Reduction of CO_2 Emission and Production Costs by Using Pozzolans in Lamerd Cement Factory

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ABSTRACT: *Two major concerns for cement factories are environmental aspects and production costs. The number of cement factories is increasing in Iran which from an environmental point of view is not favorable. Different pozzolans such as brick, potted clay, volcanic rocks, sedimentary rocks and rice bran were used in the cement produced by Lamerd factory in the south of Iran. Among these additives, rice bran fails to be proper pozzolan. This research shows that using pozzolans up to 10% does not have a significant effect on the quality of Lamerd cement. Almost the similar textures of compositions for differently mixed types of cement were determined using XRD and XRF experiments. Considering these additives, volcanic and sedimentary rocks seem to be more favorable regarding both quality and price. In fact, the additives can reduce both the emission of CO_2 (reduction of more than around 400 tons CO_2 per day) and the production costs (the money saved is around $76000 per day) in cement factory of Lamerd.*

KEYWORDS: *Pozzolans; Cement; Carbone emission; Additives; Air pollution.*

INTRODUCTION

The two largest producers of carbon dioxide are power plants (producing electricity) and cement factories [1-4]. Portland cement manufacturing is an energy-intensive process that grinds and heats a mixture of raw materials such as limestone, clay, sand and iron ore in a rotary kiln. The product called clinker is cooled, ground and then mixed with a small amount of gypsum to produce cement. Cement is mixed with aggregate and water to make concrete.

About 5% of the worldwide man-made emissions of carbon dioxide belong to Cement production, of which 50% is from the chemical process and 40% from burning fuel [5, 6]. About 900 kg of CO_2 is emitted from the fabrication of every ton of cement [7, 8]. Cement manufacturing factories produce greenhouse gases in two ways; one, directly through the production of carbon dioxide when calcium carbonate is thermally decomposed, producing lime and carbon dioxide [9] second, burning huge amount of fuel to heat up rotary furnace up to 1200 C^0. Overall, the top 10 cement-producing countries in 1994 accounted for 63% of global carbon emissions from cement production [10, 11].

The major question is that what can we do to mitigate environmentally unfavorable CO_2 emission and at the same time decreasing the production cost and enhancing the cement quality? One of emission mitigation options includes CO_2 removal from fuel gases in clinker kilns. Using different kinds of pozzolans as additives to make

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mixed cement is a very essential remedy to decrease CO_2 emission and production costs [12-18].

Pozzolan is a siliceous material that can be used as an inexpensive substitute for cement in mortar mixtures [19]. Most pozzolans are plentiful and because of current uses for them are limited, they represent a potential source of inexpensive construction material. Some pozzolans can be processed into a material with characteristics similar to Portland cement, so it is feasible that a significant portion of cement in a concrete mixture may be replaced by pozzolan. The properties of concrete mixes after the addition of various pozzolan specimens have been studied by many researchers [20-25]. In this research we are using Brick, potted clay, volcanic rock, sedimentary rock and rice bran as an additive in cement.

EXPERIMENTAL SECTION

Preparation of cement paste

The exact amount of 300 gr cement sample is mixed with water (the weight of water is 28% of the cement weight). The cement powder must be screened with 1.18 mm sieve (sieve no. 16 in ASTM system). First water is added to the mixer when mixer runs slowly and then cement is added slowly for a period of 30 seconds. The mixer is stopped for 15 seconds for cleaning the cement which is adhered to the mixer with a trowel, and then the mixer is run fast for one min.

Moulding of the paste

It is recommended to quickly form the cement paste into a ball with gloved hands and toss six times from one hand to the other, maintaining the hands about 15 cm apart. Press the ball, resting in the palm of the hand, into the larger end of the conical ring held in the other hand, completely filling the ring with the paste. Remove the excess at the larger end by a single movement of the palm of the hand. Place the ring on its larger end onto the non- absorptive plate, and slice off the excess paste at the smaller end at the top of the ring by a single oblique stroke of the trowel held at a slight angle with the top of the ring. Smooth the top of the specimen, if necessary, with one or two light touches of the pointed end of the trowel. Immediately after the melding, penetration measurements are being made. The specimen shall remain in the conical mould, supported by the non-absorptive plate throughout the test period. Before commencing the setting time test, the consistency test was conducted to obtain the water required to give the paste normal consistency.

The consistency test

To obtain the water required to give the paste normal consistency. The Vicat rod with the needle of 10 mm diameter at the end of the rod was placed in the Vicat system and the rod was adjusted. The mould was placed under the rod and the needle was balanced at the surface of the mould. After opening the rod screw for 30 sec, the rod penetrated into the paste and the length of penetration was measured. The penetration of the needle should be 10 mm so we corrected the amount of water based on this value.

