Study on Properties of Environment-friendly Concrete Containing Large Amount of Industrial by-products

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Abstract. This study aims to reduce CO₂ discharged from the cement and concrete industries by effective use of industrial by-products, such as fly ash, blast furnace slag, and so on. In this paper, the properties of concrete containing large amount of industrial by-products and very small amount of alkaline activator including cement or sludge from ready mixed concrete plant are analyzed. As the result, it was confirmed that concretes containing large amount of industrial by-products can achieve sufficient compressive strength. However, these concretes showed poor frost resistance. It was thought that the reason was coarsening of air void system and this caused their poor frost resistance. Therefore, in order to micronize the air void system and improve frost resistance, the combination of air entraining agent and antifoaming agent was applied. By this method, it was confirmed that the frost resistance of some these concrete improved. In this study, other properties of these concretes, such as fresh properties and other durability were evaluated and it was confirmed that these concretes show sufficient properties.

1. Introduction
In the recent years, a reduction in the amount of resources required for infrastructure construction has been demanded. Moreover, minimizing the life cycle cost of structures serves to reduce CO₂ emissions. The use of high-strength concrete allows increasing durability of structural components, thus leading to reductions in life cycle costs. However, when large amounts of cement are used in the production of high-strength concrete, the environmental load is high. In cement manufacturing, CO₂, which is a greenhouse gas, is discharged in large quantities. Among the sectors of the Japanese economy, the manufacturing industry in general, and the cement industry in particular, account for 46% and about 4% of CO₂ emissions, respectively. To manufacture 1000 kg of cement, it is supposed that the total amount of CO₂ emissions is 800 kg, including materials, fuel and other sources [1]. For this reason, if the use of Portland cement can be reduced through effective utilization of fly ash and blast furnace...
slag, which are industrial by-products, reductions in CO\textsubscript{2} emissions can be realized.

Under these circumstances, some new cement compositions that are more environmentally suitable have been studied recently. One of them is the so-called alkaline cement; it is produced by alkali activating silico-aluminous materials. The research on the mixture of Metakaolin and calcium hydroxide shows that sodium aluminosilicate is the main reaction product. Additionally, the formation of C-S-H gel as a secondary product is also observed [2], [3]. Geopolymer is another secondary product [4]. Some experiments were performed on the blended cements containing 30\% Portland cement and 70\% fly ash. The powdery material was mixed with two different alkaline solutions for alkaline activation. The mechanical strength developed by this blended cement differed significantly depending on the hydrating solution used. All samples consisted of a mixture of amorphous gels (C-S-H + N-A-S-H gel).

In this research, Portland cement was either not used or the quantity used was greatly reduced, and instead large quantities of industrial by-products such as blast furnace slag and fly ash were used, with the objective of developing high strength concrete with a compressive strength of 60 N/mm\textsuperscript{2} after standard curing for 28 days.

To achieve satisfactory performance of such concrete, alkaline activators must be added and their performance is very important.

In this paper, 3 types of calcium hydroxide, 2 types of Portland cement and concrete sludge from ready-mixed concrete plants were used as alkaline activators. The hardened properties, the fresh properties, and the durability of these concrete were investigated. Low frost resistance was observed in the first test series, and in the second test series, poor frost resistance was improved.

2. Test series I: Fundamental properties of environment-friendly concrete produced using various alkaline activators

2.1. Outline of tests

2.1.1. Materials used.

The materials used are shown in table 1. The main materials were fly ash and blast furnace slag. Anhydrous gypsum was also used as an admixture in order to ensure early strength. Fly ash and blast furnace slag do not harden if alkalinity is not supplied. Therefore, 3 types of calcium hydroxide were used: ultra-fine porous calcium hydroxide (TK) with BET specific surface area of 46m\textsuperscript{2}/g, special calcium hydroxide (CHs), and usual calcium hydroxide (CH1) with a purity and cost lower than CHs. The property values of calcium hydroxide are shown in table 2. Concrete sludge (SD) from ready-mixed concrete plants obtained by drying the sludge for 24 hours at 200\degree C and pulverizing to a fine powder was used as an alkaline activator. In addition, 2 types of cement were used as the most common alkaline activators: ordinary Portland cement (OPC) and a prototype cement (MPC).
Table 1. Materials.

