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SUPERSULPHATED CEMENT FROM WASTE PHOSPHOGYPSUM

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Introduction

Supersulphated cement /SSC/ is a sulphate resisting hydraulic cement produced by intergrinding or intimately blending a mixture of ground granulated blast furnace slag and gypsum anhydrite with a small amount of cement clinker or portland cement which act as activators. The cement is suitable for massive concrete constructions exposed to sea water. In India, granulated slag is available in plenty from pig iron plants situated in East and South East. However, bulk of reserves of mineral gypsum are located in the Western parts namely Rajasthan and the transport cost is high. Further, Scarcity of high purity gypsum required to produce anhydrite for making SSC and its requirement in much larger quantities /20-25% compared to 4-5% in ordinary portland cement/ have been deterrents to the production of SSC in India. However, phosphogypsum is available to the extent of 0.8 million tonnes per annum from the superphosphate plants located in different parts of India. In fact, some of these plants are situated close to slag granulation plants. Investigations were, therefore, taken up to study its suitability for making SSC.

Chemical composition of a representative sample of phosphogypsum is reported.

TABLE I

Chemical Composition of Phosphogypsum

Constituents	Precent
SiO_2	5.02
$Al_2O_3+Fe_2O_3$	0.41
CaO	31.11
MgO	-
SO_3	42.39
P_2O_5	0.60
F	0.40
Loss on ignition	20.45
Total	100.38

The material contains impurities of phosphates, fluorides and organic matter which adversely affect the development of strength if used as an additive to cement clinker. Soluble impurities present on the surface of the gypsum crystals or in intergranular spaces can be washed out with water. However, phosphate ions $/HPO_4/^{2-}$ are known to substitute sulphate ions $/SO_4/^{2-}$ /Berryand Kuntze 1972/ because of their similar ionic parameters and are present in the crystal lattice. Same is true of AlF_5^{2-} ions also /Kitchen and Skinner, 1971/. These impurities dissolve out slowly on hydration and adversely affect the hydration characteristics and strength development of cement. Attempt has been made to inactivate the impurities by heating the material to 650-850°C for four hours. Phosphoanhydrite thus produced was shaken in saturated lime water in a mechanical shaker for four hours. The extract was tested for phosphate No phosphate could be detected indicating that the impurity had been rendered insoluble and hence inactive. It appears that the impurity existing as $CaHPO_4.2H_2O$ gets converted to pyrophosphate $/Ca_2P_2O_7/$ which is no longer troublesome. Similar findings were observed by Eipeltener /1973/ also.

The calcined phosphogypsum was tested quantitatively for the impurities. Results are reported on sample as such and on ignited basis.

TABLE II

Impurities in Phosphogypsum

Sample	P_2O_5 as such	P_2O_5 on ignited basis	F as such	F on ignited basis
Phosphogypsum	0.60	0.75	0.40	0.50
Phosphogypsum anhydrite	-	0.75	-	0.41

Results show that there is no loss of phosphate on heating but about 19 percent of fluoride volatilises away. Since the fluoride may attack the refractory lining of calcining kiln, due precautions should be taken to protect the lining of the calcination unit.

Suitability of the phosphoanhydrite thus produced was investigated for making SSC. Besides phospoanhydrite the other raw materials taken were

a/ Granulated slag of composition reported in TABLE III. It had the following characteristics.

Bulk density	- 1028 kg/m^3
Glass content	- 95 per cent
Refractive index	- 1.636

TABLE III

Chemical Composition of Slag

Constituents	Percent
SiO_2	31.92
Al_2O_3	24.49
FeO	0.85
MnO	1.13
CaO	36.36
MgO	5.23
SO_3	t_2
S	0.62
Total	100.60

b/ Cement Clinker. Its Chemical Composition is reported.

TABLE IV

Chemical Composition of Clinker

Constituents	Percent
SIO_2	22.96
Al_2O_3	4.83
Fe_2O_3	2.75
TiO_2	0.20
P_2O_5	0.09
CaO	63.05
MgO	3.92

Polished section of the clinker etched with HF was examined under reflected light. Hexagonal alite phase and round shoped BC_2S were estimated with the help of integrating stage under the microscope. Aluminate and ferrite phases were estimated by X ray diffractometric method. Results are reported.

