

A FLUX FOR CEMENT

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This invention relates to compositions of the additive for manufacturing cements.

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In order to accelerate the formation of cement clinker minerals, a small quantity of mineralizer is often added to the raw materials of cement. In recent years, a composite mineralizer of gypsum and fluorite has been developed, which may be beneficial to the melting of the raw materials but easily results in the defects such as the so called "ring formation" and bringing a fluctuation in the quality of cement. The wollastonite is a mineral which has discovered a wide application through years. This mineral can be used as a component of ceramic material to greatly reduce its firing temperature and firing time. So far no report has been found that the wollastonite can be used as a component in the composite mineralizer for cement.

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An object of the invention is to develop a new mineralizer, by a generalization of employing the low-grade wollastonite, to reduce the firing temperature of cement or shortening its firing time, thus to save energy in manufacturing cements and to improve the productivity.

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According to the present invention there is provided use of wollastonite as a flux in the production of cement.

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According to the present invention there is further provided a flux for producing cement, which flux comprises wollastonite and a mineralizer.

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The wollastonite belongs to the calcium silicate minerals ( $\text{CaSiO}_3$ ), having the chemical composition  $\text{Ca}$ , ( $\text{Si}_2\text{O}_6$ ) wherein  $\text{CaO}$  is 48.3% and  $\text{SiO}_2$  is 51.7%, all based on weight throughout the application. Since the wollastonite has a needle structure, it may improve the strength of ceramic body, and give the latter a good compressibility. The invention, using the successful experience of applying wollastonite in ceramics for the production of cement and combining the components such as gypsum and fluorite of mineralizer in the prior art, has developed novel fluxes for cement with the following compositions:

1. wollastonite 50-100%, tremolite 0-50%;
2. wollastonite 50-100%, fluorite 0-15%, gypsum 0-35%;
3. wollastonite 50-100%, fluorite 0-20%, slag 0-30%.

Preferably the fluxes according to the present invention comprise a mineralizer comprising tremolite, fluorite and gypsum.

The fluxes can be made by two steps: raw materials breaking and grinding. And the products have particle sizes from 60 to 160 meshes (US standard) preferably from 80 to 100 meshes.

The flux according to the invention is added during the preparation of cement raw materials and the flux admixed is preferably 1-10% of the latter, and 3-5% is most preferable. In order to find the optimal value, an adjustment should be given after the sampling examination of free  $\text{CaO}$  in the cements produced based on different quantities of flux admixed, and the strength of the cement involved.

#### Embodiment 1

Based on the composition 2 of the flux for cement.

(1) preparation; the percentage of individual components were listed in Table 1;

(2) firing: grinding the all-black raw materials into a control system, preparing the pellets with diameters from 15 to 30 mm, preferred 25 mm, firing them in an electric oven. In comparison with the conventional method of making cement the required firing temperature in the present invention was 100 °C lower and the required time for being kept at a constant temperature was reduced by 30%. The pellets are fired for 20 minutes at 1350 °C. The analysis was then made to determine the chemical composition of the clinker formed and its possible mineral contents (%). The results are shown in Table 2.

(3) properties: manufacturing a slag cement using the clinker made by the above-mentioned method. The ratio involved was

clinker: slag: gypsum=50:50:2

and the physical properties of the cement made are shown in Table 3.

#### Embodiment II

The percentages of individual components in the flux for cement based on the composition 3 were listed in Table 4.

Under the condition that the percentages of both limestone and slag were kept unchanged and the percentages of fluorite, gypsum and wollastonite were all adjusted, the raw material pellets were prepared. During a firing, firing time at a high temperature was reduced from the original 30 minutes to less than 20 minutes. The general chemical composition and possible mineral contents of the

obtained clinker are listed in Table 5.

During the above firing for making clinker, a reduction of 30% in the coal consumption and a reduction of 30% in the firing time were achieved. The respective ratios for making cement were that

" Clinker prepared: gypsum=100:4

and in a preparation of the slag cement

clinker: slag: gypsum=50:50:4.

The physical properties of the cement are listed in Table 6.

The distinguished effectiveness of the embodiments in comparison with the prior art is shown in Table 7.

