# Cementitious Materials of Pozzolanic Type Prepared from Red Mud

# and Fly Ash with Gypsum and Portlandite as Activators

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#### **Abstract**

Bauxite from Australia contains boehmite which remains intact in the red mud after extraction of alumina. Therefore, this kind of red mud can be used as cementitious mateirals without clinkering process. Gypsum and/or portlandite were added to the red mud as activators. Two series of mixtures were prepared to produce ettringite and/or  $C_4AH_{13}$ . These cementitious mixtures called the red mud mixes are hydraulic themselves. Howevr, they are no use as cementitious materials due to the unstable hydration strength. To improve this defect fly ash was introduced to the red mud mixes together with 7 percent extra addition of portlandite to the fly ash. Thus, cementitious materials of pozzolanic type with moderately high strength have been obtained by water curing, resulting compressive strength up to 9.7, 16.4 and 20.1 MPa at 7, 28 and 91-day ages, respectively. Depressions of strength encountered in some specimens especially in air curing have been improved by blending fly ash and more activators. The depressions are closely related to the disintegrations of ettringite,  $C_4AH_{13}$  and/or  $C_4AH\bar{C}H_{12}$ .

#### 1. Introduction

Alumina is usually manufactured from bauxite by the Bayer process, smelting with sodic solution in autoclaves. After extraction of alumina from bauxite, there remains huge amount of waste called "red mud", mainly composed of hematite. The annual production of this by-product reaches 2 million tons in Japan<sup>1)</sup>, although full operation is now restricted due to international economic competitions.

Australian bauxite exported to Japan comprises some amount of boehmite,  $Al_2O_3 \cdot H_2O$ , in addition to gibbsite,  $Al_2O_3 \cdot 3H_2O$ , as Al-bearing mineral due to weak metamorphism of ores. Accordingly, boehmite remains intact in the red mud because of the incapability of dissolving this mineral by the Bayer process completely. Therefore, cementitious materials of pozzolanic type can be produced from this kind of red mud by introducing some effective activators into the red mud to react with boehmite. Since energy crisis of petroleum, constructions of power stations of coal combution types have been becoming popular in Japan and the production of byproduct fly ash is estimated to be 12 million tons near the end of this century in Japan<sup>2)</sup>. We should, therefore, pay keen attention to the effective use of red mud and fly ash in view of conservations of natural resources and environmental problems arising from simple reclamations.

<sup>\*</sup>Department of Mining and Mineral Engineering Cement chemical notations, C: CaO, A:Al<sub>2</sub>O<sub>3</sub>, S:SiO<sub>2</sub>, H:H<sub>2</sub>O, \$\bar{S}:SO\_3\$ \$\bar{C}:CO\_2\$

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The possibility of the production of this kind of cementitious materials utilizing red mud and fly ash has been already reported in the previous work in which stress was placed on the hydration and SEM observations<sup>3)</sup>. It is pointed out that present cementitious materials of pozzolanic type are apt to deteriorate in long term, especially in air despite the moderately high strength. In this paper mixing proportions including more activators will be studied and the optimum conditions of mixing will be investigated.

# 2. Experimental

#### 2.1 Red mud

The red mud used in this study is soda-reduced red mud commercially sold from a company. They wash the soda-rich red mud with water, employing 7-stage anticurrent thickenners to reduce soda content down to 3 percent. It is generally said that the soda content of raw red mud is around 10 percent in alumina factories. According to XRD studies following minerals were identified in small amount in addition to hematite and boehmite: sodalite,  $2Na_2O \cdot 1 \cdot 7Al_2O_3 \cdot 3SiO_2 \cdot nH_2O^4$ , quartz, kaolinite, calcite and vaterite<sup>3)</sup>. The latter two minerals are not essential ones, but are secondary derivatives during washing process, since the washing water dissolves some lime as precipitation agent. Chemical composition of the soda-reduced red mud is given in Table 1. The amount of boehmite is estimated to be 13.7 percent in the red mud by calculation, neglecting the small presence of quartz.

#### 2.2 Fly ash

The fly ash used in this study is ordinary one from domestic coal. The chemical composition is given in Table 1. Small amount of quartz and mullite were found as crystalline phases in the glassy matrices of the fly ash by XRD and SEM.

