Utilization Of Manganese Sulphate Sludge For Manufacturing Building Materials

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The article highlights the use of manganese sulphate sludge in the development of value added products like tiles, bricks, blocks and partial replacement of cement. The compressive strength of cement cubes at 28 days incorporating 10% sludge passing 300μ is 7% more and with 15% sludge content, the strength is comparable to control. With the use of superplasticizer the compressive strength is 25% more with 5% blending and at 15% blend; the strength is 5% more when compared to control. In case of sludge passing 45μ the compressive strength without superplasticizer at 15% blend is comparable to control. However with the use of superplasticizer the strength is approximately 20% more compare to 5% in case of 300μ passing. The flooring tiles 300x300x22mm prepared with binder content varying between 20-30% and sludge 30-35%, the transverse strength has been found to be around 30Kg/cm^2. Compressive strength of the briquettes cast with 10% sludge from soil of different places has been found to be comparable to the control soil.

When manganese oxide is reacted with sulphuric acid to form manganese sulphate solution, the aqueous solution is extracted leaving behind the cake which is non-hazardous in nature. This residual mass is approximately 40%, which needs to be disposed of in proper manner.

Introduction

The use of industrial wastes and unprocessed micro-fillers in the development of value added products have received maximum attention over the last decade. Considerable work has been done in the utilization of flyash, slag, and silica fume due to their pozzolanic nature. The use of flyash in the manufacture of cement results in the saving of energy and reduction in carbon dioxide and sulphur dioxide emissions. Other factors prompting use of waste materials are the dwindling resources, steadily increasing volume of waste materials and the ecological and environmental problems associated with quarrying and exploitation of cement raw materials [1]. Partial replacement of cement (in concrete) by slag, flyash, rice husk ash and rock mineral is very beneficial in terms of mechanical and durability characteristics of concrete. Lime stone dust poses disposal and environmental problems and has been suggested as an additive to Portland cement. The Canadian standard allows up to 5% addition to type I and III cement. The use of ground limestone is now widely used in the manufacture of composite cements, also in proportions up to 27%, according to French Specifications [2].

In view of energy saving and economical considerations, a number of waste materials has been investigated as possible blending components. Among these by-products are steel LD slag [3], silico-manganic slag [4], and nonferrous metallurgy by-products. There are other wastes which have found use in the development of building materials [5-8]. Though these wastes at the moment have a limited interest, nevertheless the industrial utilization could grow, according to the changes in the technology and advancement in the research.

Sustainable, Portland clinker based cement can be made with 0.5 or even lower clinker factor using waste produced from various industries and flyash etc. Cements containing a high volume of complementary cementing materials can now be manufactured in accordance with ASTM C 1157- a new standard specification for hydraulic cement, which is performance-based.

The present study is about the utilization of sludge when manganese oxide is reacted with sulphuric acid to form manganese sulphate solution. The aqueous solution is extracted leaving behind the cake which is non-hazardous in nature. This residual mass is approximately 40%, which needs to be disposed off in proper manner. In order to utilize this waste into development of various building components, a detailed study as partial replacement of cement, bricks, blocks and flooring tiles has been undertaken.

Materials Used

Cement: Ordinary Portland cement 43 grade was used in the present study. The physical and chemical properties are given in Table 1.

Sludge: The manganese sulphate sludge was supplied by M/S Reshmika Minerals and Chemicals, Pune. The physical and chemical properties are given in Table 2.

Admixture: Chemical admixture Sulphonated Naphthalene Formaldehyde Condensate (SNF) conforming to BIS 9103: 2003 was used.

Clay: Soil samples from Pune and Bahrauch (Gujrat) were supplied by the industry concerned for trial in the development of bricks. X-ray of the sludge is shown in Fig. 1. The physical analysis of the soil is given in Table 7.

