STUDIES ON THE REACTIONS BETWEEN GAS AND SOLID. PART I. VELOCITY OF ABSORPTION OF MOISTURE BY QUICKLIME.

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1. Velocity of Absorption of Moisture at Constant Vapour Pressure.

Method of the Experiment. Fine CaO powder of 100 gr. contained in a 500 c.c. beaker (sectional area = 79.4 cm^2.) was placed in a glass vessel with some water in the bottom. The change of weight was measured occasionally. This experiment was set about on Dec. 11th, 1929, and by dint of the warming equipment of the chamber, the temperature did not deviate much from the mean temperature of 14°C. during the whole course of time.

Result of the Experiment. The relations between the weight increase and time are shown in Table 1.

Table 1.

Time in days (t)	5	10	20	30	40	50	60	74
Weight increase (W_t) (obs.)	8.2	16.6	23.7	28.9	32.3	34.0	35.1	36.3
Weight increase calc. by eqn. (1).	8.4	14.8	23.7	29.0	32.2	34.1	35.2	36.2
Difference	+0.2	− 1.8	0.0	+ 0.1	− 0.1	+ 0.1	+ 0.1	− 0.1

From this result the following experimental formula was obtained :

$$W_t = 37.0\,(1-e^{-0.0510t}) \quad \ldots\ldots\ldots\ldots\ldots\ldots \quad (1)$$

The calculated value by this equation shows a coincidence with the observed one. (See Table 1 and Curve A of Fig. 1).

Consideration of the Results. If the temperature, humidity, surface nature and other conditions are kept constant, the velocity of absorption of moisture by CaO may be considered to follow the equation :

$$\frac{dW_t}{dt} = k_1(W_\infty - W_t) \quad \ldots\ldots\ldots\ldots\ldots\ldots \quad (2)$$

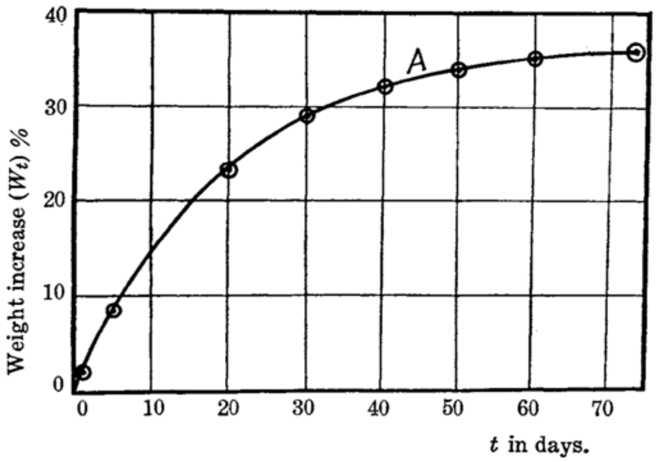

Fig. 1. Absorption of moisture by CaO at constant humidity.

where W_t: weight of moisture absorbed by 100 gr. of CaO during the t (days); W_∞: means $(\lim_{t\to\infty} W_t)$; $(W_\infty - W_t)$: absorbing capacity of the CaO in future; k_1: a constant, indicating the rate of absorption.

From the equation (2) we have

$$W_t = W_\infty(1-e^{-k_1 t}) \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots (3)$$

and

$$k_1 = \frac{1}{0.4343t}\log_{10}\left(\frac{W_\infty}{W_\infty - W_t}\right) \quad \ldots\ldots\ldots\ldots (4)$$

Equation (3) quite agrees with equation (1) in the form, and we have $k_1 = 0.0510$ and $W_\infty = 37.0$.

W_∞ cannot be calculated by the equation

$$CaO + H_2O = Ca(OH)_2 \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots (5)$$

to be equal to 32.14, because there may be some parts of moisture, which are merely adsorbed on the surface, and which make W_∞ greater than 32.14. The value: $37.0 - 32.14 = 4.86$, can therefore be regarded as the part due to adsorption.

