- SiO_2
PRI NÍZKYCH TEPLOTÁCH

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Experimentálne sa sledoval vznik reakčných produktov v sústave kalcit-kremeň (molárny pomer 1 : 1) pri teplotách 700—1000 °C v závislosti od atmosféry výpalu. Použili sa atmosféry vzduchu, vodnej pary, oxidu uhličitého, vodíka a zmesi H_2O — CO_2 . Konverzné závislosti možno popísať exponenciálnym vzťahom $\alpha_i = 1 - \exp(-Bt^z)$, v ktorom stanovená hodnota z poukazuje na difúzny mechanizmus riadiaceho procesu. Exponent B je funkciou zloženia atmosféry výpalu. Vodná para urýchľuje prechod zložiek CaO a SiO_2 do silikátovej väzby. V atmosférach obsahujúcich CO_2 nastáva tvorba kremičitanov vápenatých priamou reakciou uhličitanu vápenatého s kremeňom (700 °C). Pri syntéze vzniká prednostne Ca_2SiO_4 a v ďalšom priebehu reakcie CaSiO_3 . V atmosfére vodíka je vznik wollastonitu potlačený. Z kinetického popisu študovanej reakcie, z údajov o možných prechádzajúcich zložkách v sústave a z porovnania hodnôt koeficientov objemovej difúzie Ca^{2+} v Ca_2SiO_4 a CaSiO_3 vyplýva, že mechanizmus reakcie je založený na povrchovej difúzii vápenatých iónov polykryštalickým vrstvou produktov, t. j. Ca_2SiO_4 a CaSiO_3 .

- Obr. 1. Rovnovážna tenzia CO_2 pre reakcie I až 3; I — oblasť vzniku CaSiO_3 , II — CaSiO_3 a Ca_2SiO_4 , III — CaSiO_3 , Ca_2SiO_4 a CaO . Znakmi sú vyznačené použité zloženia pevných atmosfér vzhľadom k pomeru ich zložiek.
Obr. 2. Vývoj fázového zloženia v zmesi $\text{CaCO}_3 + \text{SiO}_2$ pri 700 °C.
Obr. 3. Závislosť $\alpha_C - \alpha_S$ v zmesi $\text{CaCO}_3 + \text{SiO}_2$. Bodmi sú znázornené experimentálne hodnoty konverzie po 120minútovom výpale.

ВЛИЯНИЕ СОСТАВА АТМОСФЕРЫ
НА СКОРОСТЬ И МЕХАНИЗМ РЕАКЦИЙ В СИСТЕМЕ CaCO_3 — SiO_2
ПРИ НИЗКИХ ТЕМПЕРАТУРАХ

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Исследовали экспериментальным путем образование продуктов реакции в системе кальцит — кварц (молярное отношение 1 : 1) при температурах 700—1000 °C в зависимости от атмосферы обжига, состоящей из воздуха, водяного пара, углекислого газа, водорода и смеси H_2O — CO_2 . Конверсионные зависимости можно описать с помощью экспоненциального отношения $\alpha_i = 1 - \exp(-Bt^z)$, в котором установленная величина z соответствует диффузионному механизму управляющего процесса. Экспонент B является функцией состава атмосферы обжига. Водяной пар ускоряет переход компонентов CaO и SiO_2 в силикатную связь. В атмосфере, содержащей CO_2 наступает образование силикатов кальция прямой реакцией карбоната кальция с кварцем (700 °C). При синтезе образуется преимущественно Ca_2SiO_4 и далее протекает реакция образования CaSiO_3 . В атмосфереводородообразование wollastonита уступает. Из кинетического описания исследуемой реакции, из данных относительно летучих компонентов в системе и из сопоставления величин коэффициентов объемной диффузии Ca^{2+} в Ca_2SiO_4 и CaSiO_3 следует, что механизм реакции основывается на поверхностной диффузии кальциевых ионов поликристаллическим слоем продуктов, т.е. Ca_2SiO_4 и CaSiO_3 .

Рис. 1. Равновесное давление CO_2 для реакций 1—3; I — область образования CaSiO_3 , II — CaSiO_3 и Ca_2SiO_4 , III — CaSiO_3 , Ca_2SiO_4 и CaO . Знаками обозначаются изменяемые составы атмосферы печи включая отношение их компонентов.

Рис. 2. Развитие состава фаз и смеси $\text{CaCO}_3 + \text{SiO}_2$ при 7000°C .

Рис. 3. Зависимость $\alpha_C - \alpha_S$ в смеси $\text{CaCO}_3 + \text{SiO}_2$. Точками обозначаются экспериментальные величины конверсий после 120 минут обжига.