Determination of initial and final setting time

All setting times were accomplished as per IS: 4031-1966 using Vicat instrument conforming to IS: 5513-1976 and balance with a load of 1000 g with an accuracy of ±1.00 g. Gauging trowel (conforming 10086-1982) is used to gauge the cement paste. A cement paste with normal concentration using standard instruction was prepared and after moulding, it is placed in the moist environment and waits until setting started.

Initial setting time

Place the test block under the rod bearing the needle (1 mm diameter). After 30 sec. lower the needle gently in order to make contact with the surface of the cement paste and release quickly allowing it to penetrate the test block for 30 sec. Measure and write down the size of penetration. Now clean the needle and change the position of the pasted block so that the needle contact with the new point on the paste surface. Repeat the procedure for every 15 min. until the needle penetrates the test block for 25 ± 0.5 mm. The time period elapsing between the time water is added to the cement and the time the needle penetrates the test block for 25 ± 0.5 mm, is the initial setting time.

Final setting time

Replace the above needle by the one with an annular attachment. The cement should be considered as finally set when upon applying the needle gently to the surface of the test block, the needle makes an impression therein (penetration of 0.05 mm, while the attachment fails to do so). The period elapsing between the time, water is added to the cement and the time the needle makes an impression on the surface of the test block, while the attachment fails to do so, is the final setting time. The experiment conditions must be carefully considered. The temperature of the air at the vicinity of mixing dry cement location, moulds and base plates and temperature of mixing water must be held around 23 ± 3 C^0. Relative moisture of the mixing room should not be less than 50%.

Bending and compressive strength test

The standard method of 393 for measuring bending and the compressive test is used for regular cement. For these tests, standard cement blocks with a dimension of 40 x 40 x 10 mm were used. The paste using for the blocks consisted of 1 part by weight cement, 3 parts standard sands and 1/2 part water (water to cement ratio was 0.5). The specification of the sand used in the paste must be according to the national standard of Iran, 3040. After compression and moulding, the moulds were located in the wet area for 24 hours. Then unmoulding blocks are placed in water with a constant temperature for a specific period of time before bending and compressive strength tests are done. During the bending strength test, the blocks break in half and then each half block was used for the compressive strength test.

XRD and XRF Analysis

Crush the sample by hand in a porcelain mortar. Take representative amounts of the crushed sample (around 50 g) using sample divider PT 100. A jaw crusher can be used, but automatic milling devices which could induce shear stress of amorphization such as ball mills should be avoided. The sample is ground by disk mill up to 75 M. Then tablets are prepared from this sample for XRD and XRF experiments. Two kinds of tablets were used; 1- fused tablet, using a sample with flux material such as lithium borate to help to melt, 2- Pressed tablets, which in this case, the sample powder is mixed with an inert and sticky material then under pressure, it is converted to a tablet. Powder sample size for XRF is 10 to 20 g and for XRD test is between 1 to 2 g. However, the size of samples of soils and rocks for both experiments are between 80 to 100 g.

RESULTS AND DISCUSSION

The used additives in this research are Powders of brick, potted clay, volcanic rock, sedimentary rock and rice bran. All these additives were individually added to cement (Portland cement type II) either 2 or 5 percent by weight. Setting tests were used on this mixed pozzolanic cement and the results are shown in Table 1.

As Table 1 shows, the initial and final setting times of mixed cement compared to the pure cement (no additive) are almost the same (as standard deviation shows; rice bran is not included) except for brick powder that small increasing in setting time is seen and for rice bran that setting time is very short. However, rice bran additive did not work as a pozzolan for Lamerd cement and the results were negative. This happened because the rice bran adsorbs water and swallows, leaves the concrete with less water and this shorten the setting time to ten min with respect to the standard setting time of 45 min. Similarities of initial and final setting times regarding pure cement and pozzolanic cement using volcanic rock are shown in Fig. 1. Setting times of 2% and 5% volcanic rock as additives are very close to pure cement setting time.

The values of setting times for the mixed cement of the sedimentary rock as is shown in the Fig. 2 are similar to the pure and mixed cement using volcanic rock as an additive.

Data in Table 2, show that bending and compressive strengths of mixed cement are very close (as standard deviation shows), and sometimes better than pure cement. The quality of Lamerd cement is very good and a higher percentage of additives at the end may not have any significant effect on its concrete physical and chemical properties.