2. Relations between the Velocity of Absorption of Moisture and Temperature and Humidity.

Method of the Experiment. Each 10 gr. of CaO powder, contained in a weighing tube of 4.9 cm^2 wide, was placed in a vessel each containing sulphuric acid or some salt solution of a known concentration, and the increase of weight was measured occasionally, at 10, 20, 30 and 40°C. respectively. Special care was taken to equalize the fineness and compactness of the powder.

Results of the Experiment. The results are shown in Tables 2 to 5.

Table 2. Temp. $= 9.9 \pm 0.9$°C. (corresponding to Fig. 2)

Solution		Water	Sulphuric acid	
concentration %		100	43.75	66.0
vapour tension (mm. Hg)		9.1	4.4	1.1
humidity %		100	48 3	12.1
	time hrs.			
weight increase (gr.)	19.75	0.0756	0.0319	0.0095 ?
	25.25	0.1021	0.0425	0.0087
	43.25	0.1919	0·0752	0.0137

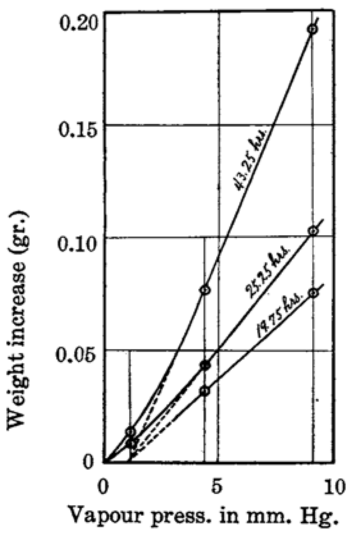

Fig. 2. Relation btw. absorption of moisture and humidity. Temp. $= 9.9 \pm 0.9$°C.

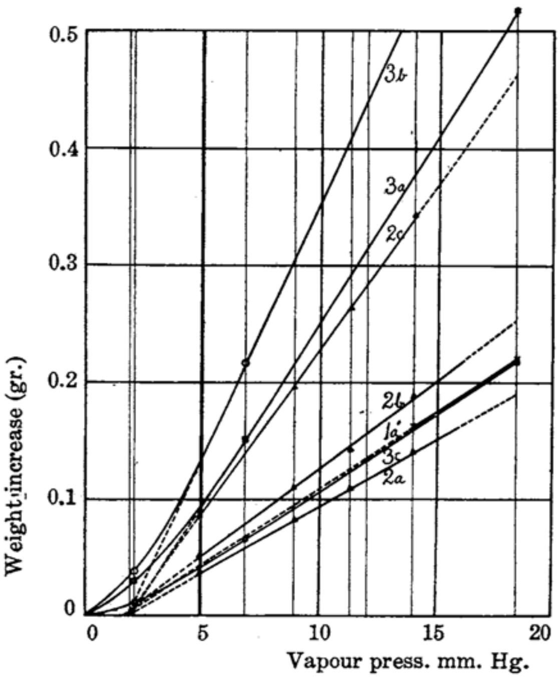

Fig. 3. Relation btw. absorption of moisture and humidity. Temp. $= 20.8 \pm 0.3$°C.

Table 3. Temp. = 20.8±0.3°C. (Fig. 3)

Solution			H_2O	NaCl	NH_4NO_3	H_2SO_4				
concentration %			100	Sat.	Sat.	37.69	43.75	50.00	55.00	65.20
vapour press. mm. Hg			18.4	14.0	12.0	11.3	8.86	6.8	4.9	2.1
humidity %			100	74.6	65.2	61.4	48.2	37.0	26.6	10.3
weight increase (gr.)	No.	time (hrs.)								
	1_a	22.5		0.1615						
	2_a	17.9		0.1399		0.1075	0.0823		0.0356	
	2_b	23.66		0.1877		0.1419	0.1085		0.0509	
	2_c	40.5		0.3414		0.2625	0.1953		0.0853	
	3_a	43.8	0.5017					0.1496		0.0291
	3_b	60.9	0.7207					0.2151		0.0412
	3_c	17.0	0.2171		0.1311			0.0641		0.0107

1_a: very compactly charged,

3_c: very coarsely charged.

