

Geothermal waste: An alternative replacement material of Portland cement

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Energy generation from geothermal resources is attractive since it is a clean and self-renewing resource; it is also relatively inexpensive compared to other forms of energy generation. Nonetheless, one of the most significant disadvantages is the generation of relatively large amounts of solid wastes that must be land filled, and this frequently impedes the progress of flashed geothermal brine power plants development in many areas of the world. Such geothermal waste (GW) is obtained as a mixture of geothermal brine and steam (naturally pressurized) that undertakes a series of stages towards heat extraction. As its temperature is reduced (from about 200 °C) a solid precipitates from the mixture, the composition of which is mostly amorphous SiO₂ and also NaCl and KCl. One such power plant operates in Mexico generating waste amounts up to 50 000 tons/year.

Regarding cementitious materials, it is well known that replacing Portland cement by various materials rich in silica, mostly byproducts such as silica fume, rice husk ash, Hi-Sil amorphous silica, etc., enhances the properties of mortars and concretes [1–3]. The combined microfiller effect (reducing the porosity) and pozzolanic behavior (reaction with Ca(OH)₂ generated by the cement hydration) bring about these advantages [4, 5]. It is also known that many replacement materials, as the aforementioned, greatly accelerate the cement hydration [6, 7]; such materials are considered to act as nucleation sites for the precipitation of Portland cement hydration products.

Following from this background, and since there is very limited information about the use of the GW in Portland cement and its properties [8], this paper presents results from research aimed to investigate in more detail the pozzolanic behavior of GW, as well as its effect on the Portland cement hydration. The GW was characterized and experiments were carried out to determine its effect on the development of compres-

sive strength in blended cement pastes at different replacement levels. X-ray diffraction (XRD) and thermogravimetric analysis (TGA) were employed to study the pozzolanic reaction.

The materials used were a commercial ordinary Portland cement (OPC), admixed with calcite at the plant; its chemical and phase compositions are given in Table I. The GW was from Cerro Prieto (Mexican Federal Electricity Commission). The GW was washed with water at 80 °C to eliminate the chlorides [9] and dried 48 h at 105 °C, its chemical composition before and after washing is shown in Table I. Fig. 1 presents the GW XRD patterns before and after washing, its amorphous character is evident by the hump at about 20–30 °2θ. The GW is white with a density of 2.1 g/cm³, surface area of about 30 m²/g [10], and the loss on ignition was 5%. For observation under the scanning electron microscopy the GW particles were ultrasonically dispersed after dilution in an aqueous solution of HCl and methanol with pH = 3; the suspension was evaporated and the powder was mounted in a bronze plate and further carbon coated. Fig. 2 shows that the GW had an irregular morphology and a particle size of 70–200 nm. In Fig. 3 is shown the Fourier transform infrared spectra for the GW. A peak of absorption at ~1100 cm⁻¹, was present related to the Si–O–Si bond, this feature has also been reported for other wastes of amorphous silica [3]. Also there is evidence of the presence of tridymite (802 cm⁻¹) [3].

The pozzolanic activity of the GW was evaluated by the method proposed by Luxan [11]. A plastic flask containing 400 ml of Ca(OH)₂ saturated aqueous solution was placed in a water bath at 40 °C, then 10 g of GW was added under continuous stirring. The pH and electrical conductivity (with compensation mechanism to 25 °C) of the solution were monitored as part of the test. The results are presented in Fig. 4. The Ca(OH)₂ saturated solution at 40 °C had a pH of 11.92 and electrical

TABLE I Chemical composition and phases of geothermal waste and Portland cement (OPC)

	SiO ₂	CaO	Al ₂ O ₃	Fe ₂ O ₃	MgO	Na ₂ O	K ₂ O	TiO ₂	MnO	SO ₃	Total
GW _i	87.97	1.62	0.98	–	0.43	6.90	1.24	0.79	–	–	99.93
GW	94.67	1.72	1.04	–	0.53	0.66	0.53	0.84	–	–	100.00
OPC	18.16	67.53	3.50	2.52	1.89	0.89	0.57	–	0.14	4.05	99.23
Phase	C ₃ S	C ₂ S	C ₃ A	C ₄ AF	Calcite	Gypsum	Quartz				Total
%	66.9	7.33	2.37	7.17	8.18	2.65	4.8				99.42