#### 2.3 Activators

Gypsum and portlandite (slaked lime) of JIS first grade were employed as activators. Physical characteristics are given in Table 2 together with those of the other raw materials.

#### 2.4 Red mud mixes

As shown in Fig.1 and Table 3 two series and 10 mixtures were prepared by mixing red mud with gypsum and/or portlandite. These red mud mixes are hydraulic themselves. The series P has been already investigated in the previous work<sup>3)</sup>, and re-

Table 1 Chemical compositions of the red mud and the fly ash.

	$\mathrm{SiO}_2$	$TiO_2$	$\mathrm{Al_2O_3}$	$\mathrm{Fe}_2\mathrm{O}_3$	MnO	CaO	MgO	Na₂O	K <sub>2</sub> O	$SO_3$	lg. loss
Red mud	9.14	8.55	19.88	48.86	-	2.47	***	3.02	-	_	8.51%
Fly ash	58.00	1.10	21.40	5.22	0.04	2.84	2.64	1.40	2.29	0.18	4.40*

<sup>\*</sup>Mainly carbon.

Table 2 Physical characteristics of raw mater	nal	ria	ria	er:	e:	tε	ìt	a'	na	n	W	ray	of	S	l characteristics	al	ivsica	Ph	2	hle	Та	
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Red mud	8,600	cm²/g	3.33
Gypsum	1,900		2.32
Portlandite	11,600		2.24
Fly ash	1,600		2.03

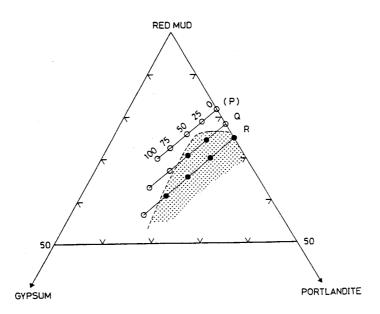


Fig. 1 Triangular representation of the mixing proportions of the red mud mixes. See the text 3.2 and Table 6 for the shaded part, showing stable strength.

Table 3 Mixing proportions of the red mud mixes

		Mix-100	Mix-75	Mix-50	Mix-25	Mix-0
Series(P)*	Red mud	70.0	73.0	76.0	78.9	81.9%
	Gupsum	18.4	13.8	9.2	4.6	-
	Portlandite	11.6	13.2	14.8	16.5	18.1
Series Q	Red mud	63.3	67.1	70.9	74.6	78.3%
	Gypsum	23.3	17.5	11.6	5.8	-
	Portlandite	13.4	15.4	17.5	19.6	21.7
Series R	Red mud	56.8	61.3	65.8	70.3	74.8
	Gypsum	28.1	21.1	14.0	7.0	
	Portlandite	15.1	17.6	20.2	22.7	25.2

<sup>\*</sup>Previous work3) and the base of mixing.

presented here again for convenience. Mixing proportions of each series were determined on the basis of those of series P. First of all, mixes of two extremes, mix-100

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(100-0) \* and mix-0 (0-0) \* were determined to give maximum formations of ettringite or  $C_4AH_{13}$  at 7-day, respectively. The other mixes, 75, 50 and 25 were determined by simply dividing the amount of activators between the two extremes into following proportions, 3:1(75-0)\*, 1:1(50-0)\* and 1:3(25-0)\*. Gypsum and portlandite act reversely each other. Neglecting the potential of C-S-H and the minor Ca-carbonate in the red mud, series R accords with stoichiometric compositions to form ettringite and  $C_4AH_{13}$  other than sodalite and kaolinite in this manner in coincidence.

# 2.5 Red mud mixes with fly ash

In order to improve long term strength of the red mud mixes, fly ash blended with 7 percent extra portlandite was added to the red mud mixes in proportions of 1:1(-

	1:1	1:2	1:3
Red mud mix	50.0	33.3	25.0%
Fly ash	46.8	62.3	70.1
Portlandite-extra	3.2	4.4	4.9

Table 4 Contents of the red mud mixes with fly ash.

1)\*\*, 1:2(-2))\*\* and 1:3(-3)\*\* in the increasing order of the fly ash. This portlandite acts as an extra activator in appearance. The contents of these mixtures are given in Table 4.

