Chemical and Thermal Activation of Perlite-Containing Cementitious Mixtures

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ABSTRACT

Perlite is a volcanic mineral abundant in Turkey, China, Japan, the US and several EU countries. Expanded perlite has been widely used in producing lightweight concrete. Recent research suggests the use of ground perlite as a pozzolan to partially replace cement. This study investigates strength properties of high-volume perlite mixtures and the influence of chemical and thermal activation on their strengths at early and later ages. Both activation types can increase early-strength gain rates and strength values achieved by pure portland cement mixtures can be exceeded in as early as 28 days with some activators and be maintained. Findings indicate that ground perlite is a successful natural pozzolan. Results also suggest that perlite-only mixtures can be activated to produce geopolymers. The consistency of its chemical composition compared to those of artificial pozzolans and its abundance in several developing countries makes perlite attractive for producing sustainable concretes with reduced carbon footprints.

INTRODUCTION

Perlite is an amorphous mineral of volcanic origin which contains 2–6% chemically combined water. Upon heating to ~900°C, this water is lost, expanding it to a cellular material of extremely low bulk density. Consequently, in addition to its use in horticulture and pharmaceuticals, expanded perlite has been widely used by the construction industry as an aggregate in the production of lightweight concretes, insulation products etc. [TPI, 2009].

Although much-less known, due to its glassy nature and its chemical composition (70–75% SiO_2 and 12–18% Al_2O_3), finely-ground perlite possesses pozzolanic properties, as demonstrated in recent studies. Yu et al. [2003] reported pozzolanic activity of perlite. Erdem et al. [2005] used ground perlite to produce blended cements and mortars, concluding that the grinding of perlite is less energy-intensive than portland cement clinkers. It was found that perlite-containing mixtures conformed to standard limitations on setting time, soundness and compressive strength. Uzal et al. [2007] used ground perlite at high cement-replacement fractions in concrete and reported normal consistency water contents and setting times similar to those of a portland cement-only control concrete and that the concretes had very low permeability after a few weeks. The strengths were lower compared to the control mixture, at

all ages up to 91 days. Turanlı et al. [2005] reported significant decreases in compressive strength, particularly at early ages, compared to a pure portland cement mixture.

A decrease in strength plagues most high-volume pozzolan mortars and concretes. Chemical and thermal activation have been suggested to improve particularly the early-age strengths of such mixtures. Sodium sulfate (Na_2SO_4) has been shown to be effective in increasing early-strength and sulfate resistance [Freeman and Carrasquillo, 1995]. Wu and Naik [2003] used several chemical activators in mixtures containing high volumes of coal ash blended cements and also reported that sodium sulfate (Na_2SO_4) was one of the most effective and economical chemicals in improving early-strength. Shi and Day [2001] concluded that calcium chloride dihydrate ($CaCl_2.2H_2O$) was very effective in increasing the pozzolanic reaction rate of lime-natural pozzolan mixtures and that thermal activation increased early strength while decreasing ultimate strength. Acid treatment of pozzolans to increase reactivity has also been suggested [Alexander, 1955; Feng et al., 2004].

Chemical activation of pozzolan-only mixtures not containing any portland cement have also been reported. Palomo et al. [1999] found that sodium or potassium silicates were more effective activators than solutions of alkali hydroxides. Fernandez-Jimenez and Palomo [2005] observed that sodium hydroxide and sodium silicate used together to activate a low-calcium fly ash significantly increased strength over their separate use, by forming a geopolymer. Other methods of geopolymerization of artificial and natural pozzolans have been reported [Davidovits, 2008].

