THE EFFECT OF MAGNESIUM SULPHATE ADDITION ON THE PROPERTIES OF ARTIFICIAL POZZOLANIC CEMENTS

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Pozzolanic cements are characterised by a low rate of development of strength, low rate of heat evolution but improved resistance to sea and sulphate waters. This paper describes the effect of magnesium sulphate addition on the properties of artificial pozzolanic cement and mortars. The addition of one per cent magnesium sulphate by the weight of the artificial pozzolanic cements increases the rate of compressive strength, chemical resistance specially to the attack of magnesium sulphate solutions and heat of evolution. The water permeability of the mortars made with Portland or Pozzolanic (with or without adding magnesium sulphate) cements remains unchanged.

Introduction

The powdery volcanic lava found near Pozzuoli, Italy and in several other places in Europe has been employed as a construction material since ancient times. It is mainly silica and alumina and possesses hydraulic properties. A pozzolana is defined as material which, though not cementitious in itself, combines with lime at ordinary temperatures to form stable insoluble cementing compounds related to those in set Portland cement. *Artificial pozzolanic cement*, the use of which is becoming popular in United States, is made by intergrinding Portland cement with a portion of such pozzolana as diatomaceous earth, pumice, burnt clay or shale. This cement is characterised by a low rate of development of strength, a low rate of heat of hydration and high resistance to the chemical attack. Pozzolanas combine with the lime liberated during setting of Portland cement and a lime-pozzolana compound of cementitious value is formed. The calcium hydroxide does not add to the strength of set cement and is readily subject to the chemical attack. The lime also reacts with certain siliceous constituents of the aggregate and causes premature failure of concrete. The partial replacement of Portland cement with pozzolana therefore controls the alkali-aggregate reaction and increases the resistance of concrete to the attack of alkalines salts. Pozzolanic cements increase the workability and reduce segregation and bleeding in concrete mixes.

The substitution of pozzolana reduces the strength obtained at the earlier stage though the ultimate strength is more than that of Portland cements. Pozzolana concretes develop lower strength if cured in air and require a long period of wet curing if the best results are to be obtained. The slow rate of setting hinders the progress of construction. The rate of development of strength has been increased [1] by finer grinding, by increasing gypsum additions to 3.3-3.5 per cent and by using a clinker having a high content of calcium tri-silicate. The additions of $CaCl_2$,[2] and $CaOCl_2$ [3] have also been tried to hasten the hardening process so that the compressive strength at 28 days is obtained equal to that of pure Portland cement. The present paper deals with the use of magnesium sulphate for accelerating the early rate of compressive strength and for improving chemical resistance to sulphate attack of artificial pozzolanic cements.

Setting Times of Portland and Artificial Pozzolanic Cements

The temperature of 850°C. to which a moderately burnt brick is fired in this country, has been reported[4] to be the best average temperature to make pozzolana from ordinary brick making clays. Burnt bricks obtained from Hyderabad, West Pakistan were therefore crushed to cement fineness and used as artificial pozzolana throughout in this investigation. In the sub-continent of India and Pakistan, the powdered burnt brick is known as *surkhi* and this has been employed since ages in mortars and renderings based on pozzolana-lime mixes. The artificial pozzolanic cements were prepared by replacing Portland cements and clinkers from 5 to 30 per cent (by weight) with *surkhi* and setting times determined with the help of Vicat needle apparatus. The initial and final setting times of Portland and pozzolanic cements recorded in Table 1 show that the substitution of 15-20 per cent *surkhi* in Portland clinkers gives the desired period of 45 minutes specified for initial settings and eliminates gypsum addition during the manufacture of Portland cements. Daudkhel Portland cement was prepared in the laboratory by adding 2 per cent Khewra gypsum to the clinker obtained from Daudkhel Cement Factory. The gypsum retarded the clinker approximately to the same extent as the partial replacement of clinker with 30 per cent surkhi. The replacement of Portland cement with *surkhi* increases slightly both initial and final setting times. The addition of 1 per cent magnesium sulphate in the artificial pozzolanic cement made by intergrinding 70 parts of Portland cement and 30 parts by weight of *surkhi* decreased the initial setting from 2 hrs. 52 minutes to 2 hrs. 41 minutes and final setting time from 4 hrs. 7 minutes to 3 hrs. 38 minutes.

