



Effects of binder and CaCl_2 contents on the strength of calcium carbide residue-fly ash concrete

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ABSTRACT

This paper presents a concrete that utilizes a calcium carbide residue and fly ash mixture as the concrete binder instead of Portland cement. The ground calcium carbide residue (CR) was mixed with classified fly ash (FA) at a ratio of 30:70 (CR:FA) by weight and used as a binder to cast CR-FA concrete specimens. The effects of binder content, water to binder (W/B) ratio, and CaCl_2 dosages on the compressive strength of CR-FA concrete were evaluated. In addition, the modulus of elasticity of CR-FA concrete was measured. The results indicated that the CR-FA mixture could be used as a cementitious material for concrete without using Portland cement. Increasing the binder content and reducing the W/B ratio improved the compressive strength of CR-FA concrete, similar to normal concrete. The addition of 3% CaCl_2 by weight of binder yielded CR-FA concrete that exhibited high workability and accelerated the compressive strength at early ages. In particular, the 450 kg/m³ of CR-FA binder content with 3% CaCl_2 at a W/B of 0.35 yielded a compressive strength as high as 24.3 MPa at 90 days, even though this concrete did not contain Portland cement.

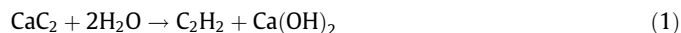
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1. Introduction

Cement production is known to contribute to the greenhouse effect due to the emission of CO_2 gas during the clinker manufacturing process. The amount of CO_2 emissions is related to the clinker to cement ratio, technology, and energy consumption in the cement production process [1]. The worldwide cement demand is estimated to reach 2.8 billion tons in 2010, and about 2.07 billion tons of CO_2 emissions will be released into the atmosphere [2]. Mehta [2] proposed ways for reducing the CO_2 emissions of the cement industry as targets for the next 20 years: consume less concrete, consume less cement in concrete mixtures and consume less clinker in cement. Gartner [3] and Damtoft et al. [4] suggested that the use of pozzolanic materials such as fly ash, blast-furnace slag, silica fume, metakaolin, and natural pozzolans, to replace Portland cement clinker helped to reduce CO_2 emissions associated with cement production. In addition, Damineli et al. [5] proposed two indices (binder intensity and CO_2 intensity) for measuring the efficiency of cement use within concrete construction. Several studies on consuming less cement in concrete by using high-volume fly ash have been reported [6–9]. New cementitious materials have also been developed, such as geopolymer-based materials [10,11], which completely replace Portland cement as the binder.

Several pozzolans such as fly ash, rice husk-bark ash, and palm oil fuel ash, which are agricultural or industrial by-products, are found in Thailand. Many studies found that these pozzolans can be used to replace some portion of cement to achieve high compressive strength of concrete [12–14]. However, their utilizations are limited because of insufficient data and lack of confidence; thus, most of these materials are disposed of in landfills.

Calcium carbide residue is a by-product from an acetylene gas (C_2H_2) production process. This gas is used as a fuel for lighting, welding, metal cutting, and space heaters, and to ripen fruit. The calcium carbide residue is produced by a simple process, which is obtained from the reaction between calcium carbide (CaC_2) and water (H_2O) according to the following equation:



The main oxide of calcium carbide residue is calcium hydroxide (Ca(OH)_2) in a slurry form. The huge amount of calcium carbide residue in Thailand has accumulated over time. An acetylene gas factory, which provided the calcium carbide residue for this study, produces approximately 1000 metric tons/month of calcium carbide residue, and a use for the residue is rarely found. Most of the residue is sent to landfills as waste (Fig. 1), causing many environmental problems, especially in terms of the groundwater pollution due to alkaline contamination.

According to ASTM C 618 [15], pozzolanic materials are siliceous or siliceous and aluminous materials, which in finely divided

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Fig. 1. Disposal area of calcium carbide residue.

form and in the presence of moisture, can react with calcium hydroxide (Ca(OH)_2) in cement paste to form additional calcium silicate hydrate (C–S–H). Since calcium carbide residue is rich in Ca(OH)_2 , it is believed that it can react with siliceous or siliceous and aluminous materials in pozzolans to form C–S–H.