| Materials   | Symbol | Type                                      | Density (g/cm³) |
|-------------|--------|-------------------------------------------|-----------------|
| Binder      | FA2    | Fly ash Type 2 (JIS A 6201)               | 2.20            |
|             | BS4    | Blast furnace slag (JIS A 6206, Specific surface area 4000 cm²/g) | 2.90            |
| Alkaline    | AG     | Anhydrous gypsum                          | 2.90            |
| Activator   | TK     | Ultra-fine porous calcium hydroxide        | 2.24            |
|             | CHs    | Special calcium hydroxide                 | 2.24            |
|             | CH1    | Type 1 calcium hydroxide                  | 2.24            |
|             | SD     | Ready-mixed concrete sludge               | 2.21            |
|             | OPC    | Ordinary Portland cement (JIS A 5210, similar to CEM I 42.5N) | 3.16            |
|             | MPC    | Prototype cement                          | 3.16            |
| Water       | W      | Tap water                                 | 1.00            |
| Sand        | S      | Crushed sand                             | 2.63            |
| Gravel      | G      | Crushed stone                            | 2.64            |
| Chemical    | SP     | High-range water reducing agent (Polycarboxylic acid ether) | 1.08            |
| Admixture   | DF     | Anti-foaming agent (Polyalkylene glycol conductor) | 1.00            |

The prototype cement had a high quantity of C₃S (alite) compared with OPC, so it was expected to increase the strength. Table 3 shows the chemical compositions and Blaine values.

Table 2. Properties of calcium hydroxide.

| Quality | TK | CHs | CH1 |
|---------|----|-----|-----|
| BET specific surface area (cm²/g) | 469000 | 15000 | 12000 |
| Average particle size (µm) | 6.0 | 9.4 | 12.0 |
| CaO (%) | 73.4 | 73.9 | Over 70 |

Table 3. Chemical compositions, Blaine values and mineral compositions of OPC and MPC.

| Symbol | Ig- loss (%) | SiO₂ | Al₂O₃ | Fe₂O₃ | CaO | MgO | SO₃ | TiO₂ | Specific surface area (cm²/g) | C₃S | C₂S | C₃A | C₄AF |
|--------|--------------|------|-------|-------|-----|-----|-----|------|-------------------------------|-----|-----|-----|------|
| SD     | --           | --   | --    | --    | --  | --  | --  | --   | --                            | --  | --  | --  | --   |
| OPC    | 0.99         | 20.69| 5.52  | 3.14  | 63.44| 2.03| 2.27| 0.30 | 3330                          | 52.97| 19.54| 9.32| 9.56 |
| MPC    | 1.06         | 19.24| 5.37  | 3.42  | 64.82| 1.91| 2.80| 0.28 | 4780                          | 68.71| 3.50 | 8.44| 10.41|

Table 4. Mixing conditions.

| Slump flow (mm) | Air content (%) | W/(B+A)* (%) | S/(B+A)* (%) | Xv (%) |
|-----------------|-----------------|--------------|--------------|--------|
| 650±50          | ¥3.0            | 20.0         | 32.0         | 37.5   |

*B+A: Binder +Alkaline Activator
Table 5. Powder composition and mix proportions of concrete.

| Blend No. | Alkaline activators | W/(B+A)* (%) | Mass ratio (%) | Unit content (kg/m³) |
|-----------|---------------------|--------------|----------------|---------------------|
|           |                     | FA2 | BS4 | AG | A.A** | W | FA2 | BS4 | AG | A.A** | S | G |
| 1         | TK                  |     |     |    |        | 168| 336| 336| 84  | 84  | 269| 990|
| 2         | CHs                 |     |     |    |        | 168| 336| 336| 84  | 84  | 269| 990|
| 3         | CH1                 |     |     | 20 |        | 168| 336| 336| 84  | 84  | 269| 990|
| 4         | SD                  |     |     |    |        | 168| 336| 336| 84  | 84  | 269| 990|
| 5         | OPC                 |     |     |    |        | 171| 342| 342| 86  | 86  | 274| 990|
| 6         | MPC                 |     |     |    |        | 171| 342| 342| 86  | 86  | 274| 990|

