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PROPERTIES OF PORTLAND BLAST FURNACE SLAG CEMENT PRODUCED USING PHOSPHOGYPSUM

By Manjit Singh, S. S. Rehsi and C. A. Taneja

Extensive work carried out in Japan on Japanese phosphogypsum has shown that when phosphogypsum produced by the dihydrate process was used to control the setting time of cement, the impurities (phosphate, fluoride and organic matter) present in the phosphogypsum considerably influenced the setting time and early strength development.

INTRODUCTION

Not only the setting time of cement was found to be greatly retarded but there was also a marked reduction in its early strength. Investigations carried out in other countries suggest that beneficiated phosphogypsum can be used in place of mineral gypsum without any adverse effect.

India produces about 1.5 million tonnes of phosphogypsum every year. Some work on the use of beneficiated phosphogypsum produced in India as a set retarder in cement has already been reported.

The properties of portland blast furnace slag (PBFS) cement prepared in the laboratory by intergrinding portland cement clinker and granulated blast furnace slags with unprocessed and processed phosphogypsum samples are described here.

EXPERIMENTAL

Materials used

1. Phosphogypsum : It was procured from M/S Coromondal Fertilizer Ltd., Vishakhapatnam. Its chemical composition is shown in Table 1.

Table 1

Chemical Analysis of Phosphogypsum

Constituents	*Percentage*
Total P_2O_5	0.65
Water-Soluble P_2O_5	0.29
Crystal lattice-Substituted P_2O_5	0.33
Insoluble P_2O_5	0.03
Total F	0.44
Water-Soluble F	0.28
Organic Matter	0.11
SiO_2	5.14
R_2O_3	0.85
CaO	31.47
MgO	0.43
Na_2O	0.32
SO_3	41.98
H_2O	19.78

The phosphogypsum was of high purity (90.25%). It was used as such and after beneficiation by the wet sieve analysis technique[15]. The fraction passing 150 micron IS sieve was used.

2. Portland Cement Clinker : It was procured from M/S Orissa Cement Company, Rajgangpur. Its chemical composition is shown in Table 2.

Table 2

Chemical composition of cement clinker

Constituents	*Percentage*
SiO_2	23.29
Al_2O_3	5.63
Fe_2O_3	1.90
CaO	63.56
MgO	4.30
SO_3	—
L.O.I.	1.10

3. Granulated Blast Furnace Slags : The granulated blast furnace slag samples numbered A, B, C, D, E & F were received from M/S Hindustan Steel Ltd., Rourkela. Their chemical composition is shown in Table 3.

Hydraulic indices employed for evaluating potential hydraulicity of slags as recommended in IS : 455-1976 and computed from Chemical Composition are shown in Table 4.

Central Building Research Institute, Roorkee (U.P.)

Table 5

Properties of PBFS cement produced using mineral selenite gypsum

Slag Designation	PBFS cement composition S* : C* : G*	Fineness cm²/g (Blaine's)	Normal consistency (%)	Setting Time (minutes) Initial	Final	Compressive Strength (kg/cm²) 1d	3d	7d	28d	90d	Autoclave Expansion (%)
A	40 : 60 : 5	4039	23.5	180	230	150	242	437	484	670	0.20
	50 : 50 : 5	4085	24.5	235	290	146	224	367	478	650	0.22
B	40 : 60 : 5	4064	23.2	170	200	128	208	333	514	666	0.46
	50 : 50 : 5	4018	24.0	210	275	130	203	290	456	572	0.5
C	40 : 60 : 5	4009	23.2	170	230	115	192	294	422	682	0.32
	50 : 50 : 5	4000	24.2	285	355	108	180	277	394	510	0.31
D	40 : 60 : 5	4085	23.5	215	245	122	202	290	434	640	0.31
	50 : 50 : 5	4085	23.7	190	255	110	178	182	366	618	0.41
E	40 : 60 : 5	4039	24.2	145	215	171	285	409	417	500	0.22
	50 : 50 : 5	4000	25.5	160	210	156	225	321	528	576	0.26
F	40 : 60 : 5	4064	25.5	150	195	142	238	345	389	660	0.21
	50 : 50 : 5	4064	25.0	165	197	133	206	355	391	519	0.24
	0 : 100 : 5	3111	22.0	180	225	144	260	305	592	611	0.31
IS: 455-1976 Limits		2250	—	30	600	—	160	220	—	—	0.80

* S = slag; C = cement clinker; G = Mineral Selenite Gypsum.