Therefore, using the flux of the invention in the production of cement can shorten the firing time, reduce the amount of coal consumption, improve the discharge of flue gas, reduce the "ring formation" in the oven and increase the compression strength of the cement by about 100 Kg/cm<sup>2</sup> or more, and the bending strength of the cement by about 10 Kg/cm<sup>2</sup> or more.

Table 1

| Component<br>(%)<br>Material | Design<br>% | Rate of<br>ignition<br>loss % | SiO <sub>2</sub> | Al <sub>2</sub> O <sub>3</sub> | Fe <sub>2</sub> O <sub>3</sub> | CaO   | MgO      | CaF <sub>2</sub> | SO <sub>3</sub> | Other | Total |
|------------------------------|-------------|-------------------------------|------------------|--------------------------------|--------------------------------|-------|----------|------------------|-----------------|-------|-------|
| limestone                    | 66.50       | 28.74                         | 0.86             | 0.15                           | 0.05                           | 36.08 | 0.49     |                  |                 | 0.13  | 66.50 |
| clay                         | 12.50       | 0.90                          | 8.26             | 1.90                           | 0.78                           | 0.05  | 0.31     |                  |                 | 0.30  | 12.50 |
| iron powder                  | 2.00        |                               | 0.25             | 0.06                           | 1.35                           | 0.10  | 0.06     |                  |                 | 0.18  | 2.00  |
| wollastonite                 | 2.50        | 0.64                          | 0.54             | 0.01                           |                                | 1.26  | 0.02     |                  |                 | 0.03  | 2.50  |
| fluorite                     | 1.00        | 0.01                          | 0.15             | 0.01                           | 0.01                           | 0.01  |          | 0.76             |                 | 0.05  | 1.00  |
| gypsum                       | 2.50        | 0.29                          | 0.03             | 0.01                           |                                | 0.89  | 0.01     |                  | 1.26            | 0.01  | 2.50  |
| coal                         | 13.00       | 9.96                          | 1.69             | 0.83                           | 0.24                           | 0.17  | 0.06     |                  |                 | 0.05  | 13.00 |
| Total                        | 100         | 40.54                         | 11.78            | 2.97                           | 2.43                           | 38.56 | 0.95     | 0.76             | 1.26            | 0.75  | 100   |
| 100% clinker                 |             | —                             | 19.81            | 4.99                           | 4.09                           | 64.85 | 1.60     | 1.28             | 2.12            | 1.26  | 100   |
| Rate                         |             | KH = 0.98                     | N = 2.18         |                                |                                |       | P = 1.22 |                  |                 |       |       |

Note: KH - Saturation coefficient of lime

N - Rate of silicic acid

P - Rate of iron

Table 2 (%)

| Rate of ignition loss | SiO <sub>2</sub> | Al <sub>2</sub> O <sub>3</sub> | Fe <sub>2</sub> O <sub>3</sub> | CaO   | HgO  | Total  | f-CaO | KH   | n    | p    | C <sub>3</sub> S | C <sub>2</sub> S | C <sub>3</sub> A | C <sub>4</sub> AF |
|-----------------------|------------------|--------------------------------|--------------------------------|-------|------|--------|-------|------|------|------|------------------|------------------|------------------|-------------------|
| 1.76                  | 20.32            | 6.17                           | 4.69                           | 65.85 | 1.25 | 100.00 | 2.02  | 0.91 | 1.87 | 1.32 | 56.37            | 15.75            | 8.40             | 14.26             |

Table 3

| Specific surface (cm <sup>2</sup> /g) | Fineness (%) | Water quantity added at standard consistency (%) | set time          |                  | Safety     | Compression strength (kg/cm <sup>2</sup> ) |       |        | Bending strength (kg/cm <sup>2</sup> ) |       |        |
|---------------------------------------|--------------|--------------------------------------------------|-------------------|------------------|------------|--------------------------------------------|-------|--------|----------------------------------------|-------|--------|
|                                       |              |                                                  | Initial (hr, min) | Ending (hr, min) |            | 3 day                                      | 7 day | 28 day | 3 day                                  | 7 day | 28 day |
| 3160                                  | 7            | 21.5                                             | 1.30              | 3.20             | Acceptable | 307                                        | 523   | 648    | 59.00                                  | 74.50 | 89.50  |

