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# Effectiveness of different mineralizers in cement manufacture

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In view of the shortage of energy sources there is greater demand for saving as much energy as possible in cement manufacturing process. The use of mineralizers is one of the ways to help in lowering the clinkering temperature. The results were obtained on the relative efficacy of eight mineralizers on clinkering. The basis of assessment was the estimation of free lime in the clinker prepared at different temperatures and the strength development in the cements so prepared from these clinkers. The fluoride bearing mineralizers were found effective at all the temperatures studied (i.e. 1200-1400°C). The zinc oxide was found effective only at higher clinkering temperatures. Calcium chloride was not found effective particularly at lower clinkering temperatures. However, a combination of fluoride and sulphate was found overall to be more effective than other individual mineralizers studied. A specially prepared compound mineralizer (MTM) has been found most effective. Whenever the temperature increased above a certain level, efficacy of mineralizer diminished.

In the manufacturing process of cement, calcination and grinding of clinker are major energy consuming steps. A calcination system which consumes approximately 80% of total energy that is normally required can be of great value in curtailing the energy requirement in this process. The thermal energy used in the manufacture of cement by dry process is established to be 850-950 kcal/kg clinker as against 1350-1550 kcal/kg clinker in the wet process. If the clinkering temperature is lowered, reduction in energy consumption may follow. It is reported that a lowering of 100°C in clinkering temperature may result in saving of 60-120 kcal/kg clinker[1]. It is possible to lower the temperature of melt phase formation, enhance the liquid phase formation and increase the rate of sintering of lime with silica, alumina and iron oxide by the use of mineralizers[2]. The role of mineralizers has been studied quite extensively but contradictions on the efficacy of such mineralizers have also been observed[3].

Although in recent times commissioning of large scale cement plants is preferred for the production of cement, growth of mini cement plants especially in the developing countries is also taking place. Mini cement plants are based on semi-dry process and consume a thermal energy of about 1100-1200 kcal/kg clinker. Besides this the main drawback of the mini cement plant, its less efficient quality control on the calcination of cement raw mix results in a variable quality of cement produced. The role of mineralizers may be to lower the clinkering temperature and in promoting strength of cement with the same raw mix. Mineralizers may be used in dry, semidry or wet processes.

There are a number of compounds having characteristics of mineralizers and there is need to compare their efficacy to select a suitable mineralizer for the desired purpose. This has been the rationale for undertaking this work and also to investigate the possibility of reduction in the fuel consumption in cement clinkerization.

## Experimental Procedure

*Materials*—Analytical grade compounds, viz., $CaF_2$, $MgSiF_6$, $Na_2SiF_6$, ZnO, $CaCl_2$, $CaSO_4$ and a mixture of some of these compounds were used as mineralizers. A specially prepared compound mineralizer designated as MTM was also used for clinkerization. High calcium oxide bearing limestone, loamy clay and red iron oxide were used for preparing the raw mix to obtain the cement clinker; the percentage composition of the raw meal was: silica 13.41, alumina 3.01, ferric oxide 4.05, calcium oxide 43.63, magnesia 0.41, alkalies 0.24 with loss on ignition at 34.91 per cent.

*Methods*—Predetermined quantities of limestone, clay and iron oxide were ground to pass through 200 mesh, to form the cement raw mix. Nine samples were prepared with this cement raw mix by adding 1.0 per cent of different mineralizers and homogenised in the pot mill. Pellets of these mixes were prepared by adding a small amount of water and were dried at 105-110°C. These pellets of every mix were calcined in a laboratory furnace at different temperatures at intervals of 50°C in the range of 1200-1400°C and were maintained at these temepratures for a period of one hour. The calcined pellets were taken out from the furnace for air quenching. The prepared clinker was ground in pestle mortar to pass through 200 mesh.

Free lime in the cement was determined according to the modified Franke method. The compressive strength development was determined on 1.2 cm cubes prepared with neat cement pastes having water/cement ratios from 0.3-0.4 by maintaining similar workability. The cubes were removed from the moulds after 24 h moist curing and then curing was done under water at 27°C.

X-ray diffractogram of cement prepared with and without MTM mineralizer was also carried out.

## Results and Discussion

The amount of free lime after clinkerization of cement raw mix provides information on the progress of the reaction of lime with other constituents. The values are shown in Fig. 1.

