は、各組成域での末端 OH 基、または中間 OH 基の脱出によって生ずべき鎖状磷酸塩の鎖長または分岐構造における分岐点数の増大によって説明される。また、分子屈折の増大は、水素イオンのためにその電子雲をひきしめられていた隣接酸素原子が、OH 群の脱出とともにその分極性を回復することによると説明される。

(5) 水分の減少に伴う密度および屈折率の減少は、一応、構造的に体積増加をもたらす結果として理解されるが、anomalous glass に属する MgO -および ZnO - P_2O_5 系ガラスの場合、中間 OH 基の脱出が起らざるを得ないような組成的条件の下では、膨脹よりもむしろ構造収縮が起きるという特異性が認められた。

(6) $\text{H}_2\text{O}/\text{P}_2\text{O}_5$ 比を一定にそろえた系列試料について、その密度と屈折率を R_{MH} に対してプロットして得られる曲線では、 $R_{\text{MH}}=1$ の組成において、 MgO - P_2O_5 系ガラスははげしい不連続的急変をみせ、 CaO -および CdO - P_2O_5 系ガラスでは単なる屈曲点を生じた、この現象によっても、含水磷酸塩ガラスの組成変動に伴う構造変換に対しては、 H_2O をも考慮に入れた R_{MH} が決定的な組成パラメーターとなることが明らかになった。

本研究における磷酸塩中の水分の定量法について有益な御教示を頂いた工業技術院電気試験所並河洋氏に対して深甚なる謝意を表します。

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7. Presence of Syngenite in Commercial Portland Cement

By

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1. Introduction

The commercial portland cement usually contains a few percent of non-evaporable water and on the amount of which the limitation has been imposed according to JIS-R 5210 not to exceed four weight percent as a weight loss by ignition. The main source of such non-evaporable water may be ascribed to gypsum which was added to cooled clinker in a mill, the combined water thereof however, might be released from by the heat

generated through ball milling and recombine to form any other hydrate than gypsum. The present work was undertaken in the hope of obtaining the information about the species and quantities of the hydrates present in commercial portland cement.

2. Experimental

2.1. Samples of portland cements and clinkers

Table 1. Chemical analysis of portland cements and clinkers (wt. %).

Cnstituents	Ig. loss	Insol.	SiO ₂	Al ₂ O ₃	Fe ₂ O ₃	CaO	MgO	SO ₃	Na ₂ O	K ₂ O
Sample										
Cement No. 58	0.6	0.4	22.9	5.2	3.0	64.3	1.4	1.5	0.35	0.54
59	0.6	0.5 ₅	22.1	5.0	3.1	65.1	1.6	1.7	0.17	0.26
60	0.7	0.5	21.8	5.1	3.0	65.3	1.2	1.7	0.24	0.51
61	0.9	0.7 ₅	22.4	4.9	2.9	64.3	1.1	2.0	0.33	0.46
62	0.6	0.9	22.0	5.3	3.0	64.5	1.5	1.5	0.44	0.33
63	1.0	0.1	21.9	5.1	3.1	64.4	1.7	1.6	0.45	0.59
64	0.4	0.8	21.3	5.2	3.2	64.7	1.4	2.2	0.25	0.61
65	0.4	0.5	22.8	4.9	3.1	64.6	1.6	1.4	0.39	0.51
66	0.8	0.9	22.2	5.1	3.1	63.6	1.4	1.9	0.50	0.68
01	0.8 ₅	0.8	22.1	5.4	3.1	63.6	1.4	2.0	0.36	0.72
02	0.8 ₅	0.7	23.6	4.1	4.0	63.4	1.1	1.8	0.10	0.38
03	0.7 ₅	0.8	21.1	4.7	2.7	65.5	1.5	2.5	0.21	0.47
Clinker No. 1	0.4	—	—	—	—	—	—	—	0.21	0.62
2	0.3	—	—	—	—	—	—	—	0.31	0.53
3	0.5	—	—	—	—	—	—	—	0.20	0.32

In the present work twelve samples of commercial portland cements and three of clinkers were used. The results of chemical analysis for them are shown in Table 1.

2.2. Chemical analysis

The methods for chemical analysis of portland cement and clinker are described in JIS-R 5202-1962. The content of free lime was determined by the modified alcohol-glycerol method recommended by The Cement Association of Japan.

2.3. Differential thermal analysis

The arrangement for differential thermal analysis (DTA) is illustrated in Figure 1 with sample and reference standard (Al_2O_3) placed in holes drilled in a ceramic holder. The thermocouple of Chromel-Alumel (0.15 mm ϕ) was directly placed in the sample and reference, and the e.m.f. developed was amplified and recorded at a full scale of 250 μ volt. A heating rate of 10°C/min. was used.

