Utilization of Industrial By-Products and Waste in ECO-Cement

Konstantin SOBOLEV, European University of Lefke, Civil Engineering Department, Lefke – TRNC
Metin ARIKAN, Middle East Technical University, Civil Engineering Department, Ankara - Turkey

Abstract

This paper presents a new approach to the production of High Volume Mineral Additive (HVMA) or ECO-cement. ECO-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 indigenous mineral additives in the cement composition.

The research results demonstrate that a high volume of natural materials (natural pozzolans, aluminosilicates, limestone, sand) 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 ECO-cement. The maximum quantity of mineral additives in ECO-cement depends on the type of mineral admixtures and the desired strength/durability level. The optimization of the composition of ECO-cement allows the production of the cement with maximal strength and at minimal cost.
Introduction

In the past 25 years, there has been considerable interest in realizing the potential of construction materials for the utilization of industrial by-products and waste (IBPW) [1-5]. Following industrial development the volume of IBPW has significantly increased and will dramatically expand in the future; this is creating a number of economical and ecological problems. Consequently, there is a demand for the development and application of technologies to reduce IBPW and transform it into useful products.

There are many examples of the successful utilization 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 [4-11]; highway construction: blast furnace/steel slag, glass and waste ash as aggregate in hot mix asphalt and base/sub-base filler material [2, 12-18]; dam construction: using blast furnace slag and fly ash [14]; and ready mix and precast concrete industry: utilization of fly ash and silica fume [3, 7, 9-14].

The following IBPW have been successfully used in construction [2-30]:

- Blast furnace slag
- Coal fly ash
- Coal bottom slag
- Flue gas desulfurization waste
- Glass
- 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 of industrial waste and contaminated soil (Fig. 1) utilize cement, bentonite, zeolite or lime for this purpose [19-23]. The final products of the process have been marketed as soil cement, cement treated base (CTB), bentonite mix and roller compacted concrete. Generally, the use of industrial by-products to replace cement is strictly defined by existing standards [7, 9]. 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 in incorporating radioactive and hazardous waste. Extensive research demonstrated the ability of immobilization of different types of IBPW including nuclear isotopes and heavy metals in cement hydrates, especially, in the structure of C-S-H gel [19].

At the same time, for many types of industrial by-products and waste the rate of utilization is limited by less than 5% [19, 22-24], mainly because of the destructive nature of the IBPW. In this case, the compatibility of the product and cement system in respect of simultaneous reactions and structure formation is a most important criterion for the utilization of IBPW. It is 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 [7-10]. 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 [20-26]. The mechano-chemical approach presented in [31] for improving properties of the cement has been successfully applied in 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 had no reduction in strength; and up to 30-45% of waste was utilized in binders with strength of normal cement (Fig. 2).
Fig. 1. Binding Materials Used for IBPW Stabilization/Immobilization

Fig. 2. Products Based on HP Cement Technology
High-Performance Cement

A newly developed technique using a special admixture during the cement grinding process helps to significantly improve the properties of ordinary cement. This approach resulted in the formulation of a new high-tech product: High-Performance (HP) Cement. 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 (Fig. 3). 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 making a wide range of concrete including high-performance concrete (Fig. 2).

The use of the specially formulated admixture provides the following effects:
- pulverization of cement clinker and mineral additives;
- formation of optimal size distribution of cement;
- creation of highly active amorphous structures;
- physical and chemical modification of the minerals.

Fig. 3. High-Performance Cement Technology
HVMA Cement

Importantly, 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 special 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 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 the HVMA cement:

- natural pozzolanic materials;
- natural sand;
- limestone;
- granulated blast furnace slag;
- fly ash;
- glass or ceramic breakage.

Two possible approaches to HVMA cement production: optimal and economical are presented in the Fig. 4.

![Diagram: High Performance Cement](image)

**Fig. 4. Types of High Volume Mineral Additive (HVMA) Cement**
Experimental Program

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 of alum process.

