Reprint from the "Indian Concrete Journal," April 1961

THE MANUFACTURE OF SUPERSULPHATED CEMENT FROM INDIAN SLAG

Experimental Work at the Central Building Research Institute

by **S. K. Chopra and Kishan Lal***

The article describes investigations carried out at the Central Building Research Institute into the physical properties of supersulphated cement prepared from Indian slag characterised by relatively low CaO/SiO_2 and SiO_2/Al_2O_3 ratios. The cement possesses strengths and resistance to the attack of sulphate and acidic waters comparable to those being produced in other countries. The manufacture of this cement is recommended in India, particularly in view of the doubtful stability of high alumina cement in the tropics and the lower cost of production of supersulphated cement.

The Editor would, however, point to the fact that the sample of slag used in this study was the same that was found eminently suitable for making Portland blastfurnace slag cement in studies made some time ago. Since then, there appears to be growing difficulty in obtaining slag of a sufficient lime content and a comparatively low silica content, and the conclusions reached here—as indeed in the case of Portland blastfurnace slag cement—may therefore need to be considerably modified.

INVESTIGATIONS on the development of Portland blastfurnace slag cement from Indian slags have been reported earlier.[1] In the near future,[2] over 3½ lakh tons of this cement will be produced by the Associated Cement Companies, Limited, at their Chaibasa Works, using slag granulated in a quenching plant at the Tata Iron and Steel Works at Jamshedpur.

TABLE I. Chemical composition of Indian slags

Constituent	Slag from the Mysore Iron & Steel Works, Bhadravati	Slag from the Tata Iron & Steel Works, Jamshedpur	Slag from the Indian Iron & Steel Works, Burnpur
SiO_2, per cent	30 – 37	30 – 34	28·5
Al_2O_3	25 – 30	22 – 28	29·5
CaO	26 – 30	36·5 – 38·2	36·2
MgO	2 – 4	3·0 – 3·6	3·0
FeO	2 – 3	0·1 – 0·9	0·9
S	0·1 – 1·2	0·8 – 0·9	1·0
MnO	0·56 – 1·25	0·5 – 1·3	0·5
SO_3	Trace	Trace	Trace

The other important cement which can be manufactured with this slag is supersulphated or slag-sulphate cement. Since Indian slags have a relatively low CaO and a relatively high Al_2O_3 content, its sulphate activation was studied first, this study being reported elsewhere.[3,11] This article deals mainly with the preparation and physical properties of supersulphated cement, with particular reference to its resistance to the attack of sulphate and acidic waters for which this cement is highly valued.

Preparation

Supersulphated cement is a product of grinding about 80 parts of granulated slag with about 12–15 parts of gypsum and about 5 parts of Portland cement clinker. Since slag is the main constituent of supersulphated cement, its chemical and physical properties are important and a great deal has been written about its requirements in these respects.[4] Generally speaking, slags which would yield a good Portland-slag cement and contain not less than 12 per cent alumina are considered suitable for making supersulphated cement. However, the latest studies of Keil and Locher, and of Tanaka, Sakai and Yamane have clearly defined the field of maximum activity of slags in the system CaO–SiO_2–Al_2O_3, with and without MgO, for sulphate activation.[5,6] According to the latter workers, synthetic slags of a composition in the range of 24–34 per cent SiO_2,

* Senior Scientific Officer and Scientific Assistant, respectively, at the Central Building Research Institute, Roorkee.

TABLE 2. Mix composition and strength of trial cements containing gypsum as activator

Mix composition, per cent				Compressive strength, kg/cm²*	
Slag	Gypsum	Clinker	Slaked Lime	3 days	7 days
	Series A				
80·0	17·5	2·5	..	214	296
80·0	15·0	5·0	..	267	305
80·0	7·5	7·5	..	199	274
80·0	10·0	10·0	..	266	289
	Series B				
80·0	17·5	..	1·5	223	246
80·0	15·0	..	2·5	289	282
80·0	17·5	..	5·0	252	312
80·0	10·0	..	10·0	223	276
	Series C				
75·0	22·5	2·5	..	223	330
75·0	20·0	5·0	..	283	391
75·0	17·5	7·5	..	307	342
75·0	15·0	10·0	..	296	330

* Determined on 1-in cubes prepared from neat cement paste of standard consistency.

16–20 per cent Al_2O_3, and 46–50 per cent of CaO are best for supersulphated cement. *Table* 1 shows that Indian slags have a lower lime and a higher alumina content than this and, apparently, cannot be considered very suitable for making supersulphated cement.