With a known total worldwide reserve base of ~7 billion tons [USGS-a, 2009], perlite is quite abundant. Countries like Turkey, China, Japan, the US, and some EU countries like Greece and Italy share a majority of the reserves. As some of these countries are major producers (and some major users) of portland cement, relatively small increases in the fraction of pozzolans used in concrete, while still meeting desired strength and durability requirements, can result significant environmental and economical savings, as well as technical improvements. From an environmental point of view, artificial pozzolans are clearly preferred over natural pozzolans, for cement replacement. Natural pozzolans lack the waste reuse advantage while being burdened by the resource depletion disadvantage. From an economical point of view, such a comparison is intricate as it depends on availability, price, and state of the pozzolans. While energy is required to grind many natural pozzolans like perlite, and some artificial pozzolans like blast furnace slag, others like fly ash are ready to use. Some regions or countries may be rich in natural pozzolans but not generate substantial amounts of artificial pozzolans. In the eastern part of Turkey, for example, there are no steel mills or coal-burning power plants, however very large reserves of perlite. From a technical point of view, again such a comparison is difficult. Natural pozzolans from the same quarry often show less chemical variation over time than artificial pozzolans from one source, such as a thermal power plant. This greatly improves repeatability and facilitates the widespread adoption of the findings of studies using natural pozzolans. As such, studies on chemical activation of artificial pozzolans using the same chemicals report different 'ideal' proportions of activators.

The amounts of the major oxides in perlite vary less than a few percentage points from one source to another and even less within the same pit. Therefore, it is expected that the results shown in this study can be repeated universally, any variation resulting mainly from differences in the portland cements used. The paper presents results of experimental investigations of the effectiveness of chemical and thermal activation in increasing the early- and late-age strengths of mortars containing high volumes of perlite.

EXPERIMENTAL INVESTIGATION

Materials

A CEM I 42,5R portland cement and perlite from a quarry in Erzincan, Turkey were used as cementitious materials in this study. The cement met the requirements of TS EN 197-1 [TS EN, 2002]. Table 1 provides the chemical compositions of the portland cement and perlite used, as determined using X-ray fluorescence.

Table 1. Oxide Analysis of the Powder Materials Used

	CEM I 42,5R	**Perlite**
SiO_2	19.56	71.1
Al_2O_3	5.00	13.0
Fe_2O_3	3.68	1.6
CaO	64.55	1,6
MgO	1.57	0.5
SO_3	2.41	1.6
K_2O	0.66	3.8
Na_2O	0.77	4.2
Loss on ignition	2.89%	-

The Portland cement had a Blaine fineness of 3370 cm^2/g. The perlite was ground alone in a laboratory ball mill to a Blaine fineness of ~4580 cm^2/g. The specific gravity of the cement and ground perlite were determined as 3.09 and 2.43, respectively. CEN Standard sand and distilled water were used in preparing the mortars. Five chemicals were used for activation: NaOH, Na_2SiO_3, Na_2SO_4, $CaCl_2$, and HCl. The NaOH, Na_2SO_4, and $CaCl_2$ were in solid form with >97%, >90%, and 84% purity. The 38.5 % solids Na_2SiO_3 and 37 % HCl were used as solutions. The use of only NaOH gave poor results for the 25 % perlite mortars and was abandoned for the 50 % perlite mortars.

Mixture proportions and Curing Conditions

This study attempted the chemical and thermal activation of mortar mixtures containing 25-50-80-100 % (by weight) perlite, using the five activators named in the previous section. Three different amounts of chemicals, 2, 4, and 6 % by weight of the cementitious materials, were used in the 25 and 50 % perlite mixtures. Based on intermediate results, it was decided to select only 50 % perlite mixtures with 2 % activator for thermal activation. Thermal activation involved steam curing at 55°C or 85°C for 3 or 10 hours. Results from mixtures with no activation, only chemical activation, and both chemical and thermal activation were compared with each other and to the control mixture containing only portland cement. Due to space limitations, here only the results of the 2% activator case for the mortars containing 25, 50 and 80 % perlite, and one mortar containing 100 % perlite, are presented. It should be noted that the use of 2% activator gave the best performance for most of the mixtures in both the heat-cured and room temperature cases. The 100 % mixture was activated in a dry oven at 65°C using both NaOH and Na_2SiO_3.

Table 2 presents the mixture proportions used in the different categories of mortars for which test results are presented.

