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# Clinker Activation of High Manganese High Alumina Glassy Slags

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The slag from the blast furnaces of Rourkela Steel plant which employs LD process for steel making and makes addition of pyrolusite to the furnace burden is different from other Indian slags in having comparatively high manganese oxide content. Earlier investigations[1] showed that a glassy slag containing MnO as high as 2.3 per cent was suitable for clinker activation under optimum conditions. Based on these investigations, a safe limit of 2.0 per cent of MnO in the slag was introduced in the revised IS: 455-1967 specification for Portland Blast Furnace Slag (PBFS) cement. However, with the change in the blast furnace technology in the recent past, MnO content in Rourkela slag has gone up to more than six per cent. In view of this, laboratory investigations were considered necessary to study the activation of these slags by clinker and their suitability for cement manufacture.

## Materials Taken

### (A) Granulated Slag

*Chemical composition:* Six samples of granulated slag were received from Rourkela Steel Plant, Rourkela. Their chemical compositions are reported in Table I.

Hydraulic indices employed for evaluating potential hydraulicity of slags as recommended in IS: 455-1967 and computed from chemical composition are reported in Table II.

*Physical properties:* Representative samples of slags were oven dried at 105°C and examined for their glass content[2] and bulk density (Table III).

As per recommendations, glass content in slags should not be less than 90 per cent. The slag samples pass this requirement.

**TABLE I: Chemical Compositions of Blast Furnace Slags, Rourkela**

| Constituents | Composition percent | | | | | |
|---|---|---|---|---|---|---|
| | 1 | 2 | 3 | 4 | 5 | 6 |
| $SiO_2$ | 30.00 | 33.80 | 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 II: Hydraulic Indices of Blast Furnace Slags, Rourkela

| Formula | | Slag samples | | | | | |
|---|---|---|---|---|---|---|---|
| | | 1 | 2 | 3 | 4 | 5 | 6 |
| $\frac{CaO+MgO+1/3Al_2O_3}{SiO_2+2/3Al_2O_3}$ | $\geqslant$ 1 | 1.00 | 0.94 | 0.82 | 0.80 | 0.93 | 0.77 |
| $\frac{CaO+MgO+Al_2O_3}{SiO_2}$ | $\geqslant$ 1 | 2.19 | 1.82 | 1.64 | 1.61 | 1.78 | 1.66 |
| $\frac{CaO+CaS+\frac{1}{2}MgO+Al_2O_3}{SiO_2+MnO}$ | $\geqslant$ 1.5 | 1.97 | 1.59 | 1.48 | 1.36 | 1.51 | 1.39 |

TABLE III: Glass Content and Bulk Density of Blast Furnace Slags, Rourkela.

| Sample No. | Glass content (±1%) | Bulk density kg/m³ |
|---|---|---|
| 1 | 96 | 700 |
| 2 | 99 | 634 |
| 3 | 98 | 968 |
| 4 | 96.5 | 834 |
| 5 | 95 | 997 |
| 6 | 93 | 672 |

(B) CEMENT CLINKER

A cement clinker from a nearby cement plant was employed. Its chemical composition is reported in Table IV.

Photomicrograph of polished section (Fig. 1) shows mainly $\beta$-$C_2S$ crystals. Alite crystals have many $\beta$-$C_2S$ inclusions. The dark prismatic phase is that of $C_3A$.

TABLE IV: Chemical Composition of Clinker

| Constituents | Percentage |
|---|---|
| $SiO_2$ | 23.46 |
| $Al_2O_3$ | 5.42 |
| $Fe_2O_3$ | 2.76 |
| MnO | 0.09 |
| CaO | 63.97 |
| MgO | 1.70 |
| $Na_2O+K_2O$ | 1.05 |
| $H_2O+CO_2$ | 1.10 |

(C) GYPSUM

Bikaner gypsum of 95 per cent purity was used.