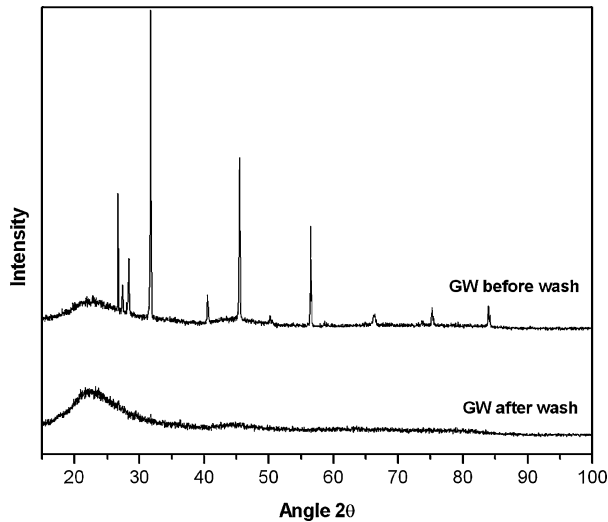


Figure 1 X-ray diffraction pattern of the GW before and after wash.

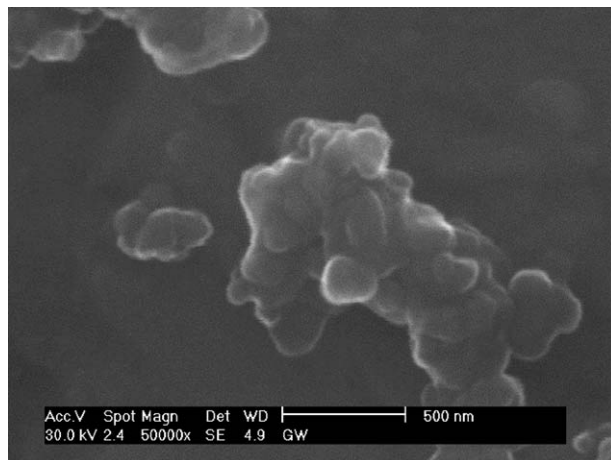


Figure 2 Micrography of the GW by SEM.

conductivity of 8.2 mS/cm. After adding the GW, these values decreased with time; this indicated that Ca^{2+} and OH^- concentration in the solution dropped, which can be attributed to an interaction with the GW. The drop in the electrical conductivity after the addition of the GW was of 2.3 mS/cm (at 2 min of measurement), which

TABLE II Pastes contents of GW and SP

Identification	GW (%)	SP (%)
P ₀	0	–
P ₁₀	10	1.00
P ₁₅	15	1.25
P ₂₀	20	1.50

according to Luxan indicates a good pozzolanic activity. The pH value was directly related to the amount of free OH^- in the solution, while the electrical conductivity depended mainly on the effective concentration of Ca^{2+} and OH^- ions in the solution.

For the characterization of compressive strength development, the GW was used in different amounts as indicated in Table II, the ratio water/solids was 0.5; a superplastizicer was required in view of the GW high surface area. Like most of the replacement materials of nanometric particle size, the GW had to be deagglomerated to better homogenize it in the mixture with OPC. Preliminary tests showed that mixing the GW with the required water, and then adding slowly the OPC was the most efficient means to minimize agglomeration. Cubes of 5 cm were cast and maintained isothermally for 24 h at 20 °C and relative humidity of 90%. After demolding the cubes were aged in plastic containers with water saturated with $\text{Ca}(\text{OH})_2$ at 20 °C. After ageing periods of 3, 7, 14, 28, and 90 days the compressive strength was measured from the average of four cubes. Fragments of the cubes were dried in a vacuum oven at 105 °C during 24 h and further ground in agate containers in a planetary ball mill to pass a 106- μm mesh, for XRD and TGA characterization.

Fig. 5 presents the results of compressive strength vs. time for all the studied mixes. The addition of 10 and 15% of GW resulted in progressively increased compressive strength, but for 20% GW the strengths were lower than those obtained for 15%. However, it seems that in all cases the addition of GW was beneficial. For the first 14 days of ageing the strength of P₁₅ was 55% higher than P₀, the difference reduced to 20% after 90 days of ageing. After 28 days onwards