Preparation and testing of PBFS cement

Slag samples and cement clinker were intergrounded in the proportions of 40 : 60 and 50 : 50 with 5% of unprocessed and processed phosphogypsum to a fineness of about 4,000 cm^2/g (Blaine's). For comparative tests, a portland cement sample was also prepared by grinding cement clinker with 5% of high purity mineral gypsum (97.75%).

The cements produced were tested for physical properties by the methods specified in IS : 4031-1968[20].

RESULTS & DISCUSSION

Properties of PBFS cement

a) With Mineral Gypsum : The effect of mineral gypsum on the physical properties of PBFS cement is shown in Table 5 (P.26). It can be seen that the experimental PBFS cement samples produced complied with setting and strength requirements of IS : 455-1976[21].

Table 3

Chemical composition of blast furnace slags, Rourkela

Constituents	*Composition in %*					
	A	B	C	D	E	F
SiO_2	30.00	33.8	36.40	36.00	33.00	34.00
FeO	0.72	0.70	0.69	0.46	1.29	2.10
Fe_2O_3	—	—	—	—	1.42	0.43
Al_2O_3	26.80	22.87	24.60	24.64	21.54	25.90
CaO	31.50	32.50	29.50	27.50	33.30	27.80
MgO	7.32	6.12	5.76	5.94	3.76	2.90
MnO	2.29	3.30	2.40	4.83	4.94	6.17
S	0.62	0.58	0.60	0.48	0.65	0.58

Table 4

Hydraulic indices of blast furnace slags, Rourkela

Sl. No.	*Formula*	*Slag Samples*							IS : 455—1976 *requirements*
		A	B	C	D	E	F		
1.	$\frac{CaO+MgO+\frac{1}{3}Al_2O_3}{SiO_2+\frac{2}{3}Al_2O_3}$	1.00	0.94	0.82	0.80	0.93	0.77	>	1.0
2.	$\frac{CaO+MgO+Al_2O_3}{SiO_2}$	2.19	1.82	1.64	1.61	1.78	1.66	>	1.0
3.	$\frac{CaO+CaS+\frac{1}{2}MgO+Al_2O_3}{SiO_2+MnO}$	1.97	1.59	1.48	1.36	1.51	1.39	>	1.5

Table 6

Properties of PBFS cement produced using unprocessed phosphogypsum

Slag Sample Designation	PBFS cement composition S*	: C*	: UPG*	Fineness cm^2/g (Blaine's)	Normal consistency (%)	Setting Time (minutes) Initial	Final	Compressive Strength (kg/cm^2) 1d	3d	7d	28d	90d	Autoclave Expansion (%)
A	40	60	5	4000	22.8	250	375	110	190	343	450	595	0.10
	50	50	5	4209	23.5	285	390	102	170	305	435	600	0.12
B	40	60	5	4100	22.0	220	265	92	117	275	485	598	0.20
	50	50	5	4100	22.0	276	325	85	169	215	470	577	0.15
C	40	60	5	4000	21.0	235	280	75	160	225	388	589	0.08
	50	50	5	4090	21.5	305	380	70	145	215	375	506	0.11
D	40	60	5	4065	23.0	240	300	95	185	250	390	565	0.11
	50	50	5	4200	24.0	224	325	88	160	220	378	545	0.11
E	40	60	5	4000	23.0	190	240	130	240	370	399	555	0.075
	50	50	5	4000	23.0	215	255	126	205	317	360	575	0.090
F	40	60	5	4100	22.5	188	238	115	200	280	345	570	0.10
	50	50	5	4165	23.5	195	248	105	180	299	355	512	0.10
	0	100	5†	3111	22.0	180	225	144	260	305	592	611	0.30

* S = Slag

C = Cement clinker

UPG = Unprocessed phosphogypsum

† = Mineral Selenite gypsum

The autoclave expansion was also within the specified limit of 0.8% maximum.

b) With Unprocessed Phosphogypsum : The use of unprocessed phosphogypsum as an additive to PBFS cements adversely affected the setting time and compressive strength (Table 6,

As can be seen, the setting time was prolonged and the compressive strength was decreased at 1, 3 & 7 days respectively. However, the later age strength at 28 and 90 days was not affected appreciably. In fact, later age (90 days) strength was nearly similar to that obtained with mineral selenite gypsum. The autoclave expansion values were within specified value of 0.8% maximum.