* B+A: Binder + Alkaline Activator  **A.A: Alkaline Activators

2.1.2. Test conditions.
The blending conditions are shown in table 4. The water powder ratio was 20%, the fine aggregate to powder ratio was 32%, and the coarse aggregate absolute volume ratio Xv was 37.5% with the reference to the findings from the previous study [5]. The quantity of high-range water reducing agent was adjusted to obtain a slump flow of 650±50 mm, and the quantity of anti-foaming agent was adjusted to achieve an air content of 3.0% or less. Table 5 shows the powder composition. The mixing proportions of fly ash, blast furnace slag, anhydrous gypsum, and alkaline activator were constant for all mixes.

2.1.3 Method of blending and mixing.
A biaxial forced mixing type of mixer with a nominal capacity of 90 liters was used for mixing the concrete. The method of blending and mixing was to first add the powder and aggregate and carry out dry mixing for 1 minute, then water and water reducing agent were added and mixing was carried out until the target fluidity was obtained.

2.1.4. Test items.
(1) Fresh properties
(a) Slump flow tests
The slump flow tests were carried out in accordance with JIS A 1150. Concrete fluidity was measured in order to evaluate the quantity of SP added to achieve the required slump flow.
(b) Air content tests
Air content tests were carried out in accordance with JIS A 1128
(2) Hardened properties
(a) Compressive strength tests
Compressive strength tests were carried out in accordance with JIS A 1108. The strength was measured at 7 and 28 days after curing in water at 20°C.
(b) Static elastic modulus tests
Static elastic modulus tests were carried out in accordance with JIS A 1149. Measurements were carried out at 28 days after curing in water at 20°C.
(3) Durability
(a) Drying shrinkage tests
Drying shrinkage tests were carried out in accordance with JIS A 1129-3. The test specimens were prismatic test specimens 10×10×40 cm. Measurements were started after curing for 7 days in water at 20°C. The drying conditions were temperature 20°C and 60% relative humidity.
(b) Accelerated carbonation tests
Accelerated carbonation tests were carried out in accordance with JIS A 1153.
(c) Freezing and thawing tests
Freezing and thawing tests were carried out in accordance with JIS A 1148.

2.2. Test results and discussion

2.2.1. Fresh properties.
The fresh property test results are shown in table 6. When TK and SD were used as alkaline activators, the quantity of SP added to obtain the required fluidity was increased in both cases. This is considered to be caused by the following reasons – in the case of TK the particles were extremely fine and the specific surface area was high, so a large quantity of free water and water reducing agent were adsorbed, and in the case of SD its water adsorption is high. In these tests, especially in the case of SD, the dilatancy property was observed. Dilatancy easily occurs in mixtures of powders with uniform particle size and could be a problem in the casting process. The quantity of air was in the range 1.4 to 2.7\% as anti-foaming agent was used.

2.2.2. Hardened properties.
The results of the hardened property tests are shown in table 7. In the blends where TK, CHs, CH1, and SD were used as the alkaline activators, it was not possible to achieve 60 N/mm$^2$ at 28 days or higher. However, when cement was used as an alkaline activator, compressive strengths of about 70 N/mm$^2$ were obtained. In three cases where calcium hydroxide was used as the activator, the static elastic modulus obtained was slightly smaller.

