STUDIES ON THE REACTIONS BETWEEN GAS AND SOLID. PART II. ABSORPTION OF CO_2 BY CaO AND $Ca(OH)_2$.

By Takeo AONO.

Received September 17th, 1931. Published December 28, 1931.

1. Absorption of CO_2 by CaO. Fine powders of lime (100 gr.) were placed in dry CO_2 and the change of weight was measured at 14°C. The results are given in Table 1.

Table 1.

Time in days	1	3	5	9	17	30	50	96	150	222	302
Increase in weight (%)	0.305	1.115	1.457	2.048	2.272	2.332	2.378	2.470	2.694	3.130	3.618

From the results it is clear, as it is ever said, that dry CO_2 does not react with dry CaO, or the velocity is very small at common temperature. The initial change of weight might be caused by a lack of care in the experiment, namely the CaO might have absorbed some moisture during its weighing, or the CO_2 gas might have contained a trace of water vapour, though it had been dried with sulphuric acid.

The rapid decrease of the carbonation velocity will be due to the facts, that the carbonation takes place only on the surface of CaO, and its rate of proceeding inwards is very slow. Hence, if the surface is covered with $CaCO_3$, the carbonation will practically cease.

This will also be true in the case of carbonation of CaO at high temperatures. To confirm this the following experiment was carried out. 7.0473 Gr. of CaO was heated in a stream of dry CO_2 for 2.5 hours, the temperature being kept at 600°C., and 0.5302 gr. of CO_2 was combined. The product was placed with untreated lime side by side, in an atmosphere which was saturated with water vapour at 50°C., and the rate of absorption of moisture was measured. At first the rate of absorption by the carbonated lime was exceedingly small. For example, the increase of weight of the carbonated lime was only 0.5% after 17 hours, while the untreated one increased 10.5%. But afterwards the rate increased more and more approaching to that of the untreated one. This fact shows that the carbonated lime has a coating of $CaCO_3$ on its surface, and is protected from water vapour. But after a certain time the water adsorbed on the surface will reach the fresh part of lime by diffusion through the coating of $CaCO_3$.

Quick lime with water changes to slaked lime with an increase of volume. Thus the crust of $CaCO_3$ is cracked off from the surface of lime and the slaking of quicklime proceeds more and more rapidly.

2. Absorption of Moist CO_2 by $Ca(OH)_2$ and its Velocity. Each 10 gr. of $Ca(OH)_2$, which had been kept in a saturated water vapour for 7 days to absorb moisture, were placed in an atmosphere of a constant composition of air and CO_2 which was saturated with water vapour (the total pressure was equal to 1 atm.) at 14°C. and their increase of weight was measured after 2 hours.

The results are shown in Table 2.

Table 2.

Absorption of moist CO_2 by 10 gr. of moist $Ca(OH)_2$ in 2 hours.
Relation between increase of weight and concn. of CO_2.

Concentration. C. (vol. % of CO_2)	1.33	3.87	6.44	13.0	32.0	64.7	78.5	100
Increase of weight % (W_t) obs.	1.21	2.88	5.47	9.40	16.84	24.63	26.26	—
Increase of weight calc. from eq. (1)	1.08	3.00	4.80	8.88	17.37	24.78	26.35	27.99
Difference	+0.13	−0.12	+0.67	+0.52	−0.53	−0.15	−0.09	—

In this table the volume concentration, C %, of CO_2 was calculated from the partial pressure of CO_2 saturated with water vapour by the following equation:

$$C = \frac{p_{CO_2}}{P} \times 100 = \frac{p(P-p_{H_2O})}{P^2} \times 100,$$

where P is the total pressure; p the partial pressure of moist CO_2; and p_{CO_2} and p_{H_2O} the partial pressure of CO_2 and H_2O respectively.

In the previous paper(1) on the absorption of moisture by CaO the author has obtained the following equation:

$$W_t = W_{h,\infty}(1-e^{-\alpha_1 ht}) \quad \ldots\ldots\ldots\ldots\ldots\ldots \quad (1)$$

---

(1) This Bulletin, **6** (1931), 294.

where W_t is the increase of weight in per cent in the time t, $W_{h,\infty}$ is $\lim_{t\to\infty} W_t$, α is the velocity constant of absorption of moisture, and h is vapour pressure.