The retardation of setting is due to the watersoluble impurities of phosphogypsum which enter gradually into aqueous phase of hydrating cement paste. Among impurities of phosphates and fluorides, the water-soluble fluorides retard the setting time to a relatively greater extent. This observation complies the findings of Kobeyashi[10], Mori and Sudo[5] who used monocalcium phosphate, dicalcium phosphate and sodium silico fluoride as the representative water soluble impu- [illegible] and found greater retardation in setting time with sodium silico fluoride than mono or dicalcium phosphate. The extent of retardation was in proportion to the amount of reagents incorporated into the cement.

The rate of retardation was found to be more pronounced in case of PBFS cement than portland cement. It was further observed that while sodium silico fluoride alone prolonged the setting time greatly, its mixture with phosphates caused further retardation. The presence of small amount of organic matter showed no ill effect on setting, but when present with phosphates and fluorides, the setting was greatly prolonged.

The impurities in phosphogypsum react with lime released by hydration of cement to form insoluble calcium salts ($Ca_3(PO_4)_2$ & CaF_2) which coat the cement particles, thereby preventing their hydration in the initial stages.
c) With Processed Phosphogypsum : The properties of PBFS cement produced using processed phosphogypsum (wet sieved through 150 micron IS sieve and washed) are shown in Table 7. It can be seen that the use of processed phosphogypsum accelerated the setting time and increased the compressive strength at 1, 3 & 7 days.

The level of strength obtained was more or less similar to that attained with mineral gypsum. The later age strength at 28 & 90 days was not affected appreciably. The autoclave expansion data was within the specified limit of 0.8% maximum. The processed phosphogypsum is thus suitable for use in place of mineral selenite gypsum.

Conclusions

From the present investigation, it can be concluded that processed phosphogypsum (wet sieved through 150 micron IS sieve and washed) can be used in place of mineral selenite gypsum. Being available in the eastern and southern parts of the country where mineral selenite gypsum is not available, the use of processed phosphogypsum would be a definite economic advantage.

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References

1. K. Takemoto, I. Ito and S. Suzuki, Influence of Chemical By-Product Gypsum on the Quality of Portland Cement, Semento Gijutsu Nenpo, Vol. 11, 1957.

2. K. Takemoto, M. Kataoka and S. Suzuki, Utilization of By-Product Gypsum for Portland cement, Sekko Sekkai, Vol. 33, pp 1627-1636, 1958.

3. T. Yamaguchi, Sekko Sekkai, Vol. 58, pp. 149-154, 1962.

4. Kuzumi & Murasugi, Onoda Kenkyu Iho, Vol. 10, pp 174-182, 1958.

5. H. Mori & G. Sudo, Influence of Phosphates on the hardening of Portland cement & Blast Furnace Slag Cement, Semento Gijutsu Nenpo, Vol. 14, p. 67, 1960.

6. M. Hanado, Report on Meeting for Study on Utilization of Chemical Gypsum, for Portland Cement, 1966.

7. H. Tanaka, Influence of Phosphogypsum on the Hydration of Portland Cement, CA, Vol. 69, 1968, 61335J.

8. K. Murakami, Application of By-Product Gypsum to Portland Cement, Semento Kon Kusito, Vol. 274, pp 2-11, 1967 (In Japanese); CA, Vol. 72, 1970, 70233p.

9. K. Murakami, Utilization of Chemical Gypsum for Portland Cement, Proc. International Symposium on the Chemistry of Cement, Part IV, pp. 457-503, 1968.