TABLE V

Compound Composition of Clinker

Phase	Percent
Alite	46.0
C_2S	37.0
Aluminate	6.1
Ferrite	8.4

The optimum proportions of SSC as determined by Tanaka et.al. /1958/ are slag 80-85%, anhydrite 10-15% and clinker 2.5%. However, while investigating the suitability of TISCO slag for making SSC, Chopra and Lal /1961/ showed that the optimum proportions using Indian slag are slag 70-75%, anhydrite 20-25% and clinker 5%. Higher percentage of anhydrite used for activation is because of the high alumina content of Indian slags. Further studies on the suitability of waste fluoro anhydrite for making SSC /Taneja and Malhotra 1974/ showed that the optimum requirements of anhydrite and clinker were 20 and 10 per cent respectively.

Preparation of Cements

SSC may be prepared by intergrinding or separate grinding and blending granulated slag and anhydrite with small proportion of cement clinker. However, since granulated slag and cement clinker-are harder to grind than anhydrite which is much softer, it is preferable to grind them separately and blend them in desired proportions for making SSC. Nine mixes were prepared by blending slag, anhydrite and clinker in the proportions of 75:20:5, 70:20:10 and 65:20:15 respectively to fineness of 4000 cm^2/g /Blains/. The mixes were tested for physical properties as per IS 4031-1968, Results of the best mix are reported.

TABLE VI

Properties of SSC

Setting Time /minutes/		Compressive strength /kg/cm²/		
Initial	Final	3 days	7 days	28 days
125	210	220.6	307.2	406.0

The mix complied with the requirements of IS 6909-1973. The optimum temperature of calcination of phosphogypsum was found to be 750°C and the amount of clinker required for activation was 10-15 per cent.

Special Properties

The above mix was tested for its heat of hydration as per IS 4031-1968 at 3, 7 and 28 days of hydration. Results are reported.

TABLE VII

Heat of Hydration of SSC

Heat of dissolution /Cals/g/				Heat of hydration /Cals/g/		
Unhydrated	Hydrated					
	3d	7d	28d	3d	7d	28d
515.1	494.2	476.7	459.3	20.9	38.4	55.7

Heat of hydration is within the specified limits of IS 6909-1973 and BS 4298-1968 and hence can be recommended for use in mass concrete constructions. Besides, SSC prepared from Indian slag has been shown to be resistant to sulphate and weak acids /Chopra and Lal, 1961/ which ordinarily attack normal portland cement concrete.

Energy Savings

In the production of SSC heat is mainly consumed in the calcination of gypsum to anhydrite and for drying of wet granulated slag. For producing one tonne of SSC heat consumption has been estimated to be 900 M. Joules against 5860 and 3350 M. Joules for portland cement clinker produced by wet and dry process respectively.

Grindability of the samples of granulated slag and cement clinker used in the above investigations was studied as per Bond's grindability test /Kannewurf, 1957/. Data obtained is reported.

TABLE VIII

Grindability of Materials

Material	Grindability gm/revolution	Work index KWH/Tonne	Fineness cm^2/g /blains/	Power required KWH
Slag	0.74	22.84	4000	56.0
Clinker	0.85	20.41	3200	30.2
			4000	50.0

Power consumption for grinding slag was considerably higher than for clinker. However, for producing clinker, additional power is required for winning, crushing and grinding of raw materials, running of kiln and the total power consumption is estimated to be 95 KWH per tonne. Hence there is considerable saving in the production of SSC.

Conclusions

Since cost of transport of material gypsum from Rajasthan to the different steel plants producing by-product granulated slag is very high and waste phosphogypsum is available within short distance, the latter can prove to be an economical substitute of natural gypsum for making anhydrite for the production of SSC. Its utilisation will bring in the market a new type of cement having special properties of low heat of hydration and sulphate resistance and would solve the problem of its disposal.

Manufacture of SSC has a special significance since fuel and power consumption are much lower than for portland cement and the major raw materials are industrial wastes available in plenty.

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Melléktermék gipszből gyártott nagy szulfáttartalmú cement

A nagytisztaságú természetes gipsz hiánya akadályozza Indiában a gipszsalakcement gyártását, ugyanakkor azonban az ország foszforsav gyáraiban évenként 0,8 millió tonna hulladék foszfogipsz keletkezik. A foszfogipsz fő szennyezői a foszfátok, fluoridok és szerves anyagok, melyek kedvezőtlenül befolyásolják a gyártott gipszsalakcement szilárdságát. Megkíséreltük a szennyezéseket magas hőmérsékletű hőkezeléssel hatástalanítani. A hevített mintákat gondosan összekevertük granulált salakkal és cementklinkerrel és a különböző arányú keverékeket szabványos módszerekkel vizsgáltuk meg. Megállapítottuk, hogy a foszfogipsz optimális hőkezelési hőmérséklete 750°C és az optimális keverési arány 70% salak, 20% anhidrit és 10% klinker. Az így gyártott cement kielégíti az indiai szabványok követelményeit. A kötéshő kicsi, így ez a cement különösen ajánlható tömegbetonok előállításához. A gipszsalakgyártás beruházási igénye csak tört része a klinkergyártásának és ezért előállítása gazdaságos. A cement előnyös tulajdonságai közé tartozik a szulfátállóság és a kis hidratációs hő. Gyártása továbbá környezetszennyező hulladék feldolgozását eredményezi.

