Self-compacting concrete produced with limestone waste

K Kopecskó
Budapest University of Technology and Economics, Hungary

E-mail: kopecsko.katalin@epito.bme.hu

Abstract. The aim of the research was to design powder type self-compacting concrete containing high amount of limestone quarry waste as aggregate and fines. The light colour aggregate mixed with white cement resulted in esthetical surfaces of exposed concrete for architectural purposes. Large amount waste originated from the limestone mining process requires deposition with further treatment. In our study we tried to replace also the limestone powder fines by the slurry produced during the cut of limestone blocks. Seven recipes were examined during the research: three mixtures of quartz aggregate with different particle size distributions were used as reference mixtures, three mixtures composed of crushed limestone aggregate and one with mixed quartz-limestone composition, respectively. In the recipe of mixed limestone-quartz aggregate dried quarry waste slurry was successfully applied instead of direct ground limestone powder. In the research different test methods were used to determine the fresh properties as well as the hardened properties of concretes.

Keywords: self-compacting concrete, limestone waste, chloride ion migration

1. Introduction
The nature of mining processes creates a potential negative impact on the environment both during the mining operations and after the mine is closed. The limestone mining in Hungary dating back to Roman times, has been to present a number of operating mines and surface engineering to pursue stone processing. The mining and processing of limestone results in large amount of unusable stone blocks and also wet lime stone cutting slurry, which are considered as mining waste and requires deposition with further treatment. It is important to use the excavated limestone to the greatest extent minimizing the debris have permanently disposed of, and positioned as a mining waste, thereby further reducing the environmental impact, the landscape damaging effect [1]. Reuse of these materials may reduce the environmental impacts.

Self-compacting concrete (SCC) is a type of structural concrete which strongly deviates from ordinary concrete in the fresh state, as it de-aerates and flows without the application of additional compaction energy [2]. The definition of self-compacting concrete (SCC) was described by Ozawa et al. [3], then Okamura and Ozawa [4]. We can distinguish the powder type and the stabilizer type self-compacting concretes. The main difference in composition between normal concrete and powder type SCC is the use of higher amount of fines in SCC to reach the suitable, approximately 30% higher amount of paste content which ensures the high fluidity in fresh state. Application of fines is necessary in order to prevent bleeding and segregation. Direct ground limestone powder is well suited additional material for SCCs. Quarry waste limestone slurry could replace the limestone powder products in concrete decreasing the material and energy consumption.
The aim of the present research was to design powder type SCC containing high amount of limestone waste for architectural purposes (e.g. facades, street furniture).

2. Experimental programme
In the mix design we have followed the Okamura method [5] which is based on a three-fold approach considering the paste, mortar and concrete phases [2]. In figure 1 the volume fractions are given for these phases.

In the Okamura method paste, mortar and concrete phases are distinguished and the desired volume ratios are given for these phases:
- estimation of air content, usually 2-3 vol% ($V_{air}$);
- limitation of the coarse aggregate content (4-16 mm) in 50 vol%, then to determine the mortar volume ($V_{mortar} = V_{concrete} - V_{air} - V_{aggr, 4/16}$);
- limitation of fine aggregate content (0-4 mm) in the mortar phase in 40 vol%, then to determine the paste volume ($V_{paste} = V_{mortar} - V_{aggr, 0/4} = V_{water} + V_{powder}$);
- determine the composition of the paste volume by defining the volume ratio of filler and cement ($V_{filler}/V_{cement}$), experimentally measuring the water demand of the powder (cement-filler), mix $\beta_{powder}$, calculating the necessary water content ($V_{water} = V_{paste} \cdot \beta_{powder}$) and powder content ($V_{powder} = V_{paste} - V_{water}$);
- experimental optimization of the resulting phases (paste, mortar and concrete).

In our mix design the limitations for concrete volume fractions (coarse aggregate 4/16 < 50 vol %) were not taken into account because in the mixtures 4 mm maximum grain size of aggregate ($d_{max}$) was chosen. It means that in our case the fine aggregate content was equal with the total aggregate content. Instead of the difficult determination of water demand ($\beta_{powder}$) the water/cement ratio was chosen 0.45 based on the result of the trial mixing.