# 2.6 Curing and testing

Cementitious materials of the red mud mixes were tested on flexural and compressive strengths at 3, 7, 28 and 91-day ages. Small scale test pieces were prepared in the molds of  $1 \times 1 \times 4$  cm dimension in state of paste with W/S 0.40, i.e., two pieces for flexural strength and derived four for compressive strength. Demolding after 3-day curing in humid air of 90 percent R.H., the test pieces were cured in water in semi-

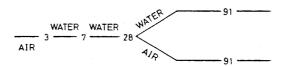


Fig. 2 Curing scheme of the cementitious materials.

<sup>\*</sup> Identical to the numerical notations in Tables 5 and 7, the last zero indicating no blend of the fly ash, i.e., the red mud mixes themselves.

<sup>\*\*</sup> Identical to the last numerals of the notations in Tables 6 and 7, when fly ash is introduced.

airtight plastic containers at 20°C. As illustrated in Fig. 2, the test pieces were divided into two groups at 28-dag age. The water curing was continued for one group, whereas air curing was carried out in 90 percent R.H. condition for the other group. The air circulates spontenously. The object of this curing is to study the deteriorations, when cured in air.

## 2.7 Identification of hydrates

Test pieces after the strength test were preserved in acetone and served for the identification of hydrates by means of XRD, using Mn-filtered Fek $\alpha$  radiation at  $30 \mathrm{KV}$  and  $10 \mathrm{mA}$ .

# 3. Results and Discussion

# 3.1 Strength of the red mud mixes

Results of the strength test are summarized in Table 5. Generally speaking, for both series Q and R decreasing of flexural strength is remarkable as found in series P in previous wrok<sup>3)</sup>. This trend is also observed on compressive strength in many specimens especially in later ages. The mixes 0-0 of both series contain no gypsum and show low strength.

Table 5 F	Flexural and	compressive	strengths	for t	he rec	l mud	mixes.
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3	7	28	91	—days—	3	7	28	91
3.9	3.1	1.7	1.6	Q100-0*	8.3	8.1	8.6	6.4
			(1.5)					(6.8)
5.4	3.2	5.1	4.1	75-0	10.1	10.4	13.9	16.4
			(1.7)					(13.6)
3.8	5.6	3.7	2.6	50-0	13.9	17.4	17.3	15.6
			(1.3)					(19.6)
2.6	3.2	2.5	2.3	25-0	7.7	8.8	9.3	8.9
			(0.5)					(6.0)
0.9	1.3	0.5	0.6	0-0	2.4	3.2	4.1	2.6
			(0.2)			٠		(2.5)
3.1	2.6	2.1	2.3	R100-0*	8.2	6.9	5.8	5.1
			(2.1)					(7.4)
3.1	2.3	2.3	2.2	75-0	7.8	7.2	7.2	5.9
			(1.9)					(6.7)
4.7	4.2	3.8	3.8	50-0	10.4	12.2	11.6	12.3
			(-)					(6.8)
3.6	3.4	3.1	2.7	25-0	8.3	11.6	10.8	11.9
			(-)					(8.4)
1.1	1.0	0.2	1.0	0-0	1.8	2.5	2.7	3.4
			(0.4)					(2.6)

Mean values in MPa. () air curing. \* 0 indicating no fly ash.

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For series Q mixes 75-0 and 50-0 give rise generally good results. However, at 91 -day age some depressions are noticed on these mixes. Though the compressive strength is higher for 50-0 cured in air, the flexural strength becomes very low, i.e., specimens become brittle. The mix 25-0 shows unstable strength at 91-day age with great fluctuation, when cured in air.

For series R mixes 50-0 and 25-0 show the saturation of strength, probably due to the exhaution of boehmite reacted with the sufficient amount of activators and depressions take place at 91-day age, when cured in air, showing cracks on the specimens and the flexural strength is too unable to be determined.

# 3.2 Strength of the red mud mixes with fly ash

Table 6 Flexural and compressive strengths for the red mud mixes with fly ash.

