

## **MULTI-LEVEL CHEMICAL CHARACTERIZATION OF DUTCH FINE RECYCLED CONCRETE AGGREGATES: A COMPARATIVE STUDY**

**Marija Nedeljković (1, 2), Jeanette Visser (2), Timo G. Nijland (2), Siska Valcke (2) and Erik Schlangen (1)**

(1) Microlab, Faculty of Civil Engineering and Geosciences, Delft University of Technology, The Netherlands

(2) TNO Buildings, Infrastructure & Maritime Delft, The Netherlands

### **Abstract**

In the Netherlands, beside cement replacement with more green cement types, there is also an urgent need for alternative materials for natural sand in new concrete in order to make it circular. Furthermore, the recyclers have raised questions regarding upscaling and the potential of fine recycled concrete aggregates (fRCA) in structural concrete elements since the availability of recycled construction rubble is increasing. The variations in their chemical and physical properties and lack of standards for their quality evaluation is the main reason for not yet using fRCA in new concrete.

In this paper, an in-depth characterization of different fRCA is performed in order to define their chemical properties. The properties can be eventually related to concrete mix design and performance (next step), so that fRCA can be classified as a material that can be used in more advanced applications. This is achieved with a multi-level chemical characterization of individual and total fractions (0-0.25 mm, 0.25-4 mm and 0-4 mm) for finding type and content of the original sand and cement phases and potential contamination of selected fractions. The tests include quantification of element composition with X-ray fluorescence (XRF), qualitative and quantitative phase analysis with X-ray diffraction (XRD) and Rietveld method. In addition, cement paste content, chlorides and sulfates of each type of fRCA was measured in order to evaluate contamination of studied material. It was shown that fRCA from different origins have similar chemical and mineralogical composition and contain comparative chloride content. The chemical composition testing can provide a first line control regarding composition and potential contamination of fRCA. After that, it can be decided which additional tests are necessary to be done in order to evaluate the suitability of fRCA for replacement of primary natural fine aggregates in new concrete.

Keywords: Fine recycled concrete aggregates, phases, contamination, XRF

## 1. INTRODUCTION

In the coming decade, sustainable construction materials with low environmental impact will have a crucial role in achieving a circular economy (CE). The Dutch CE strategy aims to make the Netherlands 'fully circular' by 2050 with an interim target of a 50% material reduction of primary raw materials (minerals, fossil fuels and metals) by 2030 [1]. Therefore, in the Netherlands, beside cement replacement with more green cement types, there is also an urgent need for alternative materials for replacement of natural sand. Despite the potential that industrial waste has for concrete production, mainly as replacement for cement, resources for aggregates are not sufficient and concrete rubble is necessary to be included in the stream of alternative raw materials. The largest source of aggregates is the construction and demolition (C&D) waste and its quantity will be significantly increasing due to aging and deterioration of our concrete infrastructure.

The variations in the chemical and physical properties of fine recycled concrete aggregates (fRCA) [2, 3], lack of experience and lack of standards for their quality evaluation are the main reasons for a large quantity of fRCA being mainly used for low grade applications such as road pavements, sub-basements, soil stabilization, improvement of sub-ground [4]. Recent laboratory studies have shown the development of mortars and concretes with different fRCA replacement levels [5, 6]. However, fRCA have not been employed yet in practice. The key question for application as sand replacement in concrete is which properties would hamper the performance of concrete and, related to this, which quality indicators should be used, so that fRCA can be classified as a material that can be used in more advanced applications.