Table1: Physical and Chemical analysis Of Ordinary Portland Cement

Property	OPC (43 G)	
SiO_2 (%)	20.65	
Insoluble residue	2.01	
Magnesia	1.42	
Al_2O_3	5.13	
Fe_2O_3	3.95	
Alkalies	0.35	
SO_3	2.55	
LOI	1.45	
Specific Surface cm²/g	2950	
CaO	60.25	
Specific gravity	3.14	
Setting Time (mins.)		
Initial	145	165
Final	230	255
Compressive Strength (Kg/cm²)		
1day	215	
3day	435	
7day	510	
28day	630	

Table 2: Physical and Chemical Analysis of Sludge

Physical form	Solid (cake)
Colour	Black
Water holding capacity	69.05%
pH	7.34
Silica	23.30
Combined Oxide	30%
SO_3	7.06
Fe_2O_3	14.17%
CaO	5.8
LOI	14.8
Al_2O_3	15.83

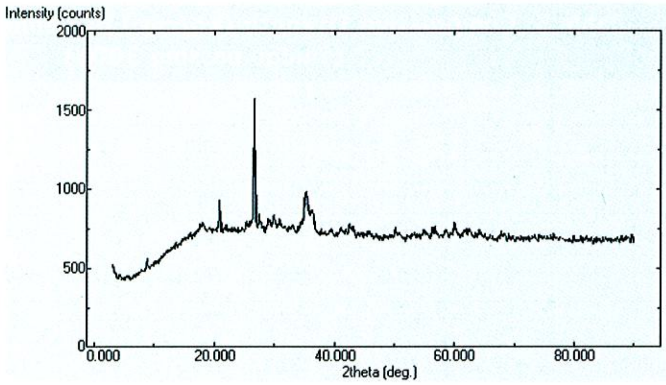

Fig 1: X-ray Diffraction Of Mangnese Sulphate Waste

Experimental Works

Partial Replacement Of Cement

In order to replace cement by the sludge various percentages of this waste (5, 10, 15 and 20%) was added in the cement. Two fractions of waste, 300 µ and 45 µ were taken. All the studies were carried out at standard consistency of cement. The water required to achieve same consistency with and without superplasticizer is given in Tables 3 & 4. One inch cubes were cast with and without

Table 3: Consistency of Cement-Sludge (<300µ)

System	Without Admixture	With Admixture
Control	128ml. (32%)	118ml. (29.5%)
5% Sludge	131ml. (32.75%)	117ml. (29.25%)
10% Sludge	136ml. (34%)	125ml. (31.25%)
15% Sludge	144ml. (36%)	132ml. (33%)
20% Sludge	150ml. (37.5%)	140ml. (35%)

Table 4: Consistency Of Cement-Sludge (<45µ)

System	Without Admixture	With Admixture
Control	128ml. (32%)	118ml. (29.5%)
5% Sludge	141ml. (35.25%)	125ml. (31.25%)
10% Sludge	150ml. (37.5%)	133ml. (33.25%)
15% Sludge	165ml. (41.25%)	140ml. (35%)
20% Sludge	180ml. (45.0%)	150ml. (37.5%)

Table 5: Compressive Strength (Kg/cm²) of Cement-Sludge System (Sludge passing 300µ)

	Without Admixture				With Admixture (0.5%)			
Sample	1d	3d	7d	28d	1d	3d	7d	28d
Control	170.0	275.0	330.0	385.0	254.5	399.04	485.5	591.7
5%	166.0	230.0	317.0	365.5	205.0	364.64	460.0	495.0
10%	97.0	220.0	344.0	412.8	116.9	247.70	330.2	481.6
15%	77.6	185.5	295.0	370.5	85.4	200.7	275.5	401.4
20%	37.8	145.0	213.0	316.5	76.5	151.4	192.64	326.5

Table 6: Compressive Strength (Kg/cm²) of Cement-Sludge System (Sludge passing 45µ)

	Without Admixture				With Admixture (0.5%)			
Sample	1d	3d	7d	28d	1d	3d	7d	28d
Control	170.0	275.0	330.0	385.0	254.50	399.04	485.5	591.7
5%	132.50	302.7	405.9	571.0	206.40	385.30	426.6	577.9
10%	61.50	172.0	275.0	426.6	110.10	309.6	440.32	584.8
15%	53.60	145.5	225.0	355.8	80.40	265.4	320.50	454.5
20%	41.30	123.8	172.0	272.6	63.40	137.2	185.76	357.

superplasticizer and kept at constant temperature at 27± 2°C. The cubes were demoulded after 24 hrs. and tested at 1, 3, 7 and 28 days. The results are given in Tables 5 & 6.