3	7	28	91	—days— 3 7	28	91	3	7	28	91	—days—	3	7	28	91
-	1.7	4.6	4.0	Q100-1* - 3.5	10.1	15.1	_	1.6	3.2	5.7	R100-1*	_	3.3	5.2	15.2
			(2.3)			(12.9)				(0.8)					(2.8)
-	4.3	5.0	2.9	75-1 - 9.4	13.2	18.5	-	1.8	4.5	3.7	75-1	~	4.0	10.1	14.9
			(1.2)			(6.0)				(2.5)					(16.0)
-	4.1	4.3	3.1	50-1 - 8.1	12.2	16.8	-	4.6	4.4	3.8	50-1		9.7	16.4	20.1
			(2.8)			(15.1)				(5.0)					(18.8)
-	2.6	2.7	3.7	25-1 - 7.2	15.2	16.6	-	4.1	4.4	4.6	25-1	-	9.2	13.0	17.7
			(2.8)			(15.6)				(3.3)					(17.7)
-	1.6	2.8		0-1 - 6.9	12.0	14.0	-	3.1	3.1	3.3	0-1	-	6.5	12.1	14.6
			(2.4)			(13.0)				(3.3)					(13.4)
~	0.8	3.8	3.3	Q100-2* - 1.8	7.1	11.2	-	0.8	3.4	3.8	R100-2*	-	1.7	7.0	13.9
			(1.8)			(10.3)				(0.6)					(3.9)
	2.8	3.9	3.6	75-2 - 5.6	8.8	13.5	-	0.9	3.3	2.6	75-2	-	1.9	6.4	13.6
			(0.3)			(2.4)				(2.2)					(12.3)
-	2.5	3.5	3.2	50-2 - 5.0	9.0	14.2	-	2.8	3.6	3.8	50-2		6.0	11.3	14.6
			(2.1)			(11.3)				(3.8)					(16.9)
-	2.0	3.0	3.8	25-2 - 4.7	8.7	12.0	-	3.0	3.0	3.6	25-2	-	5.1	9.4	11.4
			(2.6)			(11.8)				(3.5)					(11.4)
-	1.3	3.4	3.3	0-2 - 4.8	10.4	7.8	-	2.9	3.1	3.3	0-2	-	4.3	9.0	11.4
			(2.1)			(10.8)				(2.5)			-		(11.2)
-	0.6	2.6	2.4	Q100-3* - 1.2	4.8	8.1	-	0.5	3.6	3.6	R100-3*	-	1.2	6.5	10.7
			(0.6)			(4.2)				(0.4)					(2.9)
-	1.9	2.7	2.7	75-3 - 4.2	7.1	11.3	-	0.8	2.3	2.6	75-3	-	1.8	5.5	11.2
			(0.3)			(3.0)				(2.0)					(10.1)
-	1.5	2.5	2.3	50-3 - 3.2	5.6	9.6	-	1.7	2.7	2.9	50-3	-	4.1	9.2	12.0
			(8.0)			(8.2)				(2.8)					(12.8)
***	0.8	2.4	3.2	25-3 - 2.9	7.3	9.4	-	1.8	2.4	2.8	25-3		3.3	6.3	10.5
			(2.1)			(8.4)				(2.4)	•				(8.9)
-	1.4	2.4	2.7	0-3 - 3.4	8.3	9.2	-	1.9	2.3	3.0	0-3	-	3.3	8.0	10.5
			(2.0)			(7.8)				(2.1)					(8.7)

Mean values in MPa. () air curing. \* Numerals 1, 2 and 3 indicating the ratios 1:1, 1:2 and 1:3, respectively.

Results of the strength test are summarized in Table 6. Generally speking, for both series Q and R decreasing of flexural strength is not found up to 28-day age and only observed at 91-day age in many specimens of both types of curing. The strength is dependent on the content of fly ash, especially in early age, i.e., more fly ash makes the strength decrease in early age, but it is worthy to note that the depressions of strength are improved in some specimens of series Q and many specimens of series R.

In series Q abrupt depressions of flexural and compressive strengths are observed at 91-day age for the specimens, 75-1, 75-2, 75-3, and 100-3 cured in air. For specimens 0-2 cured in water depressions are also noticed at 91-day age. On the whole mixes 50-1, 50-2, 25-1 and 25-2 are superior to the others and no depressions of compressive strength were encountered.

