High Volume Mineral Additive for ECO- Cement

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Abstract

This paper presents a new approach to the production of High Volume Mineral Additive (HVMA) cement. HVMA cement technology is based on the intergrinding of portland cement clinker, gypsum, mineral additives, and a special complex admixture, Supersilica. This new method increases the compressive strength of ordinary cement to 140 MPa and also permits the utilization of a high volume (up to 60%) of inexpensive indigenous mineral additives in the cement.

The research results demonstrate that a high volume of natural materials (alumosilicates, limestone, sand, natural pozzolans) and industrial by-products (granulated blast furnace slag, fly ash) and waste (chemical wastes, broken glass and ceramic) can be used as mineral additives in HVMA cement. The maximum quantity of mineral additives in HVMA cement depends on the type of mineral admixtures and its desired strength/durability level. The optimization of the composition of HVMA cement allows the production of a cement with maximal strength and at minimal cost.

Introduction

In the past 25 years, there has been considerable interest in developing new construction materials incorporating industrial by-products and waste (IBPW) [1-5]. Accompanying industrialization the volume of IBPW has significantly increased and will dramatically expand in the future creating a number of economical and ecological problems. Consequently, there is a demand for the development and application of new technologies to reduce IBPW and transform it into useful products. The process named “high performance cement technology” was found to be very effective for the utilization of IBPW in high volumes.

High-Performance and HVMA Cement

A newly developed technique using a special admixture during the cement grinding process helps to significantly improve the properties of ordinary cement [4-6]. This approach resulted in the formulation of a new high-tech product: High-Performance (HP) Cement (Fig. 1).
The main idea of HP Cement is the addition of a new reactive silica-based complex admixture (Supersilica) during the grinding of the portland cement. Thus, in the case of HP Cement, the clinker is ground in a ball mill together with mineral additives, gypsum and Supersilica. The resulting cement is then available for producing a wide range of concrete including high-performance concrete.

In the production of HP Cement the amount of expensive and energy-consuming clinker can be drastically reduced. Even at high volumes of mineral additives the particular qualities of the Supersilica admixture provide a blended HP Cement that is far superior to ordinary cement.

As a result, HP Cement can be made to order: from super-strong cements with rugged durability to low cost cements with up to 70% mineral additives. To use a high volume of inexpensive mineral additives (sand, limestone or various industrial by-products) has an important economic and ecological impact.

The following indigenous mineral additives were applied successfully in manufacturing HVMA cement [4]:
- natural pozzolanic materials;
- natural sand;
- limestone;
- granulated blast furnace slag;
- fly ash;
- glass cullet or ceramic waste.

Two possible approaches to HVMA cement production (optimal and economical) are presented in the Fig. 2.

Fig. 1. High-Performance Cement Technology
Experimental Program

Several research projects involving a number of mineral additives have been carried out in order to evaluate the potential of HP cement technology in manufacturing of HVMA cement.

The following materials were used in the experimental program:
- portland cement (NPC);
- complex admixture Supersilica;
- finely ground mineral additives (FGMA): limestone, natural sand, perlite, fly ash, blast furnace slag, waste glass, spent catalyst, waste from alum process.

The NPC had the following Bogue's composition:
- $C_3S-64\%$
- $C_2S-14\%$
- $C_3A-14\%$
- $C_4AF-4\%$

The NPC had a compressive strength of 55.2 MPa and flexural strength of 8.2 MPa at the age of 28 days (according to ASTM C109). The fly ash had an intermediate activity according to the Pozzolanic Potential Index (PPI=0.74) and corresponded to class F according to ASTM C618. All FGMA were ground up to the Blaine specific surface area of 400-850 m$^2$/kg in the laboratory vibrating mill (LVM).

The composition of HVMA cement included a ternary blend of NPC, Supersilica, and FGMA. HVMA cement was manufactured by intergrinding all the components in LVM for 20 minutes in order to realize the mechano-chemical activation.