The sample of slag from the Tata Iron and Steel Works which had been found eminently suitable for making Portland blastfurnace cement in an earlier study[1] was mostly used in the present investigation. The CaO/SiO_2 and SiO_2/Al_2O_3 ratios for this slag are 1·11 and 1·47, respectively, and its glass content is about 95 per cent. The value of the hydraulic potential is about 75 cal/g against the recommended value of 70–80 cal/g.[7] For making trial cements, the slag was ground in a laboratory ball mill to a fineness of about 3,500 cm²/g. The other two constituents, *viz*, a commercial sample of gypsum (91·03 per cent purity) and Portland cement clinker were also ground separately to the same fineness. The mixing was done first in a laboratory mixer and then in a ball mill till the final product had a specific surface of 4,000 cm²/g.

The strengths of the trial cements prepared from the above materials in proportions normally recommended in literature[8] are given in *Table* 2. In general, the strength development is not satisfactory. Hydrated lime was also tried as an excitor in place of clinker (Series B); but it did not result in any improvement of strengths. Since lime is known to deteriorate on storage, only clinker was used in the subsequent trials.

TABLE 4. Oxide composition of supersulphated cements

Constituents	Commercial supersulphated cements		Supersulphated cement *K* 55 prepared from Indian slag
	Sealithor cement (Belgian)	Frodingham cement (British)	
SiO_2, per cent	27·00	28·8	25·71
Al_2O_3	11·93	12·8	15·67
CaO	45·41	44·0	39·77
MgO	2·61	3·7	2·47
Fe_2O_3	1·07	0·95	1·50
TiO_2	0·30	0·60	Tr
Mn_2O_3	1·18	0·80	1·80
S	0·84	0·95	0·62
SO_3	6·72	5·65	13·41
Alkalies	1·09	0·9	—
Loss on ignition	1·00	0·2	—

Though the chemistry of supersulphated cement is still not fully understood, it is generally accepted that its initial setting and hardening is associated with the formation of calcium sulpho-aluminates from the slag constituents and added calcium sulphate. In view of the higher alumina content of the slag under investigation, the quantity of the slag was reduced to 75 parts. The strengths of this series (C) of trial cements showed a general improvement; the mix 75 : 20 : 5 showed highest strengths. The optimum amount of clinker was found to be 5 per cent. In the next series (*Table* 3) the sulphate content was increased because sulphate was being depleted in the above mixes in 3 to 7 days. Gypsum burnt at an optimum temperature of 750°C was used as an activator.[3] The strengths of the four trial cements prepared by using increasing amounts of the activator showed an overall improvement, the cement K55 showing the maximum strength containing 25 per cent burnt gypsum. Since the cement K54 also possesses equally good strengths, the optimum quantity of activator may be taken as 20–25 per cent against the usually recommended value of 10–15 per cent.[8] The influence of the increased sulphate content on the stability and nature of the hydration products which in turn influence the strength and other properties of the cement are discussed at length elsewhere.[3, 11]

TABLE 3. Mix composition and strength of trial cements using burnt gypsum as activator

Identity	Composition, per cent			Compressive strength, kg/cm² *			
	Slag	Gypsum (burnt at 750°C)	Clinker	3 days	7 days	28 days	90 days
K 44	78·0	17·0	5·0	268	404	432	605
K 54	75·0	20·0	5·0	284	375	423	789
K 55	70·0	25·0	5·0	345	401	521	757
K 56	60·0	35·0	5·0	167	258	344	463

* Determined on 1-in cubes prepared from neat cement paste of standard consistency.

TABLE 5. A comparison of the physical properties of K 55 with Belgian and British supersulphated cements

Test	*K* 55 from Indian slag	Sealithor (Belgian)	Frodingham (British)
Fineness			
Specific surface area, cm^2/g, by air permeability method	4,000	4,980	5,000
Standard Consistency			
(Water required, per cent) ..	27·0	..	28·0
Setting Time (min)			
Initial	235	18–85	120–240
Final	420	85–205	180–360
Soundness			
Le Chatelier expansion, mm	0·0	0·5–1·0	1·0
Autoclave expansion, per cent	0·112	0·05	..
Mortar Compressive Strength, kg/cm^2 1 : 3 cement-sand vibrated cubes			
3 days	169	311	197
7 days	246	495	282
28 days	449	671	493
90 days	817	..	599
180 days	858	..	..
Concrete Compressive Strength, kg/cm^2 10-cm cubes, mix 1 : 6 by volume, w/c = 0·6,			
28 days	423–458	401	338

As a result of the above findings the final proportions of the constituents of supersulphated cement, *viz* slag, artificial anhydrite, and clinker, were chosen as 75:20:5. A large quantity of this cement was prepared as described earlier. The final oxide composition of this cement in comparison to some of the commercial cements is given in *Table* 4.

