LIMESTONE IN FLUE GAS DESULPHURIZATION IN OXYGEN-ENRICHED ATMOSPHERES – PART I: THE EFFECT OF CO_2 ON LIMESTONE CALCINATION

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The article describes the testing of four selected samples of limestone originating from four commercially exploited deposits. The tests of sorbents included a physicochemical analysis and calcination in different atmospheres. The main aim of the tests was to determine the possibilities for using limestone during combustion in oxygen-enriched atmospheres. Tests in a synthetic flue gas composition make it possible to assess the possibility of $CaCO_3$ decomposition in atmospheres with an increased CO_2 concentration.

Keywords: calcination, limestone, CO_2

1. INTRODUCTION

Limestone is a sorbent that is most commonly used in the processes of dry flue gas desulphurization in power plants equipped with circulatory fluidized-bed boilers. The dry flue gas desulphurization process involves feeding of dry sorbent to the boiler's combustion chamber. If the CO_2 partial pressure in the system is lower than the equilibrium limestone decomposition pressure, then indirect limestone sulphation reactions will occur. Under temperature, limestone decomposes first into CaO and CO_2 as a result of the calcination process and then, by reacting with SO_2 present in the flue gas, it forms $CaSO_4$ as the by- product of the sulphation reaction. This reaction proceeds in boilers in which coal is burned in a conventional method, that is in atmospheric air (Hu et al., 2007; Szymanek, 2008).

Due to its significant influence on the success of dry flue gas desulphurization methods, the calcination process is one of the key elements of the desulphurization process. It can be described by the following chemical reaction:

$$CaCO_3 \rightarrow CaO + CO_2 \qquad (1)$$

The calcium carbonate calcination temperature is closely related to the partial pressure of CO_2. This process will only occur when the CO_2 partial pressure in gases is lower than the equilibrium pressure at the furnace temperature. The lowest calcination temperature is 660°C, however, this process usually takes place at temperatures from approx. 750 to 930 °C. The variability of calcination temperature is due to the presence of admixtures of other chemical compounds in the limestone structure. For example, the process of decomposition of $CaCO_3$ contained in atmospheric pressure flue gas including 5% H_2O and 15% CO_2 requires a temperature in excess of 750 °C. The above process can be accelerated by increasing the temperature and removing the CO_2. Favourable conditions for

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the calcination process are provided by fluidized-bed combustion that takes place at a temperature of 830-920 °C, with the CO_2 partial pressure amounting to 10-25% (Hu et al., 2006; Szymanek, 2008).

Calcination is an endothermic process, so the reaction rate is governed by the heat and mass exchange rate which, in turn, is determined by the size of grains subjected to calcination. The thermal dissociation reactions consist of many partial chemical and physical processes. The basic ones include:
1. Heat transfer:
   - from the source to the grain surface,
   - from the interior of an individual grain to the interface.
2. Liberation of gaseous products:
   - releasing of gas molecules from the crystal lattice of the substrate,
   - chemisorption of gas molecules on the reactive surface of a grain,
   - diffusion of the gas through the solid reaction products to the boundary of the individual grain,
   - diffusion from the sample surface to the surrounding atmosphere.
3. Formation of a new solid phase:
   - formation of nuclei on active centres,
   - nucleus growth,
   - the processes of recrystallization of the reaction product solid phase (Szymanek, 2008; Wieczorek-Ciurowa, 1995).