Krammart et al. [16] reported that Ca(OH)_2 in calcium carbide residue could react with silica, alumina, and ferric oxides in a fly ash by the pozzolanic reaction to form C–S–H, similar to those obtained from the cement hydration process. They also showed that the optimal ratio of calcium carbide residue to fly ash mixture to achieve the highest compressive strength of mortar was 30:70 by weight. Furthermore, the pozzolanic reaction between calcium carbide residue and fly ash gave mortar a compressive strength of 8.3 MPa at 28 days, which increased to 20.9 MPa at 90 days. In 2003, Jaturapitakkul and Roongreung [17] observed a pozzolanic reaction between calcium carbide residue and rice husk ash and reported that the highest compressive strength of mortar was 15.6 MPa at 28 days. This previous research has revealed that the calcium carbide residue can participate in a pozzolanic reaction. However, the compressive strength of materials produced from calcium carbide residue and pozzolan was rather low. This may be due to the slow nature of the pozzolanic reaction [18]. Therefore, it is necessary to accelerate the reaction between calcium carbide residue and fly ash in order to achieve high compressive strength of concrete.

Calcium chloride (CaCl_2) is a well-known inexpensive accelerator that is used to accelerate the setting and compressive strength of concrete [19–22]. Ghataora et al. [20] used 2% CaCl_2 by weight of cement in mortar and indicated that the CaCl_2 improved the compressive strength at early age. Moreover, Singh et al. [21] found that CaCl_2 is a good accelerator for accelerating the reaction between pozzolans and Ca(OH)_2 obtained from cement hydration. Cheikh-Zouaoui et al. [22] indicated that the compressive strength development was not significantly increased in the long term when CaCl_2 was used in concrete. Generally, 2% CaCl_2 is widely used in concrete and is the upper limited given by the ACI committee 212 [23] due to concerns about steel bar corrosion. However, several discussions showed that dosages up to 3–4% could be used and the compressive strength of concrete still increased [24,25].

This study focuses on a binder from ground calcium carbide residue and classified fly ash to produce a new concrete that contains no Portland cement. Techniques to improve the strength such as increasing binder content and lowering the water to binder (W/B) ratio were considered. Moreover, 1%, 3%, 5%, and 10% of CaCl_2 by weight of binder were used to evaluate the effect of CaCl_2 on the compressive strength of such concretes. This new concrete, which is made from a calcium carbide residue and fly ash mixture, not only reduces CO_2 emissions by not using Portland cement but also reduces the environmental problems associated with disposal of the two waste materials in landfills.

2. Experimental program

2.1. Materials

The materials used in this study were calcium carbide residue, fly ash, Portland cement, a commercial grade of calcium chloride, natural river sand, crushed limestone, water, and naphthalene formaldehyde superplasticizer (Type A&F) conforming to ASTM C 494 [26].

Calcium carbide residue in slurry form was collected from the disposal area of an acetylene gas factory in Samutsakorn province in Thailand (see Fig. 1). Because the calcium carbide residue had a high moisture content (approximately 52%), it was sun-dried for approximately 3–4 days to reduce the moisture content to about 2–4%. After that, it was ground in a grinding machine until the particles retained on a 45- μm sieve were about 15% by weight and was designated as CR.

Original fly ash (designated as OF) was collected from the Mae Moh power plant in Lumpang province in Thailand. Although approximately 1.5 million tons of Mae Moh fly ash have been used annually as a pozzolanic material in concrete [27], it is only 50% of the total amount of fly ash production. The original fly ash was classified with an air classifier machine to obtain small particles, from which 1% by weight were retained on a 45- μm sieve, and was designated as FA.

Local river sand with fineness modulus of 2.68 was used as a fine aggregate. Crushed limestone was used as a coarse aggregate; it had maximum size of 19 mm and a fineness modulus of 6.90. The

specific gravities and water absorptions of the fine and coarse aggregates were 2.60%, 2.73% and 0.94%, 0.39%, respectively.