Properties

In the absence of relevant standards for testing supersulphated cement, the fineness, setting times and soundness of the cement K 55 were determined as per Indian Standard 269 : 1958 for Ordinary Portland Cement. The test results (*Table* 5) compare well with those for the British supersulphated cement[9] prepared from slag of relatively low CaO/SiO_2 ratio. The initial and final setting times of the cement K 55 are greater than for 'Sealithor', the well known Belgian Cement.[8,10] Le Chatelier's expansion and autoclave expansion were found to be 0·0 mm and 0·112 per cent, respectively, showing thereby the soundness of the cement.

Whilst the mortar and concrete compressive strengths with K 55 are comparable to those obtained with the British cement, the early strengths are lower than those obtained with "Sealithor". This may be due partly to its lower fineness and partly to the nature of the Indian slag.

The reaction of slag of specific surface 4,000 cm^2/g with distilled water showed that lime equivalent to 0·094 per cent was liberated immediately and that hardly any more

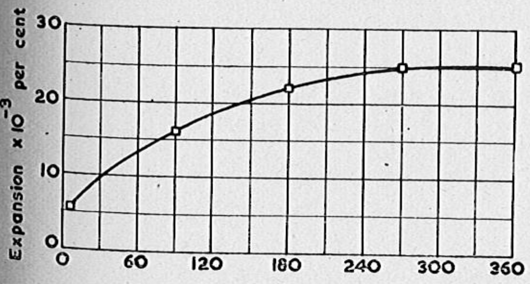

Fig 1 Expansion of 1:3 mortar bars of K 55 in 5 per cent sodium sulphate solution

lime was released on continued leaching with water. Presumably further hydration was stopped because of the deposition of silica and alumina gels on the slag grains. In the hydration and hardening of supersulphated cement these gels are removed either by dissolution or by forming crystalline compounds by their reaction with the ions, mainly Ca^{++}, OH' and SO_4'', present in the solution and thereby exposing new surfaces of the grains for further attack. The main reaction in the early stages of hydration is between CaO, Al_2O_3 and $CaSO_4$ to form high sulphate sulphoaluminate. On this assumption, it may be inferred that the rate of the above reaction in *K* 55 which shows lower early strengths is comparatively slow in the beginning. According to Blondiau, this can happen if the solubility of calcium sulphate is not maintained at an adequate level

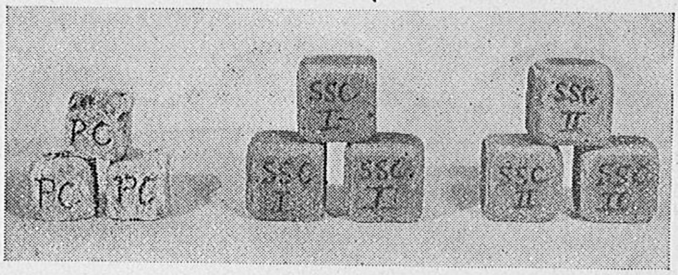

Fig 2 Mortar cubes made with supersulphated cement and ordinary Portland cement after 1 year's immersion in a 2.0 per cent sulphuric acid solution. Note the much better condition of the former

in order to permit the solution in proportion to the contents of lime and soluble alumina.[7] It may also be due to the different nature of gels formed in the Indian and Belgian slags on hydration. However, the early strengths are not critical. In fact, supersulphated cement is seldom employed on account of its strength. Its resistance to the action of sulphate and acidic water and lower heat of hydration are more important properties.

Since *K* 55 contained a greater quantity of burnt gypsum than that used hitherto, its volume stability on storing under water over a period of 12 months was also studied. The maximum expansion of 1 : 3 mortar bars in twelve months was found to be 0·011 per cent, which is negligible, showing thereby that there is no danger of delayed expansion due to the formation of ettringite at later stages. In fact the quantity of ettringite was found to decrease after 28 days.[3]

Supersulphated cement is well known for its high sulphate-resistance. Test 1 : 3 mortar bars (10 in × 1 in × 1 in) of the cement *K* 55 were placed in a 5 per cent solution of sodium

TABLE 6. Relative resistance to the attack of sulphate and acidic waters

Cement	Compressive strength of 1 : 3 mortar cubes (vibrated), kg/cm^2, on immersion for 12 months			
	Distilled water	Solution of 1 per cent *KCl* 3 per cent *Na Cl* 2 per cent $MgSO_4$	Distilled water saturated with CO_2	2 per cent sulphuric acid
Ordinary Portland cement	470	400	404	277
Supersulphated cement *K* 55	899	858	746	358

sulphate after initial curing in water for 7 days. The changes in the length of the bars measured at various intervals up to the age of one year are shown in *Fig* 1. The total expansion of about 0·025 per cent in 360 days is hardly significant showing thereby that cement *K* 55 possesses excellent resistance to the attack of sulphate waters.