Calcination is a process that, by influencing the porosity, specific surface, and pore structure of calcinates, determines their properties. This is caused by the fact that the thermal dissociation of calcium carbonate proceeds practically under non-isothermal conditions at different CO_2 partial pressures (Szymanek, 2008; Wieczorek-Ciurowa, 1995). Experimental data shows that the temperature of the $CaO/CaCO_3$ interface is variable during calcination and, at the same time, much lower than the flue gas temperature. This is illustrated by the diagram below (Wieczorek-Ciurowa, 1995):
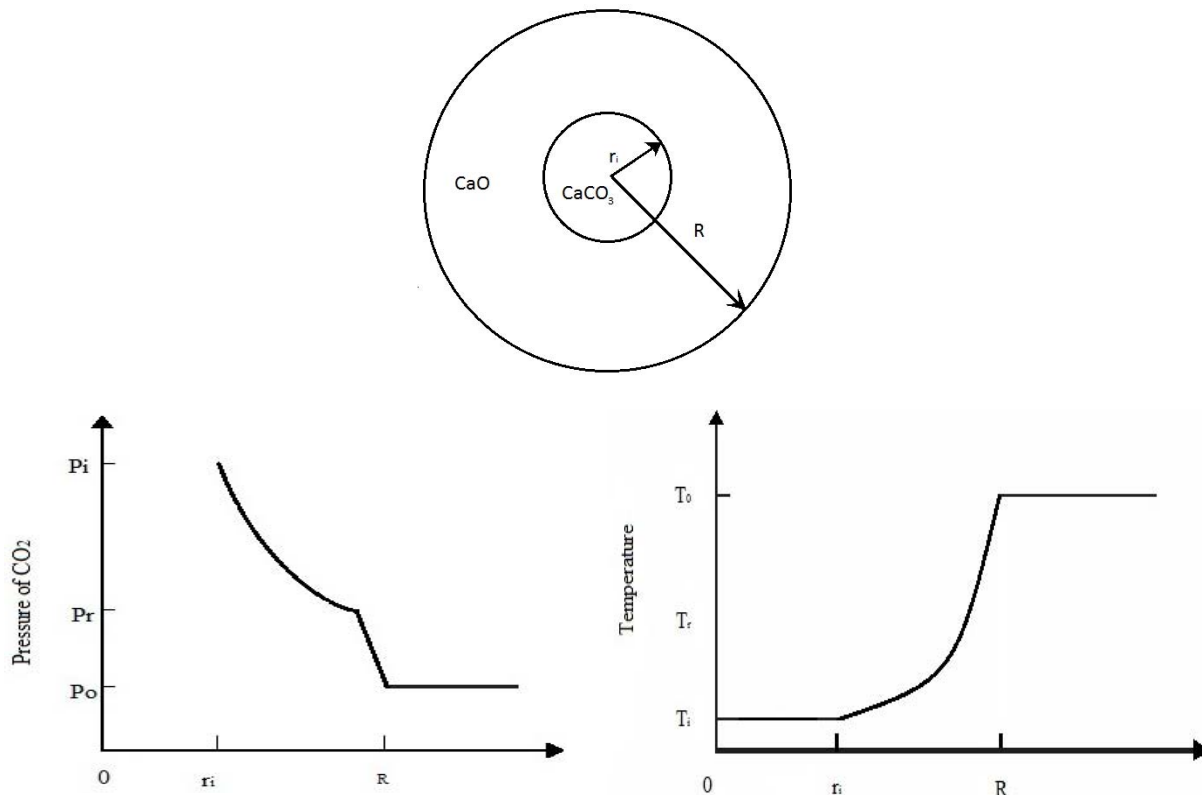

Fig. 1. Limestone calcination (Wieczorek-Ciurowa, 1995);
P_0, P_r, P_i – partial pressures, respectively: in the particle surrounding atmosphere, on the particle surface, at the $CaCO_3/CaO$ interface; T_0, T_r, T_i – respectively, ambient temperature, temperature at the particle surface, temperature at the $CaCO_3/CaO$ interface; R – calcinated particle radius; r_i – radius of the unreacted $CaCO_3$ core

As indicated by the diagram above, the heat is transferred through the calcium oxide layer to the calcium oxide-carbonate interface, which gives rise to the formation of zones of lowered temperature. These conditions are favourable to the formation of calcium sulphite. Only the increase in particle temperature, caused by the completion of the calcination process, makes the oxidation of calcium sulphite to calcium sulphate possible (Wieczorek-Ciurowa, 1995).

The aim of the tests was to determine the possibilities for using limestone during combustion in oxygen-enriched atmospheres. The tests in a synthetic flue gas composition enable one to assess the possibility of $CaCO_3$ decomposition in atmospheres with an increased CO_2 concentration.

2. TESTING METHODOLOGY

Four limestone samples selected previously, derived from four commercially exploited deposits, were subjected to testing. The test limestones originated from different geological periods, so they are characterized by different physicochemical and sorption properties.

