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Effect of chemical additives on the carbon dioxide in the sustainable production of portland pozzolanic cement

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ABSTRACT

This research aims to investigate the reduction of CO_2 emissions in the cement production process by producing pozzolanic portland cement (PPC) with the characteristics of ordinary portland cement (OPC) using quality-improving chemical additives including calcium nitrate (CN), calcium formate (CF), triethanolamine (TEA) and triisopropanolamine (TIPA). To this end, CN and CF (1, 2 and 3% wt of binder) were added to PPC mortar during the making process, and TEA and TIPA (0.003, 0.006 and 0.01% wt of binder) were added as a solution to the mixture of clinker and natural pozzolan during grinding. The results obtained from compressive strength tests illustrated that, on average, PPC samples containing 15% natural pozzolan led to a 2.7% decrease and a 17.3% increase in the compressive strength respectively compared to OPC with 1% CF and 0.01% TEA. Accordingly, for cement production, clinker can be reduced by 15%, and natural pozzolan be replaced; the reduction in resistance caused by adding natural pozzolan can also be compensated by using chemical additives. Hence, the possibility of replacing 15% of natural pozzolan with clinker, while maintaining the quality of produced cement and reducing the emission of 135 kg of CO_2 per ton of cement production is one of the results of this research.

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1. Introduction

Power plants and cement plants are the largest emitters of carbon dioxide (CO_2) (Scrivener et al., 2018). Portland cement production is an energy-intensive process that involves heating a ground mixture of raw materials such as limestone, clay, silica, and iron ore in a rotary kiln. The product, called clinker, is cooled, ground, and then mixed with a small amount of gypsum to form cement. About 5% of global CO_2 emissions are from cement production, with 60% from chemical processes and 40% from fuel combustion (Locher, 2006). About 900 kg of CO_2 are emitted per ton of cement produced (Shen et al., 2014). Cement plants produce greenhouse gases in two ways. First, directly through the production of CO_2 when calcium carbonate is thermally decomposed to produce calcium oxide and CO_2, the second, a large amount of fuel is burned to heat the rotary kiln to a temperature of 1400 °C (Loreti, 2009). Overall, the top 10 cement producing countries accounted for 63% of the global carbon emissions from cement production in 2022 (Canadell and Peter, 2022). Therefore, reducing fuel consumption in clinker kilns and using different types of pozzolans as additives for making blended cement is a crucial solution to reduce CO_2 emissions and production costs (Ramasamy and Tikalsky, 2012).

According to the definition provided in the Iranian National Standard No. 3433, natural pozzolans are siliceous or siliceous-aluminous materials or a combination of both that do not have adhesive properties by themselves, but in powder form, in the presence of moisture and at normal ambient temperature, they react chemically with calcium hydroxide and produce adhesive gels such as calcium silicate and calcium aluminosilicate. As the above gel hardens, mortar and concrete made with these materials gradually increase in strength, and as the internal spaces decrease and the density and permeability of mortar and concrete increase, their durability in various environments increases.

One of the disadvantages of Portland cements containing natural pozzolan is the decrease in compressive strength at early ages (day 2 and day 7) compared with plain Portland cement. The reason for this is the weak activity of pozzolans, which is attributed to the high density and chemical stability of the glassy surface layer of pozzolans. This layer is an obstacle to the reaction of the porous and amorphous inner layers with higher pozzolanic activity and the silica-alumina chain. In Portland cements containing pozzolanic materials, with an increase in the ratio of pozzolan to cement clinker, the initial compressive strength decreases and the setting time of the cement increases (Taylor, 1997). To prevent the decrease in compressive strength of Portland cements containing pozzolanic materials, various methods can be used, including increasing the softness of the cement (mechanical activation), the use of superplasticizers and chemical additives (activators or quality improvers) (Allahverdi et al., 2018).

One of the methods to achieve a desirable level of early compressive strength of Portland cements containing pozzolanic materials is the use of chemical quality-improving additives. These quality-improving additives are a group of cement additives used to improve early and final strengths. In this method, chemicals are added during the grinding of Portland cements containing pozzolanic materials or during the production of mortar or concrete. The use of chemical additives accelerates the pozzolanic reaction and, as a result, increases the early compressive strength of concrete. Today, adding chemicals to cement or concrete is considered one of the most effective and economical methods to increase the compressive strength of concrete (Gök and Kilinç, 2015).