Two major groups of HVMA cement were investigated:
- at optimum content of Supersilica (at 15% of Supersilica in HVMA cement);
at economical content of Supersilica (at Supersilica to NPC ratio of 15:85 or FGMA – HP cement blend).

FGMA content in HVMA cement was varied from 15% to 60%.

The strength characteristics of HVMA cements were determined in accordance with a specially developed accelerated test procedure. The compressive strength of mortar consisting of cement, standard sand and water (in a quantity, required to obtain a flow of 106-115 mm) at a cement to sand ratio of 1:1 using 4x4x16 cm prismatic samples, cured for 8 hours at 80 °C in a steam chamber.

**Strength Properties of HVMA Cement**

It was found that the optimum content of Supersilica in HP Cement is 15% [4]. This amount of Supersilica ensures the maximum strength of HP Cement: compressive strength of 135.4 MPa and flexural strength of 18.1 MPa (W/C of 0.14). Tested under the same conditions, the NPC demonstrated compressive strength of 68.0 MPa and flexural strength of 8.3 MPa (W/C of 0.23) [4,7].

The replacement of the portland cement component in HP Cement by FGMA at optimal Supersilica content provides an increase in compressive strength (Table 1-3):
- 135.8 MPa at limestone content of 60% (Fig. 3);
- 140.5 MPa at sand content of 60% (Fig. 3);
- 145.2 MPa at fly ash content of 15% (Fig. 4);
- 165.6 MPa at waste glass content of 30% (Fig. 5).

Further increase in the FGMA content above these limits leads to a proportional reduction of strength (Fig. 3-5).

**Table 1. Effect of Mineral Additives on HVMA - Cement Compressive Strength**

<table>
<thead>
<tr>
<th>Mineral Additive</th>
<th>Type</th>
<th>Compressive Strength, MPa @ Volume of Mineral Additive, %</th>
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<tbody>
<tr>
<td></td>
<td>0 15 30 45 60</td>
<td></td>
</tr>
<tr>
<td>Limestone</td>
<td>Economical* 135.4 129.7 108.5 82.1 79.4</td>
<td></td>
</tr>
<tr>
<td></td>
<td>Optimal* 135.4 134.2 132.7 133.9 135.8</td>
<td></td>
</tr>
<tr>
<td>Sand</td>
<td>Economical 135.4 121.1 112.7 89.9 81.2</td>
<td></td>
</tr>
<tr>
<td></td>
<td>Optimal 135.4 133.3 131.9 136.1 140.5</td>
<td></td>
</tr>
<tr>
<td>Perlite</td>
<td>Economical 135.4 121.4 95.7 79.9 42.3</td>
<td></td>
</tr>
<tr>
<td></td>
<td>Optimal 135.4 131.1 122.2 110.3 85.9</td>
<td></td>
</tr>
<tr>
<td></td>
<td>*according to Fig. 2.</td>
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</tbody>
</table>

**Table 2. Effect of Fly Ash and GBFS on HVMA Cement Compressive Strength**

<table>
<thead>
<tr>
<th>Mineral Additive</th>
<th>Type</th>
<th>Compressive Strength, MPa @ IBPW Content, %</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>0 15 30 45 60 90</td>
<td></td>
</tr>
<tr>
<td>Fly Ash</td>
<td>Economical* 135.4 121.5 84.2 73.1 61.4 35.2</td>
<td></td>
</tr>
<tr>
<td></td>
<td>Optimal* 135.4 145.2 128.0 104.0 94.5 -</td>
<td></td>
</tr>
<tr>
<td>GBFS</td>
<td>Economical 135.4 117.2 82.3 71.9 54.7</td>
<td></td>
</tr>
<tr>
<td></td>
<td>Optimal 135.4 124.1 119.8 111.5 82.3</td>
<td></td>
</tr>
<tr>
<td></td>
<td>*according to Fig. 2.</td>
<td></td>
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</tbody>
</table>
Fig. 3. Effect of Mineral Additives on the Compressive Strength of HVMA Cement