Table 2. Proportions of Materials Used for Mortar Mixtures

	Category 1	Category 2	Category 3	Category 4	Category 5
Mixture designation	Control	P25	P50	P80	P100
Cement (mass % of Cm[*])	100	75	50	20	0
Perlite (mass % of Cm)	0	25	50	80	100
Activator (mass % of Cm)	None	None / 2	None / 2	2	~14 (total solids)
Activating chemical	None	one of the five chemicals named	Na_2SiO_3 or Na_2SO_4 or $CaCl_2$ or HCl	$CaCl_2$	NaOH and Na_2SiO_3
Thermal Act. Temp.	None	None	None / 55°C / 85°C	85°C	65°C
Thermal Act. Duration	-	-	3 h / 10 h	10 h	48 h

[*] Cm = Cementitious materials (Cement + Perlite)

In accordance with the findings of Uzal et al. [2007], the consistency of the mortar mixtures did not change noticeably with the addition of perlite and the water-to-cementitious materials ratio for all mixtures was set to 0.485, except for the 100 % perlite mixture which had a water-to-perlite ratio of 0.4. The sand-to-cementitious material ratio for all mixtures was 2.7. Mortars were mixed at room temperature, following the durations and order of mixing described in ASTM C 305. Specimens to be thermally activated were placed in the oven immediately after casting.

RESULTS AND DISCUSSIONS

Compressive Strength Development

The efficiency of the activation attempts was judged solely by comparison of early-age and later-age strengths of the mortars with those of the non-activated perlite-incorporating mortars and the control case. Although it could be expected that high amounts of perlite addition could affect setting time and that the use of some chemicals may influence durability, the goal was to eliminate some of the chemicals and chemical/thermal combinations before investigating a broader range of properties of successful mixtures providing desirable strength development. Three 4*4*16 cm prisms were cast for testing at every age. The prisms were tested in three-point bending and the two halves from each tested in uniaxial compression. Only the results of compressive strength are presented. The flexural strengths of the mortars were ~15-25 % of the compressive strengths at 56 days.

The mean compressive strengths of 25% perlite mixtures, with different activators and no heat-curing, are compared to the non-activated mortar and the control mortar in Table 3. Figure 1 shows the strength values at each age normalized against the control mixture (Category 1) strength to make it easier to compare results. A value greater than 1.0 indicates that the strength of that mixture exceeds that of the control Portland cement mixture at that age. Normalized strength is only shown up to 56 days to better show detail at early ages.

Table 3. Compressive Strengths of Chemically Activated P25 Mortars (MPa)

| Activator	Age					
	1 day	**3 days**	**7 days**	**28 days**	**56 days**	**91 days**
None	8.77	23.12	31.70	42.88	55.00	57.05
NaOH	7.42	12.60	14.55	24.20	29.38	31.55
Na$_2$SiO$_3$	6.47	19.65	28.18	41.73	47.18	50.24
Na$_2$SO$_4$	12.63	25.23	31.80	39.30	47.60	51.09
CaCl$_2$	12.27	29.73	35.98	57.10	58.63	71.30
HCL	5.80	24.55	33.55	52.90	55.83	60.10
Control	13.43	24.50	34.53	44.93	52.00	55.70
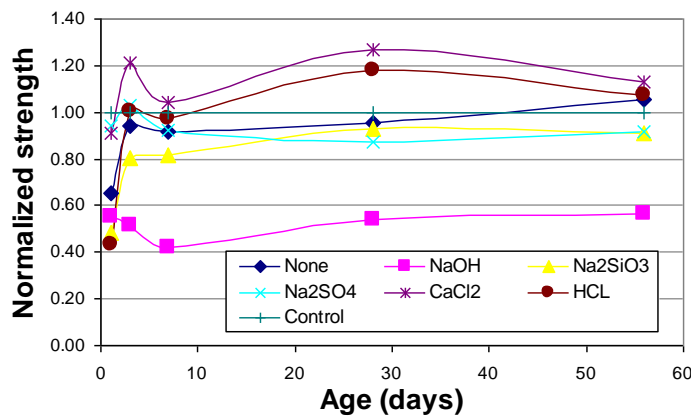
Fig. 1. Compressive Strengths of Chemically Activated P25 Mortars Normalized Against the Pure Cement Control Mortar Strengths