Various chemical admixtures have been used to obtain concrete with sufficient strength at early ages, calcium chloride has been the most widely used in the past for setting and hardening accelerators. However, the presence of chloride causes serious problems with corrosion of reinforcing bars embedded in reinforced concrete. For this reason, the use of chloride-free chemical admixtures such as calcium nitrate, and calcium formate has been on the agenda of researchers (Chikh et al.,, 2007).

Another chemical additive used in the cement industry is triethanolamine, TEA, which is a tertiary alkanolamine, used as an anti-wear agent in the cement production process and as a main component in the composition of certain concrete admixtures. Depending on the type of cement and the amount added, TEA can act as an accelerator or retarder of setting time. For example, adding 0.02% TEA to type I Portland cement acts as a setting accelerator, while at 0.25% it acts as a mild setting retarder, at 0.5% it acts as a severe setting retarder, and at 1% it acts again as a strong setting accelerator. The effect of this compound on increasing the strength of cement pastes also depends on the amount of TEA added. The addition of small amounts of alkanolamines such as triisopropanolamine and TEA has caused a significant increase in the strength of cement pastes at different ages (Yaphary et al., 2017).

The use of pozzolanic materials to reduce CO_2 emissions and conserve energy in the production of Portland pozzolanic cement was investigated by Ragab et al., (2022), the results showed that by replacing 15% of basalt in the production of cement clinker, CO_2 emissions and energy consumption in the clinker industry can be reduced (Ragab et al., 2022). The reduction of CO_2 emissions and production costs by using different types of pozzolans including brick, potting clay, volcanic rocks, sedimentary rocks and rice bran in the Lamerd cement factory was investigated by Abdollahi and Zarei (2015). They concluded that among these additives, rice bran cannot be a suitable pozzolan. This study showed that the use of pozzolans up to 10% did not have a significant effect on the quality of Lamerd cement. Among the additives used, volcanic and sedimentary rocks were more desirable in terms of both quality and price. In fact, the additives were able to reduce both CO_2 emissions (reduction of more than 400 ton/day of CO_2) and production costs (economic savings of about $76,000/day) in the Lamerd cement plant (Abdollahi and Zarei 2018). The amount of CO_2 greenhouse gas emission reduction in the environment by replacing local mineral pozzolan as part of cement in concrete with an emission reduction approach was evaluated by Rangrazian et al., (2022). Therefore, in order to find the optimal design for replacing local mineral pozzolan with part of cement, four types of mixing designs with 5, 10, 15 and 20 wt% were investigated and its effect on the compressive strength of concrete and the amount of CO_2 greenhouse gas emission and its ability to reduce the amount of environmental pollution compared with conventional cement concrete were evaluated. The results showed that the best amount of this pozzolan to replace cement in concrete is 15 wt%, which increases the strength by 2.4%. Moreover, this pozzolan emits 15.20 kg less CO_2 per 1 m^3 of concrete than conventional cement concrete. This amount is similar to other widely used pozzolans. Therefore, considering the desirable effects in strengthening the structure and reducing cement consumption in concrete, the studied pozzolan was introduced as a cement-reducing and environmentally friendly material (Rangrazian et al., 2022).

The changes in the early strength of a fly ash-based cement blend with a ratio of 70% ordinary Portland cement and 30% fly ash using accelerating chemical additives such as sodium thiocyanate, diethanolamine, and glycerol (glycerin) were investigated separately and in combination by Hoang et al., (2016). The chemical additives were in the form of 40% sodium thiocyanate solution, 85% diethanolamine solution, and 85% glycerol, each of which was used alone or in combination. The results indicated an increase in the compressive strength of the cement containing the combined additives by 64 and 14%, respectively (Hoang et al., 2016).