Bending and compressive strengths of pozzolanic cement using brick as an additive with respect to the pure cement is shown in Fig. 3. These strengths are almost the same and pozzolanic cement quality remains the same as pure cement. For other additives in this research except for rice bran, we see the same trends and similarities (figures are not shown).

Bending and compressive strength variation during 28 days of hardening can be shown in Fig. 4. The lines related to compressive and bending strength for pozzolanic cement of 5% brick (A) and pure cement (B) are almost the same. As figure shows, the bending and compressive strengths for the mixed cement are even

Table 1: Initial and Final Setting Time of mixed Pozzolanic Cement.

Additives	Initial Setting (min)	Final Setting (min)
No additives	170	205
Brick powder (2%)	176	212
Break Powder (5%)	185	225
Potted clay Powder (2%)	168	205
Potted clay Powder (5%)	170	208
Volcanic rock (2%)	171	203
Volcanic rock (5%)	172	205
Sedimentary rock (2%)	173	203
Sedimentary rock (5%)	171	209
Rice bran (2%)	10	Negative
Rice bran (5%)	10	Negative
Std.Dev.	5.06	6.91

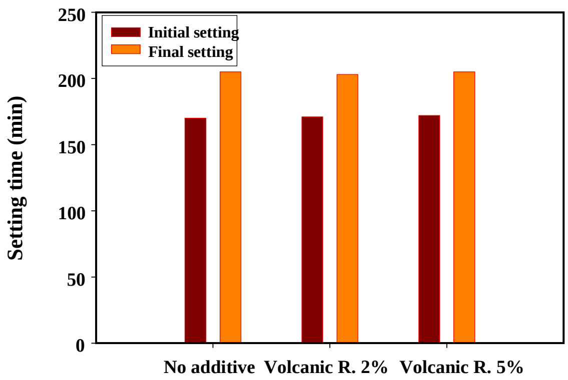

Fig. 1: Initial and final setting times of pure and mixed cement using volcanic rock as an additive.

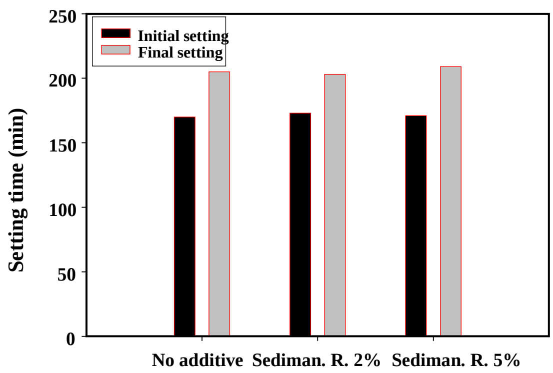

Fig. 2: Initial and final setting times for pure and mixed cement using sedimentary rock as an additive.

more than pure cement. It seems that the hardening process enhances the effective role of additives in the cement.

The chemical composition of pure Lamerd cement and mixed cement using XRF analysis is shown in Table 3. Data in this Table show that there are'nt significant differences between pure cement and 2% or 5% mixed pozzolanic cement (as is shown from their standard deviations). As Table 3 shows the concentrations of different oxides in pure and mixed cement change simultaneously.

Carbon dioxide is the most abundant oxides in the cement as Fig. 5 shows. Because the main constitute of cement raw material is calcium carbonate, and SiO_2, Al_2O_3, and Fe_2O_3 are the next abundant oxides respectively. Quantitative similarities in compositions illustrate that mixed cement has almost the same quality as pure cement, however the mixed cement production is cheaper and environmentally friendlier.

The experiment of X-Ray Diffraction (XRD) is used to determine the main phases of the mixed pozzolanic cement and the results of the analysis are shown in Table 4.

Analysis of XRD shows that different phases such as C_3S (Tricalcium silicate), has a higher percentage of pure and pozzolanic cement but its variation in different additives are almost uniform (as standard deviation shows).

Table 2: Bending and Compressive strengths (Kg/cm2) of mixed Pozzolanic cements by the hardening Time.