2.2. Mix proportions of concrete, casting, and testing

For calcium carbide residue-fly ash (CR-FA) concrete, a weight ratio of 30:70 for CR:FA was used as a binder to cast concrete as suggested by Krammart et al. [16]. All concrete mixture proportions and the workability of fresh concrete are summarized in Table 1. Three main proportions of CR-FA concrete mixtures were assessed to evaluate the effects of binder contents (300, 375, and 450 kg/m³) and W/B ratios (0.50, 0.40, and 0.35) on the compressive strength of CR-FA concrete. In the three main mixtures, calcium chloride (CaCl₂) at 1%, 3%, 5% and 10% by weight of binder were added to observe the workability and the acceleration of the compressive strength. The CR-FA concretes containing binder contents of 300, 375, and 450 kg/m³, which contained no CaCl₂, were also cast, and the slumps of fresh concrete were maintained between 50 and 100 mm by using superplasticizer. Cylindrical concrete specimens of 100 mm in diameter and 200 mm in height were cast, and the compressive strengths of CR-FA concrete were determined at 7, 14, 28, 60, and 90 days. The elastic modulus of all CR-FA concretes were determined at 28 days in accordance with ASTM C 469 [28] and compared with those of the normal concretes (NC300, NC375, and NC450), in which Portland cement was used as a binder. It was noted that the normal concretes had W/B ratios of 0.65, 0.53, and 0.45, and no superplasticizer or calcium chloride was applied to the mixtures.

3. Results and discussion

3.1. Fineness and particle shape of materials

The physical properties of CR, OF, and FA are summarized in Table 2, while Fig. 2 shows the particle size distribution curves obtained with a Mastersizers Malvern Instrument. The CR, OF, and FA had specific gravities of 2.32, 2.19, and 2.39, respectively. It was noted that the specific gravity of CR was slightly higher than those reported by Jaturapitakkul and Roongreung [17] and Krammart and Tangtermsirikul [29], which were 2.21 and 2.26, respectively. The mean particle sizes (d_{50}) and the weight of particles retained on a 45- μ m sieve for CR, OF, and FA were 14.3, 27.1, 12.1 μ m and 14.8%, 42.6%, 0.2%, respectively. Fig. 3a–c presents the particle shapes of CR, OF, and FA using scanning electron microscopy (SEM), respectively. It was seen that the CR had irregular and angular shapes, while the Mae Moh fly ashes OF and FA had spherical shapes. The results indicated that the CR was porous and had larger size than the FA. The classified fly ash (FA) had a higher fineness than the original fly ash (OF); the mean particle size (d_{50}) was reduced from 27.1 to 12.1 μ m, while the specific gravity increased from 2.19 to 2.39. This observation is consistent with the results of Kiattikomol et al. [12], Slanicka [30], and Angsuwattana et al. [31], who reported that the use of an air classifier machine to classify fly ash could reduce the particle size and could accelerate the pozzolanic reaction. In addition, the FA had a specific surface area of 4770 cm²/g or about two times higher than that of the OF (2370 cm²/g).

Table 1
Concrete mixture proportions.

Concrete designation	Mixture proportions (kg/m ³)								W/B	Slump (mm)
	Cement	CR	FA	Water	Fine agg.	Coarse agg.	SP	CaCl ₂		
300	–	90	210	150	840	1070	3.00	0.00	0.50	90
300CI1	–	90	210	150	840	1070	3.00	3.00	0.50	70
300CI3	–	90	210	150	840	1070	3.00	9.00	0.50	80
300CI5	–	90	210	150	840	1070	3.00	15.00	0.50	180
300CI10	–	90	210	150	830	1060	3.00	30.00	0.50	220
375	–	112.5	262.5	150	810	1030	3.75	0.00	0.40	80
375CI1	–	112.5	262.5	150	810	1030	3.75	3.75	0.40	115
375CI3	–	112.5	262.5	150	805	1025	3.75	11.25	0.40	115
375CI5	–	112.5	262.5	150	800	1020	3.75	18.75	0.40	125
375CI10	–	112.5	262.5	150	790	1005	3.75	37.5	0.40	210
450	–	135	315	157.5	760	965	6.75	0.00	0.35	100
450CI1	–	135	315	157.5	760	965	6.75	4.50	0.35	175
450CI3	–	135	315	157.5	755	960	6.75	13.50	0.35	210
450CI5	–	135	315	157.5	750	955	6.75	22.50	0.35	160
450CI10	–	135	315	157.5	735	935	6.75	45.00	0.35	160
NC300	300	–	–	195	825	1055	–	–	0.65	70
NC375	375	–	–	200	800	1025	–	–	0.53	70
NC450	450	–	–	203	760	975	–	–	0.45	90

Notes: Numbers of 300, 375, and 450 indicate the binder content in kg/m³; CI stands for CaCl₂. For example, 450CI3 means concrete containing binder content of 450 kg/m³ and 3% of CaCl₂ by weight of binder. NC is normal concrete using Portland cement as a binder.