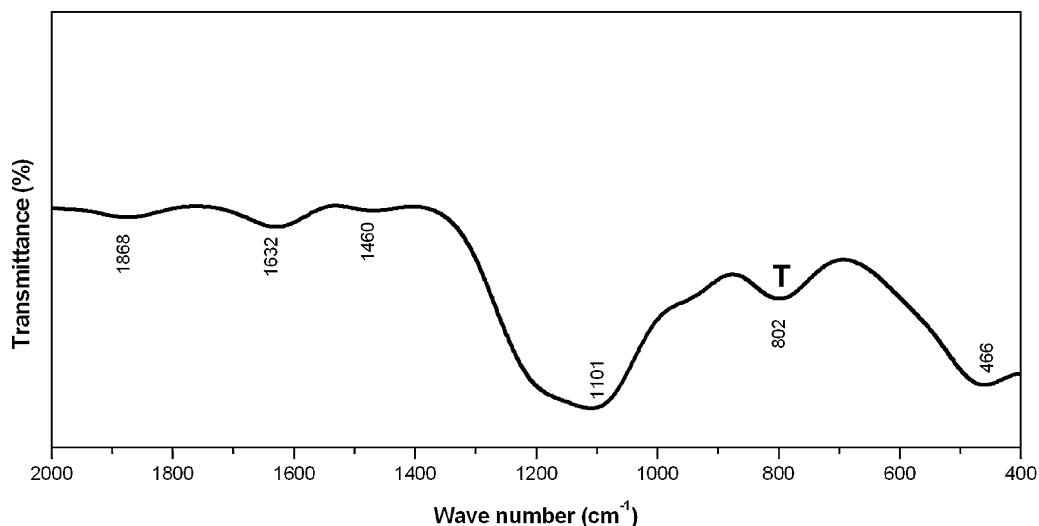


Figure 3 Infrared spectra of the GW.

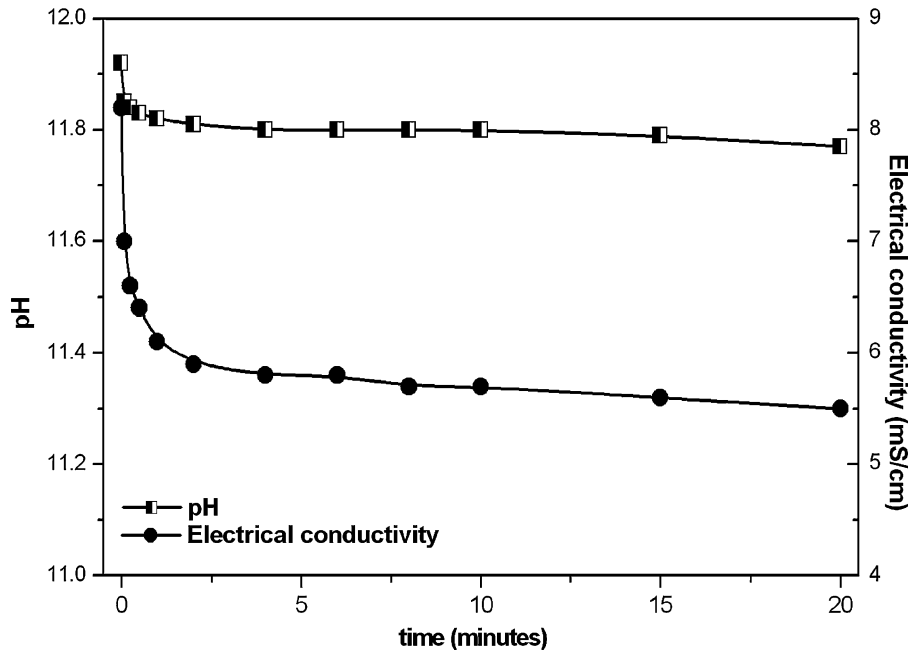


Figure 4 Electrical conductivity and pH measurements of the GW.