Samples	1 day		2 days		3 days		7 days		28 days	
	bending	compression	Bending	compression	bending	Compression	bending	compression	bending	compression
No additive	21	100	33	205	43	250	56	323	70	480
Brick (2%)	22	101	32	198	41	238	56	342	71	472
Brick (5%)	22	97	34	208	45	242	58	348	70	498
Potted clay (2%)	23	102	34	199	44	248	54	341	71	472
Potted clay (5%)	20	95	35	198	44	250	52	355	69	480
Volcanic R. (2%)	22	104	34	203	40	243	55	348	71	479
Volcanic R. (5%)	21	100	30	192	42	240	51	338	67	494
Sedimentary R. (2%)	25	105	33	199	43	248	51	338	65	470
Sedimentary R. (5%)	22	99	34	193	44	243	51	336	68	470
Rice bran	--	--	--	--	--	--	--	--	--	--
Std.Dev.	1.41	3.16	1.48	5.22	1.61	4.44	2.63	9.09	2.08	10.3

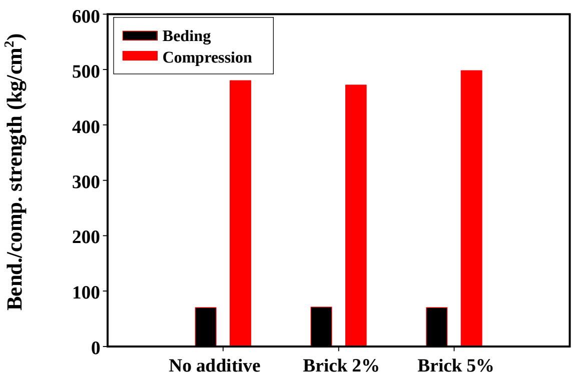

Fig. 3: Bending and compressive strengths of mixed cement using brick as an additive after 28 days.

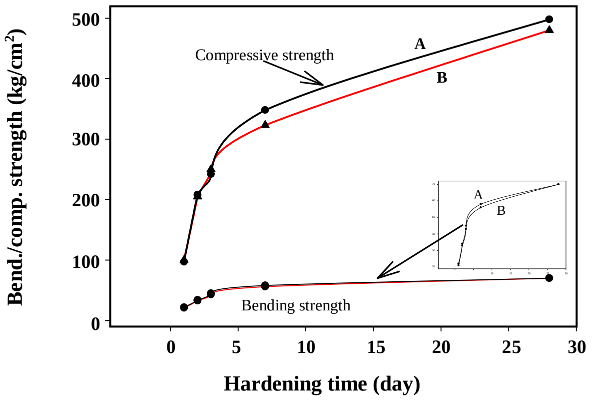

Fig. 4: Bending and compressive strengths of A: mixed cement with 5% brick and B: pure cement vs. hardening time (day).

For other phases such as C_2S (Dicalcium silicate), C_3A (Tricalcium aluminate), and C_4AF (Tetra-calcium aluminoferrite) uniformity exist as is shown in the Fig. 6.

The maximum amount of pozzolan that can be used without decreasing the quality of cement was tested and the result is shown in the Fig. 7. In this Figure, the pozzolanic additives were added up to 20% by weight to Lamerd cement. From this Figure, we can deduce that addition of additives up to 8% has no risk of losing the cement quality. However, more than 8% additives, the curves for both compressive and bending strengths are no longer linear. In fact, the quality of Lamerd cement compared to other cement factories in Iran has gained a higher reputation and quality and even addition of additives up to 10% may be allowed. Here the result for volcanic rock additives is shown and of course, the test for rice bran as was shown before did not work.

CONCLUSIONS

Additives such as brick, potted clay, volcanic rocks and sedimentary rocks can be used in Lamerd cement without losing the quality of the concrete. The results, of course, depends on the availability of specific pozzolan and its price. Iran is a mountainous country and there are plenty of volcanic rocks. Using even 10% of volcanic rock additive still can hold the quality of the Lamerd

Table 3: Compositions of mixed pozzolanic cement determined by XRF.

Cement	% additives	FCaO	SiO_2	Al_2O_3	Fe_2O_3	CaO	MgO	SO_3	IR	LOI
Pure	0	1.12	21.64	4.61	3.99	63.34	2.41	1.62	0.42	0.77
Brick	2	1.17	22.52	4.51	3.88	62.62	2.70	2.12	0.77	1.12
Brick	5	1.28	22.38	4.51	3.81	62.92	2.66	1.98	0.70	1.08
Potted clay	2	1.22	21.45	4.12	3.95	63.62	2.65	1.90	1.32	2.10
Potted clay	5	1.17	21.91	4.11	3.18	62.75	2.52	1.70	1.21	2.10
Volcanic	2	1.17	21.52	4.66	3.77	63.39	2.55	2.39	1.22	2.36
Volcanic	5	1.03	21.17	4.70	3.68	63.05	2.62	2.50	1.00	2.50
Sedimentary	2	1.08	22.5	4.22	3.66	64.04	2.88	1.88	1.28	1.99
Sedimentary	5	1.01	21.62	4.17	3.88	63.45	2.54	1.63	1.25	1.88
Std.Dev		0.087	0.498	0.243	0.243	0.450	0.133	0.317	0.318	0.618

Table 4: XRD analysis, % composition of different phases in mixed and pure cement.