Table 2
Physical properties of calcium carbide residue (CR), original fly ash (OF), and classified fly ash (FA).

Physical properties	CaC ₂ Residue (CR)	Original fly ash (OF)	Classified fly ash (FA)
Specific gravity	2.32	2.19	2.39
Retained on a 45- μ m sieve (%)	14.8	42.6	0.2
Mean particle size, d_{50} (micron)	14.3	27.1	12.1
Blaine fineness (cm ² /g)	4350	2370	4770

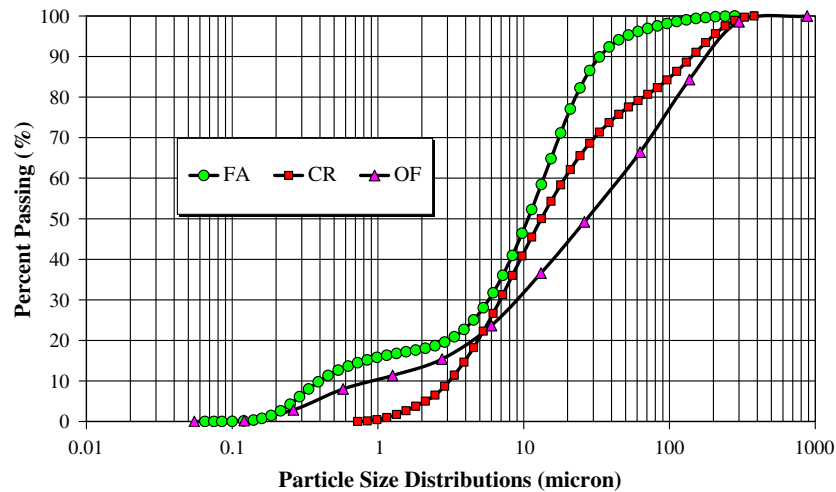


Fig. 2. Particle size distributions of materials.

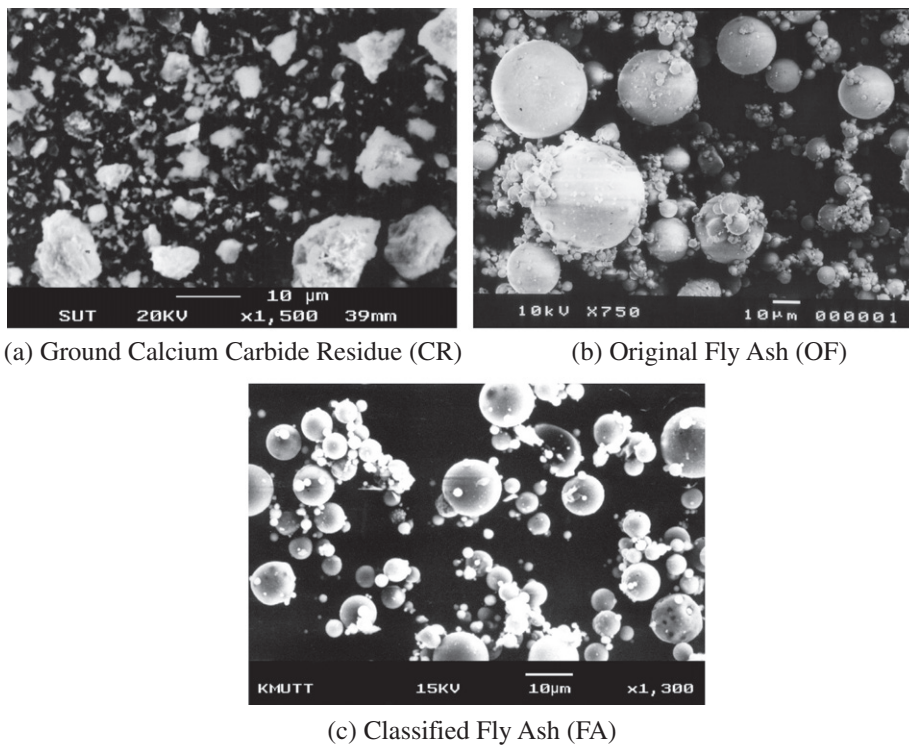


Fig. 3. Scanning electron microscopy of CR, OF, and FA.