The thermal decomposition of sorbents was examined by the methods of thermogravimetry (TG), differential thermogravimetry (DTG) and simultaneous differential thermal analysis (SDTA) using TGA/SDTA 851e thermal analyzer supplied by Mettler Toledo. Thermogravimetry involves the recording of variations in the mass of a substance as it is heated or cooled as a function of time or temperature, or the measurement of a variation in the mass of an isothermally heated substance as a function of time. In order to improve the legibility of the curves, differential thermogravimetry is performed, which is the first derivative of the thermogravimetric relationship with respect to time and temperature. Simultaneous differential thermal analysis, on the other hand, enables detection of thermal effects that accompany the physical and chemical transformations, as well as identification of compounds that, in the temperature range examined, undergo exothermal and endothermic transformations. This involves recording of the temperature difference between the substance tested and the standard substance with respect to time or temperature.

In the tests carried out, a dynamic temperature programme was employed, whereby sorbent samples were heated under atmospheric pressure in the following atmospheres: neutral (N_2), oxidizing (O_2), CO_2, and mixtures of: CO_2 80% O_2 20%, CO_2 60% O_2 40%, CO_2 40% O_2 60%, CO_2 20% O_2 80%, with a gas flow coefficient of 50 ml/min, in the temperature range of 25-900 ^{o}C - 1000 ^{o}C, and with a heating rate of 15 ^{o}C/min. During each experiment was carried out sample of mass 7mg.

In addition, physicochemical examination of limestones was performed using the following testing methodologies:
- Calcium (CaO) content determination – a volumetric method with EDTA – this involves the compleximetric titration of calcium with a standard solution of sodium versenate in the presence of Patton and Reeder's indicator, after prior dissolving of the sample in a diluted hydrochloric acid solution. Any possible effect of interfering cations (Fe, Al) is removed by the addition of triethanolamine.
- Loss on ignition (LOI) determination – a gravimetric method – the principle of this method relies on the ignition of a weighed sample of ash at a temperature of 800±15 ^{o}C to a constant mass and then the gravimetric determination of the mass loss.
- Silica (SiO_2) content determination – a gravimetric method – the principle of this method relies on the dissolving of a sample in diluted hydrochloric acid, filtering off the insoluble matter and co-melting it with an alkali metal alloy. The content of silicon in the form of silicic anhydride (SiO_2) is determined by a gravimetric method via the dehydration process by evaporation with hydrochloric acid, as the mass loss of the residue after it being treated with hydrofluoric acid.

- Determination of carbonates (CO_2) – a volumetric method – the method involves the acidimetric titration of the excess of the standard hydrochloric acid solution, added to the sample solution to decompose the carbonates, with a standard solution of NaOH in the presence of orange as the indicator.
- Determination of the contents of (Al, Fe, Mg, Na, K, S, Cu, Ni, Zn, Cr, Cd, Mn, Pb) cations by the inductively coupled plasma optical emission spectrometry (ICP-OES) technique – the method involves the microwave mineralization of a specific weighed sample in a pressurized closed system, in a system of concentrated mineral acids ($HCl+HNO_3+HF$ 5:2:1, v/v). In the obtained clear mineralizates, the intensity of emitted radiation of a wavelength characteristic of a given element is measured by the optical emission spectrometry technique with excitation in inductively coupled argon plasma (ICP-OES).
- Determination of the hydrochloric acid insoluble matter – made using the procedure prescribed by the EN 196-2:2005 standard: "Cement testing methods" - Part 2: "Chemical analysis of cement".
- Moisture content determination – made using procedures based on the PN-76/B-04350 standard: "Limestone and quicklime and hydrated lime - Chemical analysis".
- Particle size distribution – was made by laser scattering methods with use laser analyser Coulter LS 13320.

3. ANALYSIS OF THE OBTAINED RESULTS

3.1. Physicochemical limestone examinations

The physicochemical examinations of sorbents included the analysis of their chemical composition, identification of the phase composition by the FTIR method, surface analysis using scanning microscopy and grain composition analysis. The chemical composition was determined based on the contents of calcium (CaO), magnesium (MgO), aluminium (Al_2O_3), iron (Fe_2O_3), potassium (K_2O), sodium (Na_2O), sulphur (SO_3), carbonates (CO_2), silica (SiO_2), organic matter, hydrochloric acid insoluble matter (NR), free water (H_2O) and the metals: Cu, Ni, Zn, Cr, Cd, Mn and Pb. Chemical composition of the samples tested is shown in Table 1.