Table 6. Fresh properties test results.

| Blend No. | Alkaline activators | Slump flow (mm) | Air (%) |
|-----------|---------------------|-----------------|---------|
| 1         | TK                  | 658             | 1.5     |
| 2         | CHs                 | 643             | 1.5     |
| 3         | CH1                 | 645             | 1.4     |
| 4         | SD                  | 690             | 2.7     |
| 5         | OPC                 | 710             | 1.6     |
| 6         | MPC                 | 678             | 1.8     |

Table 7. Hardened properties test results.

| Blend No. | Alkaline activator | Compressive strength (N/mm$^2$) | Static elastic modulus (kN/mm$^2$) |
|-----------|--------------------|---------------------------------|-----------------------------------|
|           |                    | 7-day  | 28-day  |                                      |
| 1         | TK                 | 40     | 56      | 35.5                               |
| 2         | CHs                | 39     | 53      | 35.7                               |
| 3         | CH1                | 34     | 49      | 32.0                               |
| 4         | SD                 | 42     | 52      | 39.4                               |
| 5         | OPC                | 55     | 67      | 38.3                               |
| 6         | MPC                | 56     | 79      | 37.6                               |
2.2.3. Durability.

(1) Drying shrinkage tests

The results of the drying shrinkage tests are shown in figure 1. In three cases in which calcium hydroxide (TK, CHs, CH1) was used, it was found that the amount of drying shrinkage tended to increase. In particular, it was found that for Blend No. 1, which used TK, the shrinkage was large. Drying shrinkage is caused by the surface tension effect acting between the particles of gel that constitute the cement paste, and the capillary tension effect acting on the meniscus formed by water between the particles. It is considered that by using TK the fine particle component of the powder is increased, so the number of fine voids increases, and hence the amount of shrinkage of Blend No. 1 increased. The amount of shrinkage was also small for Blend No. 5 and 6, which used cement as alkaline activator. This is considered to be due to the high compressive strength and high static elastic modulus.

However, the amount of drying shrinkage of all blends was not so large comparing to usual concrete. Therefore, it is thought that it is not such a severe problem.

(2) Accelerated carbonation tests

The variation in carbonation depth is shown in figure 2. In the blend which used SD and OPC as activators, it was found that the progress of carbonation was fast. This is considered to be conditioned by the fact that the calcium hydroxide content was low compared with the other three blends. On the other hand, in the previous research [6], the carbonation depth was about 13 mm at 26 weeks for ordinary concrete with W/C = 55%. Therefore, it is considered that the carbonation resistance is about the same as that for ordinary concrete.

![Figure 1. The tests results of drying shrinkage.](image-url)
(3) Freezing and thawing tests

The results of the freezing and thawing test are shown in Figure 3. Blends with sufficient frost resistance could not be obtained for all blending conditions. In particular, for three blends that used calcium hydroxide (TK, CHs, CH1) as the alkaline activator the degradation was large after 30 cycles. Normally to increase frost resistance it is effective to entrain 3 to 6% entrained air using an AE agent. However, in these tests an anti-foaming agent was used, with the aim of obtaining high strength concrete with improved resistance to freezing damage. However, for Blend Nos. 5 and 6, which had 28 day strengths of about 70 N/mm², the results showed large degradation in frost resistance. Therefore, in the next tests an appropriate amount of air was entrained using AE agent.

Figure 3. Frost resistance test results.
3. Test Series II: Tests to investigate the improvement in frost resistance in environment-friendly concrete

3.1. Outline of tests
In Test series II, the aim was to improve frost resistance by adding AE agent.

3.1.1. Materials used.
The materials used in this test are shown in table 1. An air entraining agent (AE) was used in addition to the materials used in Series I. And for alkaline activators, CHs, CH1, SD and OPC were used.

3.1.2. Test conditions.
The blending conditions are shown in table 8, and the powder composition is shown in table 9. In order to improve frost resistance, an appropriate quantity of AE agent was added to achieve an air quantity of 3.5±1.0% (All blend) and 4.5±1.0% (OPC blend only). Also, for the same reason the quantity of FA was reduced to 25%, the quantity of BS was increased to 50%, and the quantity of alkaline activator was increased to 15%.

3.1.3. Test items.
The test items of fresh properties were the same as for Test Series I, and compressive strength tests and freezing and thawing test were carried out in the same way as in Test Series I.