Given the breadth and potential of sustainable development in environmental, economic, social and industrial relations, this phenomenon has quickly become the most important debate and one of the most prominent challenges of the twenty-first century (Darvishi et al., 2023). In the past, man may have instinctively understood that the secret of his survival lay in harmony with nature and that the decline of nature was his decline. In this regard, the Rio Declaration on Environment and Development addressed this important issue in its twenty-seven principles. According to principles 3, 4, 6, and 8 of the United Nations Conference on Environment and Development held on June 30, 1992, sustainable development is defined as

"Sustainable development is a process of change in the use of resources, the direction of investments, the orientation of technological development and institutional change that is consistent with present and future needs" (Vahdat and Towhidi 2009). As the quality of materials, including cement, increases, their lifespan increases, and as the lifespan of materials such as cement increases, its consumption decreases under the same conditions. Accordingly, the need for its production decreases and, consequently, the pollutants resulting from its production decrease. In addition, fewer natural resources are consumed for the production of cement, and therefore these natural resources are preserved for future generations (Fode et al., 2023). In this study, the reduction of CO_2 emissions in the cement production process by producing pozzolanic Portland cement with the characteristics of pure Portland cement using quality-improving chemical additives was investigated, which is a step forward towards achieving sustainable development in the cement industry.

2. Materials and Methods

2.1 Chemicals

For this study, gypsum was obtained from the Zarrinkamar mine in Shahrood, north of Iran, natural pozzolan of volcanic ash type from the Qahavand mine located in Hamedan province, west of Iran, and clinker from the Golestan Peyvand Cement Company. In Table 1, the chemical analysis and physical properties of these materials as well as the potential chemical composition of the bog clinker are shown.

Table 1 Chemical composition and physical properties of Clinker and Gypsum and Pozzolana

Physical properties	Clinker	Gypsum	Natural pozzolan
Grindability (Kwh/Sh.ton)	11.09		7.73
Chemical analysis (Wt%)			
CaO	65.03	32.63	4.01
SiO_2	22.16	1.66	56.14
Al_2O_3	5.29	0.40	17.53
Fe_2O_3	3.78	0.38	8.60
MgO	2.48	-	1.24
SO_3	0.22	44.50	1.64
Cl	0.01	-	0.03
K_2O	0.53	-	2.35
Na_2O	0.31	-	0.41
LOI	0.56	20.26	8.37
Free CaO	1.18	-	-
Bogue potential chemical compounds (Wt%)			
C_3S	55.13	-	-
C_2S	21.78	-	-
C_3A	7.62	-	-
C_4AF	11.50	-	-

2.2 Experiments

In order to prepare cement mixtures, similar to the cement production process, raw materials including clinker, gypsum and natural pozzolan were ground simultaneously in a cylindrical laboratory ball mill with a length and diameter of 0.1 m and 0.45 m, respectively, until reaching a specific surface area (Blin) of 3200 ± 20 cm^2/g.

Plain Portland cement with a composition of 96% clinker and 4% gypsum and Portland cement containing natural pozzolan with a composition of 81% clinker, 15% natural pozzolan and 4% gypsum were produced in a laboratory mill. To investigate the effect of chemical additives on the engineering properties of cement mixtures, TEA and TIPA were added to the mixture of materials as an aqueous solution during grinding. For this purpose, a certain amount of the additive was dissolved in 10 ml of distilled water and spread it dropwise at different points on the surface of the materials inside the mill, and then the grinding operation was started. CN and CF additives were added to the water used during mortar preparation. The type and amount of chemical additives used are reported in Table 2.

Table 2 Cement mixtures and chemical admixture and corresponding dosage

Sample Code	Sample Name	Clinker (%)	Natural Pozzolan (%)	Gypsum (%)	Chemical Additive	Chemical additive (wt% of cement)
M0	OPC	96	0	4	-	0
M1	PPC	81	15	4	-	0
MCN1	PPC+CN1	81	15	4		1
MCN2	PPC+CN2	81	15	4	$Ca(NO_3)_2.4H_2O$ (CN)	2
MCN3	PPC+CN3	81	15	4		3
MCF1	PPC+CF1	81	15	4		1
MCF2	PPC+CF2	81	15	4	$Ca(CHO_2)_2$ (CF)	2
MCF3	PPC+CF3	81	15	4		3
MTEA0.003	PPC+TEA0.003	81	15	4		0.003
MTEA0.006	PPC+TEA0.006	81	15	4	Triethanolamine (TEA)	0.006
MTEA0.01	PPC+TEA0.01	81	15	4		0.01
MTIPA 0.003	PPC+TIPA0.003	81	15	4		0.003
MTIPA 0.006	PPC+TIPA0.006	81	15	4	Triisopropanolamine (TIPA)	0.006
MTIPA 0.01	PPC+TIPA0.01	81	15	4		0.01