Compressive Strength

Zeal Pak Portland cement and artificial pozzolanic cements were mixed dry separately with Malir sand passing sieve No. 8 in the proportion of 1:3 by volume. The grading of this sand has been reported earlier.[5] The water-cement ratio, which was inclusive of the water absorbed by the dry aggregate, was kept at 0.45. The hand-mixed mortars were compacted manually in 2-inch cube moulds. Similar cubes were moulded adding 1 per cent commercial magnesium sulphate to the pozzolanic mix of 70 parts Zeal Pak Portland cement and 30 parts *surkhi*. The mortar cubes were removed from moulds after 24 hrs. of curing in water and tested for compression at 3, 7, 14 and 28 days. The compressive strengths, recorded in Table 2, show that magnesium sulphate in pozzolanic cement increases the rate of early strength and 28 days' compressive strength is higher than that of Portland cement.

TABLE 1.—THE EFFECT OF CRUSHED BURNT BRICK (SURKHI) ON SETTING TIMES OF PORTLAND CEMENT AND CLINKERS.

Portland Cement or Clinker	Cement/Clinker replaced with *surkhi* (by weight) %	Setting Times: Initial Hrs.	Setting Times: Initial Mts.	Setting Times: Final Hrs.	Setting Times: Final Mts.	Water by weight of Cement/mix %
Daudkhel Clinker	nil	0	12	0	22	33 (Distilled water)
,,	10	0	18	1	15	33 ,,
,,	20	0	55	2	7	33 ,,
,,	30	1	45	2	57	33 ,,
Zeal Pak Clinker	nil	0	22	—	—	31 (Tap water)
,,	10	0	40	—	—	31 ,,
,,	20	1	10	—	—	31 ,,
,,	30	1	29	—	—	31 ,,
Daudkhel Cement	nil	1	48	3	10	33 (Distilled water)
,,	10	1	57	3	15	33 ,,
,,	20	2	10	3	25	33 ,,
,,	30	2	13	3	31	33 ,,
Zeal Pak Cement	nil	2	18	3	42	33 (Distilled water)
,,	10	2	28	3	50	33 ,,
,,	20	2	37	3	57	33 ,,
,,	30	2	52	4	7	33 ,,

TABLE 2.—THE EFFECT OF SURKHI AND MAGNESIUM SULPHATE ON THE EARLY RATE OF COMPRESSIVE STRENGTH OF (1:3) MORTAR CUBES.

Cement/ Zeal Pak Portland Cement%	Mixture Brick dust (Surkhi) %	Additive by weight of Mixture	Wet compressive strength in lbs. per sq. inch at 3 days	7 days	14 days	28 days
100	—	—	2833	3584	4368	5375
90	10	—	2587	3192	4130	5113
70	30	—	2044	2453	3668	4575
70	30	1% magnesium sulphate	2442	3460	4144	6200

Sulphate Resistance

The sulphate resistance of Portland and pozzolanic cements was determined by the accelerated test.[6] The mortar cubes, for this purpose, were removed from water at the age of 14 days and dried in oven at 100°-110°C. for about 24 hrs. The dried cubes were cooled to room temperature and dipped in 5 per cent solutions of commercial sodium and magnesium sulphate seperately. At the age of 21 days, the cubes were removed from the sulphate solutions, redried at 100-110°C. cooled, and redipped for the chemical attack on mortars. The second cycle of drying, cooling and dipping is to accelerate the sulphate action on set cements. The compressive strengths of different compositions measured at the age of 28 days are shown in Table 3. The addition of magnesium sulphate in pozzolanic cements not only improves chemical resistivity but such cements gain compressive strengths when dipped in magnesium sulphate solution for the accelerated determination of sulphate resistance.

TABLE 3.—THE EFFECT OF SURKHI AND MAGNESIUM SULPHATE ON THE SULPHATE RESISTANCE OF (1:3) MORTAR CUBES.

Cement/Zeal Pak Portland cement %	Mixture Brick dust (Surkhi) %	Additive by wt. of mixture	Wet compressive strength per sq. inch at 28 days after 2 cycles in 5 per cent solution of commercial	
			Sodium sulphate	Magnesium sulphate
100	—	—	4244	4669
90	10	—	4556	4844
70	30	—	4351	5107
70	30	1% Magnesium sulphate	5755	7455

Water Permeability

The water repelling properties of Portland and artificial pozzolanic cements were determined by measuring moisture penetration through mortar slabs by the device reported earlier.[7] The results show that the permeability of mortars, cured upto two months in water, is not influenced by the substitution of *surkhi* for Portland cement and by adding magnesium sulphate to pozzolanic cements.