**Experimental**

(a) *Grindability of slags and clinker:* To decide on intergrinding or separate grinding and blending of experimental portland blast furnace slag (PBFS) cements, grindability of samples 1, 2, 3 and 4 vis-à-vis that of cement clinker was studied as per Bond's grindability test.[3] Work index and approximate power required to grind the material to fineness of 4000 cm²/gm (Blains) were calculated from the equation

$$W = \frac{10\,W_i}{\sqrt{P}} - \frac{10\,W_i}{\sqrt{F}}$$

where $W$ is the work in kWh/tonne and $W_i$ is the work index. $P$ and $F$ are the 80 per cent passing sizes in micron of the product and feed material respectively. Results are given in Table V.

(b) *Optimum proportions of slag & clinker:* Slag sample 2 and cement clinker were interground in the proportions of 40:60 and 50:50 with 4 per cent of gypsum to fineness of ~ 4000 cm²/gm (Blains). A control cement was also prepared by grinding cement clinker with 4 per cent of gypsum. The cements produced were tested for physical properties as per IS: 4031–1968 using three fraction standard Ennore

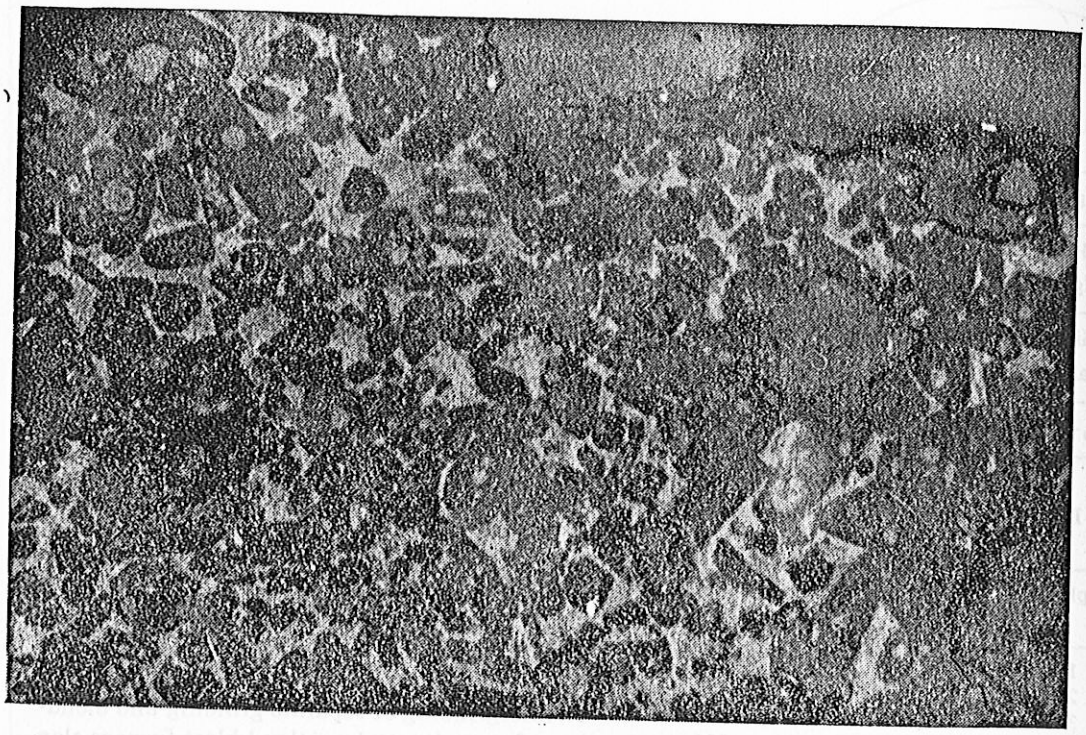

Fig. 1—Photomicrograph of the used cement clinker. ×800

TABLE V: Results of Work Index and Power Requirement Calculations

| Material | Grindability gm/rev | Work index kWh/tonne | Power required to grind material to 4000 cm²/gm kWh/tonne |
|---|---|---|---|
| Slag 1 | 0.80 | 21.45 | 52.72 |
| Slag 2 | 0.82 | 21.06 | 51.77 |
| Slag 3 | 0.81 | 21.25 | 52.23 |
| Slag 4 | 0.78 | 21.97 | 54.00 |
| Clinker | 0.86 | 20.41 | 50.00 |

sand for making mortar. The results are reported in Table VI.