The compressive strength of cement samples was measured according to ASTM C109 standard. For this purpose, EN-DIN-1164 standard sand was used. Considering that adding natural pozzolan to cement leads to an increase in the water required to reach normal density, the water to cement ratio in the mortar making stage is one of the factors affecting the compressive strength of cement. Therefore, to eliminate the effect of water to cement ratio on compressive strength, according to ASTM C230 standard, flow table test and use of mortar with solvency within the normal range of 110% ± 5, i.e.

the upper limit of solvency (115%) for plain Portland cement mortar and the lower limit of solvency (105%) for other cement mixtures (containing pozzolan) were considered. After conducting numerous tests, the optimal water to cement ratio was determined to be 0.51. The cement mixture mortars were molded in 40 × 40 × 160 mm molds. The molds were kept in a box with a humidity of more than 95% and a temperature of 20 ± 2 °C for the first 24 hr. The specimens were cured according to ASTM C192 standard in water saturated with calcium hydroxide at a standard temperature of 23 ± 2 °C and for a period of 2, 3, 7, 28 and 56 days. To achieve the desired type and ratio of chemical additives, the compressive strength of the specimens was measured at ages 1, 2, 3, 7, 28 and 56 days and the cement mixture with the highest compressive strength was selected as the optimal mixture. Then, calculations related to the reduction of CO_2 gas were performed and its extracted amount was reported.

2.3 Characterization

To measure the compressive strength of the cured mortar specimens, a ToniZEM digital uniaxial hydraulic compressive strength testing machine (Toni tecnick) with a capacity of 200 kN, an accuracy of 0.01 kN, and a loading speed of 2.4 kN/s was used in the laboratory of Golestan Peyvand Cement Company, Iran. Three mortar specimens were used in each measurement and their average was reported. The minimum and maximum standard deviation values for the measurements were calculated to be 0.06 and 1.76 Mpa, respectively.

3. Results and Discussion

3.1 X-Ray diffraction pattern

The X-ray diffraction (XRD) pattern of natural pozzolan is shown in Fig. 1(a) and gypsum in Fig. 1(b). In Fig. 1(a), it is observed that the dominant crystalline phase in natural pozzolan is quartz with the chemical formula SiO_2. According to ASTM C311 and ASTM C618 standards, the resistance activity index was used to evaluate pozzolanic activity and its value was reported to be 80.53% for day 7 and 85.92% for day 28. In addition, in Fig. 1(b), it is observed that the dominant crystalline phase of gypsum is gypsum with the chemical formula $CaSO_4.2H_2O$.