Table 4. Temp. = 30.3±0.5°C. (Fig. 4)

Solution			H_2O	NH_4NO_3	H_2SO_4	
concentration. %			100	Sat.	50	66
vapour pressure mm. Hg.			32.4	19.3	12.1	3.5
humidity %			100	59.5	37.3	10.8
weight increase (gr.)	No.	time (hrs.)				
	1_a	17.25	0.3967	0.2188	0.1188	0.0215
	1_b	22.92	0.5436	0.2969	0.1646	0.0289
	1_c	40.17	0.9280	0.5480	0.3012	0.0522
	1_d	45.50	1.1163			
	1_e	28.83	1.7112			
	1_f	89.83	2.1658			

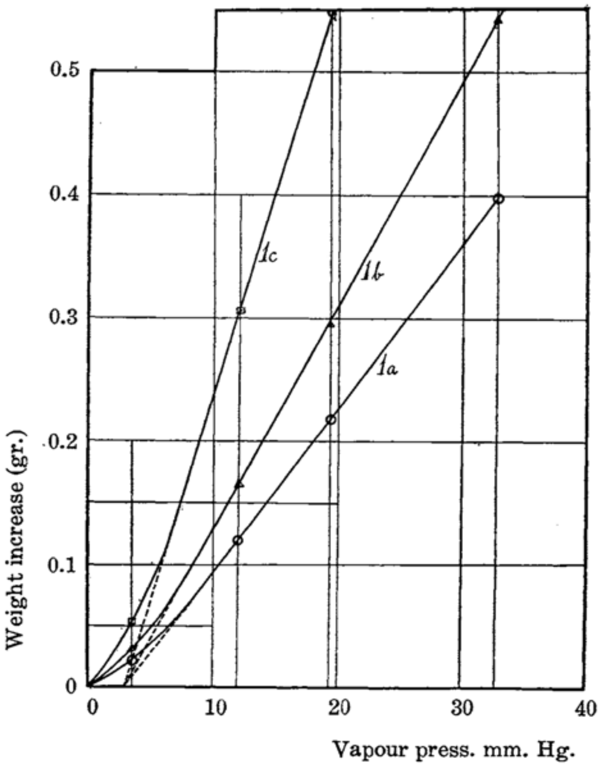

Fig. 4. Relation btw. absorption of moisture and humidity.
Temp. = 30.3 ± 0.5° C.

Table 5. Temp. = 39.9±0.1°C.

Solution		H_2O	NaCl	H_2SO_4	
concentration %		100	Sat.	50.0	66.0
vapour pressure mm.Hg		55.0	41.2	21.3	5.4
humidity %		100	74.9	38.6	9.8
weight increase (gr.)	time hrs.				
	18.08	0.8417	0.5760	0.2464	0.0481

Theoretical Part

The increase of weight (W_t) of quicklime due to moisture must be the sum of water adsorbed by CaO, water chemically combined to form $Ca(OH)_2$ (W_t') and hygroscopic water on the $Ca(OH)_2$ (w_t). It may be assumed that the water adsorbed by CaO is relatively small because it soon combines with CaO to form $Ca(OH)_2$, and $Ca(OH)_2$ formed absorbs rapidly the hygroscopic water, the quantity of which must be considerable. Then we have

$$W_t = W_t' + w_t \qquad (6)$$

This w_t may be regarded to consist mainly of the water adsorbed on the surface of $Ca(OH)_2$, and as $Ca(OH)_2$ produced from the CaO forms very fine powders, the area of the surface may be regarded to be proportional to the mass. Then from Langmuir's equation of the adsorption isotherm we have

$$w_t = \lambda W_t' \qquad (7)$$

$$w_t = \left(\frac{\lambda' h}{1+ah}\right) W_t' \qquad (8)$$

where a and λ' are constants and h is the vapour pressure. From equations (6) and (8) we have

$$W_t = W_t'(1+\lambda) = W_t'\left(1+\frac{\lambda' h}{1+ah}\right) \qquad (9)$$

and combining this equation to equation (2), we have

$$\frac{dW_t'}{dt} = k_1(W_\infty' - W_t') \qquad (10)$$

where $W_\infty' = \dfrac{W_\infty}{1+\lambda} = 32.14\%$ of initial weight of pure CaO .... (11)