The P25 mixtures without any chemical or thermal activation shows an expected strength loss compared to the control at early ages. However, the pozzolanic reaction appears to increase strength to within 5 % of the control at 3 days and exceeds it between 28 and 56 days. Of the activated mixtures without thermal activation CaCl$_2$ and HCl give the highest ultimate strengths while NaOH appears detrimental and give the lowest strengths of all mixtures beyond 1 day. Despite its high ultimate strength the mortars activated with HCl possess a 1-day strength about 65 % and 43 % of the non-activated P25 and control mixtures, respectively. Na$_2$SO$_4$ also slightly improves early-strength but slightly decreases strength after 28 days. Thus, without any thermal activation, and to overcome the drawback of early strength loss for the P25 mixtures, CaCl$_2$ and Na$_2$SO$_4$ appear to be most effective and a choice may be based on the specific application conditions, such as whether the concretes will be reinforced or plain. It is apparent that perlite is an effective pozzolan, even without thermal activation.

The compressive strengths of 50% perlite mixtures, with different activators and no heat-curing, are compared to the non-activated mortar and the control mortar in Table 4. Figure 1 shows the values at each age normalized against the 100 % Portland cement control mixture strength.

Table 4. Compressive Strengths of Chemically Activated P50 Mortars (MPa)

Activator	Age					
	1	3	7	28	56	91
None	6.62	15.58	18.68	30.45	38.90	47.00
Na_2SiO_3	4.52	13.80	16.58	31.53	37.97	42.90
Na_2SO_4	7.08	15.88	19.90	31.83	39.10	33.10
$CaCl_2$	5.90	12.75	18.38	33.15	43.07	51.20
HCL	4.28	11.60	18.40	34.05	43.37	50.40
Control	13.43	24.50	34.53	44.93	52.00	55.70
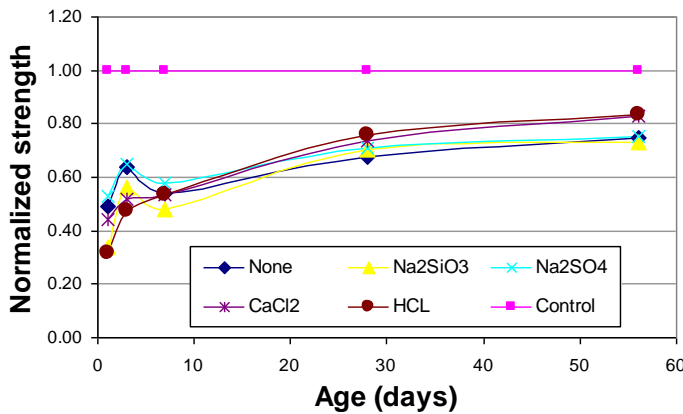
Fig. 2. Compressive Strengths of Chemically Activated P50 Mortars Normalized Against the Pure Cement Control Mortar Strengths

The P50 mixture without any chemical or thermal activation has about half the strength of the control mixture until 7 days, after which this difference diminishes. The strength did not attain that of the control within the testing period but was within 10 % after three months. It is expected that the control strength would be matched and exceeded eventually reinforcing the effectiveness of perlite even at 50% cement replacement. The early-age strengths of all activated P50 mixtures were much lower than the control, similar to the unactivated case. In fact none of the chemical activators appeared satisfactory at later ages with the highest strength achieved using HCl or $CaCl_2$ being only ~10 % higher than the unactivated mixture. Nevertheless all room temperature-cured P50 mixtures had sufficient ultimate strengths for structural use. Similar to the P25 mortars HCl caused reduced early strength despite giving high ultimate strength. The early strength improvement provided by addition of Na_2SO_4 was minor, about 10 % over the non-activated mortar. It appears that for the 50 % cement replacement case, thermal activation may be needed, to overcome losses in early-age strength.