Table 1. Chemical composition analysis

Determined parameter	Test sample			
	Sorbent I	Sorbent II	Sorbent III	Sorbent IV
CaO content [%]	54.90	52.00	55.00	55.00
MgO content [%]	0.30	1.52	0.18	0.26
Al_2O_3 content [%]	0.096	0.34	0.12	0.077
Fe_2O_3 content [%]	0.054	0.47	0.23	0.054
K_2O content [%]	0.017	0.060	0.018	0.018
Na_2O content [%]	0.026	0.026	0.020	0.031
SO_3 content [%]	1.10	2.20	0.27	0.40
CO_2 content [%]	43.80	40.80	43.10	43.70
SiO_2 content [%]	0.54	1.84	0.40	0.25
Moisture content [%]	0.01	0.04	0.05	0.06
HCl insoluble matter contents [%]	1.30	2.86	1.26	0.69
Loss on ignition, LOI (800°C) [%]	43.60	43.10	43.70	44.0

From the obtained results we can find that the main component of the examined sorbents is calcium carbonate. Magnesium oxide occurs only in the form of a double salt, $CaCO_3 \cdot MgCO_3$, and is in the largest amount in sorbent II. This sorbent is also characterized by the highest contents of sulphates and aluminium and silicon compounds, which in turn results in higher contents of matter insoluble in HCl. All of the examined sorbents are characterized by either a lack or small contents of organic matter, as indicated by the high loss on ignition values which are, to a large extent, consistent with those of carbonate contents. Tables 2 and 3 show the results of phase composition and heavy metal content examinations.

Table 2. Phase composition of the examined sorbents

Probable chemical compound	Contents [wt%]			
	Sorbent I	Sorbent II	Sorbent III	Sorbent IV
$CaCO_3$	95.9	86.3	97.4	97.1
$CaCO_3 \cdot MgCO_3$	1.4	6.9	0.8	1.2
$CaSO_4$	1.9	3.7	0.5	0.7
Aluminosilicates	0.6	2.2	0.5	0.3
Total	99.8	99.1	99.2	99.3

Table 3. Heavy metal contents

Determined parameter	Test sample			
	Sorbent I	Sorbent II	Sorbent III	Sorbent IV
Cu content [ppm]	0.9	2.1	2.3	2.4
Ni content [ppm]	1.8	2.8	1.7	8.1
Zn content [ppm]	7.6	83	41	8.2
Cr content [ppm]	3.0	3.8	1.6	3.6
Cd content [ppm]	0.4	1.2	0.6	0.8
Mn content [ppm]	31	110	86	29
Pb content [ppm]	5.4	46	20	2.7

Table 4. Fractional distribution of sorbents

Fraction μm	Mass fraction [%]			
	Sorbent I	Sorbent II	Sorbet III	Sorbent IV
< 0.5	1.01	1.38	1.08	1.81
0.5 – 1.0	6.43	9.22	7.11	11.69
1.0 – 5.0	22.46	20.60	15.71	28.40
5.0 – 10.0	11.00	16.30	13.40	12.50
10.0 – 50.0	8.70	17.80	14.20	11.60
50.0 – 100.0	7.70	7.70	5.20	7.80
100.0 – 150.0	9.60	7.60	9.70	6.80
150.0 – 200.0	18.10	11.80	18.00	12.50
200.0 – 250.0	12.40	6.20	12.70	6.10
> 250.0	2.60	1.40	2.90	0.80

The obtained examination results indicate a considerable variation of composition of the sorbents tested. The content of $CaCO_3$, which is of key importance to desulphurization, ranges from 85% to 97%, while the $CaCO_3 \cdot MgCO_3$ content, from 0.8 to 7. To determine the particle size was performed granulometric analysis. The results are shown in Table 4.

Based on the obtained results we can state presence of two fractions, fine < 50µm and coarse > 50 µm. The nature of the distribution of fines fraction varies between sorbents I, IV and sorbents II, III. In sorbents I and IV there exist meaningful increase of fraction in the range of 1.0 – 5.0 µm, although in sorbents 1 and 3 exist higher share of fraction in the range of 1.0 and 50.0.