Supersulphated Cement from Waste Phosphogypsum

Scarcity of natural gypsum of high purity prevents the production of supersulphated cement (SSC) in India. Waste gypsum is available to the extent of 0,8 million tonnes per annum from the phosphoric

acid plants. This contains impurities of phosphates, fluoride and organic matter which affect adversely the development of strength when the material is used as a component of the cement. Attempt was made to inactivate the impurities by heating the material to high temperature. Suitability of anhydrite thus produced was investigated for making SSC by intimately blending separately ground mixture of anhydrite, granulated slag and cement clinker in different proportions and testing as per standard test methods. Results showed that the optimum temperature of calcination of gypsum was 750°C. Optimum proportion was found to be 70:20:10::Slag:anhydrite:clinker. The cement thus produced complied with the physical requirements of the Indian standard. Its heat of hydrations was found to be low and hence its use can be recommended for massive structures. Capital investment and energy consumption are much less in the production of SSC than in portland cement and is hence more economical to produce. The cement has special properties of sulphate resistance and low heat of hydration. Moreover, its production will solve the problem of disposal of the waste.

Aus Abfallgips hergestellter Zement mit grossem Sulphatgehalt

Der Mangel an reinem Naturgips hindert das Herstellen von Gips-Schlacke-Zement in Indien, obwohl sich in den Phosphorsärefabriken des Landes jahrlich 0,8 Millionen Tonnen Abfall Phosphogips bildet. Die wichtigsten Unreinigungen des Phosphogipses sind Phosphate, Fluoride und organische Stoffe, die die Festigkeit des Gips-Schlacke-Zementes unmittelbar beeinflussen. Wir haben probiert die Unreinigungen durch Hochtemperaturbehandlung unwirksam machen. Nach der Wärmebehandlung wurden die Proben mit granulierter Schlacke und Zementklinker sorgsam vermengt und die Gemische mit verschiedenem Zusammensatz nach genormten Methoden untersucht. Wir konnten feststellen, dass die optimale Wärmebehandlungs-Temperatur 750°C ist, und das optimale Mischungsverhältnis 70% Schlacke, 20% Anhydrit und 10% Klinker ist. Der derart hergestellte Zement entspricht den indischen Zementnormen. Seine Bindungswärme ist klein, und so kann dieser Zement für Massenzement Zwecke angeboten werden. Die Investitionskosten der Gipsschlacke-Herstellung beträgt nur einen Bruchteil der Klinkerherstellung, und deswegen ist ihre Produktion wirtschaftlich, Zu den Vorteilen dieses Zementes gehört auch seine Sulphatbeständigkeit und seine niedrige Hydratationswärme. Dieses Verfahren ermöglicht das Aufarbeiten eines die Umgebung verunreinigenden Abfalles.

Гипсошлаковый цемент из фосфоргипса

Отсутствие в Индии естественного гипса высокой чистоты является препятствием для производства гипсошлакового цемента. В то же время на заводах по производству фосфорной кислоты ежегодно образуется в качестве отхода производства 0,8 млн тонн фосфоргипса. Основными примесями фосфоргипса являются фосфаты, фториды и органические вещества, которые оказывают отрицательное влияние на прочность гипсошлакового цемента. Были сделаны попытки устранения вредного влияния примесей путем обработки фосфогипса при высокой температуре. Образцы фосфогипса, подвергнутые тепловой обработке, смешивались в различных пропорциях с гранулированным шлаком и цементным клинкером, и полученные таким образом пробы подвергались стандартным испытаниям на прочность. Было установлено, что оптимальной температурой для обработки фосфогипса является 750°С, а оптимальным соотношением компонентов смеси: 70 % шлака, 20 % ангидрида и 10 % клинкера. Полученный таким образом цемент удовлетворит требования индийских стандартов. Теплота твердения маленькая, поэтому этот цемент особенно предлагается для приготовления массового бетона. Капиталовложения производства гипсошлакового цемента составляют только часть производства клинкера, таким образом производство его является экономичным. К благоприятным свойствам этого цемента является экономичным. К благоприятным свойствам этого цемента является сульфатостойкость и низкая теплота гидратации, кроме того, его производство основано на утилизации отхода производства.