10. W. Gutt et al, A survey of Locations, Disposal and Prospective use of Major Industrial By-Products and Waste Materials, pp 36-51, BRE, Current Paper (19/74), Feb. 1974.

Table 7

Properties of PBFS cement produced using processed phosphogypsum

Slag Designation	PBFS cement composition S*	C*	PPG*	Fineness cm²/g (Blaine's)	Normal consistency (%)	Setting Time (minites) Initial	Final	Compressive Strength (kg/cm²) 1d	3d	7d	28d	90d	Autoclave Expansion (%)
A	40	60	5	4009	23.0	190	250	147	220	405	470	615	0.10
	50	50	5	4000	23.5	250	320	141	220	350	450	625	0.10
B	40	60	5	4200	22.2	180	220	124	190	315	499	632	0.15
	50	50	5	4100	22.9	235	290	121	180	290	490	588	0.18
C	40	60	5	4100	22.0	185	240	110	180	280	430	640	0.10
	50	50	5	4064	22.0	290	370	100	170	255	400	535	0.10
D	40	60	5	4000	23.0	230	260	124	195	275	420	600	0.08
	50	50	5	4085	23.5	210	275	108	175	280	406	599	0.08
E	40	60	5	4100	23.0	160	230	166	270	410	521	600	0.10
	50	50	5	4147	24.0	180	230	154	218	325	522	580	0.10
F	40	60	5	4009	24.0	170	228	138	215	325	370	620	0.10
	50	50	5	4200	22.0	180	235	129	199	340	385	551	0.10
	0	100	5†	3111	22.0	180	225	144	260	305	592	616	0.30

* S = Slag

C = Cement clinker

PPG = Processed phosphogypsum (wet sieved through 150 micron IS sieve and washed)

† = Mineral selenite gypsum

11. A. A. Tabikh and F. M. Miller, The Nature of Phosphogypsum Impurities and their Influence on Cement Hydration, Cement and Concrete Research, Vol. 1, pp 663-678, 1971.

12. A. V. Vasilev, Use of Phosphogypsum to Control the Setting Time of Cement, CA, Vol. 81, No. 6, 1974, 28833v.

13. Yu. V. Nikifored et al, Phosphogypsum as a substitute for Gypsum in Clinker Grinding, Tsement, Vol. 1, pp 19-21, 1976, CA, Vol. 85, 1976, 8250u.

14. Drolji. & Stane, Phosphogypsum as a Setting Regulator during Hydration of Portland Cement, Cement (Zagrab), Vol. 18, No. 1, pp 19-23, 1975 (Croat), CA, Vol. 84, No. 1, 1976, 8383g.

15. C. A. Taneja & Manjit Singh, Evaluation of Suitability of Phosphogypsum for Use in Preparation of Different Building Materials, Research & Industry, Vol. 21, No. 4, pp. 263-265, 1976.

16. C. A. Taneja, & Manjit Singh, Phosphogypsum — A Substitute for Mineral Gypsum in Cement Manufacture, Cement, Vol. 10, No. 33, pp. 35-37, April-June 1977.

17. S. K. Chopra, K. C. Narang & H. C. Visvesvarya, Utilization of By-Product Gypsum in Cement Industry; Chemical Age of India, Vol. 28, No. 2, pp 101-107, Feb. 1977.

18. C. A. Taneja & S. K. Mulhotra, Utilization of By-Product Gypsum as an Additive to Cement Clinker, Research & Industry, Vol. 18, No. 1, pp. 24-25, 1973.

19. A. Das Gupta: Gypsum Waste as Set Controller in Cement, Cement, Vol. 11, No. 1, pp. 10-15, Oct/Dec. 1977.

20. Specification for Methods of Physical Tests for Hydraulic Cement, Indian Standard Institution, Manak Bhavan, 9, Bahadur Shah Zafar Marg, New Delhi 1.

21. Specification for Portland Blast Furnace Slag Cement, Indian Standard Institution, Manak Bhavan, 9, Bahadur Shah Zafar Marg, New Delhi 1.

22. K. Kobayashi, Influence of the Impurities on the Development of Strength and the Setting Time of Portland Cement, Semento Gijutsu Nenpo, Vol. 18, pp. 79-85, 1963.