Table 4

| Component<br>(%)<br>Material | Design<br>% | Rate of<br>ignition<br>loss % | SiO <sub>2</sub> | Al <sub>2</sub> O <sub>3</sub> | Fe <sub>2</sub> O <sub>3</sub> | CaO      | H <sub>2</sub> O | CaF <sub>2</sub> | SO <sub>3</sub> | Other    | Total |
|------------------------------|-------------|-------------------------------|------------------|--------------------------------|--------------------------------|----------|------------------|------------------|-----------------|----------|-------|
| limestone                    | 67.50       | 28.25                         | 1.04             | 0.49                           | 0.16                           | 36.21    | 0.37             |                  |                 | 0.98     | 67.50 |
| slag                         | 17.00       | 3.11                          | 8.16             | 3.08                           | 0.82                           | 0.87     | 0.24             |                  |                 | 0.72     | 17.00 |
| coal                         | 8.00        | 6.08                          | 1.05             | 0.49                           | 0.10                           | 0.07     | 0.06             |                  |                 | 0.14     | 8     |
| fluorite                     | 0.7         |                               | 0.05             | 0.01                           |                                |          |                  | 0.60             |                 | 0.04     | 0.7   |
| gypsum                       | 3.80        |                               |                  |                                |                                | 0.97     |                  |                  | 1.39            | 1.44     | 3.8   |
| wollastonite                 | 3           | 0.87                          | 0.43             | 0.01                           | 0.01                           | 1.50     | 0.07             |                  |                 | 0.11     | 3     |
| sum                          | 100         | 38.31                         | 10.73            | 4.09                           | 1.09                           | 39.62    | 0.74             | 0.60             | 1.39            | 3.43     | 100   |
| 100% clinker                 |             |                               | 17.40            | 6.63                           | 1.77                           | 64.22    | 1.20             | 0.97             | 2.25            | 5.56     | 100   |
| Rate                         |             | KH = 1.06                     |                  |                                |                                | N = 2.07 |                  |                  |                 | P = 3.74 |       |

Note: KH - Saturation coefficient of lime

N - Rate of silicic acid

P - Rate of iron

Table 5 (%)

| mm   | SiO <sub>2</sub> | Al <sub>2</sub> O <sub>3</sub> | Fe <sub>2</sub> O <sub>3</sub> | CaO   | MgO  | Sum   | f-CaO | KH   | n    | P    | C <sub>3</sub> S | C <sub>2</sub> S | C <sub>3</sub> A | C <sub>4</sub> AF |
|------|------------------|--------------------------------|--------------------------------|-------|------|-------|-------|------|------|------|------------------|------------------|------------------|-------------------|
| 1.32 | 18.82            | 5.85                           | 2.02                           | 63.94 | 1.18 | 93.13 | 3.44  | 0.95 | 2.39 | 2.90 | 60.78            | 8.10             | 12.07            | 6.14              |

Table 6

| material | Specific surface (cm <sup>2</sup> /g) | Fineness (%) | Water quantity added at standard consistency (%) | set time          |                  | Safety     | Compression strength (kg/cm <sup>2</sup> ) |       |        | Bending strength (kg/cm <sup>2</sup> ) |       |        |
|----------|---------------------------------------|--------------|--------------------------------------------------|-------------------|------------------|------------|--------------------------------------------|-------|--------|----------------------------------------|-------|--------|
|          |                                       |              |                                                  | Initial (hr, min) | Ending (hr, min) |            | 3 day                                      | 7 day | 28 day | 3 day                                  | 7 day | 28 day |
| Clinker  | 3310                                  | 65           | 22.5                                             | 2.10              | 4.31             | Acceptable | 342                                        | 484   | 646    | 59                                     | 68    | 85     |
| slag     | 3215                                  | 7            | 22.5                                             | 2.50              | 5.42             | Acceptable | 129                                        | 256   | 462    | 33                                     | 61    | 82     |