Assuming that the velocity of formation of $Ca(OH)_2$ is proportional to the vapour pressure h, namely

$$k_1 = a_1 h \qquad (12)$$

At the earlier stage of slaking, where W_t' is negligibly small compared with W_∞', we have

$$\frac{dW_t'}{dt} = a_1 h W_\infty' \qquad (13)$$

or

$$W_t' = a_1 h W_\infty' t \qquad (14)$$

and from (9) and (14),

$$W_t = \alpha_1 W'_\infty ht\left(1+\frac{\lambda' h}{1+ah}\right) \dots\dots\dots\dots\dots\dots \quad (15)$$

or

$$\omega \equiv \frac{W_t}{h} = \alpha_1 W'_\infty t\left(1+\frac{\lambda' h}{1+ah}\right) \dots\dots\dots\dots \quad (16)$$

Taking a certain value of ω' corresponding to h', we have, for every common time t,

$$\frac{h-h'}{\omega-\omega'} = \left(\frac{1+ah'}{\alpha_1 W'_\infty \lambda' t}\right)(1+ah) \dots\dots\dots\dots \quad (17)$$

Therefore, if the equation (15) truely holds, $\frac{h-h'}{\omega-\omega'}$ must be in linear relation with h.

Now, discussing this relation from the observed values :

From	Table 3 No. 3c (20°C.)				Table 4 No. 1a (30°C.)				Table 5 (40°C.)			
$h_{mm.}$	2.1	6.8	12.0	18.4	3.5	12.1	19.3	32.4	5.4	21.3	41.2	55.0
$\frac{h-h'}{\omega-\omega'}\times10^{-3}$	—	1.09	1.69	2.43	—	2.34	3.05	4.72	—	5.95	7.03	7.77

we see that $\frac{h-h'}{\omega-\omega'}$ stands in linear relation with h (Fig. 5) and therefore that the equation (15) holds, and consequently the above assumptions are quite plausible.

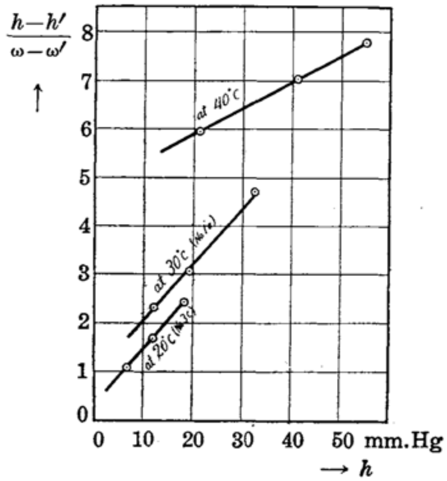

Fig. 5.

For the equation of absorption of moisture by quicklime at constant temperature we have the following general equations

$$\frac{dW_t}{dt} = \alpha_1 h \left\{(1+\lambda) W'_\infty - W_t\right\} \qquad (18)$$

and

$$W_t = (1+\lambda) W'_\infty \left\{1 - e^{-\alpha_1 h t}\right\} \qquad (19)$$

where

$$\lambda = \frac{\lambda' h}{1+ah} .$$

Summary

(1) From the experimental study, it has been found that the mechanism of absorption of moisture by quicklime can be explained as follows: free CaO absorbs moisture to form $Ca(OH)_2$, the velocity of which being proportional to the humidity, and the $Ca(OH)_2$ formed, getting off from the mother CaO in fine powders, and swelling in its volume, quickly adsorbs moisture, the amount of which being proportional to the amount of $Ca(OH)_2$ formed.

(2) The general equation of the velocity of the increase of weight at constant temperature has been given as

$$\frac{dW_t}{dt} = \alpha_1 h \left\{(1+\lambda) W'_\infty - W_t\right\}$$

and

$$W_t = (1+\lambda) W'_\infty \left\{1 - e^{-\alpha_1 h t}\right\} ,$$

where

$$\lambda = \frac{\lambda' h}{1+ah} ,$$

(3) The effect of temperature elevation has also been studied.

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