Bricks

Before casting of full size bricks, small briquettes were cast (Fig. 2 - 4) with different soils and sludge samples. Initially the soil samples, control and various sludge percentages (10%, 20%, 25% and 30%) were mixed with appropriate water content and kept for 24hrs. Again this soil was properly mixed and kept for 1 hr. The brass moulds used for making briquettes were filled with the soil and demoulded immediately. These briquettes were kept in the sun for 24 hrs. and dried in oven at 110°C for 24 hrs. so that the moisture is completely removed. Dimension and dry weight of the briquettes were recorded. These briquettes were fired at 1000°C and 950°C depending upon the temperature at which strength and other properties like water absorption and compressive strength has been found better.

The water absorption and compressive strength are given in Table 8. Full size bricks of size 225x100x75mm were cast and fired at 1000° C for three hours. Fig. 5 - 7 show photographs of green and fired bricks. The mechanical properties of the fired bricks are given in Table 9.

Flooring Tiles

The flooring tiles are simply the compressed mass of predetermined dimension containing cement binder, sludge, sand, marble chips and

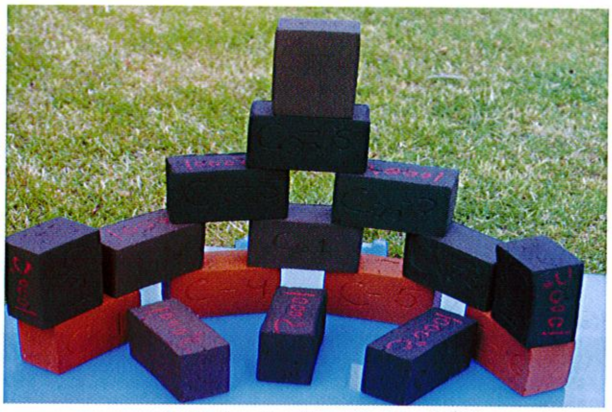

Fig 3: Briquettes From Roorkee Soil

Fig 2: Briquettes From Pune Soil

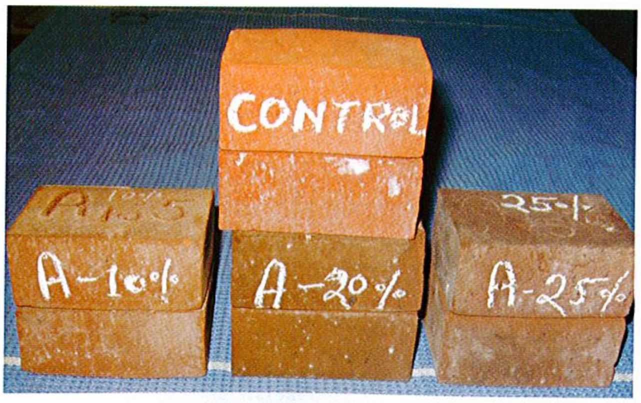

Fig 4: Briquettes From Bharuch Soil

Table 7: Physical Analysis Of Different Soils				
Soil	Particle size Passing	Soluble salts (%)	pH	Bulk density
Roorkee	<4mm, 100% <2mm, 97.8% <1mm, 77.1%	0.680	8.325	1.40
Pune	<4mm, 93.9% <2mm, 86.8% <1mm, 33.1%	0.805	6.566	1.28
Bharuch	<4mm, 88.9% <2mm, 89.9% <1mm, 28.9%	0.565	8.696	1.28