In series R abrupt depressions of flexural and compressive strengths are observed at 91-day age for the specimens 100-1, 100-2 and 100-3, when cured in air. On the whole, the mixes 50-1, 50-2, 50-3, 25-1 and 25-2 are superior. Although, the mix 0-1 is good in strength, it may be difficult to use in practice owing to low workability of the paste<sup>3)</sup>.

#### 3.3 Hydrates

Hydrates identified are summarized in Table 7 only limiting at 91-day age for saving space.

#### 3.3.1 For the red mud mixes

When gypsum is present, formation of ettringite prevails as seen in the mixes 100 and 50-0. However, C<sub>4</sub>AH<sub>13</sub> begins to form gradually with occasional carbonation and finally no ettringite exists in the mix 0-0 containing no gypsum. It is curious that no C<sub>4</sub>AH<sub>13</sub> forms in the mixes 100-0 and 75-0 having some potentials of  $C_4AH_{13}$ . This may be explained to consider the limited solid solution series of  $C_6A\bar{S}_3$  $H_{32}$  –  $C_6AH_{32}$  <sup>5,6)</sup>. Sometimes  $C_4AH_{13}$  (strictly saying this should be  $C_4A\bar{C}_{0.5}H_{12}$  <sup>7)</sup>) converts to C<sub>4</sub>A\(\bar{C}\)H<sub>12</sub> by carbonation, especially in later age. Disintegration of ettringite takes place in some specimens cured in air. This will be discussed later in detail. Calcite exists from the beginning of curing, since the red mud contains some calcite and vaterite. However, most of the calcite would be derived from admixed portlandite due to carbonation. Much calcite is detected in the specimens cured in air at 91-day age. Formation of Ca-monosulphate was scarcely detected. Presence of type II C-S -H was reported in the previous work<sup>3)</sup> by means of SEM, but the C-S-H probably formed was not clearly identified by XRD. Judging from the amount of activators left in specimens cured in water at 91-day age, gypsum is wanting for the reactions except 100-0, while portlandite is sufficient except 0-0 in serise Q. In series R gypsum is also wanting except 100-0, while portlandite is in excess. It is found that most of the depressinos of strength is caused by the disintegrations of ettringite, C<sub>4</sub>AH<sub>13</sub> and/or  $C_4A\bar{C}H_{12}$  as seen in Table 5.

#### 3.3.2 For the red mud mixes with fly ash

Hydrates are similar to those of the red mud mixes. When gypsum is present, ettringite forms preferentially. With increasing content of portlandite,  $C_4AH_{13}$  is

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observed as well as C<sub>4</sub>ACH<sub>12</sub>. Since these mixes comprise fly ash blended with 7 percent extra portlandite, increase of the content of portlandite takes placee into two directions. One is the direction from mix 100 to mix 0 via mixes 75, 50 and 25. The other is the direction from mix 1:1 to mix 1:3 via mix 1:2. Therefore, formations of  $C_4A\bar{H}_{13}$  and  $C_4A\bar{C}H_{12}$  become popular, when compared with the hydration of the red mud mixes, especially in mixes 1:2 and 1:3. Formation of Ca-monosulphate is scarce and not distinct generally. Calcite exists from the beginning more or less and much formation of this mineral is seen in specimens cured in air at 91-day age. Disintegrations of ettringite  $C_4AH_{13}$  and  $C_4A\bar{C}H_{12}$  are worthy to note. These phenomena are closely related to the depressions of strength at 91-day age, when cured in air as seen in the specimens 75-1, 75-2, 75-3, and 100-3 in series Q, and 100-1, 100-2, and 100-3 in series R. Other depressions are also mostly related to these disintegrations as seen in Table 6. It seems that the rate of consumption of gypsum is fast and the amount is generally wanting, while that of portlandite is slow and is generally sufficient. Portlandite is apt to convert to calcite especially in air curing at 91-day age. C-S-H probably formed was not clearly identified by XRD8. However, this may be present as reported previously by SEM<sup>3)</sup>.