3.2. Chemical compositions of materials

The chemical compositions of CR, OF, and FA determined by using X-ray Fluorescence analysis are tabulated in Table 3. It was found that the major chemical constituents of CR were CaO (51.9%) with a high value of loss on ignition (LOI) at 41.7%. This LOI was particularly high because it was determined at temperatures of 950–1000 °C. Furthermore, the CR mainly consisted of $\text{Ca}(\text{OH})_2$, which decomposed into CaO and H_2O (gas) at approximately 550 °C [17]. This high LOI value is similar to that reported by Krammart and Tangtermsirikul [29], which was 31.7%.

The chemical compositions of FA differed slightly from those of OF; similar results were obtained by Angsuwattana et al. [31]. The

Table 3

Chemical compositions of calcium carbide residue (CR), original fly ash (OF), and classified fly ash (FA).

Chemical compositions (%)	CR	OF	FA
SiO_2	3.4	44.9	44.6
Al_2O_3	2.6	23.7	23.5
Fe_2O_3	0.3	10.8	10.4
CaO	51.9	13.8	13.8
MgO	0.5	3.5	3.3
K_2O	0.0	2.4	2.6
Na_2O	0.0	0.1	0.1
SO_3	0.2	1.3	1.2
Loss on ignition (LOI)	41.7	0.5	0.8

OF and FA had total oxide contents ($\text{SiO}_2 + \text{Al}_2\text{O}_3 + \text{Fe}_2\text{O}_3$) of 79.4% and 78.5%, respectively. In addition, the SO_3 content of OF and FA

were 1.3% and 1.2% with LOI of 0.5% and 0.8%, respectively. Therefore, the OF and FA in this study could be classified as a fly ash Class F, according to ASTM C 618 [15].

3.3. Workability of fresh concrete

Table 1 shows the workability of all fresh concrete mixtures in terms of slump. It was found that CR-FA concretes with binder contents of 300, 375, and 450 kg/m³ without CaCl₂ had a slump of fresh concrete between 80 and 100 mm, within controlled ranges (50–100 mm). The CR-FA concretes with binder contents of 300, 375, and 450 kg/m³ required a superplasticizer at 3.0, 3.75, and 6.75 kg/m³, respectively; a similar result was also obtained by Faroug et al. [32], who reported that the concrete with lower W/B ratio and higher binder content required more superplasticizer to maintain the same workability of concrete. Mostly, the workability of fresh CR-FA concrete increased with the increasing of CaCl₂ content because the CaCl₂ absorbed moisture in ambient environment especially at high relative humidity. This resulted in increasing of free water in the mixture and increasing the slump of fresh CR-FA concrete. For example, 300CI1, 300CI3, 300CI5, and 300CI10 concretes had slumps of 70, 80, 180, and 220 mm, respectively.

Table 4
Compressive strength and modulus of elasticity of concrete.

Concrete designation	Compressive strength (MPa)					Modulus of elasticity at 28 days (GPa)
	7 days	14 days	28 days	60 days	90 days	
300	2.9	5.4	9.3	11.7	12.1	20.8
300CI1	3.2	6.5	9.1	11.0	11.8	20.9
300CI3	3.2	6.8	8.3	10.6	11.1	19.2
300CI5	5.3	8.1	8.9	12.0	12.2	20.1
300CI10	2.2	4.0	5.0	5.9	6.8	N/A
375	4.3	9.3	15.1	18.6	20.5	25.9
375CI1	4.4	9.2	10.7	12.5	13.7	23.2
375CI3	3.1	7.0	8.7	10.4	11.1	19.8
375CI5	6.4	9.4	10.9	13.8	14.9	22.3
375CI10	3.8	5.8	7.7	8.6	8.7	18.6
450	4.8	9.3	15.5	19.5	20.5	26.4
450CI1	6.5	11.2	14.9	16.4	18.3	26.5
450CI3	9.2	17.0	19.8	22.7	24.3	30.7
450CI5	5.1	9.2	10.9	12.3	14.9	23.2
450CI10	5.0	9.0	11.3	12.0	14.2	23.8
NC300	–	–	31.3	–	–	31.4
NC375	–	–	41.4	–	–	34.1
NC450	–	–	46.3	–	–	38.9

Notes: The compressive strength of 300CI10 concrete at 28 days was too low to obtain the elastic modulus value.