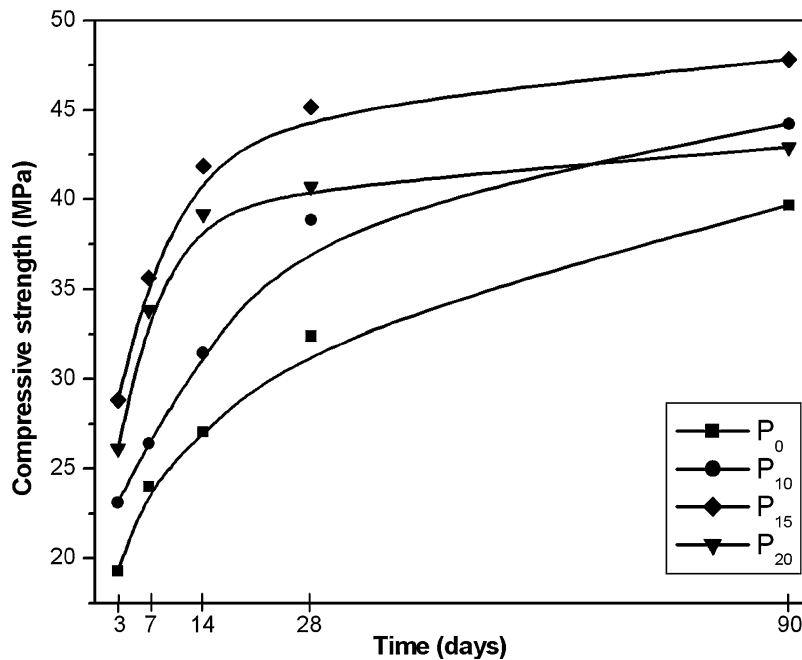


Figure 5 Compressive strength vs. time for the pastes P₀, P₁₀, P₁₅, and P₂₀ (the subscripts refer to the %GW).

the mixes P₁₅ and P₂₀ show a tendency towards low strength gain rates, while P₀ and P₁₀ indicate a trend for further strength increase even after 90 days.

The hydration reactions of OPC generate Ca(OH)₂ as a byproduct, and its concentration can be followed by thermogravimetry since it decomposes, losing water, showing a weight loss step at about 450 °C. Fig. 6 shows the %Ca(OH)₂ vs. time for all mixes. For comparative purposes all data sets were normalized to an equivalent of 80% of cement. For the P₀ mix the Ca(OH)₂ values increased as the time advanced, as expected for progressive hydration reactions. For the mixes P₁₀, P₁₅, and P₂₀ the %Ca(OH)₂ were lower compared to P₀; the values increased for the first 7 to 14 days and then the CH concentration was depleted. This is evidence for the pozzolanic behavior of the GW since the first days

of hydration. The Ca(OH)₂ consumption was greater as the %GW increased. The trend towards lower Ca(OH)₂ concentrations indicates that the pozzolanic reaction is still in progress and for the paste P₂₀ the Ca(OH)₂ was totally consumed. This pattern of pozzolanic behavior was similar to those reported for in cement pastes with silica fume [4, 5] and other replacement materials [12].

Fig. 7 presents the XRD patterns of the pastes P₀, P₁₀, P₁₅, and P₂₀ after 3 and 90 days of ageing. Rutile was added as internal standard in a ratio 1:5 (rutile:cement). It can be observed that the Ca(OH)₂ peak (interplanar distance = 2.628 Å, intensity = 100%) increased for the pure OPC from 3 to 90 days. On the other hand this peak decreased with increased %GW; after 90 days the Ca(OH)₂ quantity decreased considerably for P₁₀ and

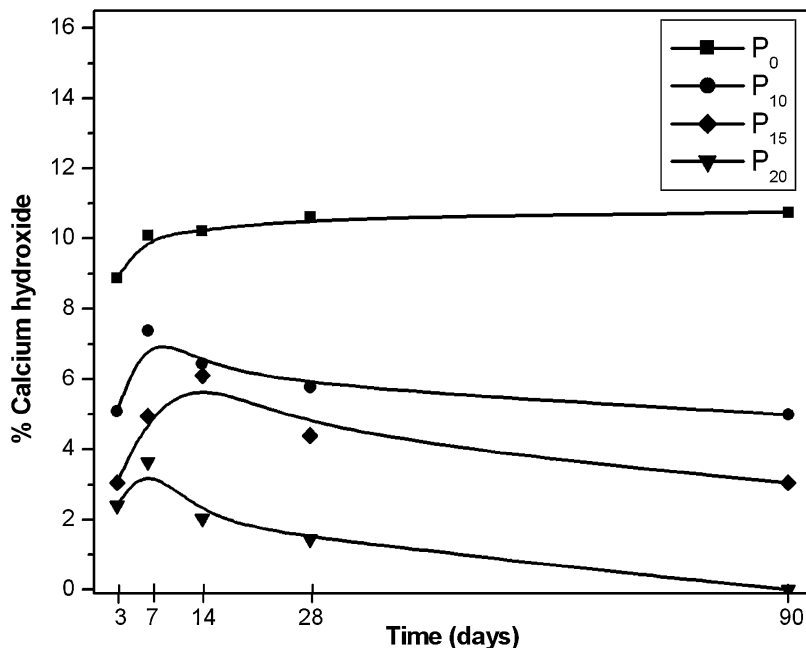


Figure 6 %Calcium hydroxide vs. time for the pastes P₀, P₁₀, P₁₅, and P₂₀. Data referred to the ignited weight (the subscripts refer to the %GW).