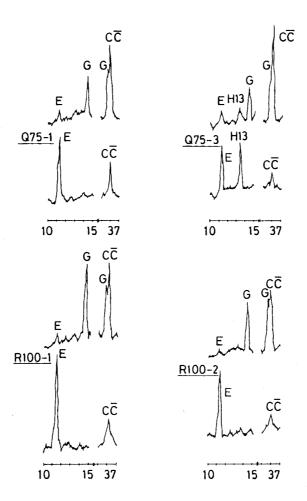


Fig. 3 XRD diagrams of FeK $\alpha$  showing the disintegrations of hydrates. Top, air curing, bottom, water curing for each set. Notations, see Table 7.

Table 7 Hydrates identified in present cements in relation to gypsum and portlandite. Listed only for 91-day age in relative amounts.

	O100 0	075.0	OFA A	005.0	Λ0.0
	Q100-0	Q75-0	Q50-0	Q25-0	Q0-0
E	++++	++++	++++	++	-
	(++++)	(++++)	(++++)	(+++)	(-)
H13	-	_	_	++	++
	(-)	()	(-)	(-)	(+)
ČH12	_		++	+ + + +	++++
	(-)	(-)	(-)	(-)	(++)
CĈ	++	+	+	+	+
	(+++)	(++++)	(++++)	(++++)	(++++)
G	+	_	_	_	_
ļ	(++)	(-)	(-)	(-)	(-)
P	+	+	+	+	
	(+)	(+)	(+)	(-)	(-)
	R100-0	R75-0	R50-0	R25-0	R0-0
E	++++	++++	++++	+++	_
	(++++)	(++)	(++++)	(++)	(-)
H13	_	_	-	++	++
	(-)	(-)	(-)	(-)	(++)
ČH12	_	_	+	++	++++
	(-)	(-)	(-)	(-)	(+++)
СĒ	+	+	+	+	+
	(++++)	(++)	(++++)	(++++)	(++++)
G	++++	_	_	_	_
_	(++++)	(+)	(-)	(-)	(-)
P	++	++	+	++	++
	(+)	(+)	(-)	(+)	(-)

	Q100-2	Q75-2	Q50-2	Q25-2	Q0-2
Е	+++	+++	++	+	-
	(+++).	(-)	(++)	(+)	(-)
H13	_	++	++	+++	++
	(-)	(-)	(-)	(++)	(+)
ČH12			-	+	++
	(-)	(-)	(-)	(+)	(+)
CĒ	+	+	+	+	+
L	(++)	(+ + + +)	(++)	(+++)	(+++)
G	-	_	-	-	_
	(-)	(++)	(-)	(-)	(-)
P	vocare	+	+	+	-
	(+)	(-)	(-)	(-)	(-)
	R100-2	R75-2	R50-2	R25-2	R0-2
Е	++++	+++	+++	+	_
	(-)	(+++)	(++)	(+)	(-)
H13	-	+	++	++	++
	(-)	(-)	(+)	(+)	(+)
CH12	-	_	-	+	++
	(-)	(-)	(-)	(+)	(+)
CĒ	+	+	+	+	+
	(++)	(++)	(++)	(++)	(+++)
G	_	_	-	_	-
	(+++)	(-)	(-)	(-)	(-)
P	+	+	_	-	+
	(-)	(-)	(-)	(-)	(-)

( ) air curing. E:ettringite, H13:  $C_4$  AH<sub>13</sub>, $\bar{C}$ H<sub>12</sub>:  $C_4$ A $\bar{C}$ H<sub>12</sub>, $C\bar{C}$ : calcite, G: gypsum, P: portlandite. Peak height of XRD, ++++: large, +++: medium, ++: small, +: detectable, -: undetectable.

DIC,		ciccian			
	Q100-1	Q75-1	Q50-1	Q25-1	Q0-1
E	++++	++++	+++	++	_
	(++++)	(+)	(+++)	(++)	(-)
H13			++	+++	++
	(-)	(-)	(+)	(+)	(+)
ĒН12	_	-	-	+	. ++
_	(-)	(-)	(-)	(+)	(+)
CĈ	+	+	+	+	+
	(++)	(+++)	(+++)	(+++)	(+++)
G		-		_	_
	(-)	(++)	(-)	(-)	(-)
P	+	+	+	+	
	(+)	(-)	(+)	(-)	(-)
	R100-1	R75-1	R50-1	R25-1	R0-1
E	+ + + +	+ + + +	+++	++	
	(+)	(++++)	(+++)	(++1)	(-)
H13	_	-	+	++	++
_	(-)	(-)	(+)	(++)	(+)
ČH12	-		-	++	++
	(-)	(-)	(-)	(+)	(+)
CĒ	+	+	+	+	+
	(+++)	(++)	(++++)	(++)	(++++)
G	_	-	_	_	
	(++++)	(-)	(-)	(-)	(-)
P		_	-		· -
	(-)	(-)	(+)	(-)	(-)