Seven mixtures of self-compacting concrete were studied during the research. Three basic recipes were designed with different particle size distributions of the coarser aggregate, where the fractions of 1/2 and 2/4 mm varied in different ratios (25:75, 35:65 and 45:55). Three mixtures were made with quartz aggregate (K1-K3, used as reference), further three mixtures were made with crushed limestone.
aggregate fractions of 1/2 and 2/4 mm (M1-M3). Based on the results one recipe was selected for mixed quartz-limestone composition (MK). The origin of the limestone is the freshwater limestone quarry Sütő (Hungary). Crushed aggregate fractions were produced in the laboratory conditions. Proposed by Daczko [6] in the mix design the 0/0.125 fraction of fine quartz sand was added to the paste phase (i.e. paste volume).

To keep the consistency and workability high performance superplasticizer admixture was applied. The amount of cement, limestone powder, fine sand (0/0.125 mm) and the total amount of the aggregate was constant for all recipes. The type of cement used in the experiment is CEM I 52.5 N white cement. The type and amount of polypropylene microfiber was the same in all recipes (0.1 vol%).

In the studied mixtures the aggregate fractions of 1/2 and 2/4 mm varied in different mass ratios:
- 25:75 in the mixtures K1 and M1;
- 35:65 in the mixtures K2, M2 and MK;
- 45:55 in the mixtures K3 and M3.
The volume fraction of fine aggregate (1/4 mm) for all mixtures was approximately 42 vol% (table 1).

Table 1. Recipe of the mixture K1 (aggregate 1/2 and 2/4 mm fractions in the ratios of 25:75).

| Material     | Type or fraction         | Density (kg/m³) | Mass (kg) | Volume (l) | Mass/mix (kg/60 l) |
|--------------|--------------------------|-----------------|-----------|------------|-------------------|
| Cement       | CEM I 52.5 N white       | 3100            | 400       | 129.0      | 24.0              |
| Limestone powder | commercial            | 2700            | 450       | 166.7      | 27.0              |
| Fine sand    | 0/0.125 mm               | 216             | 284       | 107.2      | 13.0              |
|              | 1/2 mm (25%)             | 2650            | 850       | 320.8      | 51.0              |
| Sand         | 2/4 mm (75%)             | 1134            | 427.9     | 68.0       |                   |
| Microfiber   | Fibrofor Multi           | 910             | 0.9       | 1.0        | 0.054             |
| Admixture    | ViscoCrete 20HE (2.5%)   | 1090            | 10        | 9.2        | 0.600             |
| Water        | mw/mc=0.45               | 1000            | 180       | 180        | 10.8              |
| Air          |                          |                 |           | 5          |                   |
| Sum          |                          | 2391            | 1000      |            |                   |

Commercial ground limestone powder was applied as fines (filler), except in the recipe of mixed quartz-limestone aggregate (MK), where dried quarry waste slurry was utilized. The quarry waste slurry was produced during the cut of the large limestone blocks, and it is available in large amount. The specific surface of the fines was measured by Blaine method. The specific surface of limestone waste slurry was close to the specific surface of the white cement, and higher than for the commercial limestone powder (table 2).

Table 2. Specific surface of fines

| Specific surface (m²/kg) | CEM I 52.5 N | Limestone powder | Limestone slurry |
|--------------------------|--------------|------------------|-----------------|
|                          | 417          | 343              | 407             |

The trial mixtures were made with quartz aggregate. In case of limestone aggregate the consistency and the workability was not appropriate with the same amount of mixing water because of the porosity resulting water uptake. To reach the same consistency first we measured the 30 minutes water uptake.
(4.8 m%) of the porous crushed aggregate. Before mixing the different concrete mixtures the limestone aggregate was mixed with the necessary water demand and kept to saturate for 30 minutes in the mixer. Without this treatment exclusively the increase of amount of admixture did not result adequate consistency and workability.

3. Results and Discussion

In the study various test methods were used to determine both the fresh properties (e.g. slump-flow test, T50 time, J-ring test, loss of consistency) of concrete mixtures as well as the hardened properties of concrete specimens at different ages (compressive strength, flexural tensile strength, modulus of elasticity, abrasion resistance, freeze-thaw resistance).

3.1. Fresh properties of concrete mixtures

Studying the fresh properties of self-compacting concrete has a great importance. All recipes resulted in self-consolidating, self-compacting concrete (table 3).

3.1.1. Slump-flow test, Visual Stability Index and J-ring test

As we expected specimens with limestone aggregate reached lower values of compressive and flexural strength, flexural tensile strength, modulus of elasticity, abrasion resistance, freeze-thaw resistance.