For the thermally activated mixtures, only the results of the 'lowest temperature-shortest curing time' and the 'highest temperature-longest curing time' are shown since they yielded, with a few exceptions, the minimum and maximum strengths, respectively, for a set of mortars activated using the same chemical. The compressive strengths of 50% perlite

mixtures, with different activators thermally activated at 55°C for 3 hours, are compared to the non-activated 50 % mortar and the control mortar in Table 5. Figure 3 shows the values at each age normalized against the 100 % Portland cement control mixture strength.

Table 5. Compressive Strengths of Chemically Activated P50 Mortars Cured at 55°C for 3 hours (MPa)

| Activator	Age					
	1	3	7	28	56	91
None	6.62	15.58	18.68	30.45	38.90	47.00
Na_2SiO_3	5.72	12.97	15.75	32.28	37.95	41.25
Na_2SO_4	9.85	13.85	19.50	32.65	36.40	41.55
$CaCl_2$	6.95	12.72	20.40	29.40	46.45	48.62
HCL	2.95	10.15	16.15	34.00	45.65	45.75
Control	13.43	24.50	34.53	44.93	52.00	55.70
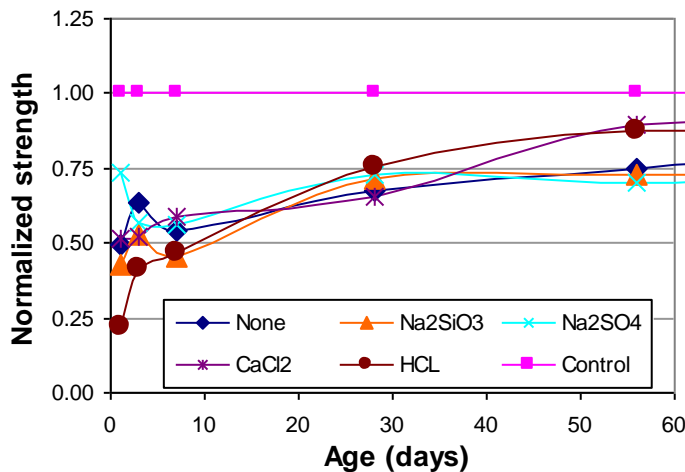
Fig. 3. Compressive Strengths of Chemically Activated P50 Mortars Cured at 55°C for 3 hours Normalized Against the Pure Cement Control Mortar Strengths

It is seen that, curing at 55°C for 3 hours improves the 1-day strength for all activated mortars except HCl, compared to the non-activated P50 mortar. The improvement is almost 40 % for the Na_2SO_4-activated mortars and 18 % and 27 % for the $CaCl_2$ - and Na_2SiO_3-activated mixtures. Even with this increase, the strengths of the chemically and thermally activated P50 mortars are 50-75 % of the control. The strengths on the following days, however, are nearly the same as those of the room temperature-cured samples suggesting that thermal activation at higher temperatures or for longer time periods may be needed. This heat-curing regimen does not appear to provide great benefits.

The compressive strengths of 50% perlite mixtures, with different activators thermally activated at 85°C for 10 hours, are compared to the non-activated 50 % mortar and the control mortar in Table 6. Figure 4 shows the values at each age normalized against the 100 % Portland cement control mixture strength.

Table 6. Compressive Strengths of Chemically Activated P50 Mortars Cured at 85°C for 10 hours (MPa)