	Q100-3	Q75-3	Q50-3	Q25-3	Q0-3
E	+++	+++	++	+	_
	(++)	(+)	(++)	(+)	(-)
H13	+	+++	++	+++	+
	(-)	(+)	(+)	(++)	(+)
ČH12	-	_	_	+	+
	(-)	(-)	(-)	(+)	(+)
CČ	+	+	+	+	+
	(++)	(++++)	(++)	(++)	(++)
G	-	_	+	-	
	(+)	(++)	. (-)	(-)	(-)
P	+	+	_	_	+
	(-)	(-)	(-)	(-)	(-)
	R100-3	R75-3	R50-3	R25-3	R0-3
E	++++	+++	++	++	_
	(-)	(+++)	(++)	(+)	(-)
H13	_	+	++	++	++
	(-)	(-)	(+)	(+)	(+)
ČH12	_	-	-	+	++
_	(-)	(-)	(+)	(+)	(+)
ČС	+	+	+	+	+
	(++)	(++)	(+++)	(++)	(+++)
G	_	-	· -	_	-
, ·		/ /	( )	(-)	(-)
	(+++)	(-)	(-)	( )	١ /
P	(+++) - (-)	(+)	( <del>-</del> ) - (+)	_ (-)	()

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# 3.3.3 Disintegrations of ettringite, $C_4AH_{13}$ and $C_4A\bar{C}H_{12}$

As seen in Fig. 3 and Table 7 disintegrations of these minerals are found to occur partly or completely in some specimens cured in air at 91-day age. Judging from XRD results, following reactions would take place in the course of curing.

For ettringite:  $C_6A\bar{S}_3H_{32}+3\bar{C}=3C\bar{S}H_2+AH_3+3C\bar{C}+23H$ 

Consequently, ettringite disintegrates into gypsum, gibbsite and calcite in addition to water, but the gibbsite is hardly detected due to the ill-crystalline nature in the early stage of formation.

For 
$$C_4AH_{13}$$
 and  $C_4ACH_{12}$ :  $C_4AH_{13}+\bar{C}=C_4A\bar{C}H_{12}+H$   
 $C_4A\bar{C}H_{12}+3\bar{C}=AH_3+4C\bar{C}+9H$ 

Consequently, the both minerals disintegrate into gibbsite and calcite in addition to water.

If these three reactions take place independently or simultanously, depressions of strength are induced, depending on the degrees of disintegrations. However, it is quite curious that no depressions of strength were encountered in haüyne-belite cement cured in steam, in which ettringite and C-S-H are essential hydrates and disintegration of the ettringite occurs, when subjected to air after the steam curing<sup>9)</sup>.

# 4. Summary and Conclusion

"Red mud cement" can be made from soda-reduced red mud, when activated with gypsum and/or portlandite. Boehmite included in the red mud plays an important role in present cementitious materials of pozzolanic type. Many kinds of hydraulic materials are able to be manufactured, varying the proportions of the red mud and the activators. However, these materials are generally unstable in strength. This defect is improved by introducing fly ash blended with 7 percent extra portlandite as seen in Table 6 and Fig.1. Thus, hardened cementitious materials, for instance, showing compressive strength of 9.7, 16.4 and 20.1 MPa at 7, 28 and 91-day ages were obtained, respectively. Some specimens show depressions of strength, when cured in air. It is found that the depressions are caused by the disintegrations of ettringite, C<sub>4</sub> AH<sub>13</sub> and/or C<sub>4</sub>ACH<sub>12</sub> being essential hydrates in present cementitious materials in addition to type II C-S-H. Further investigation would be necessary in order to make clear the disintegrations of these minerals in various curing conditions. Although present hydraulic materials show modelately high strength, they stain hands red with ease due to softness of the surface of hardened materials. This defect could be improved by coating with plaster of Paris and so on.

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