

Evaluation of the effect of various groups of waste glass on the properties of Eco-cement is important for the development and realization of this alternative way of waste-glass recycling.

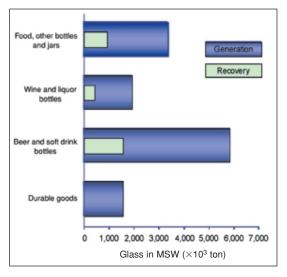


Fig. 1. Structure of waste glass stream.3

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Instituto de Ingenieria Civil, Universidad Autónoma de Nuevo León; Monterrey, Mexico lass is one of the earliest synthesized materials. It has been used for more than 9000 years. Because of its easy availability, cost effectiveness and unique mechanical, chemical, thermal and optical properties, glass is currently found in many applications. In the United States, ~20 million tons of glass products are manufactured annually with a shipment value of about \$29 billion.¹

Theoretically, glass is a 100% recyclable material: it can be indefinitely recycled without loss of quality. According to EPA official statistics, ^{2,3} the municipal solid-waste (MSW) stream in the United States contains ~5.5% of waste glass, or 12.8 million tons. In 2000, only 23% of this volume was recycled. ²⁻⁶ This means that, despite the apparent simplicity of glass recovery, its recycling rate is among the lowest (at an average MSW recovery level of 30%). ³

Waste glass comes from various sources: glass containers (bottles and jars), construction glass (windows) and electrical equipment (lamps, monitors and TVs). Most (89%) of the waste glass comes from various containers (Figs. 1 and 2).^{2,3} Generally, recovered glass containers are recycled as new glass containers; other recovered glass is used in newly emerging sectors, such as fiberglass insulation, abrasives, light-weight aggregates, concrete and asphalt.^{2–27}

Recycling of waste glass is attractive to glass manufacturers, because it decreases the costs associated with raw materials and technological processes. Recycling also lowers energy consumption and eliminates the need to dump waste glass in landfills. However, to recycle waste glass effectively within the glass industry, it must contain glass of similar composition, which has been separated from contaminants that can decrease the quality of new glass products.²

The following contaminants affect recycling of waste glass: 2,3,7-11

- Glass of fluctuating composition or color (compared with the main stream);
- Ceramics (dishware, porcelain, pottery, brick, concrete);
- Metals (including container lids or seals); and
- Organics (paper, plastics, cork, wood, plants, food residue (especially sugar)).

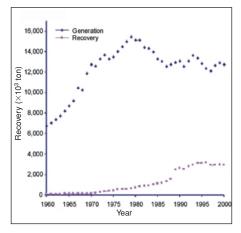


Fig. 2. Generation and recovery of waste glass in the United States.³

The inconsistency of the wasteglass stream makes it difficult to separate glass from other recycled materials and, therefore, minimize contamination. To increase the rates of recycling, glass manufacturers need a uniform supply of quality waste; this requires better colorsorting and ceramic-detection technology for waste glass.^{2,3,10} On the other hand, it also is evident that new alternative technologies that better tolerate contaminants are needed to boost the recycling of waste glass beyond the current limits of the glass industry.

The construction industry has shown great gains in recycling industrial byproducts and waste, including waste glass. 14-28 There are many examples of the successful recycling of waste glass in construction: heat insulation (fiberglass and light-weight aggregates), aggregates for concrete and asphalt, base and subbase filler materials, and cement constituent (as pozzolanic additive). Usually, considerable volumes of contaminants can be tolerated in such applications.

When waste glass is proposed as a constituent of cement (as mineral additive) and concrete (as aggregate), concern about decrease in strength and potentially deleterious alkali–silica reaction (ASR) is often expressed. ^{19–26} The usual precautions to avoid ASR (such as the application of low-alkali cement and pozzolanic additives) are found to be effective when waste glass is used

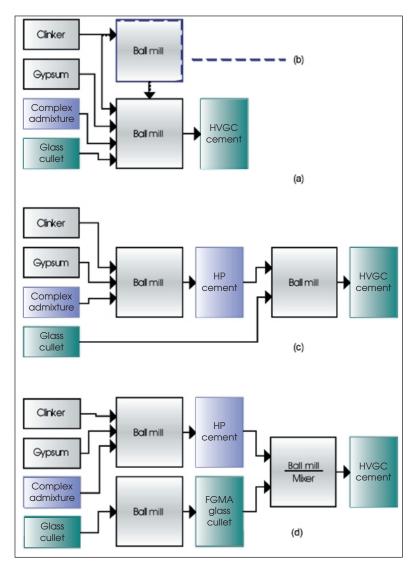


Fig. 3. Technological alternatives to manufacture ECO-cement.