From the analogy of the character of reaction, a similar relation has been assumed for the absorption of CO_2

$$W_t = W_\infty(1-e^{-\beta_1 Ct}) \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots \quad (2)$$

where C denotes the concentration of CO_2 in the moist air. The value of W_∞ cannot be calculated directly from the chemical equation: $Ca(OH)_2 + CO_2 = CaCO_3 + H_2O$, because water is adsorbed and expelled during the experiment. As the materials were always saturated with moisture, the value of W_t, however, may be regarded as a measure of CO_2 absorbed, since the water will evaporate by local heating, and the product will be $CaCO_3$ keeping a quantity of H_2O and CO_2 corresponding to the adsorption equilibrium, the total increase of weight being thus proportional to the CO_2 combined. Putting $W_\infty = 30.0$ by inspection, we have from the experimental data the following equation:

$$W_t = 30.0\,(1-e^{-0.0135\,Ct}) \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots \quad (3)$$

The value of W_t calculated from this equation, shown in Table 2 and Fig. 1, agrees fairly well with that of observed. Hence the following differential form will also be true:

$$\frac{dW_t}{dt} = \beta_1 C\,(W_\infty - W_t) \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots \quad (4)$$

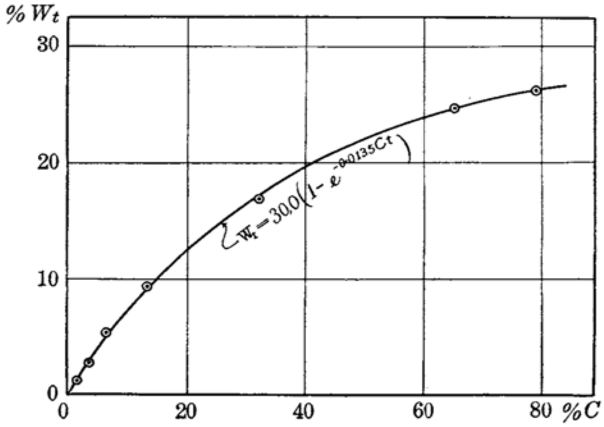

Fig. 1.

Relation btw. concn. of CO_2 and absorption of CO_2 in 2 hrs.

3. Absorption of Dry CO_2 by $Ca(OH)_2$ and its Velocity. 132.14 Gr. of $Ca(OH)_2$, prepared from 100 gr. of CaO and equivalent water, were placed in a desiccator with $CaCl_2$. It was evacuated and CO_2 (dried by conc. H_2SO_4) was introduced into it. The increase of weight was measured from time to time. The results are given in Table 3 and Fig. 2.

Table 3.

Days	1	2	4	6	8	11	16	26	39	60	124	221	301
Increase of weight %.	31.80	35.82	42.18	40.38	38.81	37.16	36.16	35.96	35.82	35.64	35.63	35.49	35.39

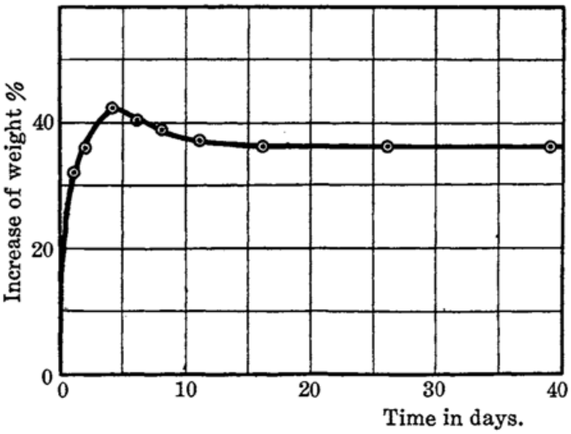

Fig. 2.

Absorption of CO_2 by dry Ca $(OH)_2$.

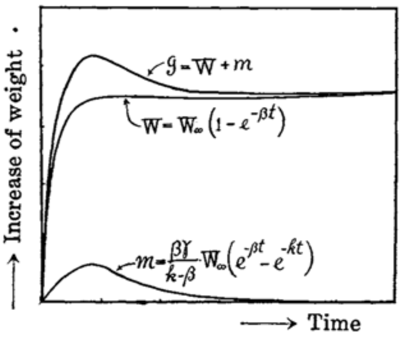

Fig. 3.