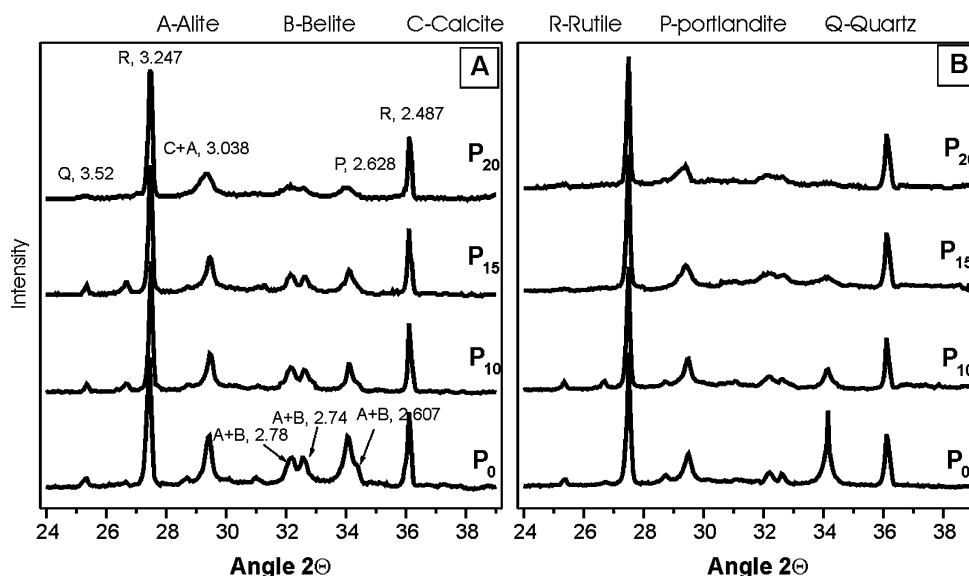


Figure 7 XRD pattern for pastes P₀, P₁₀, P₁₅, and P₂₀ (the subscripts refer to the %GW) at (A) 3 days and (B) 90 days of hydration, interplanar distances in Å.

P₁₅, and for P₂₀ the peak was not present. The effect of the GW on the reactivity of the alite and belite (the main OPC phases) can be noted by following the changes in the peaks of these phases in Fig. 7. The addition of GW reduced markedly the height of the peaks, indicating that the OPC reactions were accelerated.

From these results it can be concluded that the GW accelerated the hydration of the OPC, increasing the reactivity of the alite and belite, and possibly serving as nucleation sites. The pozzolanic behavior, observed by TGA and electrical measurements, was enhanced with the %GW and the hydration time. These factors resulted in the enhancement of the compressive strength over the time period of the tests (90 days). This could be attributed to the two effects mentioned above (acceleration of the hydration and pozzolanic behavior) and a third effect, namely acting as a microfiller due to its nanometric particle size.

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References

1. H. A. TOUTANJI and T. EL-KORCHI, *Cem. Concr. Res.* **25** (1995) 1591.
2. M. NEHDI, J. DUQUETTE and A. EL DAMATY, *ibid.* **33** (2003) 1203.
3. D. ANDERSON, A. ROY, R. K. SEALS, F. K. CARTLEDGE, H. AKHTER and S. C. JONES, *ibid.* **30** (2000) 437.
4. H. CHENG-YI and R. F. FELDMAN, *ibid.* **15** (1985) 582.
5. V. YOGENDRAN, B. W. LANGAN and M. A. WARD, *ibid.* **21** (1991) 691.
6. W. A. GUTTERIDGE and J. A. DALZIEL, *ibid.* **20** (1990) 853.

7. J. I. ESCALANTE-GARCIA and J. H. SHARP, *ibid.* **28** (1998) 1259.
8. J. I. ESCALANTE, G. MENDOZA, H. MANCHA, J. LOPEZ and G. VARGAS, *ibid.* **29** (1999) 623.
9. C. DÍAZ and J. M. RINCÓN, *Bol. Soc. Esp. Cer. Vid.* **29** (1990) 181.
10. C. DIAZ, Ph.D. Thesis, "Caracterización y purificación del residuo de sílice de la central Geotérmica de Cerro Prieto" (Universidad Autónoma de Madrid, 1994).
11. M. P. LUXAN, F. MADRUGA and J. SAAVEDRA, *Cem. Concr. Res.* **19** (1989) 63.
12. J. I. ESCALANTE, L. Y. GOMEZ, K. JOHAL, G. MENDOZA, H. MANCHA and J. MENDEZ, *ibid.* **31** (2001) 1403.

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