3.4. Compressive strength of concrete

Table 4 shows the average compressive strength values of the five concrete specimens at each testing age. The results showed that the compressive strength of CR-FA concrete increased with age, and the compressive strength at 28 days ranged from 5.0 to 19.8 MPa, depending on the W/B ratio, binder content, and amount of CaCl₂ in the concrete. Although the CR-FA concretes contained no Portland cement, the compressive strengths of concretes increased continuously and varied from 6.8 to 24.3 MPa at 90 days. This result indicated that the CR-FA mixture could be used as a cementitious material in concrete. It should be noted that the compressive strength of CR-FA concrete was obtained from a pozzolanic reaction between Ca(OH)₂ in CR and SiO₂, Al₂O₃, and Fe₂O₃ in FA, which developed with curing age: it developed quickly at early ages (up to 28 days) and then increased gradually at later ages. This behavior is similar to that of normal concrete, in which Portland cement is used as a binder.

3.5. Effect of water to binder ratio on compressive strength

Fig. 4 shows the relationship between the compressive strength and the W/B ratio of CR-FA concrete without CaCl₂. It was found

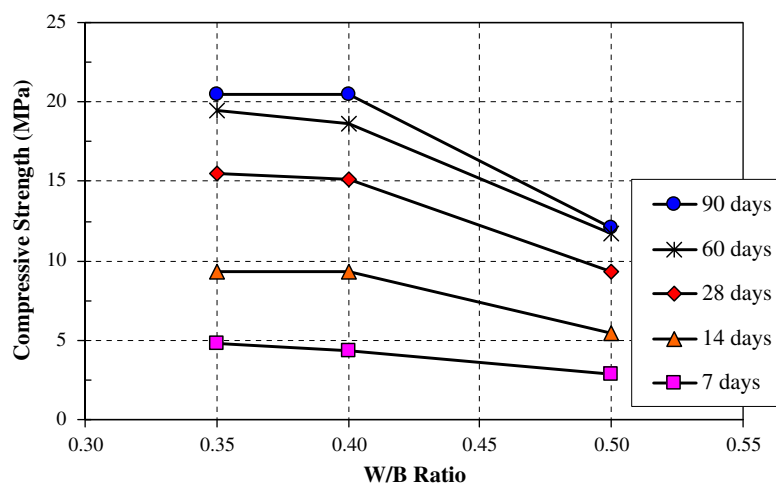


Fig. 4. Relationship between compressive strength and W/B ratio of CR-FA concrete.

that the compressive strengths of CR-FA concretes at 28 days were 9.3, 15.1 and 15.5 MPa, and increased to 12.1, 20.5, and 20.5 MPa at 90 days for concretes with W/B ratios of 0.50, 0.40, and 0.35, respectively. Moreover, the compressive strength development of concrete at the low W/B ratio (0.35) was larger than that at the high W/B ratio (0.50). At 90 days, the compressive strength of concrete for a W/B ratio of 0.35 was increased about 15.7 MPa from that at the age of 7 days while that for a W/B ratio of 0.50 increased about 9.2 MPa. This suggested that the strength development of CR-FA concrete significantly increased with low W/B ratios. The result is similar to that for normal concrete, in which Portland cement was used as a major binder [33–36]. As a result, CR-FA concrete with a low W/B ratio accelerated the reaction between CR and FA, resulting in increased compressive strength. For example, 450 concrete (W/B ratio of 0.35) had compressive strengths of 4.8, 9.3, 15.5, 19.5, and 20.5 MPa at 7, 14, 28, 60, and 90 days, respectively, although the binder contained no Portland cement. It should be noted that the compressive strength of 300 concrete (W/B ratio of 0.50) was low since the compressive strength at 90 days was only 12.1 MPa.