Fig. 4. Effect of Fly Ash and GBFS on the Compressive Strength of HVMA Cement
Table 3. Effect of IBPW on HVMA Cement Compressive Strength

<table>
<thead>
<tr>
<th>IBPW</th>
<th>Type</th>
<th>Compressive Strength, MPa @ IBPW Content, %</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>0</td>
</tr>
<tr>
<td>Waste Glass</td>
<td>Economical</td>
<td>135.4</td>
</tr>
<tr>
<td></td>
<td>Optimal</td>
<td>135.4</td>
</tr>
<tr>
<td>Spent Catalyzer</td>
<td>Economical</td>
<td>135.4</td>
</tr>
<tr>
<td></td>
<td>Optimal</td>
<td>135.4</td>
</tr>
<tr>
<td>Alum Waste</td>
<td>Economical</td>
<td>135.4</td>
</tr>
<tr>
<td></td>
<td>Optimal</td>
<td>135.4</td>
</tr>
</tbody>
</table>

*according to Fig. 2.

A feasibility analysis demonstrated that HVMA cements can be produced at a reduced cost using FGMA in the cement at an economical Supersilica content (Supersilica to NPC ratio of 15:85) [4]. It was found that the HVMA - cements with a strength level of normal cement can be manufactured with up to 45% of FGMA and with economical Supersilica content.

Fig. 5. Effect of IBPW on the Compressive Strength of HVMA Cement

IBPW Utilization

There are many examples of the successful recycling of industrial by-products in the cement industry: burning organic waste including scrap tires as cement kiln fuel and using blast furnace slag and fly ash in cement [4-12]; highway construction: blast furnace/steel slag, glass and waste ash as aggregate in hot mix asphalt and base/sub-base filler material [2, 13-19]; dam construction: using blast furnace slag
and fly ash [15]; and ready mix and precast concrete industry: utilization of fly ash and silica fume [3, 7, 10-15].

The following IBPW have been successfully used in construction [2-31]:
- Blast furnace slag
- Coal fly ash
- Coal bottom slag
- Flue gas desulfurization waste
- Glass cullet
- Mining tailings
- Municipal waste combustion ash
- Plastic
- Reclaimed concrete and asphalt
- Scrap tires
- Steel slag
- Waste rock
- Carpet fiber wastes
- Waste Paper

Many processes for recycling industrial waste and contaminated soil (Fig. 6) utilize cement, bentonite, zeolite or lime for this purpose [20-24]. Generally, the use of industrial by-products to replace cement clinker is strictly defined by existing standards [9, 10]. The requirements for by-products or mineral admixtures are summarized in separate standards. According to current standards, the IBPW or mineral admixtures must demonstrate the binding or pozzolanic properties providing a synergetic effect and compatibility with portland cement. Cement-based materials have demonstrated excellent combining properties for incorporating radioactive and hazardous waste. Extensive research demonstrated the ability of the immobilization of different types of IBPW including nuclear isotopes and heavy metals in cement hydrates, especially, in the structure of C-S-H gel [20].

At the same time, for many types of industrial by-products and waste, the rate of utilization is limited to less than 5% [20, 23-25], mainly because of the destructive nature of IBPW. In this case, the compatibility of the IBPW and cement system with simultaneous reactions and structure formation is a most important criterion for the utilization of IBPW. It is a challenging problem to provide IBPW compatibility and at the same time increase the utilization rate.