Table 8. Mixing conditions.

| Slump flow (mm) | Air content (%) | W/(B+A)* (%) | S/(B+A)* (%) | Xv (%) |
|-----------------|-----------------|--------------|--------------|-------|
| 650±50          | 3.5±1.0 / 4.5±1.0** | 20.0         | 32.0         | 37.5  |

*B+A: Binder +Alkaline Activator, **:OPC blend (Blend No.4-2) only.

Table 9. Powder composition and mix proportions of concrete.

| Blend No. | Alkaline activators | W/(B+A)* (%) | Mass ratio (%) | Unit content (kg/m³) |
|-----------|---------------------|--------------|----------------|---------------------|
| 1         | CHs                 | 166          | FA2 BS4 AG A.A** | W FA2 BS4 AG A.A** S G |
| 2         | CH1                 | 166          | 208            | 416 83 125 267 990 |
| 3         | SD                  | 166          | 208            | 416 83 125 267 990 |
| 4-1       | OPC                 | 171          | 214            | 428 86 128 274 990 |
| 4-2       | OPC                 | 168          | 211            | 422 84 127 271 990 |

*B+A: Binder +alkaline activator, **A.A: Alkaline Activators.
Table 10. Fresh property test results and compressive strength.

| Blend No. | Alkaline activators | Slump flow (mm) | Air (%) | Compressive strength (N/mm²) |
|-----------|---------------------|-----------------|---------|-----------------------------|
| 1         | CHs                 | 495             | 3.5     | 43                          | 51   |
| 2         | CH1                 | 365             | 3.5     | 41                          | 54   |
| 3         | SD                  | 40*             | 3.4     | 47                          | 73   |
| 4-1       | OPC                 | 700             | 4.0     | 58                          | 69   |
| 4-2       | OPC                 | 600             | 5.2     | 47                          | 62   |

*: slump value.

3.2. Test results and discussion

3.2.1. Fresh properties.
Fresh property test results are shown in table 10. The quantity of air was in the range from 3.6 to 5.5%.

3.2.2. Compressive strength.
Compressive strength test results are shown in table 10. For the blend using CHs and CH1, the compressive strength at 28 days was less than 60 N/mm², but the same or higher compressive strength was obtained from the other blends. It is considered that a higher compressive strength could be obtained compared with Test Series I by reducing the quantity of fly ash.

3.2.3. Frost resistance.
Frost resistance test results are shown in figure 4. In Test Series II, the quantity of air in the hardened specimens was increased in addition to reducing the quantity of FA. As a result, for the blends that used SD and OPC (Blend No.4-2) as the activator results were obtained that satisfied 300 cycles. For other blend, it was also found that frost resistance was somewhat improved.

![Figure 4. Frost resistance test results.](image-url)
4. Conclusions
In this research, it was confirmed that concrete containing large amount of industrial by-products can achieve sufficient properties except for frost resistance. However, by combining air-entraining agent and anti-foaming agent adequately, it was confirmed that frost resistance of some these concretes is improved.
1. When TK and SD were used as alkaline activators, the quantity of SP added to obtain the required fluidity was increased in both cases. In the case of SD, the dilatancy property was observed and it could be a problem in the casting process.
2. In the blends where TK, CHs, CH1, and SD were used as alkaline activators, it was not possible to achieve 60 N/mm² at 28 days or higher. However, when cement was used as an alkaline activator, compressive strengths of about 70 N/mm² were obtained.
3. In three cases using calcium hydroxide, it was found that the amount of drying shrinkage tended to increase. Also, the amount of shrinkage was small for the cases when cement was used as the alkaline activator. The amount of drying shrinkage of all blends was not so large comparing to usual concrete.
4. In the blend which used SD and OPC as activators it was found that the progress of carbonation was fast compared with the other three blends. However, it is considered that the carbonation resistance is about the same as that of ordinary concrete.
5. In Test Series I, sufficient frost resistance could not be obtained for all blending conditions. In Test Series II, the quantity of air was increased in addition to reducing the quantity of FA. As a result, for the blends that used SD and OPC (Blend No.4-2) as the activator results were obtained that satisfied frost resistance requirements.

5. References
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