The main hydrates in commercial portland cement, which are present enough to bring forth an endothermic peak in DTA curves, are gypsum, syngenite and calcium hydroxide. For quantitative estimations of these hydrates, the apparatus must be calibrated by observing the peak area corresponding to the thermal effect of respective materials, the known amount of which being incorporated in a diluent¹⁾. As a diluent, the clinker No. 2 was used to make the calibration curve for gypsum and syngenite, and the cement No. 64 for calcium hydroxide. The calibration curves thus obtained were shown in Figure 2, in which almost straight-line co-relations between peak areas and the contents of the materials mentioned could be established. From the points used to establish Figure 2, one should be able to determine upto about 10 mg of each hydrate (that is, 2 wt. % for the sample size of 500 mg) within a probable error of ± 0.5 mg of each hydrate.

2.4. Determination of moisture content by use of Karl Fischer reagent

a) cross sectional view

b) top view of ceramic holder

- ① thermal insulator
- ② Kanthal winding
- ③ silica glass tube
- ④ radiation shield (steel tube)
- ⑤ ceramic holder (alumina block, 33 mm ϕ $\times$ 13 mm)
- ⑥ electric insulator tube
- ⑦ reference standard, α - Al_2O_3 powder
- ⑧ hole for inserting thermocouple (6 mm ϕ $\times$ 13 mm)
- ⑨ silica glass tube (7 mm ϕ)
- ⑩ sample
- ⑪ Pt-PtRh thermocouple
- ⑫ Alumel wire
- ⑬ chromel wire (the ends of both wires are directly placed in holes)

Fig. 1. The apparatus used for DTA.

Fig. 2. Calibration curves for DTA of gypsum, syngenite and calcium hydroxide.

Fig. 3. Assembly for Karl-Fischer micro-electrometric titration.

The determination of moisture in cement was carried out by use of the Mitsubishi Kasei's Model KFD-8 Assembly for Karl Fischer micro-electrometric Titration (see Figure 3). The weighed sample (2~3 g) was placed in a combustion boat and inserted into a quartz glass tube furnace which had to preliminarily been dried. When the furnace was heated electrically at a rate of $5^\circ\text{C}/\text{min}$. while a slow stream of nitrogen was passed through (0.15 l/min.), water content held in the sample was released from, absorbed in a methanol-glycol solution and then titrated intermittently with Karl Fischer reagent (3mg $\text{H}_2\text{O}/\text{ml}$). To obtain a correct value, it was necessary to run through blank test and make a corresponding reduction (i.e., equivalent to 0.1~0.15 ml of the reagent) from the results of the analysis.

3. Results and Discussion

3.1. DTA curves of some commercial portland cements

DTA curves of portland cement No. 01, 02 and 03 are shown in Figure 4, in which endothermic peaks are observed at 100°C , 140°C , 270°C and 440°C respectively. The sample No. 02 has no 270°C peak. To make clear the natures of these endothermic effects, the water released from by heating was measured by use of Karl Fischer reagent and the dehydration curves thus obtained were presented in Figure 5. Up to 200°C , a continuous dehydration occurs in marked contrast to the endothermic peaks revealed in DTA. The endothermic peaks at about 100°C and 140°C may reasonably be attributed to removal of adhesive water and dehydration of gypsum respectively. On rising temperature, another dehydration occurs for sample No. 01 or No. 03 somewhat abruptly at 270°C ~ 300°C , that is likely to correspond with the 270°C peak in Figure 4, but for the sample No. 02 which has no 270°C peak, there appears also

Fig. 4. DTA curves of portland cements, No. 01, 02, 03.

Fig. 5. Dehydration curves of portland cements, No. 01, 02, 03 measured by using Karl-Fischer reagent (heating rate, $5^\circ\text{C}/\text{min}$).

no distinct dehydration at 270°C ~ 300°C , suggesting that a certain hydrous compound having a dehydration temperature of 270°C may present in the sample No. 01 and No. 03. In addition, there occurred a distinct endothermic peak at 440°C , which might be attributed to the dehydration of calcium hydroxide.

3.2. Presence of syngenite $\text{K}_2\text{SO}_4 \cdot \text{CaSO}_4 \cdot \text{H}_2\text{O}$

To elucidate the species of a hydrous compound having an endothermic peak at 270°C , some works have been done and as a result, this compound could most likely be identified with syngenite on the basis of the following facts.

1) As in the case of cement No. 01 and 03, syngenite has also an intensive endothermic peak

Fig. 6. DTA curve of syngenite.

at 270°C owing to the splitting off its hydrated water, the DTA of syngenite being shown in Figure 6. In the figure, an exothermic peak also takes place at 340°C and may perhaps be attributed to the rearrangement of some distorted structure set forth by dehydration into β - K_2SO_4 and β - $K_2SO_4 \cdot 2CaSO_4$ and another endothermic peak present at 550°C to the transformation of β - K_2SO_4 thus formed into α - K_2SO_4 in accordance with the phase diagram of the system, K_2SO_4 - $CaSO_4$.