3.2. Limestone calcination

Calcination tests were carried out according to the adopted methodology, and the results are presented in the successive figures. In Figure 2, decomposition of $CaCO_3$ in a neutral atmosphere is shown. Figure 3 illustrates decomposition of $CaCO_3$ in atmospheres of CO_2 100% and gas mixtures.

Table 5. Weight loss during calcination

Weight loss				
Atmosphere	Sorbent I	Sorbent II	Sorbent III	Sorbent IV
N2	43%	43%	43%	43%
O2	44%	44%	44%	42%
O_2 80% CO_2 20%	45%	44%	43%	44.5%
O_2 60% CO_2 40%	45%	44%	43.5%	43.5%
O_2 40% CO_2 60%	4.5%	8%	3.35%	7%
O_2 20% CO_2 80%	2.5%	2.5%	1.25%	3.75%
CO_2	1.5%	1.15%	1.2%	3.25%

Table 6. Temperature of calcination of the sorbents tested

Calcination process temperature				
Atmosphere	Sorbent I	Sorbent II	Sorbent III	Sorbent IV
N_2	570 °C - 810 °C max.770 °C	540 °C - 830 °C max.760 °C	570 °C - 830 °C max.780 °C	560 °C - 800 °C max.770 °C
O_2	600 °C - 840 °C max.780 °C	600 °C - 810 °C max.780 °C	560 °C - 840 °C max.780 °C	600 °C - 830 °C max.780 °C
CO_2 20% O_2 80%	800 °C - 900 °C max.860 °C	800 °C - 890 °C max.860 °C	810 °C - 900 °C max.860 °C	780 °C - 890 °C max.860 °C
CO_2 40% O_2 60%	860 °C - 920 °C max. 900 °C	850 °C - 930 °C max.900 °C	850 °C - 930 °C max.900 °C	870 °C - 920 °C max.900 °C
CO_2 60% O_2 40%	above 850 °C	above 800 °C	above 800 °C	above 900 °C
CO_2 80% O_2 20%	calcination stopped	calcination stopped	calcination stopped	calcination stopped
CO_2	calcination stopped	calcination stopped	calcination stopped	calcination stopped

The performed thermogravimetric analyses found that the thermal decomposition of sorbents progressed within a similar temperature range and resulted in a similar weight loss. The weight loss, resulting from the thermal decomposition of $CaCO_3$ and liberation of CO_2 and H_2O, amounted to 43-45%. With the increase in CO_2 concentration, a dramatic decrease in weight loss down to 3.35-8% was observed at 60% CO_2; 3.75-1.25% at 80% CO_2; and 3.25-1.15% at 100% CO_2. The results are given in Table 5. The calcination temperature, on the other hand, ranged from 560 ^{o}C to 930 ^{o}C with the maximum loss at a temperature from 780 ^{o}C to 900 ^{o}C, depending on the gas used, as shown in Table 6. Based on the obtained results we can state that with the addition of CO_2, an increase in calcination temperature occurs, until the calcination is completely stopped at temperatures lower than a gas mixture CO_2 content of 80%.
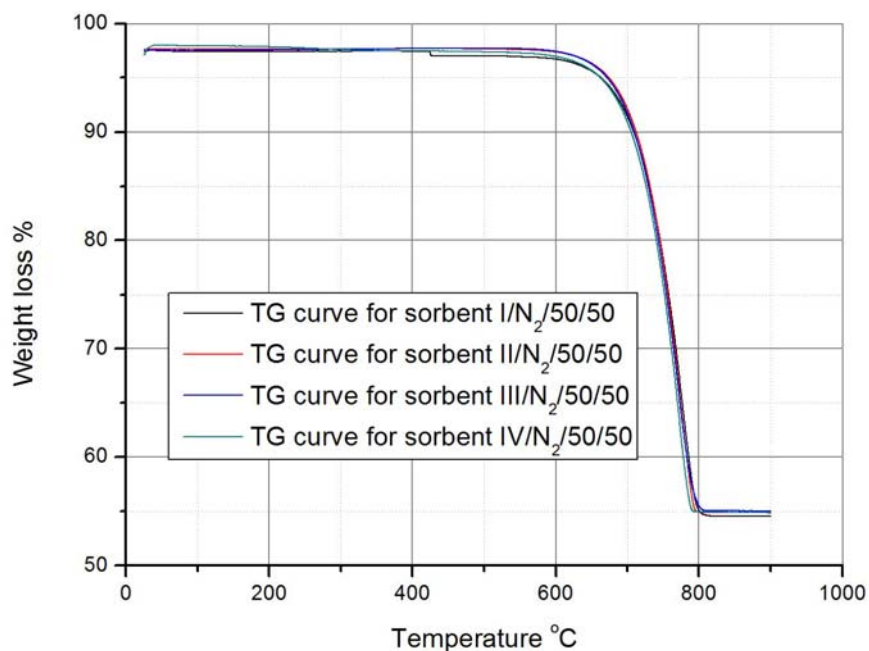