Thermal Heat of Hydration

The heat evolved during the hardening of Portland cement is reduced by the substitution of *surkhi* though not proportionately to the degree of substitution since the reaction between lime and pozzolana itself evolves some heat. As a rough approximation the percentage reduction in heat evolution at 7 or 28 days, has been reported[8] by F.M. Lea to be about one-half the percentage substitution. The heat evolutions of cements were measured by vaccum-flask method and results with and without corrections for heat losses are reported in Fig. 1. The addition of magnesium sulphate increases heat evolution in pozzolanic cement and makes it unsuitable for thick concrete constructions where a low rate of heat of hydration is desirable.

Conclusion

The magnesium sulphate addition in artificial pozzolanic cement increases the early rate of strength and the compressive strength at 28 days is obtained slightly higher than that of pure Portland cement. The magnesium sulphate can either be mixed during the manufacture of pozzolanic cements or dissolved in the mixing water while making the concrete. The substitution of 30 per cent Portland cement with *surkhi* and addition of 1 per cent magnesium sulphate to hasten the rate of hardening, will increase the production of construction cement at reduced price. Alkali resistance of cement and concrete is important in many parts of the country where

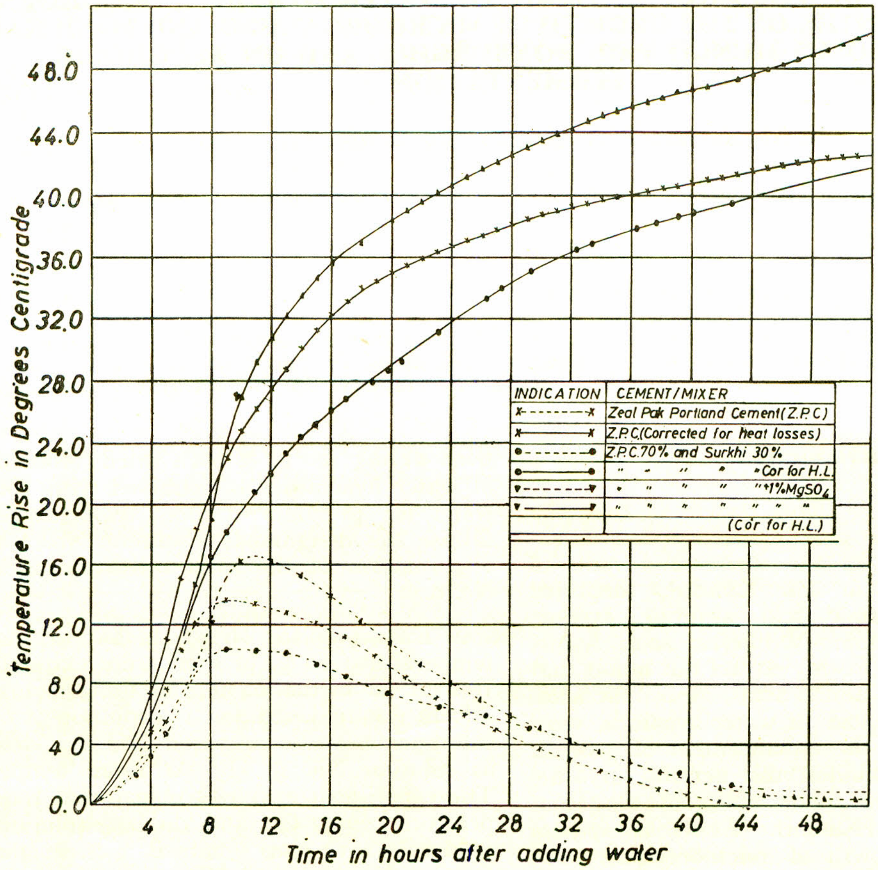

Fig. 1.—Thermal heat of hydrations of Portland and pozzolanic cements measured with vacuum flask and corrected for heat losses.

soil carries a large amount of sodium sulphate and alkaline salts. Magnesium sulphate has a far more serious effect on Portland concrete than other metallic salts. The magnesium sulphate increases alkali resistance of artificial pozzolanic cements and these cements develop appreciable strength when attacked by magnesium sulphate solution. The increased alkali resistance of this cement may also prove useful in concrete sewers as the normal sewage has alkaline reaction.

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