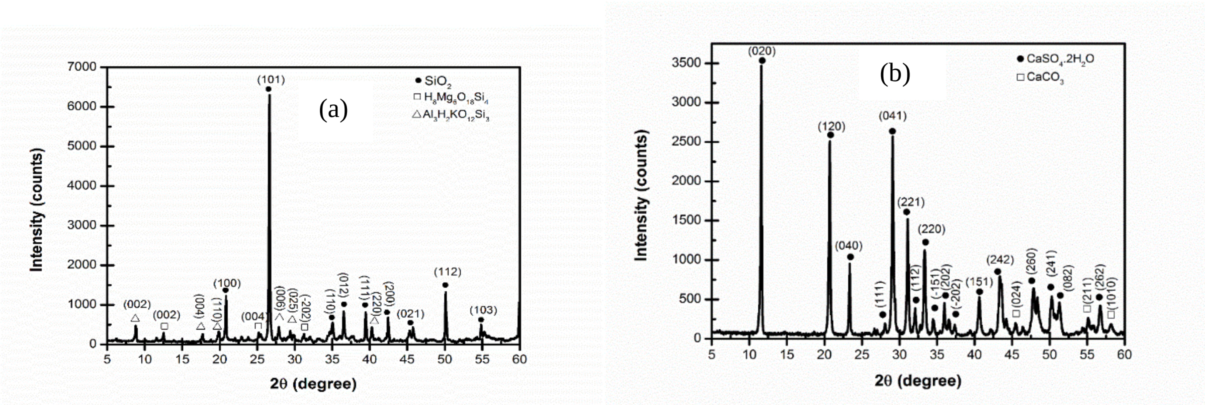

Fig.1 X-Ray diffraction pattern of pozzolan: a) and b) gypsum

3.2 Mill operating time for optimal cement production

Table 3 shows the mill operating time required to achieve the desired specific surface area for the cement produced. The results of Table 3 show that TEA and TIPA additives act as grinding aids and facilitate the grinding process, as the mill operating time was reduced to produce cement with a specific surface area of 3200 ± 20 cm^2/g.

Table 3 The operation time of the mill to obtain cement with a specific surface of 3200 ± 20 cm^2/g

Sample Code	Sample Name	Weight (kg)	Mill operation time (min)
M0	OPC	7	60
M1	PPC	7	50
MTEA0.003	PPC+TEA0.003	7	40
MTEA0.006	PPC+TEA0.006	7	35
MTEA0.01	PPC+TEA0.01	7	27
MTIPA 0.003	PPC+TIPA0.003	7	35
MTIPA 0.006	PPC+TIPA0.006	7	30
MTIPA 0.01	PPC+TIPA0.01	7	30

3.3 Residue on 45 and 90 µm sieves and special surface

Table 4 shows the residue on 45 and 90 µm sieves and the specific surface area of cement mixtures. As can be seen in Table 4, sample M1 containing 81% clinker, 15% pozzolan and 4% gypsum had the highest residue on 45 and 90 µm sieves among the other samples. While the lowest residue on 45 and 90 µm sieves was for sample MTEA0.01. The reason for this is the difference in the abrasion capacity of natural pozzolan and Portland cement clinker. According to the results in Table 1, the abrasion capacity of natural pozzolan and Portland cement clinker was reported to be 7.73 and 11.09 Kwh/Sh.ton, respectively. In sample M1, 15% natural pozzolan was replaced by Portland cement clinker compared with M0. Because the abrasiveness of natural pozzolan is lower than that of Portland cement clinker, natural pozzolan typically falls into the fine cement fraction, while unground clinker particles are categorized in the coarse clinker fraction. This results in a higher residue on the 45 and 90 µm sieves compared to the ordinary Portland cement sample (M0). Nevertheless, the lowest residue on the 45 and 90 µm sieves was for the MTEA0.01 sample. The reason for this is the use of TEA as a chemical additive in the cement abrasion process. In general, the use of alkaloamines such as TEA and TIPA facilitates the clinker grinding process by reducing the aggregation of cement particles and also prevents the formation of coatings on the surface of the grinding equipment (Gartner and Myers 1993).

3.4 Compressive strength of cement mixtures

Fig. 2 shows the values of compressive strength of cement mixtures mortar after 1, 2, 3, 7, 28, and day 56 of curing. In addition, Table 5 shows the changes in compressive strength of cement mixtures mortar containing natural pozzolan in the presence of chemical additives compared to pure Portland cement (M0).

Table 4 Amount of specific surface area (Blaine) and residue on 45 and 90 µm sieves of cement mixtures

Sample Code	45 µm sieve (wt%)	90 µm sieve (wt%)	Surface area (cm^2/g)
M0	18.4	1.4	3218
M1	25.0	5.9	3233
MTEA0.003	18.0	4.2	3218
MTEA0.006	18.4	4.3	3188
MTEA0.01	15.2	3.3	3218
MTIPA0.003	19.7	4.0	3203
MTIPA0.006	21.7	3.7	3203
MTIPA0.01	17.8	2.3	3218