3.1.1.1. Slump-flow test, Visual Stability Index and J-ring test

The flow values of limestone concrete (quartz gravel) exceeded the size of the flowtable (80 cm), so these values were fixed to 80 cm uniformly. The flow values of limestone concrete were slightly less, between 74 and 80 cm. This means that the shear-tension in the concrete mixtures made with quartz aggregate is smaller. According to the MSZ EN 206-9:2010 standard [8], all the tested concrete can be classified into the SF3 (760-850 mm) slump-flow class.

T50 times were uniformly above 2 seconds, which are to be classified into VS2. Comparing the T50 times, it can be seen that concrete mixtures made with quartz aggregate reached slower the 50 cm diameter than concrete mixtures made with limestone, which means that their plastic viscosity is higher. According to the MSZ EN 206-9:2010 standard [8], all the tested concrete can be classified into the SF3 (760-850 mm) slump-flow class.

The J-ring test can be used to determine the passing ability of self-consolidating concrete. The results of J-ring tests were significantly affected by the shelf life of the concrete. The passing abilities of limestone concretes were much better, with less than 5 cm for all three recipes. For the other recipes, the maximum difference in spread is the highest for concrete K3 (24 cm), which indicates a poor passing ability. The passing ability of MK (mixed quartz-limestone aggregate) recipe represents about the average with the 9 cm difference in spreading.

The stability of self-consolidating concrete can be observed visually by examining the concrete mass and therefore can be used for quality control of self-consolidating mixtures. Visual rating criteria were used to classify the ability of the self-compacting concrete mixtures to resist segregation (VSI, visual stability index). According to ASTM C 1611, after spreading of the concrete the passing abilities of limestone concrete was mixed with the necessary water demand and kept to saturate for 30 minutes in the mixer. Without this treatment exclusively the increase of amount of admixture did not result adequate consistency and workability.

3.1.2. Shelf life of concrete mixtures

The shelf life of concrete mixtures was also studied. At the age of 30 minutes the mixtures lost the self-compatible property; they showed rather slump than flow. The reason is the relative early setting of the CEM I 52,5 N white cement. However the drop of the efficacy of the admixture could also influence the shelf life and change the workability (table 4).
Table 3. Fresh properties of mixtures

|                      | Q1  | Q2  | Q3  | L1  | L2  | L3  | QL  |
|----------------------|-----|-----|-----|-----|-----|-----|-----|
| slump-flow test, k_1 (cm) | >80 | >80 | >80 | 75  | 80  | 74  | 77  |
| J-ring test, k_0 (cm)   | 45  | 71  | 56  | 72  | 78  | 70  | 68  |
| T<sub>50</sub> time (s) | 3.5 | 4.5 | 5.0 | 2.5 | 2.5 | 3.0 | 2.0 |
| Visual stability index (VSI) | 0   | 0   | 0   | 1.5 | 1   | 2   | 1   |

Figure 2. Spread of the Q2 mixture, VSI 0
Figure 3. Spread of the L3 mixture, VSI 0
Figure 4. Spread of the QL mixture, VSI 1
Figure 5. Spread of the L3 mixture, VSI 2
Table 4. Shelf life of the concrete mixtures

| Haegermann spread | Q1 | Q2 | Q3 | L1 | M2 | M3 | QL |
|-------------------|----|----|----|----|----|----|----|
| 0 min. (cm)       | 30 | 28 | 28 | 28 | 28 | 27 | 25 |
| 15 min. (cm)      | 28 | 25 | 26 | 20 | 24 | 20 | 22 |
| 30 min. (cm)      | 10 | 11 | 11 | n.a.| n.a.| n.a.| n.a.|

3.1.3. Air content and density of concrete mixtures
The air content in the recipes of concrete with quartz aggregate was estimated to be 0.5 vol% (5 l/m$^3$), and for concretes made with limestone aggregate to be 1.0 vol% (10 l/m$^3$). This was different from the proposed mix design where the air-void content estimated to be 2-3 vol%. Based on the test results of the air content, the Okamura's suggestion (2-3 vol% air content) can be realistically designed in SCC recipes. It is difficult to achieve lower air content with self-compacting concrete. Limestone additive concretes due to the angular shape and the coarser surface of the grains are able to keep more air content. Due to the round, smooth surface of quartz aggregates, the admixture is effective to drive out the adsorbed gas layer.