in concrete.^{23–26} The application of waste glass as a finely ground mineral additive (FGMA) in cement is another promising direction for waste-glass recycling.^{21,27} FGMA glass, with its high surface area, participates in the relatively quick pozzolanic reactions that eliminate the danger of a slower alkali–silica reaction at a later stage.²¹

It has been demonstrated that the technology of high-performance (HP) cement can be used for engineering ECO-cement with a high volume of mineral additives (HVMA).^{27,30} Supersilica, a reactive silica-based complex admixture, is added during the cement-grinding process; it promotes the mechanochemical activation of cement and imparts high strength and extreme durability to the concrete or mortar made from such cement.^{27,30} In ECO-cement, relatively large amounts (up to 70%) of portland cement clinker can be replaced with inexpensive, locally available mineral additives, including waste glass. It is expected that the complex admixture and FGMA glass containing significant amounts of amorphous, highly reactive silicon dioxide will participate in simultaneous pozzolanic

reactions, accelerated by the presence of sodium ions.

In practice, the following technological alternatives can be used to manufacture ECO-cements (Fig. 3):

- One-stage grinding process, when all the components of the cement are ground simultaneously (Fig. 3(a));
- Two-stage grinding process with clinker pregrinding (Fig. 3(b));
- Two-stage grinding process with intermediate production of HP cement (Fig. 3(c)); and
- Three-stage grinding process with intermediate production of HP cement and FGMA (Fig. 3(d)).

The selection of an appropriate method for the production of blended ECO-cements depends on the type and grinding ability of the mineral additives as well as the desired specification of the final product. For comparison study, two-stage grinding (as per Fig. 3(b)) can be considered as the most adequate; there-



Fig. 4. Waste glass materials used in the research.

Composition	Clinker	Limestone	Window glass	Monitor	Bottle glass		
				glass	Brown	Green	
SiO ₂	20.84		71.71	83.96	71.19	71.12	
Al_2O_3	5.52		1.26	2.03	2.38	1.71	
Fe ₂ O ₃	3.61		0.09	0.04	0.29	0.24	
TiO ₂	0.29		0.07	0.20	0.15	0.07	
CaO	65.57	52.05	8.44	0.37	10.38	10.02	
MgO	2.13	3.04	4.16	0.01	1.70	3.01	
Na ₂ O	0.82		13.61	7.98	13.16	13.17	
K₂Ō	0.19		0.40	5.35	0.70	0.19	
SO ₃	0.91		0.25	0.05	0.04	0.25	
Cr ₂ O ₃	0.03					0.23	
LOI	0.23	42.90					

fore, in the research program, this option of ECO-cement production has been used.

The effect of FGMA glass (waste sital glass) on the strength behavior of HP-cement-based materials has been reported in the literature. At the same time, the recycling of various types of waste glass in ECO-cement has been proposed. Consequently, the evaluation of the effect of various groups of waste glass on the properties of ECO-cement is important for the development and realization of this alternative way of waste-glass recycling.

Materials and Research Program

Four waste-glass materials (in a form of glass cullet, as per Fig. 4) were used in the research: window glass (WG), black-and-white monitor glass (MG) as well as brown and green bottle glass (BBG and GBG, respectively). ASTM Type I clinker was used in the research program.31 The reference cements included portland cement CEM-I 42.5 (NPC),³² HP cement type A and HP cement type B (HPC-BL containing 35% of limestone (LS)).^{28,29} The reactive silica-based complex admixture supersilica was used for preparation of HP cements and waste-glass ECO-cement samples. The chemical composition of these materials was analyzed using X-ray diffractometry XRD (Table I). Surprisingly, no lead was detected in the MG sample.

The experimental program had two main tasks to investigate:

- Flexural strength of waste glass cements;³³ and
- Compressive strength of waste glass cements. 33,34

Mixture Proportioning

The strength properties of seven cement samples were investigated. These included cements produced in accordance with high-performance cement technology using various types of waste glass (WG, MG, BBG and GBG) and reference cements. Waste glass (50% by weight) and complex admixture (10%) were used to produce these

cements. A small amount (5%) of quartz sand (S) was used to prepare the HPC-BL sample to facilitate grinding in the ball mill (with total LS + S amount in the cement of 40%). The composition and properties of investigated cements are presented in Table II.

The mortars were prepared according to ASTM C109.³⁴ Sand-to-cement ratio (S/C) of 2.75 was used for all mortars. These mortars were produced at a decreased water-to-cement ratio (W/C) adjusted to obtain a flow range of 140–190 mm.