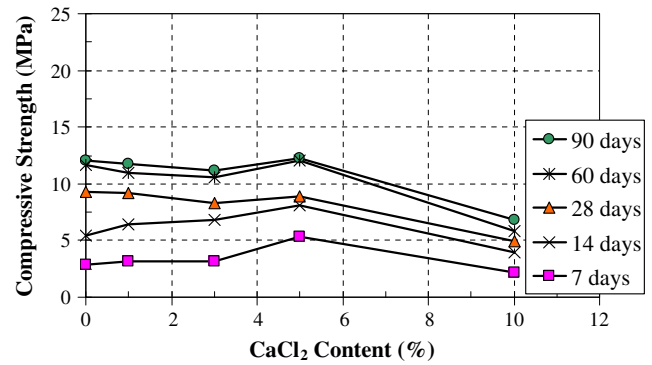
3.6. Effect of calcium chloride on compressive strength

In this study, CaCl_2 was expected to accelerate the reaction between CR and FA in order to obtain high compressive strength at early age. Fig. 5a–c presents the relationship between compressive strength and CaCl_2 content in concrete at binder contents of 300, 375, and 450 kg/m^3 , respectively. At the early age of 7 or 14 days, the use of CaCl_2 could not accelerate the compressive strength for concretes with binder contents of 300 and 375 kg/m^3 . For example, the compressive strengths at 7 days of 300Cl1, 300Cl3, 300Cl5, and 300Cl10 concretes were 3.2, 3.2, 5.3, and 2.2 MPa, respectively, which did not have much difference from that of 300 concrete. Furthermore, the effect of CaCl_2 on the compressive strength is very small when the age of concrete increases since the compressive strengths of concretes with and without CaCl_2 were almost the same when CaCl_2 was added in the concrete between 1 and 5% by weight of binder. It is also noted that the use of 10% of CaCl_2 resulted in lowering the compressive strength of CR-FA concrete compared to the one without CaCl_2 .

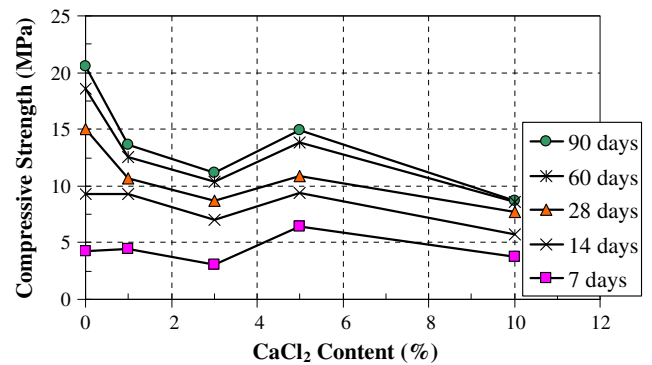
For a high binder content of 450 kg/m^3 , CaCl_2 could accelerate the compressive strength of CR-FA concrete at early age, i.e., at 7 and 14 days. It was found that at 3% CaCl_2 is the most effective for accelerating the compressive strength of CR-FA concrete. 450Cl3 concrete had compressive strengths of 9.2 and 17.0 MPa, about 2 times greater than that of 450 concrete at 7 and 14 days, respectively. At 28 days, the compressive strength of 450Cl3 concrete was higher than that of the one without CaCl_2 . This result also indicated that CaCl_2 was effective in accelerating the compressive strength of CR-FA concrete when a low W/B ratio and high binder content was used (W/B ratio of 0.35 and binder content of 450 kg/m^3). However, the effect of CaCl_2 on the compressive strength of CR-FA concretes at later ages (60 or 90 days) was not pronounced since 450 and 450Cl3 concretes did not have much difference in compressive strength (20.5 and 24.3 MPa at 90 days, respectively). This behavior agreed with the results of Ghataora et al. [20] and Cheikh-Zouaoui et al. [22], who reported that the use of CaCl_2 resulted in the high early strength of Portland cement concrete, while the increase in compressive strength was not significant in the long term.