Table 8: Physical Properties Of Briquettes			
System	Briquette	Water Abs. (%)	C.S. (Kg/cm²)
Roorkee (1000°C)	Control C+10% sludge C+20% sludge C+30% sludge	12.50 14.53 14.64 14.62	234.0 254.5 200.2 172.5
Pune (950°C)	Control C+10% sludge C+20% sludge C+25% sludge	15.44 16.44 19.00 21.77	200.0 189.0 121.4 83.9
Bharuch (900°C)	Control C+10% sludge C+20% sludge C+25% sludge	14.00 15.77 18.53 19.57	191.7 180.2 120.8 95.5

Table 9: Physical Properties Of Bricks			
System	Briquette	Water Abs. (%)	C.S. (Kg/cm²)
Pune (1000°C)	Control C+10% sludge C+20% sludge	20.00 16.44 19.00	98.0 86.0 78.0
Bharuch (1000°C)	Control C+10% sludge C+20% sludge	14.00 15.77 18.53	91.0 80.2 62.0

Fig 5: Full Size Green Bricks With Bharuch Soil (20%)

Fig 6: Full Size Green Bricks With Pune Soil (20%)

Fig 7: Fired Bricks Of Different Compositions

marble powder. The tiles are generally recommended to be prepared with two types of mixes filled in the mould. The layer bearing a mixture of cement, sludge and sand is called back layer and the other containing cement, marble powder and chips is called wearing layer. The pressed tile is placed in air in vertical position in frames designed for this purpose. After a period of 18-24 hours, the tile is placed in water for curing.

In the present study tiles of size 250x250x25 mm were prepared with mixture of cement (white/grey), marble powder, marble chips, sand and sludge. Various mix proportions of ingredients were used. The tiles were prepared in two and single layer system. To prepare tile the mixture containing cement, marble dust, marble chips and water sufficient to give a thick cream was filled in the mould and over this another mixture of cement, sludge and sand moist with water was filled. Plunger was placed over it and hydraulic load of 60T was applied and after releasing the pressure the tile was taken out and lifted to the frame designed for the purpose. The tile is allowed to remain under water and after 28 days the properties of the tiles determined as per BIS1237-1980.

Table 10: Properties Of Single Layer Flooring Tiles

Sl. No.	C gms.	Sludge gms.	Fly Ash	Sand gms.	Chips Gms.	Water ml.	TS Kg/cm²	W.Abs. (%)	WR (mm.)
1	800	800	500	400	200	580	34.4	8.9	3.0
2	800	800	500	400	200	580	36.8	9.1	3.1
3	800	800	400	400	300	530	34.0	8.5	3.3
4	800	800	500	400	200	530	32.4	8.2	3.2

C= Cement

Table 11: Properties Of Double Layer Flooring Tiles

Sl. No.	C gms.	Sludge gms.	MD gms	Sand gms.	Marble Chips	Water ml.	TS Kg/cm²	W.Abs. (%)	WR (mm.)
1	T=300		500		400	520	33.0	7.5	2.8
	B=400	800		500					
	T=400		500		300	520	35.5	6.5	2.4
	B=400	800		500					

C=cement, S=sludge, MD= marble dust, TS= transverse strength, WR= wear resistance, W. Abs.= water Absorption

The results are given in Table 10 & 11. The photograph of the tiles single/double layer is shown in Fig. 8 & 9.

Solid Bricks And Blocks

Different mix proportions (Table 12) comprising of waste, sand and cement were prepared by mixing them in dry state. Optimum quantity of water was added to each mix for shaping bricks and blocks. The bricks were shaped either by CBRICK machine based on vibro-compaction technique or by hand operated machine. The bricks were cured for 28 days. The results are given in Table 12. In case of blocks a fixed quantity of dry mix (approx. 16kg - finalized after conducting a number of experiments) was filled in the two moulds of the block making machine and used in producing 300x200x150mm. The block making machine is based on pressure-vibration technique. The blocks were cured for 28 days for development of strength. The results are given in Table 12. The photographs of the solid bricks and blocks are given in Fig. 10 & 11.