Syngenite used was prepared as follows, an equimole mixture of potassium sulfate (guaranteed reagent) and natural gypsum (high grade, $H_2O = 20.15\%$) was ground to a fineness enough to pass through 150 mesh sieve, placed in a test tube (20 mm $\phi \times 200$ mm) which was fitted with an air condenser made of glass tube (3 mm in inner diameter) to allow water released from gypsum to reflux, and heated for three hour in an oven at a temperature of 200°C. The product was identified with syngenite by X-ray diffraction data²⁾, the combined water thereof being measured to be 5.54% (Cf. theoretical value, 5.49%).

2) When the mixture of K_2SO_4 and $CaSO_4 \cdot 2H_2O$ both in powder states was allowed to stand in the saturated water vapour at any temperature up to about 200°C, so easily formed syngenite. In Figure 7, DTA curves of the equimolar mixture of K_2SO_4 and $CaSO_4 \cdot 2H_2O$ are shown. The curve a) is for the mixture as mixed and has intensive endothermic peaks at about 140°C (dehydration of gypsum) and at 550°C (transformation of β - K_2SO_4 to α - K_2SO_4) in addition to a weak exothermic peak around 340°C (formation of anhydrite $CaSO_4$ II from soluble anhydrite $CaSO_4$ III)³⁾. The curve b) is for the mixture that was kept as a thin layer (1~2 mm in depth) at 20°C overnight in a desiccator containing water to expose it to moist air, and shows the large endothermic peak at 270°C marking the presence of syngenite. The curve c) is for the mixture which was aerated as for b) and then followed by desiccation over $CaCl_2$, hence shows a similar configuration as b)

— c) the mixture aerated as b) and followed by desiccation
 a) the mixture as mixed
 - · - · b) the mixture aerated overnight at 20°C

Fig. 7. DTA curves of the mixture of gypsum and potassium sulfate.

but with a lack of endothermic peak around 100°C (removal of free water). In consequence, the presence of some condensed moisture seems to be indispensable to the formation of syngenite from the starting raw mixture as mixed.

3) When the cement clinker No. 1, K_2O content thereof being 0.62%, was subjected to aeration in the same way as described above with or without incorporation of gypsum, so the sample with gypsum gave the DTA curve exhibiting 270°C peak (see Figure 8), suggesting the formation of syngenite therein.

4) As described above, syngenite might be formed in portland cement only when K_2SO_4 , which is originally present in clinker, would react with gypsum added in a mill under a moist atmospheric condition. In some commercial clinker, K_2SO_4 could be detected^{4), 5)} and Suzukawa⁵⁾ desc-

..... clinker
 — clinker aerated with incorporation of gypsum
 - · - clinker aerated (overnight at 20°C)

Fig. 8. DTA curves of clinker No. 1 and the one which was aerated with or without incorporation of gypsum.

ribed that the SO_2 from the fuel reacts with K_2O in preference to Na_2O in the kiln at a clinkering temperatures. A moist atmospheric condition necessary for formation of syngenite would be realized in some cement mills, as stated by Pollitt⁷⁾. Namely, ball milling generates considerable heat, with consequent possibilities of dehydrating gypsum to the hemihydrate or soluble anhydrite forms. It is therefore usual to cool cement mills by external wetting, and the use of fine water sprays in the last chamber has also been advocated.

These facts are responsible for the possible occurrence of syngenite in commercial portland cement. The writers, however, could not confirm directly the presence of the mineral in commercial cement neither under microscope nor by X-ray diffraction, because that syngenite produced by aerating a mixture of K_2SO_4 and $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$ in powder state at any temperature up to about 200°C was liable to be mossy but almost amorphous aggregates in appearance, so under microscope ($\times 400$) it could hardly be distinguishable from gypsum which had been distorted by entire or partial dehydration. X-ray inspections were also carried out for the sample No. 63 having a large endothermic peak at 270°C , resulting in, however, that even the strongest diffraction line of syngenite, $2\theta = 31.34^\circ$, $d = 2.86 \text{ \AA}$ could not be detectable.

3.3. Estimation of syngenite and other hydrates in commercial portland cement.

The quantitative estimations of gypsum, syngenite and calcium hydroxide in twelve commercial cements and three pulverized clinkers were tried by measuring peak areas recorded in DTA and the results obtained were shown in Table 2.

Gypsum: In commercial cements, the contents of gypsum, possible amounts of hemihydrate being calculated as dihydrate in this work, varied over

the range from zero to 1.7 in weight percent, that is, the ratios of SO_3 content as in the form of calcium sulfate dihydrate to the total SO_3 were ranging from zero to 46% with a mean value of 12.6%, indicating that gypsum added to clinker in a mill might be almost dehydrated by the heat generated through ball milling.