The densities of the fresh concrete mixtures varied between 2250 and 2370 kg/m$^3$, the prepared concretes can be considered as concretes with ordinary density, however slightly less than for conventional concretes with quartz aggregate (without addition of large amount of limestone filler). The density of hardened concrete was measured at the age of 28 days (table 5).

Table 5. Air contents and densities of fresh and hardened concrete

|                | K1  | K2  | K3  | M1  | M2  | M3  | MK |
|----------------|-----|-----|-----|-----|-----|-----|-----|
| Air content (vol%) | 1.42| 1.58| 2.04| 2.89| 2.88| 4.36| 2.66|
| Density of fresh concrete (kg/m$^3$) | 2368| 2365| 2354| 2275| 2280| 2250| 2282|
| Density of hardened concrete (kg/m$^3$) | 2365| 2363| 2346| 2235| 2246| 2227| 2275|

3.2. Hardened properties of concrete mixtures

3.2.1. Strength and modulus of elasticity
The compressive and flexural tensile strength values were determined on 40x40x160 mm prisms (figures 6 and 7) as well as the compressive strength was determined on cubes of 150 mm (figure 8).

As we expected specimens with limestone aggregate reached lower values of compressive and flexural tensile strength than concrete with quartz aggregate. The average compressive strengths of quartz containing mixtures (K1-K3) at the age of 28 days were above 80 MPa; mixtures with limestone aggregate (M1-M3) shown about 35% smaller compressive strength as well as mixture with mixed aggregate (MK) about 20% smaller.

The moduli of elasticity of quartz containing mixtures (K1-K3) are greater than 35,000 MPa; in case of mixtures with limestone aggregate (M1-M3) are below 30,000 MPa and for mixed aggregate concrete (MK) is 33,400 MPa.

3.2.2. Abrasion resistance
The abrasion resistance was determined according to the standard MSZ EN 14157:2005 [10]. For the test the Böhme abrasion wheel tester was used. The aggregate properties affect the performance of concrete. Based on the test results mixtures containing limestone aggregate (M1-M3) are not considered abrasion resistant. This is the consequence of the different hardness of the minerals. Surface hardness of aggregates is important where aggregates are likely to wear in service. The Mohs'
relative hardness of calcite (CaCO$_3$) is 3 while the Mohs' relative hardness of α-quartz (α-SiO$_2$) is 7 [11]. The abrasion resistance of the mixture MK improved by the application mixed quartz-limestone aggregate (figure 9).

3.2.3. Freeze-thaw resistance
MIXTURES containing limestone aggregate (M1-M3) in terms of freeze-thaw resistance also performed worse than concretes containing quartz aggregate. The frost resistance test carried out in deionised water at 50 cycles. After removing the specimens the residual compressive strength was determined. The most significant decrease in compressive strength was measured in case of concrete containing mixed aggregate (MK), with an average decrease of 15 MPa (21%); the decrease in average compressive strength of concrete made with aggregate quartz aggregate is 5.00 MPa (5.8%) and for concrete made with limestone aggregate is 3.40 MPa (5.2%). Based on the results of the salt scaling tests concretes without quartz aggregate (M1-M3) are not suggested for applications required use of de-icing salt in winter.

![Figure 6. Development of compressive strength of SCC mixtures determined on prisms](image6)

![Figure 7. Development of flexural-tensile strength of SCC mixtures determined on prisms](image7)
Figure 8. Compressive strength of SCC mixtures at the age of 28 days, determined on cubes

Figure 9. Abrasion resistance of SCC mixtures at the age of 28 days, decrease of volume (mm³)

3.2.4. Chloride ion migration

Tang and Nilsson [12] developed a rapid electrical migration (HTC) method to determine the diffusion coefficient of chloride ions and the degree of chloride penetration. The method was further developed in NT Build 492 [13]. For the experiment, discs with 50±2 mm height were cut from the Ø100x200 mm cylinders (figure 10). The test started at the age of 28 days. For the comparative test all specimens were subjected to the 30 V DC for the same time (8 hours). After the measurement, the specimen has to be splitted and then the split surface is treated with silver nitrate (AgNO₃) solution for the colorimetric determination of the depth of chloride penetration. Figures 11 and 12 shows pictures after the whitish precipitation (AgCl) occurred during the reaction between AgNO₃ and Cl⁻ ions.