Cements	C_3S	C_2S	C_3A	C_4AF
Pure cement	54.9	22.0	5.5	12.1
Brick 2%	46.1	31.2	5.4	11.8
Brick 5%	48.5	29.1	5.5	11.6
Potted clay 2%	60.8	17.0	4.2	12.0
Potted clay 5%	55.0	22.8	5.5	9.70
Volcanic R. 2%	56.0	21.0	6.0	11.5
Volcanic R. 5%	53.3	23.3	6.2	11.2
Sedim. R. 2%	54.3	25.0	5.0	11.1
Sedim. R. 5%	58.6	19.2	4.5	11.8
Std.Div.	4.55	4.50	0.64	0.727

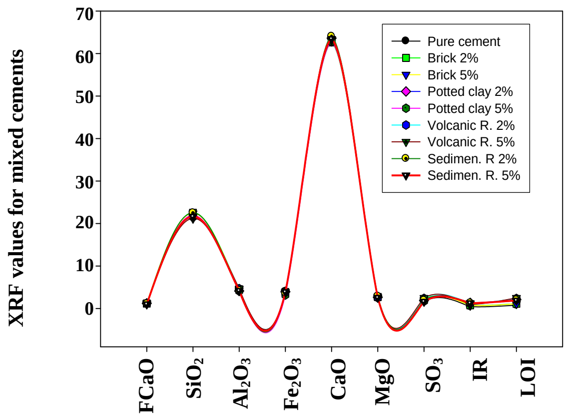

Fig. 5: XRF values of mixed cement for different additives.

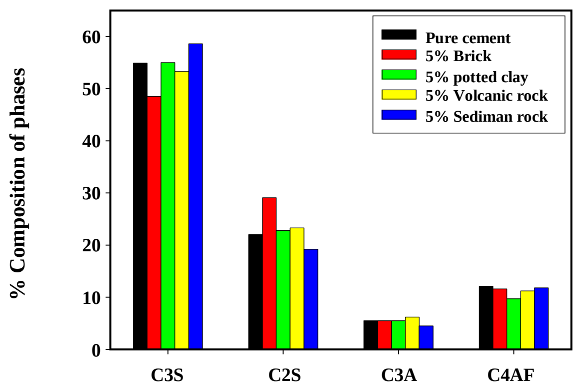

Fig. 6: Percent composition of different phases in mixed cement with respect to pure cement.

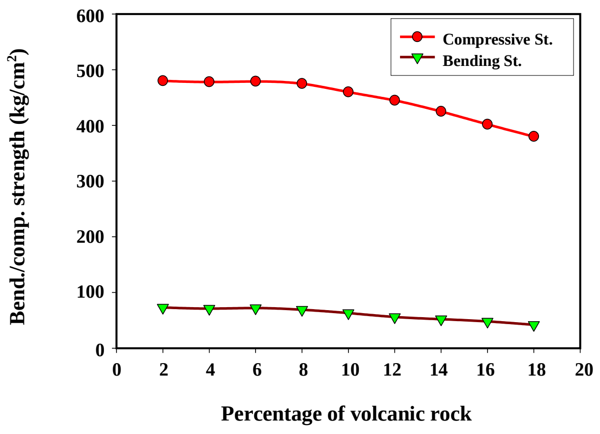

Fig. 7: Bending/compressive strength vs. percentage of volcanic rock after 28 days.

cement to a high standard. Around one ton CO_2 is emitted for each ton of cement production both as a fuel and calculations of calcium carbonate. The production of cement in Lamerd factory is 4000 ton per day. Therefore, adding 10% of pozzolans can reduce 400 tons CO_2 per day and this reduction of CO_2 gas environmentally is very important to prevent global warming. Calculation shows that production of each ton clinker for Lamerd factory costs $19, and since one-ton volcanic rock replaces one-ton clinker, then the money saved for 4000 ton cement per day will be $76000. Therefore, two main reasons, environmental and economical aspects make the production of mixed pozzolanic cement unavoidable. Regarding the production of cement in Iran we are facing with two phenomena. The first one is that the application of the proper additive to cement has a great deal of economic and environmental benefits. In fact, this can encourage the directors of the cement factories because environmental safety is involved with saving money. However, the second phenomenon is that, in spite of extensive academic research in Iran, still transferring of the knowledge from academic and research centers to industries is a big and complicated dilemma. In this regard, government, private sections, and industrial bourgeoisies have to work all together to solve or break this complicated and severe talisman.

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