Syngenite: The amounts of syngenite were estimated to be from zero to 1.2%, that is, the ratios of SO_3 content as in the form of syngenite to the total SO_3 were ranging upto 37% with a mean value of 15.5%. It is noteworthy that many cements contain a perceptible amount of syngenite with a loss of calcium sulfate dihydrate. Though

Fig. 9. The contents of syngenite versus that of K_2O in commercial portland cements.

Table 2. Contents of gypsum, syngenite and calcium hydroxide in commercial portland cements and clinkers.

Sample	$\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$	SO_3 as $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$	$\text{K}_2\text{SO}_4 \cdot \text{CaSO}_4$	SO_3 as syngenite	$\text{Ca}(\text{OH})_2$	CaO as $\text{Ca}(\text{OH})_2$	Summation (Σ)	Σ
Cement	(I)	Total SO_3	(II)	Total SO_3	(III)	Total free lime	of H_2O in hydrates I, II, III	lg. loss
No.	(%)	(%)	(%)	(%)	(%)	(%)	(%)	(%)
58	0.1	2	0.8	25	0.6	110	0.2 ₃	36
59	1.7	49	0.0	0	0.4	65	0.4 ₇	76
60	0.2	6	1.0	29	1.1	89	0.4 ₃	61
61	0.7	15	0.9	21	0.8	96	0.4 ₂	48
62	0.4	12	0.3	8	0.4	73	0.1 ₈	30
63	0.2	6	1.2	37	2.0	100	0.7 ₁	71
64	0.0	0	1.0	22	0.0	0	0.0 ₁	3
65	0.2	7	0.3	9	0.2	65	0.0 ₆	23
66	0.6	15	0.0	0	0.9	84	0.3 ₆	47
01	0.4	9	1.0	23	0.6	98	0.3 ₁	37
02	0.7	18	0.0	0	0.3	66	0.2 ₁	25
03	0.8	15	0.6	12	0.2	55	0.2 ₅	33
means	0.50	12.6	0.59	15.5	0.63	75.1	0.31	40.8
clinker								
1					0.6	59		
2					0.4	55		
3					0.4	64		

it might have been anticipated that an obvious relation between K_2O contents and the amounts of syngenite would be given for the samples tested, it appears from Figure 9 that this is not usually the case.

Calcium hydroxide: In a fresh clinker free lime is entirely present as calcium oxides, but in a ground cement a considerable portion of the total free lime has been found to present in the hydrated form as calcium hydroxide⁸⁾. The amounts of $Ca(OH)_2$ varied over the range from zero to 2.0% by weight of samples, that is, the ratios of $Ca(OH)_2$ content to the total free lime determined by means of the modified alcohol-glycerol method reached to maximum 100%, but with a mean value of 75.1%.

As seen in Table 2, the total amount of water combined to gypsum, syngenite and calcium hydroxide was found to be 0.31 wt.% on the average and the ratio of which to ignition loss shown in Table 1 be 40.8%, suggesting that as a remainder there would be a considerable amount of adhesive or loosely bound water in addition to carbonate.

4. Summary

The species of hydrous materials present in commercial portland cements were investigated by means of DTA and Karl Fischer reagent and as

a result, syngenite $K_2SO_4 \cdot CaSO_4 \cdot H_2O$, in addition to gypsum and calcium hydroxide, could be detected on several cements tested. Syngenite reveals a distinct endothermic peak at 270°C on DTA curve, and from the peak areas measured for twelve commercial cements, the syngenite contents were estimated to be maximum 1.2 wt.% with a mean value of 0.59 wt.%. The gypsum content was found to be reduced to a mean value of 0.5 wt.% presumably owing to the dehydration during ball milling, while the ratio of calcium hydroxide to the total free lime reached a value of 75.1%.

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市販ポルトランドセメント中, Syngenite の存在

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市販ポルトランド中にどのような種類の含水化合物が存在するかを、示差熱分析およびカルフィッシャー試薬を用いる水分測定法により検討したところ、試料セメントによっては、石膏、水酸化カルシウムのほかに Syngenite ($K_2SO_4 \cdot CaSO_4 \cdot H_2O$) が生成していることを認めた。Syngenite は、DTA 曲線において 270°C に顕著な吸熱ピークを示し、そのピーク面積からの定量

によると 12 個の試料のうち最大 1.2%, 平均 0.59% の含有量を示した。2 水塩としての石膏の含有量は、平均 0.5% にとどまり、おそらくボールミル粉碎中に大部分脱水していること、および全遊離石灰中、平均 75% の酸化カルシウムは $Ca(OH)_2$ の形で存在することを知った。

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