3.7. Modulus of elasticity

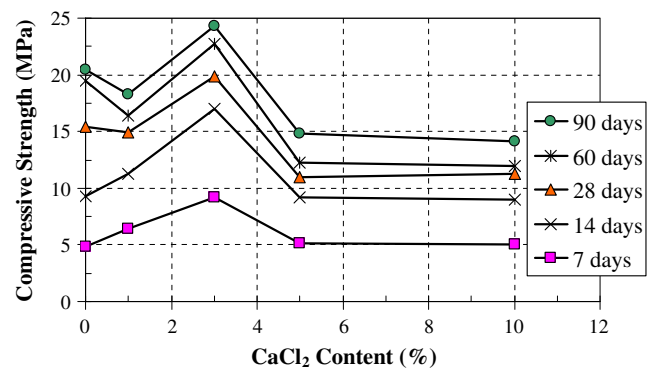
The modulus of elasticity of CR-FA concretes at binder contents of 300, 375, and 450 kg/m^3 was measured at 28 days. The average modulus of elasticity for each mixture (using five concrete



(a) Binder content of 300 kg/m^3



(b) Binder content of 375 kg/m^3



(c) Binder content of 450 kg/m^3

Fig. 5. Relationship between compressive strength of CR-FA concrete with different binder contents and CaCl_2 contents.

specimens) is tabulated in Table 4. It was found that the elastic modulus of CR-FA concretes ranged from 18.6 to 30.7 GPa, while that of normal concretes ranged from 31.4 to 38.9 GPa depending on the compressive strength of the concrete. It is well-known that the elastic modulus of normal concrete is generally related to its compressive strength: the modulus of elasticity increases with the increasing of compressive strength [14,37,38]. The elastic modulus of CR-FA concrete is similar to that of normal concrete since it increased with the compressive strength.

Fig. 6 shows the relationships between the modulus of elasticity and the square root of the compressive strength for each concrete. In order to avoid the effect of the specimen size on the elastic modulus of concrete [39], the CR-FA concrete specimen size was the same as the cylindrical size of the normal concrete. As shown in Fig. 6, it was concluded that the CR-FA concrete had compressive strength and modulus of elasticity properties similar to normal

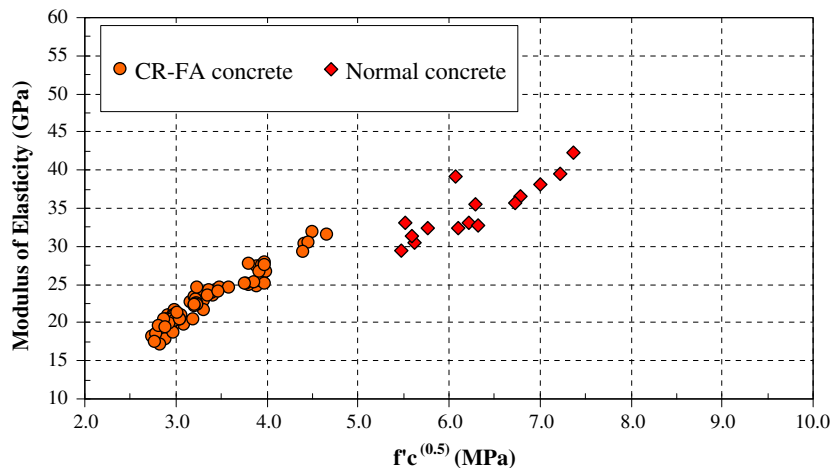


Fig. 6. Relationship between modulus of elasticity and square root of compressive strength for each concrete.

concrete, although the binder of the new concrete did not contain Portland cement.

4. Conclusions

Based on the experimental results, the following conclusions can be drawn:

1. The ground calcium carbide residue (CR) and classified fly ash (FA) mixture could be used as a cementitious material for new concrete. Although the CR-FA mixture contained no Portland cement, the compressive strength of the CR-FA concrete could be as high as 24.3 MPa at 90 days.
2. Increasing the binder content and reducing the W/B ratio of the CR-FA concrete improved the compressive strength as well as the modulus of elasticity.
3. CaCl_2 increased the slump of fresh CR-FA concrete. To accelerate the compressive strength of CR-FA concrete at early age, 3% of CaCl_2 by weight of binder should be used for high binder contents (450 kg/m^3) together with a low water to binder ratio (0.35). However, steel bar corrosion in the concrete should be a concern when using large doses of CaCl_2 .
4. The elastic modulus of CR-FA concrete increased with the increasing of compressive strength. CR-FA concrete had compressive strength and modulus of elasticity properties similar to normal concrete, although the binder of the CR-FA concrete contained no Portland cement.

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