The resistance of *K* 55 to the attack of sea water was studied by immersing 7 days old mortar specimens (1 : 3 cubes of 7·06 cm) in a solution containing 1 per cent KCl, 3 per cent Na_2SO_4 and 2 per cent $MgSO_4$. Similarly, the specimens were also immersed in distilled water saturated with CO_2 and in 2 per cent sulphuric acid for one year for testing the resistance of the cement to the attack of CO_2 bearing and acidic waters. Specimens prepared from ordinary Portland cement were also tested under the same conditions for the sake of comparison. The specimens made with supersulphated cement were found to show far greater resistance (*Fig* 2). This was also borne out by the strengths of the specimens after one year's immersion which are about twice the strengths for ordinary Portland cement specimens. The cement *K* 55 showed 4·5, 16·9 and 60·2 per cent loss in strength in salt solution, CO_2—saturated distilled water, and 2 per cent sulphuric acid, respectively, in terms of its one-year strength in distilled water taken as 100 per cent (*Table* 6).

Concrete specimens, 28 days old, prepared with Sealithor showed about 25 per cent loss in strength after six months storage in a 1·5 per cent solution of sulphuric acid.[10] Therefore, it can be concluded that the cement *K* 55 is comparable to Sealithor in its resistance to the attack of sulphate and acidic waters and is far superior to that of ordinary Portland cement.

Conclusions

Indian slag having a low CaO/SiO_2 and SiO_2/Al_2O_3 ratio can be used in the making of supersulphated cement provided the proportions of the constituents of the cement are worked out carefully. Such a cement prepared from slag from the Tata Iron and Steel Works was found to possess good strengths and resistance to the attack of sulphate [and] acidic waters. The manufacture of this cement can [be] recommended.

Acknowledgments

The authors thank Dr N. K. Patwardhan for his help[ful] suggestions and are grateful to Dr R. R. Hattiang[di,] Technical Director, the Associated Cement Compan[ies] Limited, for the supply of clinker and to the Indian I[ron] and Steel Company, Limited, for the supply of slag.

The paper is being published with the permission of [the] Director, Central Building Research Institute, Roork[ee].

References

1. CHOPRA, S. K. and PATWARDHAN, N. K. "Use of granula[ted] blastfurnace slag in the manufacture of Portland blastfurn[ace] cement." *Indian Ceramics*, March 1956. Vol. 2, No. 12.
2. —"Portland blastfurnace slag cement". Editorial, *The Ind[ian] Concrete Journal*, November 1959. Vol. 33, pp. 367–368.
3. CHOPRA, S. K. and KISHAN LAL. "Sulphate activation of [l]ime and high alumina slag." *Jour. Sc. & Ind. Res.* To [be] published.
4. KEIL, F. "Slag Cement." *Proc. Third International Sympo[sium] on the Chemistry of Cement, London*, 1952.
5. KEIL, F. and LOCHER, F. W. "Hydrauliche Eigenschaften [von] Gläsern 1. Gläser des Systems CaO–SiO_2—Al_2O_3 mit und o[hne] MgO".
6. TANAKA, T., SAKAI, T. and YAMANE, J. "Die Zusammensetz[ung] japanischer Hochofenschlacken für sulfathüttenzement. *Ze[ment]-Kalk-Gips*, November 1958. pp. 50–55.
7. BLONDIAU, L. Discussion of the paper "Chemistry of ce[ment] durability" by T. Thorvaldson. *Proc. Third Internati[onal] Symposium on the Chemistry of Cement, London*, 1952. p. 4[...]
8. LEA, F. M. The Chemistry of Cement and Concrete. Edw[ard] Arnold, London, 1956. pp. 420–422.
9. —— Frodingham supersulphated cement. Brochure 2, [...] Frodingham Cement Co, London.
10. UYTTANDAELE, J. F. "Supersulphated cement." *The Indu[strial] Chemist*, November, 1949. p. 509.
11. CHOPRA, S. K. and WILLIAMS, H. Discussion of the paper "B[last]furnace slags and slag cement" by W. Kramer. *Proc. Fo[urth] International Symposium on the Chemistry of Cement*, Washing[ton], October, 1960.

Printed by Pyarelal Sah at The Times of India Press, Bombay, India, and published by M. H. Engineer, B.A., B.Com. for the Cement Marketing Co., of India Ltd. at 'Cement House,' 121, Queen's Road, Bombay 1.