The combination of certain mineral and chemical admixtures has been found to be very effective in solving this problem [9-11]. The application of sodium silicate (liquid glass) in combination with granulated blast furnace slag (GBFS) was recognized as very effective in reducing permeability, which is essential for the utilization of the IBPW at high volumes [21-27]. The mechano-chemical approach presented in [6] for improving properties of the cement has been successfully applied in the utilization of alum waste and spent chromium-bauxite catalyzer [4]. When the maximal loading of these products in conventional cement was limited to 10-15%, a high performance cement blended with 15% waste showed no reduction in strength. The HP cement based binders with the strength of normal cement were manufactured using up to 30-45% of waste (Fig. 5,7).
Industry Development vs. Eco-Considerations

According to Cembureau’s reports [32-34], the world production of cement has increased by about 50% in the past 10 years. Following the growing demand for cement, this trend is the most significant factor affecting technological development and updating the manufacturing facilities in the cement industry. At the same time, extensive updating of existing facilities for the manufacture of clinker consumes the bulk of capital investment and yields a slow return. Therefore, the expansion of an existing cement plant requires a proportionally high rate of investment. However, in the case of HVMA cement new investments are required only to upgrade the grinding complex. This can help to increase production capacity by 30-50% without additional increase of clinker output (Table 4).

It is generally agreed that the production of cement clinker is expensive and ecologically harmful. CO₂, a principle gas contributing to the “greenhouse effect”, NOₓ and SOₓ are among the hazardous emissions generated in relatively high volumes by the conventional portland cement process. Blended cements incorporating different mineral admixtures or industrial by-products, can partly replace the cement clinker. Therefore, blended cements meet the challenges of modern society by increasing bulk production and conserving energy [35-36]. Since HVMA cement uses about 30-50% less clinker than inferior cements, it creates less ecological damage. In this way HVMA cement contributes to the reduction of carbon dioxide and other emissions at source; it uses IBPW materials economically that would be otherwise transported to landfill sites. In respect of these ecological and economical advantages an ECO- prefix is suggested for HVMA cement: ECO-cement (Fig. 2, 7).
Table 4. Expanding an Existing Cement Plant: Case of HVMA Cement

<table>
<thead>
<tr>
<th>Performance Parameters</th>
<th>Existing Plant</th>
<th>+20% Scenario</th>
<th>+40% Scenario</th>
</tr>
</thead>
<tbody>
<tr>
<td>Mineral Additive Content, %</td>
<td>30</td>
<td>50</td>
<td>70</td>
</tr>
<tr>
<td>Capacity, mil. tons per year</td>
<td>1.0</td>
<td>1.4</td>
<td>2.5</td>
</tr>
<tr>
<td>Required Investments, mil. $</td>
<td>-</td>
<td>4.3</td>
<td>15.4</td>
</tr>
<tr>
<td>Income, mil. $</td>
<td>45.0</td>
<td>64.6</td>
<td>114.2</td>
</tr>
<tr>
<td>Production Cost, mil. $</td>
<td>38.3</td>
<td>55.4</td>
<td>98.8</td>
</tr>
<tr>
<td>Gross Profit, mil. $</td>
<td>6.7</td>
<td>9.2</td>
<td>15.4</td>
</tr>
<tr>
<td>Extra Profit, mil. $</td>
<td>-</td>
<td>2.5</td>
<td>8.7</td>
</tr>
<tr>
<td>Pay Back Period, year</td>
<td>-</td>
<td>0.8</td>
<td>2.2</td>
</tr>
</tbody>
</table>
Concluding Remarks

1. The results of the research have demonstrated that the application of HP Cement technology provides:
   • control of the strength properties of the HVMA / ECO- cement;
   • use of a high volume of indigenous materials in the cement without strength loss;
   • the production of super-high strength cement using selected IBPW.

2. The technology of HP Cement gives an opportunity for using a wide range of by-products and waste. HVMA / ECO- cements are characterized by a number of environmental benefits: ability to utilize IBPW, conservation of energy and natural resources, low overall emissions, and reduced cost, all at controlled or high strength.

3. Further research is required to quantify the effect of Supersilica and mechano-chemical activation on microstructure development, strength properties and durability of HVMA / ECO- cement based materials.

References

7. Sobolev K.G. High- Strength Concrete with Low Cement Factor, Ph.D. Dissertation, Chemical Admixtures Lab, Research Institute of Concrete and Reinforced Concrete, Moscow, Russia, 1993.