The favourable effect of mineralizers on the reaction of lime with silica and $R_2O_3$ at all temperatures especially at lower temperatures studied becomes evident when compared with values of free lime in clinkers prepared without mineralizer. The free lime in the cement with fluorine bearing compound mineralizer MTM is lowered by 18, 14, 7, 4 and 2% at 1200, 1250, 1300, 1350 and 1400°C respectively as compared to cement without mineralizer. The use of mineralizer as a new component in the region of portland cement formation has lowered the temperature at which liquid formation appears and thus has influenced the reactivity of component of raw materials and rate of formation of clinker at a particular temperature. The mineralizer enters into solid solution with $C_3S$, $C_2S$ and $C_3A$ to form unstable intermediate compounds of new phases which are stable upto certain temperature and decompose above that temperature forming the stable phases[4-6]. Beside this it has been reported[7] that fluorine containing substances stimulate the breaking of Si – O – Si bonds and thus clinker formation results at lower temperatures. This was corroborated from the XRD of cement prepared

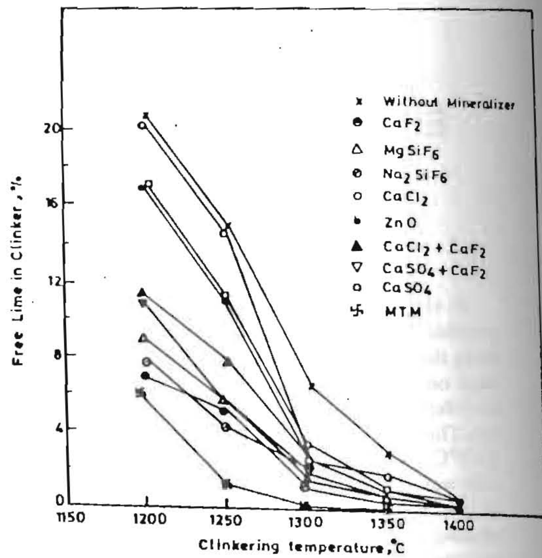


Fig. 1—Effect of clinkering temperature on lime fixation

with and without mineralizer MTM at 1250 and 1350°C shown in Fig. 2. The intensity of peaks of different phases ($C_3S$, $C_2S$) is higher in the clinker produced at 1250°C as well as at 1350°C with the mineralizer in comparison to clinker produced with the same raw mix at the same temperatures without mineralizer.

The effectiveness of mineralizer is not only linked to liquid phase formation at lower temperature but also on the accelerating effect upon CaO combination[8]. All these factors have contributed in lowering the temperature at which clinkering has taken place. Also whenever the temperature increases above a certain level the efficacy of mineralizer diminishes.

The effectiveness of the various mineralizers and some of their mixtures was found in the following order on the basis of studies here as:

$$MTM > Na_2SiF_6 > MgSiF_6 > CaF_2 > CaF_2 + CaSO_4 > CaF_2 + CaCl_2 > ZnO > CaSO_4 > CaCl_2$$

Okorokov *et al.*[9] have opined electronegativity as a specific feature of mineralizer and for anions it is decreased depending on the electronegativity as in the series

$$SiF_6^{2-} > F^- > SO_4^{2-} > Cl^-$$

for the reduction of liquid phase viscosity. This is corroborated in the present study.

The determination of the compressive strength, indicative of hydraulicity developed on clinkering, was carried out on the cement produced at 1250, 1300, 1350 and 1400°C and the results are