Activator	Age					
	1	3	7	28	56	91
None	6.62	15.58	18.68	30.45	38.90	47.00
Na$_2$SiO$_3$	12.77	14.80	16.20	22.90	26.35	30.4
Na$_2$SO$_4$	18.48	18.45	19.73	24.90	31.35	35.6
CaCl$_2$	17.43	18.12	24.65	33.70	42.90	52.1
HCL	14.80	18.67	22.50	33.73	40.75	44.1
Control	13.43	24.50	34.53	44.93	52.00	55.70
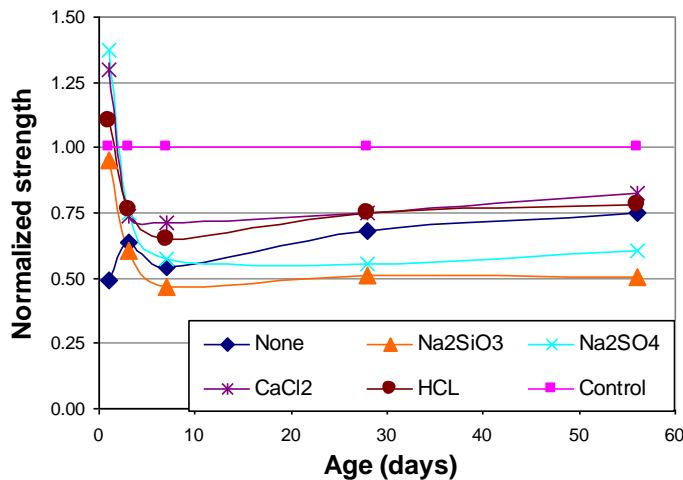
Fig. 4. Compressive Strengths of Chemically Activated P50 Mortars Cured at 85°C for 10 hours Normalized Against the Pure Cement Control Mortar Strengths

Thermal activation at 85°C for 10 hours substantially increases the early-age strength values of all P50 mortars over the room temperature cases. CaCl$_2$-activated samples once again possess the highest strength, both at early ages and later ages. HCl mortars, also similar to its behavior in the other cases, have relatively low 1-day strengths but rapidly improve between 1 and 3 days, and afterwards. All activated mortars possess 1-day strengths greater than that of the pure cement control mortar except the Na$_2$SiO$_3$-activated mortar, which shows 95 % of the 1-day control specimen strength. Also common to all activators is that their strengths relative to the control drops beyond 1-day. The lowest relative strength is at around 7 days for nearly all activated mortars with a subsequent increase, due probably to continued pozzolanic activity. Nevertheless, strengths of all thermally and chemically activated P50 mixtures are lower than those of only chemically activated, beyond 28 days. Na$_2$SiO$_3$ and Na$_2$SO$_4$ mortars have significantly lower later-age strengths than the control and the other activated mixtures. It appears, therefore, that thermal activation at 85°C for 10 hours can overcome problems caused by slow and delayed strength gain due to high perlite content.

Results for only one P80 and P100 mixture each are presented. Table 7 shows the compressive strength development of a P50 and a P80 mortar activated using $CaCl_2$ and 85°C for 10 hours. The successful activation of mixtures containing high amounts of perlite led to an additional study of their geopolymerization potentials. Table 7 also shows the 3- and 7-day strengths of a 'first attempt' P100 mixture based on [Rangan, 2008] activated using both NaOH and Na_2SiO_3 at 65°C for 48 hours.

Table 7. Compressive Strengths of Chemically and Thermally Activated P50 and P80 Cured at 85°C for 10 hours and a P100 Mortar Cured at 65°C for 48 hours (MPa)

Designation	Age					
	1	3	7	28	56	91
P50	17.43	18.12	24.65	33.70	42.90	52.1
P80	6.60	6.57	6.88	11.73	13.35	13.40
P100	-	15.86	24.80	-	-	-
Control	13.43	24.50	34.53	44.93	52.00	55.70

A comparison of the P50 and P80 mortars shows a substantial decrease in early and later-age strengths with the augmentation of pozzolan content. The P80 mixture appears to undergo reactions which give it a strength comparable to those of non-activated P50 mortars at 1 day. Surprisingly, however, the strength does not improve measurably during the following week and about doubles, at 56-days. Although such a mixture can still be used for certain applications, the limiting content for cement replacement with perlite for structural uses appears to lie between 50-80 % by weight.

The P100 mixture developed ~25 MPa strength at 7 days, after dry-oven curing and the strength increase continued at room temperature. As expected by looking at Table 1, and the successful results presented in this paper, mixtures containing only perlite as the cementitious powder can be used to develop geopolymeric materials. Improved proportioning and concentration of chemicals, and better thermal curing program are expected to substantially increase the strengths achieved.