Preparation of Samples

Clinker was preground in a ball mill for 60 min for consequent use in the research program. Waste-glass samples were washed to remove organic contaminants and crushed in the laboratory jaw crusher to a maximum size of 4 mm.

Samples of high-performance cement type A (HPC-A) were obtained by grinding a mixture composed of 85% preground clinker, 5% gypsum and 10% complex admixture in a laboratory ball mill. Subsequently, samples of glass cement were obtained by grinding a mixture composed of 35% clinker, 5% gypsum, 10% complex admixture and 50% waste glass.

The sample weight was 5 kg, and the grinding media weight was 65 kg. Grinding time for all cement samples was 60 min.

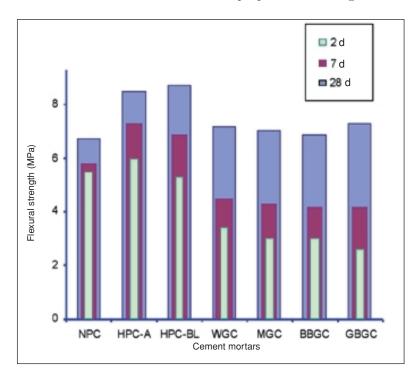
The investigated mortars were mixed following EN $196.^{35}$ The mortars were east into three-gang $(40\times40\times160~\text{mm})$ prism molds and compacted in accordance with EN $196.^{35}$

Curing and Testing

After the compaction procedure, the molds were placed in a humidity cabinet for 24 h (keeping a relative humidity of 95% and a temperature of 20°C). Following this period, the samples were removed from the molds and kept in water until the testing age.

The mortar samples were tested at the ages of 2, 7 and 28 d for flexure and compression. Compressive strength tests were conducted using the portions of prisms broken in flexure.³³ The compressive strength results indicated are the average of four values, and the flexural strength results are the average of the two values.

The flexural test results of glass cement mortars (following ASTM) are presented in Table II and Fig. 5. According to the test results, the 28 d flexural strength of the glass cement mortars is located in the relatively narrow range of 6.9–7.3 MPa. These values are slightly higher than the 28 d flexural strength of reference NPC (6.7 MPa). This difference can be explained by the decreased W/C that was used for preparation of the glass



 ${\it Fig.~5.~Flexural~strength~of~glass~cement~mortars.}$

Composition						Flexural strength (MPa)			Compressive strength (MPa)		
Туре	Clinker	Gypsum	LS + S	Supersilica	W/C	2 d	7 d	28 d	2 d	7 d	28 d
NPC	95	5	0	0	0.45	5.5	5.8	6.7	26.5	36.1	45.4
HPC-A	85	5	0	10	0.30	6.0	7.3	8.5	42.1	58.4	72.3
HPC-BL	48	2	40	10	0.28	5.3	6.9	8.7	34.8	54.8	66.7
WGC	35	5	50	10	0.30	3.4	4.5	7.2	16.4	31.0	50.1
MGC	35	5	50	10	0.30	3.0	4.3	7.0	12.1	25.0	44.5
BBGC	35	5	50	10	0.30	3.0	4.2	6.9	13.2	25.0	45.3
GBGC	35	5	50	10	0.30	2.6	4.2	7.3	11.6	25.5	46.0

cement mortars within the selected flow range. At the same time, the reference HPC-A and HPC-BL samples demonstrate the highest flexural strength at 28 d age (8.5 and 8.7 MPa, respectively).

The flexural strength values of investigated ECO-cements at the 2 d age are almost the same for the group of glass cements, with the best value of 3.4 MPa for glass cement based on WG. These values are significantly lower then the strength of the reference NPC. Similar behavior is observed at 7 d age for all investigated glass cements.

Compressive Strength of Mortars

The compressive test results of glass cement mortars (following ASTM) are presented in Table II and Fig. 6. According to the test results, the best 28 d compressive strength value of 50.1 MPa is obtained by cement produced using window glass. The monitor-glass, brown-bottle-glass- and green-bottle-glass-based cements reach a 28 d compressive strength of 44.5–46.0 MPa, which is close to the strength of reference NPC (45.4 MPa). At the same time, all ECO-cements with waste glass show strength values that are significantly lower than those of the optimized samples of HPC-A (72.3 MPa) and HPC-BL (66.7 MPa).