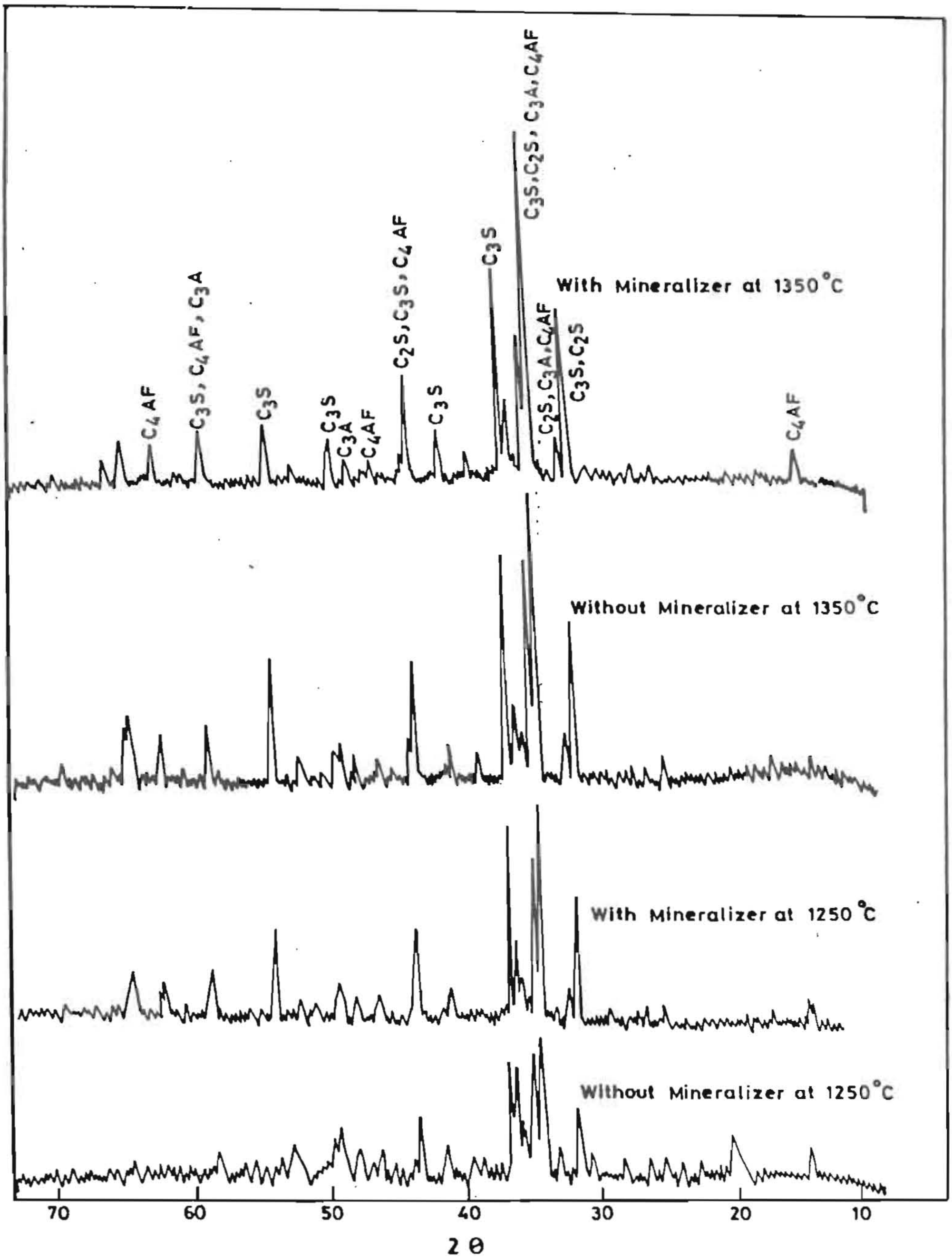


Fig. 2—X-ray diffraction patterns of clinkers prepared at 1250 and 1350°C

shown in Table 1. The cement clinkerized at 1250°C with fluorine bearing mineralizers has developed good strength even after 3 days and at all stages of curing. Especially at 28 days it becomes 4-5 times higher than the cement clinkerized at 1250°C without mineralizer. Whereas with $Cl^-$ and $SO_4^{2-}$ bearing mineralizers no such improvement has been noticed.

The development of strength with MTM mineralizer is excellent even at 1250°C.

Table 1—Compressive strength of cement produced at different temperatures with different mineralizers

| Mineralizer | Compressive strength ($kg/cm^2$) of cement prepared at | | | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | 1250°C | | | 1300°C | | | 1350°C | | | 1400°C | | |
| | days | | | days | | | days | | | days | | |
| | 3 | 7 | 28 | 3 | 7 | 28 | 3 | 7 | 28 | 3 | 7 | 28 |
| Nil | 36 | 48 | 68 | 89 | 121 | 288 | 218 | 304 | 450 | 240 | 355 | 460 |
| 1% $CaF_2$ | 108 | 201 | 300 | 213 | 323 | 443 | 256 | 342 | 523 | 276 | 390 | 533 |
| 1% $MgSiF_6$ | 171 | 218 | 260 | 182 | 304 | 475 | 264 | 446 | 608 | 290 | 470 | 550 |
| 1% $Na_2SiF_6$ | 141 | 200 | 247 | 140 | 238 | 465 | 242 | 332 | 535 | 285 | 410 | 550 |
| 1% $CaCl_2$ | 21 | 27 | 75 | 118 | 133 | 275 | 237 | 317 | 470 | 247 | 326 | 475 |
| 1% ZnO | 72 | 100 | 124 | 118 | 281 | 403 | 247 | 437 | 475 | 265 | 455 | 522 |
| 1% $CaSO_4$ | 31 | 51 | 88 | 101 | 152 | 275 | 229 | 288 | 414 | 244 | 305 | 470 |
| 0.5% $CaF_2$ + 0.5% $CaCl_2$ | 72 | 150 | 210 | 190 | 280 | 325 | 200 | 280 | 480 | 249 | 237 | 488 |
| 0.5% $CaF_2$ + 0.5 $CaSO_4$ | 88 | 170 | 220 | 197 | 282 | 340 | 267 | 300 | 470 | 270 | 340 | 480 |
| MTM | 363 | 481 | 647 | 426 | 481 | 741 | 433 | 525 | 689 | 430 | 520 | 700 |

However, if $Cl^-$ and $SO_4^{2-}$ mineralizes are partly replaced by $F^-$ containing mineralizer improvement occurs thus implying the improvement in the efficacy of mixed mineralizers. The addition of ZnO does not prove to be as effective as fluorine based mineralizer at all the temperatures studied here especially at a temperature of 1250°C.

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