ECONOMICAL AND ENVIRONMENTAL ARGUMENTS FOR USING GROUND PERLITE IN CONCRETE

The combined annual cement production of the seven countries listed in the introduction exceeds 1.7 billion metric tons, over 60 % of the worldwide production. China is increasing its annual production by ~100 thousand tons every year, greater than the individual annual production of any country in the world except India [USGS-b, 2009]. The 1:1 relationship between amount of CO_2 released per amount of portland cement downplays the greenhouse gas issue. Theoretically, producing one ton of clinker requires 1.6 GJ of energy [Liu et al., 1995]. The average specific energy consumption, however, changes from 2-3 GJ to much higher, depending on process methods and kiln technologies. Some plants in China produce clinker at an average energy consumption of 5.4 GJ [Khurana et al., 2002]. This corresponds to energy obtained by the burning of 100-150 kg of average-energy coal, which corresponds to an added 250-600 kg of CO_2 released per ton of cement produced.

As stated previously, natural pozzolans must offer significant economical or technical advantages to be preferred over industrial byproduct artificial pozzolans. However, an argument could be made for their use where artificial pozzolans are not available or variations in their compositions render them difficult to use in high-volume pozzolan applications or for important projects. The low variability of the composition of perlite increases confidence in mixtures incorporating large amounts. The use of perlite does lead to resource depletion but it still reduces the CO_2 emitted due to production. With recent moves towards taxation and trading of emissions, and one ton of carbon trading at ~15€ (in Europe), reduction of emitted CO_2 can equate to great monetary savings.

The energy that goes into preparation of ground perlite for use in concrete is due mainly to grinding and transportation. Expanded perlite is more easily pulverized but such material has already been heated to high temperatures and has a large carbon footprint. Crushing from the natural state is less energy intensive than crushing clinker and energy for transportation depends on site location. For thermally activated applications, such as production of precast members, a small amount of extra energy will be expended to maintain the chosen low temperature of the curing environment. From a different environmental perspective, some artificial pozzolans may contain and concretes made with them can eventually leach out hazardous materials, such as heavy metals. This is a problem that would not be encountered with perlite, thus rendering perlite concretes more suitable for environmentally sensitive sites. In short, concretes incorporating high volume fractions of ground perlite as a pozzolan can be a greener alternative.

CONCLUSIONS

The following general conclusions can be drawn from the study provided in the paper:

- Perlite is an effective natural pozzolan and can be used to replace up to 50 % of portland cement in concrete mixtures without a significant loss of ultimate strength
- The decrease in the early-age strength of mixtures incorporating 25 % perlite can be overcome by using $CaCl_2$ or Na_2SO_4.
- Chemical activation alone does not increase the early-age strengths of mixtures incorporating 50 % perlite very much. Addition of 2 % Na_2SO_4 by weight of the cementitious materials results a ~10 % increase at 1-day and even less later.
- The effective recovery of the early-age strength of mixtures incorporating 50 % perlite requires both chemical and thermal activation.
- Longer curing at higher temperatures increases strength at early ages but decreases or does not affect ultimate strength. Curing of samples incorporating 50 % perlite at 55°C for 3 hours improves only the 1-day strength but not at later ages.
- Curing of samples incorporating 50 % perlite at 85°C for 10 hours improved the 1, 3, and 7-day strengths with all activators except Na_2SiO_3.
- Na_2SiO_3 and Na_2SO_4 mortars incorporating 50 % perlite and cured at 85°C for 10 hours have significantly lower later-age strengths than the pure cement control and the other activated mixtures.
- The ultimate strength of the mixture with 80 % perlite increased to only ~25% of that of the control even with chemical and thermal activation.
- Use of high volumes of perlite in concrete can reduce CO_2 emissions and energy expended per unit volume of concrete.

- A "first attempt" of the geopolymerization of a 100 % perlite mixture with NaOH and Na$_2$SiO$_3$ gave ~25 MPa strength at 7 days, indicating a huge potential for the use of perlite in developing sustainable concretes.

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