Fig 8: Single Layer Tiles

Fig 9: Double Layer Tiles

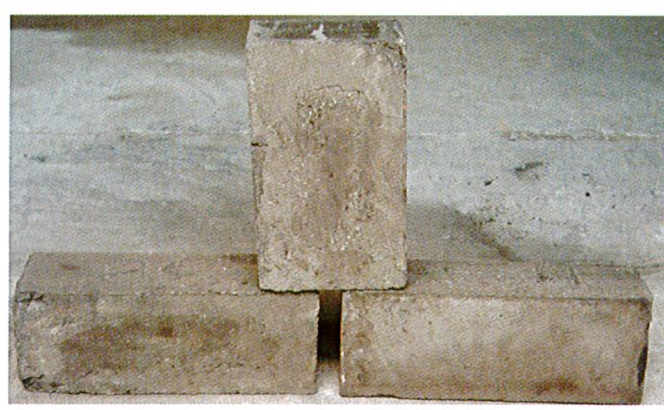

Fig 10: Solid Bricks From Sludge

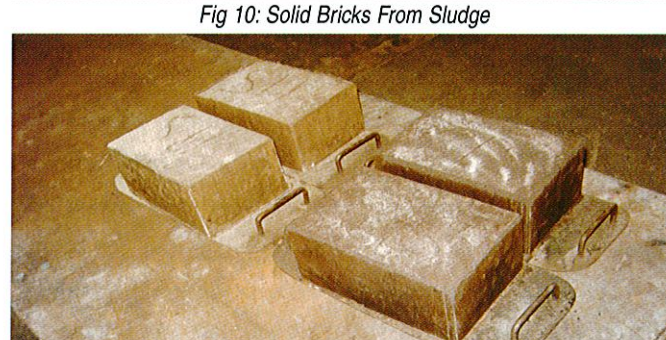

Fig 11: Blocks Of Size 300x200x150mm

Table 12: Physical Properties of Bricks and Blocks

System	Sand (%)	Sludge (%)	Cement (%)	C.S. (Kg/cm²)
Bricks	55	25	20	75-85
Blocks	55	25	20	86.7

Results And Discussion

From Tables 3 & 4 it is clear that the consistency of the cement increases from 32.0% (control) to 37.5% and 42% as the sludge content increases from 5 to 20% for 300μ and 45 μ passing without any admixture. However, with the addition of superplasticizer, the consistency varies from 29.5% (control) to 35% and 37% for 300μ and 45 μ passing sludge.

The compressive strength of the cement cubes given in Table 5 shows that with increase in sludge content there is drop in strength up to 7days except at 10% where the strength is comparable to control. However at 28 days the compressive strength at 10% is approx. 7% extra compared to control. At 15% sludge content, the strength is comparable to control, indicating that there is possibility of blending 15% sludge passing 300μ. With the use of superplasticizer the compressive strength is 25% more with 5% blending and at 15% blend; the strength is 5% more when compared to control.

Use of manganese sulphate sludge in the development of value added products like tiles, bricks, blocks and partial replacement of cement have been highlighted in this study.

It is clear from Table 6 that in case of sludge passing 45μ the compressive strength without superplasticizer at 15% blend is comparable to control. However with the use of superplasticizer the strength is approximately 20% more compare to 5% in case of 300μ passing. The extra strength found can be due to formation of dense matrix in the presence of finer particles (45μ passing) and increased hydration of silica/alumina present in the sludge with cement. The notable observation is 40% gain in strength with 5% sludge using superplasticizer. This can definitely act as a performance improver in blended cement.

The use of manganese sulphate waste has been done in the development of clay bricks. The properties of the soil collected from three locations are given in Table 7. Initially small briquettes were cast and fired at 950°C and 1000°C and its physical properties are given in Table 8. It is clear from the table that with 10% sludge incorporation in soil there is not much deterioration in the compressive strength of the brick. The studies carried out in full size bricks also shows the same trend.

The other value added product developed from this sludge waste is flooring tiles. As mentioned in the experimental procedure these tiles were cast in single and double layer, the results of these tiles are given in Tables 10 & 11. It is evident from the table that about 35% sludge can be utilized in the development of either single or double layers tiles. These tiles satisfy the requirement of Indian standard BIS1237-2006 [9].

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