Experimental PBFS cements containing 40 and 50 per cent of slag compare well with ordinary portland cement in physical properties. Therefore, slag content up to 50 per cent can be safely recommended in the manufacture of PBFS cements.

In this connection, it should be mentioned that for determining optimum safe proportion of slag, strength of PBFS cement should be

TABLE VI: Physical Properties of Experimental and Control Cements

| Mix S:C:G* | Fineness cm²/gm (Blains) | Setting time (min) | | Compressive strength (kg/cm²) | | | |
|---|---|---|---|---|---|---|---|
| | | Initial | Final | 3d | 7d | 28d | 90d |
| 40:60:4 | 4009 | 135 | 215 | 210 | 286 | 621 | 646 |
| 50:50:4 | 4009 | 240 | 340 | 209 | 321 | 506 | 574 |
| 0:100:4 | 3145 | 175 | 245 | 230 | 308 | 589 | 659 |

*S, C and G stand for slag, clinker and gypsum respectively.

compared with that of control portland cement rather than with the limits specified in the Indian Standard. Though IS: 455–1967 permits slag content up to 65% in PBFS cement, the safe limit of the samples of slag under study appears to be 50 per cent since strength data of PBFS cement when compared with that of control portland cement in Table VI show that there is substantial fall in strength though the PBFS cement still complies with the IS specification. Safe proportion of 50 per cent seems also justified by the data in Table VIII.

(c) *Optimum gypsum content:* Three mixes, each in the proportion of 50:50: :Slag:Clinker, were interground with 4, 5 and 6 per cent of gypsum to fineness of ~ 4000 cm²/gm (Blains). The PBFS cements produced were tested as per IS: 4031–1968. Results are reported in Table VII.

The data show that the strengths of the three PBFS cements are more or less equal, and no variational trend is discernible. An average value of 5 per cent was therefore chosen as the provisional optimum amount. $SO_3$ contents in 4, 5 or 6 per cent of gypsum of purity of 95 per cent are 1.77, 2.21 and 2.65 per cents. These are within the specified maximum percentage limit of 3.0. Maximum sulphide content in samples of slags is 0.65 per cent which is much below the limit of 1.5% specified for PBFS cement in IS 455:1967.

**TABLE VII: Physical Properties of Experimental Cements, with Varying Gypsum Contents**

| Mix No. | Gypsum | Setting time (min) | | Compressive strength (kg/cm²) | | |
|---|---|---|---|---|---|---|
| | | Initial | Final | 3d | 7d | 28d |
| 1 | 4 | 240 | 340 | 209 | 321 | 506 |
| 2 | 5 | 210 | 275 | 203 | 333 | 514 |
| 3. | 6 | 230 | 295 | 217 | 317 | 495 |