Fig. 2. TG curve for sorbents I, II, III, and IV; neutral atmosphere (N_2); heating rate, 15 ^{o}C/min
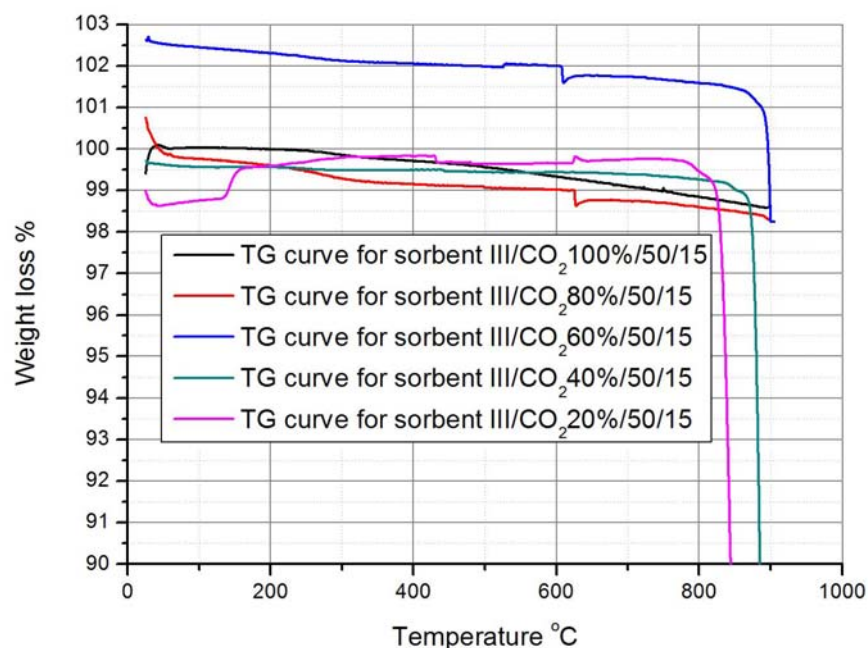

Fig. 3. TG curve for sorbent III; atmosphere, respectively: CO_2 100%, CO_2 80% O_2 20%, CO_2 60% O_2 40%, CO_2 40% O_2 60%, CO_2 20% O_2 80%; heating rate, 15 ^{o}C/min

4. SUMMARY

The presented results of physicochemical examinations of four sorbents have shown differences both in chemical composition and grain-size composition. The main component of the sorbents is calcium carbonate, which was also confirmed by infrared spectrophotometric examination. Three sorbents, I, III and IV, all contain calcium carbonate in excess of 95%. Only sorbent II exhibits a lower calcium carbonate content of 86.3%. It also contains more impurities compared to the remaining sorbent, which are in the form of calcium sulphate, the double salt $CaCO_3 \cdot MgCO_3$, aluminosilicates, as well as heavy metals.

From the limestone calcination investigation carried out it has been found that the thermal decomposition of the limestones tested progresses within a comparable temperature range and with a comparable weight loss. The weight loss in the tests amounted to 43-45%, while the calcination temperature was in the range of 560 ^{o}C - 930 ^{o}C, with the maximum weight loss taking place at a temperature from 780 ^{o}C to 900 ^{o}C, depending on the gas used in the test. The addition of CO_2 caused a dramatic decrease in weight loss down to 3.35-8% at 60% CO_2; 3.75-1.25% at 80% CO_2; and 3.25-1.15% at 100% CO_2; as well as an increase in calcination temperature, until the complete stopping of calcination at temperatures lower than 900 ^{o}C with a gas mixture CO_2 content of 80%.

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