Fig. 2 Compressive strength values of cement mixtures

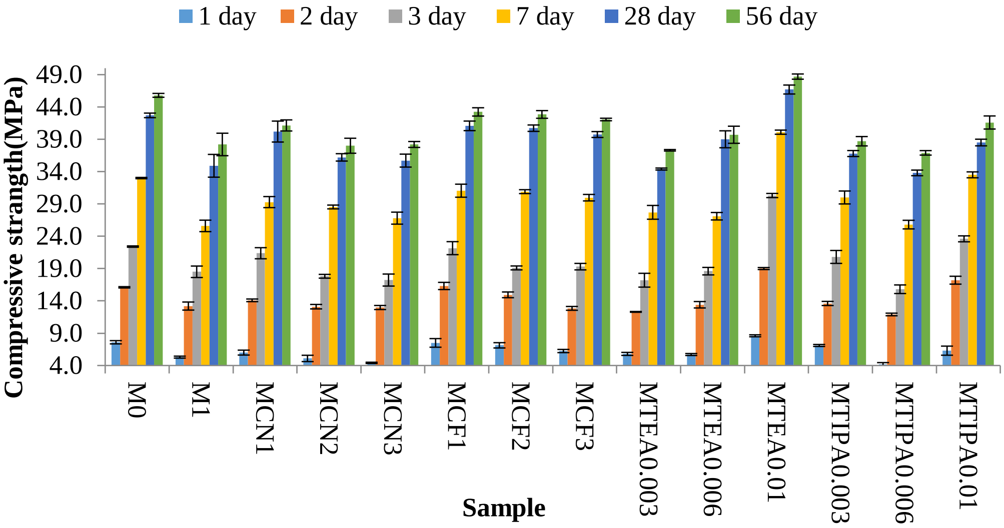

Table 5 The amount of changes in compressive strength (%) of ppc in the presence of chemical admixture compared to opc without chemical admixture

Age /Sample Code	1 day	2 day	3 day	7 day	28 day	56 day	Average
M0	0.00	0.00	0.00	0.00	0.00	0.00	0.00
M1	-30.26	-18.01	-17.41	-22.42	-18.27	-16.59	-20.50
MCN1	-21.05	-12.52	-4.59	-11.27	-5.86	-10.17	-10.91
MCN2	-32.92	-18.61	-20.49	-13.55	-15.22	-17.03	-19.64
MCN3	-41.95	-19.42	-23.12	-18.79	-16.39	-16.59	-22.71
MCF1	-1.32	1.29	-1.09	-5.92	-3.80	-5.60	-2.74
MCF2	-6.26	-7/24	-14.73	-6.36	-4.64	-6.46	-7.62
MCF3	-17.87	-20.23	-13.84	-9.19	-6.94	-8.17	-12.71
MTEA0.003	-23.68	-23.60	-23.21	-16.06	-19.44	-18.56	-20.76
MTEA0.006	-25.00	-16.77	-16.96	-17.88	-8.67	-13.32	-16.43
MTEA0.01	13.16	18.01	35.27	21.52	9.37	6.33	17.28
MTIPA0.003	-6.58	-15.53	-7.14	-9.09	-13.82	-15.50	-11.28
MTIPA0.006	-44.74	-26.09	-29.46	-21.82	-20.84	-19.43	-27.06
MTIPA0.01	-17.11	6.83	5.36	1.52	-9.84	-9.17	-3.73

The results obtained indicate that calcium formate acts as a suitable compressive strength accelerator for Portland cement, because the compressive strength of the samples with the presence of 1% calcium formate increased by 33.13 at day 1, 23.48 at day 2, 20.00 at day 3, 21.27 at day 7, 14.32 at day 28, and 13.08% at day 56 compared with the Portland pozzolanic cement sample (M1). Moreover, at ages 1 and day 2, it approached the compressive strength of the pure Portland cement sample (M0), so that the compressive strength of the mixed cement samples containing natural pozzolan with the presence of 1% calcium formate decreased by only 2.7% on average compared with the compressive strength of pure Portland cement.

Therefore, calcium formate can be classified as a suitable accelerator of compressive strength. The results of Heikal (2004) showed that calcium formate increases the early and later age compressive strength and accelerates the formation of C-S H. Its effect on calcium silicate phases is mainly attributed to the fact that the diffusion (dissolution) rate of formate ions ($HCOO^-$) is much higher than that of Ca^{2+}. Formate ions can penetrate into the hydrated layers covering the tricalcium silicate (C3S) and dicalcium silicate (β-C2S) grains. As a result, the precipitation of calcium hydroxide and the decomposition of calcium silicates are accelerated. They also showed that calcium formate increases the gel-to-space ratio and the degree of hydration (higher combined water content). In a study by Jinqing and Wang (2022) on the effect of calcium formate on increasing the compressive strength of pure Portland cement mortar, it was concluded that adding calcium formate can increase the compressive strength of Portland cement mortar at all curing ages.