The NPC had the following Bogue’s composition:

- C_3S-64%,
- C_2S-14%,
- C_3A-14%,
- C_4AF-4%.

The fly ash had an intermediate activity according to Pozzolanic Potential Index (PPI=0.74) and corresponded to class F according to the ASTM C618. All FGMA were ground up to the Blaine specific surface area of 400-850 m²/kg in the laboratory vibrating mill (LVM).

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

Two major groups of HVM A cement were investigated:

- with optimum content of Supersilica at 15% of Supersilica in HVM A cement;
- with economical content of Supersilica at Supersilica to NPC ratio of 15:85.

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

The strength characteristics of HVM A cements were determined in accordance with a specially developed accelerated test procedure: the strength of mortar consisting of cement, standard sand and water (in quantity, required to obtain flow of 106-115 mm) at a cement : 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 (at W/C of 0.14) [4,8].

The replacement of the portland cement component in HP Cement by FGM A at optimal Supersilica content provides an increase in compressive strength (Table 1-3):

- 135.8 MPa at limestone content of 60% (Fig. 5);
- 140.5 MPa at sand content of 60% (Fig. 5);
- 145.2 MPa at fly ash content of 15% (Fig. 6);
- 165.6 MPa at waste glass content of 30% (Fig. 7).

Further increase in the FGM A content above these limits leads to a proportional reduction of strength (Fig. 5-7).

Fig. 5. Effect of Mineral Additives on the Compressive Strength of HVMA Cement
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>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>0</td>
<td>15</td>
</tr>
<tr>
<td>Limestone</td>
<td>Economical</td>
<td>135.4</td>
</tr>
<tr>
<td></td>
<td>Optimal</td>
<td>135.4</td>
</tr>
<tr>
<td>Sand</td>
<td>Economical</td>
<td>135.4</td>
</tr>
<tr>
<td></td>
<td>Optimal</td>
<td>135.4</td>
</tr>
<tr>
<td>Perlite</td>
<td>Economical</td>
<td>135.4</td>
</tr>
<tr>
<td></td>
<td>Optimal</td>
<td>135.4</td>
</tr>
</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</td>
<td>15</td>
</tr>
<tr>
<td>Fly Ash</td>
<td>Economical</td>
<td>135.4</td>
</tr>
<tr>
<td></td>
<td>Optimal</td>
<td>135.4</td>
</tr>
<tr>
<td>GBFS</td>
<td>Economical</td>
<td>135.4</td>
</tr>
<tr>
<td></td>
<td>Optimal</td>
<td>135.4</td>
</tr>
</tbody>
</table>

Fig. 6. 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>Waste Glass</td>
<td>Economical</td>
<td>135.4 136.6 131.2 89.8 43.4</td>
</tr>
<tr>
<td></td>
<td>Optimal</td>
<td>135.4 157.7 165.6 149.4 80.7</td>
</tr>
<tr>
<td>Spent Catalyzer</td>
<td>Economical</td>
<td>135.4 130.7 104.5 50.5 -</td>
</tr>
<tr>
<td></td>
<td>Optimal</td>
<td>135.4 141.3 125.9 111.8 -</td>
</tr>
<tr>
<td>Alum Waste</td>
<td>Economical</td>
<td>135.4 101.5 77.1 45.9 -</td>
</tr>
<tr>
<td></td>
<td>Optimal</td>
<td>135.4 115.9 87.4 62.3 -</td>
</tr>
</tbody>
</table>

Financial analysis demonstrated that HVMA cements can be produced at a reduced cost using FGM A in HVMA 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 FGM A and with economical Supersilica content.

Fig. 7. Effect of IBPW on the Compressive Strength of HVMA Cement
CONCLUSIONS

1. The results of the research have demonstrated that the application of HP Cement technology and Supersilica admixture provides:
   - control of the properties of the HVM A /ECO- cement;
   - use 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 provides an opportunity for using a wide range of by-products and waste.

REFERENCES

8. 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.