	Notations Used to Distinguish Cement Samples
NPC	Reference portland cement
HPC-A	Reference high-performance cement type A
HPC-BL	Reference high-performance cement type B (35% of LS)
WGC	ECO-cement produced using window glass (WG)
MGC	ECO-cement produced using monitor glass (MG)
BBGC	ECO-cement produced using brown bottle glass (BBG)
GBGC	ECO-cement produced using green bottle glass (GBG)

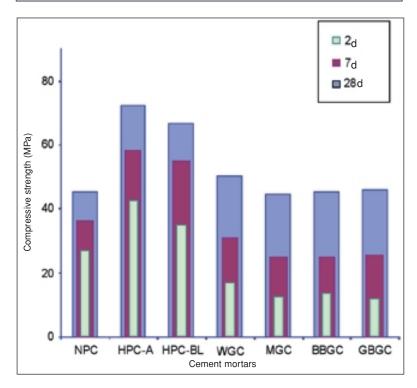


Fig. 6. Compressive strength of glass cement mortars.

The compressive strength values of investigated HP cements at the 2 d age are almost the same for the group of glass cements. Glass cement based on WG demonstrates the best compressive strength at the early ages. Similar behavior of waste-glass ECO-cements is observed at the 7 d age (Table II).

Delay in the strength development of waste-glass ECO-cements at early age, e.g., 50% at 2 d and 26% at 7 d, can be explained by low clinker content (35%) in these cements. Simultaneous pozzolanic reactions and low W/C help to offset this trend at later stages of hardening.

Discussion and Conclusions

The current economic climate makes recycling feasible only for a limited number of materials. Waste materials can be used only when they can be collected, processed and reused at a cost the same as or less than natural materials.2 As concluded in Ref. 2, "based on recent technology and conditions, the ability of the glass industry to further increase the recycling rates of waste glass is quite restricted." Therefore, alternative technologies are needed to boost the recycling of waste glass beyond the present restraints of the glass industry.

ECO-cement technology can be used in manufacturing cement with a high volume of mineral additives, including waste glass. A feasibility analysis has demonstrated a profitable production of ECO-cement with 50% of blast-furnace slag (BFS).²⁹ On other hand, it is unreasonable to expect that the use of waste glass can completely offset the additional expenses related to ECO-cement production (as in case of BFS).

However, this may be the case if ECO-cement is optimized for better performance than conventional cement or if there is a premium paid for the utilization of waste glass. At the same time, it is obvious that, with the increase in the costs of waste disposal and the introduction of ecological taxes, ECO-cement can be considered as an appropriate alternative for recycling

waste glass (including mixed and contaminated glass).

The developed ECO-cement, containing 50% of waste glass, possesses flexural and compressive strength properties at a level similar to normal portland cement, 6.9–7.3 and 44.5-66.7 MPa, respectively. Best compressive strength values have been demonstrated by the ECO-cement based on waste window and green bottle glass. Lowwater demand property of HP and ECO-cements results in high workability at low W/C. It helps to improve the strength of mortars based on these cements and to offset the use of mineral additives in the cement composition.

The selection of an appropriate method for the production of blended HP/ECO-cements is essential in the manufacture of the final product with the required specifications. This method also is associated with necessary structure of the cement and the grinding ability of the components used. For example, when the mineral additive with a grinding ability similar to clinker is used, a one-stage grinding method is suggested because of its simplicity. Application of two-stage grinding process results in bimodal cement containing fine clinker and relatively coarse particles of mineral additive (Fig. 7(a)).

The three-stage grinding process is preferable when a superfine uniform mix of all components is necessary or when FGMA is required to be finer than the clinker component (Fig. 7(b)). It is expected that the pregrinding of waste glass to obtain particles finer than those of cement clinker (in the form of FGMA) considerably improves the strength characteristics of the obtained ECO-cements.

The use of FGMA of a smaller size than the clinker component is essential for improved reaction ability and provides better packing of particles.³⁰ This approach has been used to develop high-strength HVMA/ECO-cements, including glass cements containing waste sital glass.²⁷

Based on the conducted research, it is concluded that application of

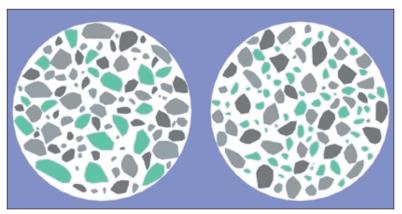


Fig. 7. Microstructural model of ECO-cement.

HP cement technology helps to recycle waste glass in ECO-cement. Additional investigations may be necessary to improve the chemical activity of waste glass in the cement system. Further research is required to explain and quantify the hydration mechanism and the structural development of ECO-cement containing large volumes of waste glass as well as to examine their resistance to a number of detrimental factors, including the possible adverse effects of the alkali–silica reaction.

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