Table 7

| No. | Title                                            | Unit               | Prior Art                                          | Embodiment                                         | Note                            |
|-----|--------------------------------------------------|--------------------|----------------------------------------------------|----------------------------------------------------|---------------------------------|
| 1.  | Heat consumption                                 | kcal/kg            | 1174                                               | 754                                                | Reduction<br>35.7%              |
| 2.  | Ignition loss                                    | %                  | 40                                                 | 36                                                 | Average reduction<br>4%         |
| 3.  | Firing time of<br>clinker at high<br>temperature | Min                | 30                                                 | 20                                                 | Less<br>33.3%                   |
| 4.  | Strength                                         | kg/cm <sup>2</sup> | Compressing strength<br>527<br>Bending strength 68 | Compressing strength<br>646<br>Bending strength 85 | Increasing 119<br>Increasing 17 |
| 5.  | Kiln sintering                                   |                    | Ring forming and<br>lumping easily                 | Hardly lumping                                     |                                 |
| 6.  | Draining of flue<br>gas                          |                    | Black                                              | White with black                                   |                                 |
| 7.  | Time period for<br>settling safety               | Day                | 15                                                 | 7                                                  | Less 8 days                     |
| 8.  | Grindability                                     |                    | Solid and compact,<br>hard for grinding            | Fragile, grinding<br>easily                        |                                 |



**CLAIMS**

1. Use of wollastonite as a flux in the production of cement.
2. Use according to Claim 1, wherein the particle size of the flux is from 60 to 160 U.S. standard meshes.
3. Use according to Claim 2 wherein the particle size of the flux is from 80 to 100 U.S. standard meshes.
4. Use according to any one of Claims 1 to 3, wherein the wollastonite is broken and then ground to produce the flux.
5. A flux for producing cement, which flux comprises wollastonite and a mineralizer.
6. A flux according to Claim 5, wherein the mineralizer comprises tremolite, fluorite and gypsum, or fluorite and slag.
7. A flux according to Claim 6, comprising not more than 50% tremolite and no less than 50% wollastonite by weight.
8. A flux according to Claim 6, comprising not more than 15% fluorite, nor more than 35% gypsum and no less than 50% wollastonite by weight.
9. A flux according to Claim 6, comprising not more than 20% fluorite, not more than 30% slag and no less than 50% wollastonite.



10. A flux according to any one of Claims 5 to 9,  
wherein the particle size of the flux is from 60 to 160  
U.S. standard meshes.

11. A flux according to Claim 10, wherein the particle  
size of the flux is from 80 to 100 U.S. standard meshes.

12. A method of manufacturing a flux in accordance with  
any one of Claims 5 to 11, the method comprising breaking  
the raw materials and grinding the broken raw materials.

13. A method of manufacturing a cement clinker, which  
method comprises preparing the raw materials for the  
clinker, the raw materials comprising wollastonite or a  
flux in accordance with any one of Claims 5 to 11, grinding  
the raw materials and firing the ground mixture.

14. A method according to Claim 13, wherein the flux is  
present in the raw materials in the range of from 1 to 10%  
by weight.

15. A method according to Claim 14, wherein the flux is  
present in the raw materials in the range of from 3 to 5%  
by weight.

16. A cement clinker comprising wollastonite or the  
flux according to any one of Claims 5 to 11.

17. A process for producing cement, comprising the step  
of blending clinker according to Claim 16 with slag and  
gypsum.

18. A cement comprising wollastonite or the flux  
according to any one of Claims 5 to 11.



19. Use of wollastonite as a flux, substantially as  
hereinbefore described.

20. A flux for producing cement substantially as  
hereinbefore described, with reference to the foregoing  
embodiments.

21. A cement clinker substantially as hereinbefore  
described with reference to the foregoing embodiments.

22. A cement substantially as hereinbefore described  
with reference to the foregoing embodiments.

23. A method of manufacturing a flux for producing  
cement substantially as hereinbefore described with  
reference to the foregoing embodiments.

24. A method of manufacturing a cement clinker  
substantially as hereinbefore described with reference to  
the foregoing embodiments.

25. A method of manufacturing a cement substantially as  
hereinbefore described with reference to the foregoing  
embodiments.

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