Table 6 The amount of changes in the compressive strength (٪) of the mortar of opc mixtures in the presence of chemical admixture compared to ppc without chemical admixture

Sample code/Age	1 day	2 day	3 day	7 day	28 day	56 day	Average
M0	43.40	21.97	21.08	28.91	22.35	19.90	26.27
M1	0.00	0.00	0.00	0.00	0.00	0.00	0.00
MCN1	13.21	6.70	15.53	14.38	15.18	7.71	12.12
MCN2	-3.81	-0.72	-3.73	11.44	3.72	-0.52	1.06
MCN3	-16.76	-1.71	-6.91	4.69	2.29	0.00	-3.07
MCF1	41.51	23.54	19.77	21.27	17.70	13.18	22.83
MCF2	34.42	13.14	3.24	20.70	16.67	12.15	16.72
MCF3	17.77	-2.70	4.32	17.06	13.86	10.10	10.07
MTEA0.003	9.43	-6.82	-7.03	8.20	-1.43	-2.36	0.00
MTEA0.006	7.55	1.52	0.54	5.86	11.75	3.93	5.19
MTEA0.01	62.26	43.94	63.78	56.64	33.81	27.49	47.99
MTIPA0.003	33.96	3.03	12.43	17.19	5.44	1.31	12.23
MTIPA0.006	-20.75	-9.85	-14.59	0.78	-3.15	-3.40	-8.50
MTIPA0.01	18.87	30.30	27.57	30.86	10.32	8.90	21.14

According to the results of Table 6, the compressive strength of pozzolanic cement samples containing 0.003 and 0.006% TEA not only did not increase significantly, but also decreased at some ages; however, the compressive strength behavior of the pozzolanic cement mixture containing 0.01% TEA was completely different from that of pozzolanic cement mixtures containing lower amounts of TEA, such that the compressive strength of this mixture increased by 60.00 at day 1, 43.69 at day 2, 63.78 at day 3, 56.77 at day 7, 29.96 at day 28, and 27.20% at day 56 compared with the control sample M1. In addition, according to the results of Table 5, the compressive strength of the mixture samples containing natural pozzolan in the presence of 0.01% TEA not only did not decrease compared with the compressive strength of pure Portland cement (M0), but also increased by an average of 17.3%. These results clearly show that TEA acts as a strong accelerator of compressive strength. The results of the study by Hongbo et al., (2019) showed that TEA can accelerate the hydration of tetracalcium aluminoferrite and tricalcium aluminate phases in cement, facilitate dissolution, and thus enhance the pozzolanic reaction of natural pozzolan. The increase in the rate of release of hydration heat in the initial reaction period is due to the accelerating effect of TEA on the reaction of tricalcium aluminate with calcium sulfate. The TEA additive can combine with some cations such as Al^{3+}, Fe^{3+} and Ca^{2+} under a highly alkaline environment. When TEA is combined with Al^{3+}, it can promote the formation of calcium sulfoaluminate hydrate (aluminoferrite trisulfate and aluminoferrite monosulfate) and accelerate the hydration process of tricalcium aluminate. The main reason for the increase in compressive strength by TEA could be attributed to the greater formation of calcium silicate (aluminate) hydrate gels (C-(A)S-H). In hydrates, with the addition of triethanolamine, the formation of hydrotalcite phase such as $Mg_6Al_2(OH)_{16}.CO_3.4H_2O$ and C-(A)S-H is accelerated, which is the reason for the increase in compressive strength (Hongbo et al., 2019). Jinqing and Wang (2022) studied the effect of TEA on increasing the compressive strength of pure Portland cement and showed that TEA had a positive effect on compressive strength at all ages until reaching the turning point, and the optimal dosage was approximately 0.013%.