In specimens made with quartz aggregate, the chloride penetration depth as well as the nonsteady-state migration coefficient was much smaller than in specimens made of limestone additives. The depth of chloride penetration depends on the permeability concrete (i.e. pore structure). The porosity of the limestone aggregate increases the permeability. It can be noticed that among the three discs of one specimen, the disc number 2 (i.e. the middle of the cylindrical specimen) has the largest value of penetration depths or migration coefficients. This can be explained by the self-compacting properties of concrete. In case of SCC there is no vibration, so the upper third is richer in the paste phase, while the lower third is denser due to the more aggregate grains.
Figure 10. Preparation of specimens (discs) for testing chloride migration

Figure 11. White precipitation of AgCl shows the depth of chloride ingress, mixture K1

Figure 12. White precipitation of AgCl shows the depth of chloride ingress, mixture M2

4. Conclusions
The aim of the present research was to design powder type SCC containing high amount of limestone waste for architectural purposes (urban furniture, cladding, etc.). The origin of the limestone is the freshwater limestone quarry Sättő (Hungary). Aggregate fractions were made crushing of the freshwater limestone in laboratory scale. Seven recipes were examined during the research: three mixtures of quartz aggregate with different particle size distributions were used as reference mixtures, three mixtures composed of crushed limestone aggregate and one further with mixed quartz-limestone composition. Based on the test results the recipe of self-compacting concrete containing combination of quartz-limestone aggregate (MK) was suggested to use in precast concrete industry. In the recipes of K1-K3 and M1-M3 commercial ground limestone powder was used as fines. In the recipe of mixed quartz-limestone aggregate (MK), instead of commercial ground limestone powder the waste limestone slurry was successfully applied. Limestone slurry is a waste material, which is produced during cut the large limestone blocks. This concrete has increased resistance against abrasion comparing with concretes containing only limestone aggregate. With the proposed concrete mixture the purpose of containing the largest possible amount of limestone waste in a self-compacting concrete with appropriate fresh and hardened properties was achieved.
Figure 13. Depths of chloride ingress (mm) and nonsteady-state migration coefficients (m$^2$/s) of SCC mixtures at the age of 28 days (migration test by 30 V DC, 8 hours).

Acknowledgements
Author acknowledges the support by the Hungarian Research Grant NVKP_16-1-2016-0019 “Development of concrete products with improved resistance to chemical corrosion, fire or freeze-thaw”.

References
[1] Mang B 2004 Az ásványi nyersanyagtermelés főbb hatásai (in English: The impact of mineral raw material production), Publication of the University of Miskolc, Series A, Mining, Vol. 66, pp. 15-21.
[2] fib Bulletin No. 51. 2009 Structural concrete. Textbook on behaviour, design and performance, Vol. 1. pp. 96-99.
[3] Ozawa K, Maekawa K and Okamura H 1990 High performance concrete with high filling capacity, Admixtures for concrete, improvement of properties, Vasquez E (Ed.), Chapman & Hall, London, Great Britain, pp. 51-62.
[4] Okamura H and Ozawa K 1996 Self compactable high performance concrete in Japan, High performance concrete, Zia P (Ed.), SP-159, ACI, Farmington Hills, USA, pp. 31-44.
[5] Okamura H and Ozawa K 1995 Mix design for self-compacting concrete, Concrete Library of JSCE, Vol. 25, No. 6, pp. 107-120.
[6] Daczko J A 2012 Self-consolidating concrete – Applying what we know, Spoon Press, Abingdon, pp. 118-137.
[7] MSZ EN 12350-8:2010. Testing fresh concrete. Part 8: Self-compacting concrete. Slump-flow test.
[8] MSZ EN 206-9:2010. Concrete. Additional rules for self-compacting concrete (SCC).
[9] ASTM C1611 / C1611M – 14 Standard Test Method for Slump Flow of Self-Consolidating Concrete.
[10] MSZ EN 14157:2005. Natural stone test methods. Determination of the abrasion resistance.
[11] http://webmineral.com/help/Hardness.shtml#WqA05nxG2Cg. Downloading date: 01/02/2018, search engine: google.hu, search terms: Mineral hardness.
[12] Tang L and Nilsson L 1992 Chloride diffusivity in high strength concrete, Nordic Concrete Research, Vol. 11, pp. 162-170.
[13] Nordtest NT Build 492. Concrete, mortar and cement-based repair materials: Chloride migration coefficient from non-steady-state migration experiments, Approved 1999-11, Finland.