When dry $Ca(OH)_2$ reacts with CO_2 to form $CaCO_3$, setting equivalent molecules of water free, the water will be kept by the surrounding lime for a time and then given off. The curve of indicating the change of weight with time will therefore have a point of maximum and inflexion. Its character will be shown in Fig. 3, curve *g*. This curve is obtained as the sum of two curves *W* and *m*, where *W* shows the weight of CO_2 absorbed and *m* that of water remaining.

The velocity of absorption of CO_2 by $Ca(OH)_2$ is, from the former experiment, given by the equation

$$\frac{dW_t}{dt} = \beta(W_\infty - W_t) \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots \quad (4)$$

or

$$W_t = W_\infty(1-e^{-\beta t}) \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots \quad (5)$$

where W_∞ is, from the equation $Ca(OH)_2+CO_2=CaCO_3+H_2O$, equal to 35.1%. The velocity of liberation of water is theoretically

$$\frac{dw_t}{dt} = \gamma\left(\frac{dW_t}{dt}\right) = \beta\gamma W_\infty e^{-\beta t} \quad \ldots\ldots\ldots\ldots\ldots\ldots \quad (6)$$

where $\gamma=18.02/25.98$ and therefore $\gamma W_\infty=24.3\%$. The velocity of evaporation of water will be given by the equation

$$-\frac{dm_t}{dt} = km_t - \gamma\frac{dW_t}{dt} = km_t - \beta\gamma W_\infty e^{-\beta t} \quad \ldots\ldots\ldots \quad (7)$$

where m_t is the amount of water held by the material at time t. By integrating the equation (7) m_t may be calculated.

$$m_t = e^{-\int kdt}\left[\int e^{\int kdt}(\beta\gamma W_\infty e^{-\beta t})\,dt + \text{const.}\right]$$

$$= m_o e^{-kt} + \frac{\beta\gamma}{k-\beta}W_\infty\left[e^{-\beta t} - e^{-kt}\right] \quad \ldots\ldots\ldots\ldots \quad (8)$$

where m_o means m_t at $t=0$. The total increase of weight after the time t is therefore

$$g_t = W_t + m_t$$

$$= W_\infty + \left(\gamma W_\infty\frac{\beta}{k-\beta} - W_\infty\right)e^{-\beta t} - \left(\gamma W_\infty\frac{\beta}{k-\beta} - m_o\right)e^{-kt} \quad \ldots \quad (9)$$

$$= 35.1 + \left(24.3\frac{\beta}{k-\beta} - 35.1\right)e^{-\beta t} - \left(24.3\frac{\beta}{k-\beta} - m_o\right)e^{-kt} \quad \ldots \quad (9')$$

If $m_o = 0$, then $g_t = g_t'$

$$g_t' = 35.1 + \left(24.3\frac{\beta}{k-\beta} - 35.1\right)e^{-\beta t} - 24.3\frac{\beta}{k-\beta}e^{-kt} \quad \ldots\ldots\ldots \quad (9'')$$

The character of the curve for equation (9) agrees with that of experimentally obtained. The equation (9) may be applied to any reactions of this sort.

These experiments were carried out in the research laboratory of the Electrochemical Manufacturing Co. Ltd., Tokyo, before April 6th, 1930 and reported to the board of directors of the Co. on that day. Grateful acknowledgment is made to Dr. M. Katayama, Prof. of the Tokyo Imperial University, for giving valuable suggestions, and to Mr. K. Hibi, Director of the Co., who gave the author the opportunity of the accomplishment of this work and allowed him to publish this report. Mr. I. Kobayashi assisted the author in this experiments.

Summary.

(1) It was determened experimentally that the velocity of absorption of CO_2 by $Ca(OH)_2$ is proportional to the concentration of CO_2 (or partial pressure of CO_2) in the air, and to the absorbing capacity of the substance:

$$\frac{dW_t}{dt} = \beta C (W_\infty - W_t)$$

(2) For the change of weight due to the absorption of dry CO_2 by dry $Ca(OH)_2$ the following equation was proposed

$$g_t = W_\infty + \left(\frac{\beta}{k-\beta}\gamma W_\infty - W_\infty\right)e^{-\beta t} - \left(\frac{\beta}{k-\beta}\gamma W_\infty - m_o\right)e^{-kt}.$$

and was also experimentally discussed.

Research Laboratory of the Electrochemical
Manufacturing Co. Ltd., Tokyo.