**TABLE VIII: Physical Properties of PBFS Cements**

| Slag sample No. | MnO % | PBFS cement composition S:C:G | Fineness cm²/gm (Blains) | Normal consistency | Setting time (min) | | Compressive strength (kg/cm²) | | | | Autoclave expansion (%) |
|---|---|---|---|---|---|---|---|---|---|---|---|
| | | | | | Initial | Final | 3d | 7d | 28d | 90d | |
| 1. | 2.29 | 40 60 5 | 4039 | 23.5 | 180 | 230 | 242 | 437 | 484 | 670 | 0.20 |
| | | 50 50 5 | 4085 | 24.5 | 235 | 290 | 224 | 367 | 478 | 650 | 0.22 |
| 2. | 3.30 | 40 60 5 | 4064 | 23.2 | 170 | 200 | 208 | 333 | 514 | 666 | 0.46 |
| | | 50 50 5 | 4018 | 24.0 | 210 | 275 | 203 | 290 | 456 | 572 | 0.50 |
| 3. | 2.40 | 40 60 5 | 4009 | 23.2 | 170 | 230 | 192 | 294 | 422 | 682 | 0.32 |
| | | 50 50 5 | 4000 | 24.2 | 285 | 355 | 180 | 277 | 394 | 510 | 0.31 |
| 4. | 4.83 | 40 60 5 | 4085 | 23.5 | 215 | 245 | 202 | 290 | 434 | 640 | 0.31 |
| | | 50 50 5 | 4085 | 23.7 | 190 | 255 | 178 | 282 | 366 | 610 | 0.40 |
| 5. | 4.94 | 50 60 5 | 4039 | 24.25 | 145 | 215 | 285 | 409 | 417 | 500 | 0.22 |
| | | 50 50 5 | 4000 | 25.5 | 160 | 210 | 225 | 321 | 528 | 576 | 0.26 |
| 6. | 6.17 | 40 60 5 | 4064 | 25.5 | 150 | 195 | 238 | 345 | 389 | 660 | 0.21 |
| | | 50 50 5 | 4064 | 25.0 | 165 | 197 | 206 | 355 | 391 | 519 | 0.24 |
| | | 0 100 5 | 3111 | 22.0 | 180 | 225 | 260 | 305 | 592 | 611 | 0.30 |
| | | IS:269–1967 | > 2250 | — | > 30 | < 600 | > 160 | > 220 | — | — | < 0.80 |

(d) *Preparation of PBFS cements:* The six samples of slags were interground with cement clinker in the proportions of 40:60 and 50:50 with 5 per cent of gypsum to fineness of ~ 4000 $cm^2/gm$ (Blains).

## Results

*Physical properties of PBFS cements:* The cements produced were tested for physical properties as per IS: 4031–1968. Results are reported in Table VIII. Physical properties of control portland cement are reported for comparison.

This shows that all the cements comply with the physical requirements of IS: 455–1967.

## Discussion

Clinker activation of Rourkela slags containing MnO as high as 6.17 per cent has shown them to be suitable for the manufacture of PBFS cement although the strength data do not show any correlation with MnO content of slags presumably on account of variations of all the chemical constituents of the slags. Earlier studies on clinker activation of Mn-containing synthetic slag glasses of compositions corresponding to those of Rourkela slags also showed improvement in strength with increase in MnO content up to 10 per cent.[4,5] These results, however, are at variance with those obtained with foreign slags in which MnO beyond 3.5 per cent has been shown to impair their hydraulic quality.[6–8] The improved performance of Mn-containing Rourkela slags appears to be due to their higher alumina content, lower $CaO/SiO_2$ ratio and lower sulphide content than foreign slags.[4] Studies of Solacolu[9] on clinker activation of synthetic slag glasses corresponding to compositions of foreign slags have shown that fall in strength of Mn-containing slag cements is due to the presence of MnS rather than MnO which was shown to improve strength. Sulphur in slag is known to have more affinity for manganese than for calcium or iron.[10] Hence Rourkela slag, being low in sulphur, contains less of MnS than some foreign Mn-containing slags and therefore, is less prone to fall in strength due to MnS on clinker activation.

X-ray diffraction studies on hydrates of clinker activated Mn-containing synthetic slag glasses[4] did not reveal the presence of any manganese hydrate. Presumably manganese may be going in solid solution in the C-S-H phase modifying the structure of the hydrate and improving strength which requires further investigation.

Data on hydraulic indices of slags (Table II) indicate that the same slag can be graded differently depending upon the choice of the index used. Hence the criterion does not seem to be reliable. Further, the indices do not bear any correlation with the strengths of PBFS cements. This is understandable because besides chemical composition, hydraulic properties depend considerably on conditions of quenching[11] which seem to vary from sample to sample as is apparent from their bulk densities.

## Conclusion

PBFS cement produced by intergrinding glassy slag and clinker in equal proportions with 5 per cent of gypsum complies with the standard specification. MnO content up to 6.17 per cent in slags has not been found to be deleterious.

## Recommendations

1. Manufacture of PBFS cement using high manganese glassy Rourkela slag is recommended.
2. Chemical requirements laid down in Notes 1, 2 & 3, clause 4 of IS: 455–1967 are redundant and should be deleted from the standards.

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