The compressive strength of pozzolanic cement mixture samples containing 0.006% TIPA not only did not increase significantly, but also decreased at most ages; however, the compressive strength behavior of pozzolanic cement mixture samples containing 0.01% TIPA and 0.003% TIPA was different, such that the compressive strength of the sample containing 0.003% TIPA increased by 34.38 at day 1, 2.53 at day 2, 12.79 at day 3, 17.19 at day 7, 2.50 at day 28, and 1.05% at day 56, compared with the control sample M1. In addition, for the mixture containing 0.01% TIPA, 19.38 at day 1, 30.05 at day 2, 27.57 at day 3, 30.86 at day 7, 7.05 at day 28, and 8.98% at day 56 increased compared with the control sample M1; therefore, the results indicate that TIPA also acted as a compressive strength accelerator for Portland pozzolanic cement. In addition, the results indicated that the performance of TEA in accelerating the compressive strength of cement mixtures was better than that of TIPA. Since TEA and TIPA additives are commonly used to facilitate the cement grinding process by reducing the agglomeration of cement particles and also preventing the formation of coatings on the surface of the grinding materials, this effect causes a true homogenization of the cement components, including clinker, gypsum and natural pozzolan, which in turn adjusts the hydration reactions and compressive strengths.

The findings of Hongbo et al., (2019) showed that TEA and TIPA can accelerate the hydration of cement up to day 28, which is the reason for the increase in compressive strength of cement up to day 28 by TIPA and TEA. However, the performance of TEA in increasing compressive strength was better than TIPA. One of the reasons for this better performance was the reduction of air bubbles in the mortar when using TEA. Another reason was the relatively weaker ability of TIPA than TEA to facilitate the formation of hydrotalcite-like phase and C-(A)S-H.

3.3 CO_2 Production

Due to the characteristics of the production process, the cement industry is one of the main sources of CO_2 emissions, accounting for about 5-8% of global emissions. About 900 kg of CO_2 is released per ton of cement produced (Pisciotta et al 2023). According to the Intergovernmental Panel on Climate Change (IPCC), greenhouse gas emissions, especially CO_2, should be reduced by about 50-80% by 2050 (Anonymous, 2020).

In this study, clinker was reduced by 15% and natural pozzolan was used instead. The use of natural pozzolans instead of cement had many economic, environmental and technical advantages. CO_2 emissions during the processing of natural pozzolans are very low compared with cement production, because natural pozzolans do not need to be calcined due to their volcanic origin, as they are naturally heated (Hayati et al., 2023). Therefore, considering the production of 900 kg of CO_2 gas for the production of 1 ton of cement and replacing 15% of clinker with natural pozzolan, the production of CO_2 gas was reduced by 135 kg.

4. Conclusion

In this study, the effect of quality-improving chemical additives including CN, CF, TEA and TIPA on CO_2 emissions in the sustainable production of Portland pozzolanic cement was investigated. The main results of this study are:

1. The effect of CN in increasing the compressive strength was not sufficient and therefore it cannot be considered as a suitable accelerator of compressive strength in the Portland cement mixture containing natural pozzolan. CF can be considered as a suitable accelerator of compressive strength of Portland cement mortar containing natural pozzolan.

2. By adding 0.01% TEA to Portland pozzolanic cement, the initial compressive strength increased by about 13.2% for day 1 and an average of 17.3% for all ages compared with the compressive strength of pure Portland cement. By adding 0.01% TIPA to Portland pozzolanic cement, the initial compressive strength decreased by about 17.1% for day 1 and an average of 37.3% for all ages compared with the compressive strength of pure Portland cement.

3. The effect of TEA in increasing the early compressive strength of Portland cement containing natural pozzolan is much better than TIPA.

4. Considering the production of 900 kg of CO_2 gas for the production of 1 ton of cement and replacing 15% of clinker with natural pozzolan, an equivalent to 135 kg of CO_2 gas production was reduced per 1 ton of cement production.

Statements and Declarations

Data availability

The data used in this research are provided in the text of the article.

Conflicts of interest

The author of this paper declared no conflict of interest regarding the authorship or publication of this paper.

Author contribution

A. Derakhshani: Original Draft Preparation, Methodology, Investigation; A. Ghadi: Research Management, Supervisor, Writing, Review and Editing; S.E. Vahdat: Supervision, Writing, Review and Editing.

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