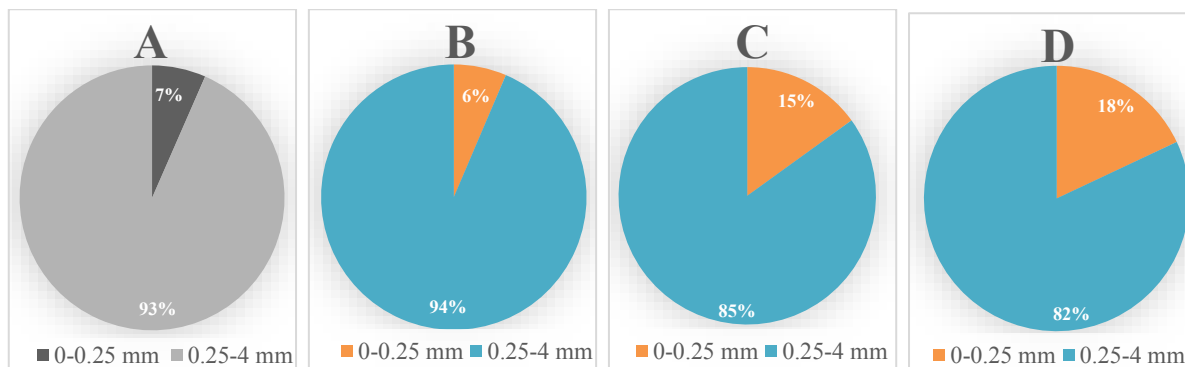
Material characterization is an important step in order to understand variations of recycled material and their key properties affecting concrete performance. For example, the type of aggregate, or strictly speaking its modulus of elasticity, influences shrinkage of concrete. Another example; one of the most critical aspects for durability of concrete, are soluble chlorides and sulfates contained in concrete components of which the amount is limited in concrete in order to prevent degradation, in this case initiation of corrosion of reinforcement or sulfate attack. Typically, chlorides can be present in concrete components, i.e. in water, cement, aggregates and in admixtures, but also concrete structures are often exposed to chloride-contaminated environments in the Netherlands, causing chloride ions to penetrate through the concrete cover. After recycling of such a concrete, chemical composition and phase analysis can be an indicator for contamination level of a recycled concrete. X-ray diffraction (XRD) analysis is a powerful tool in this regard, but challenges can arise due to the complex and often varying composition of fRCA. For this reason it is necessary to combine XRD with other characterization techniques such as X-ray fluorescence spectrometry (XRF). Multi-level characterization of Dutch fRCA such as chemical and mineralogical composition, adhered cement paste content and content of  $\text{Cl}^-$ ,  $\text{SO}_4^{2-}$  in the cement paste, is performed in this study, to demonstrate potential of this material for its use in the new concrete.

## 2. MATERIALS AND METHODS

### 2.1 Materials and sample preparation

The fRCA were supplied by three project partners. They were chosen to be representative of major Dutch fRCA. All batches were delivered fresh (no storage in meanwhile). Primary natural river sand with 95 wt.% of  $\text{SiO}_2$  was also studied to provide a baseline for comparison.

All fRCA were first dried in an oven at 105 °C. After drying, fRCA were sieved and divided into eight fractions (<0.063 mm, 0.063-0.125 mm, 0.125-0.250 mm, 0.250-0.5 mm, 0.5-1 mm, 1-2 mm, 2-4 mm, >4 mm) using a sieve tower. After evaluation of individual fractions, it was decided to choose two subfractions 0-0.25 mm and 0.25-4 mm and investigate their properties and compare to the properties of total fraction 0-4 mm. The pie charts in Figure 1 show their relative proportions in 0-4 mm in studied materials; where letters refer to primary natural sand (A) and fRCA with different origins (B, C, D).



**Figure 1: The relative proportions of particle size fractions (0-0.25 mm and 0.25-4 mm) in 0-4 mm (weight %).**

The fRCA samples were first ground with a grinding machine, Fritsch pulverizer 5, to an average particle size of 100  $\mu\text{m}$ . The machine has four grinding cups and five steel grinding balls per grinding cup. The maximum sample quantity is 225 ml. After grinding, milling with an Alpine e200 LS air jet sieve of fRCA fractions was done and particles with an average size of 25  $\mu\text{m}$  were obtained. This particle size was necessary for XRD analysis. Finally, manual grinding was applied to obtain particles with an average size of 10  $\mu\text{m}$  for XRF analysis.

## 2.2 Experimental methods

### 2.2.1 X-ray fluorescence

The fluorescence spectra of studied materials were recorded with a Bruker S8 Tiger spectrometer. A binding agent, Boreox ( $\text{C}_{12}\text{H}_{22}\text{O}_{11}$ ) from Fluxana, is used during the preparation of pressed pellets. Samples were mixed in a stainless steel grinding cup. The loss on ignition (LOI) was measured by heating the fRCA to 1050 °C. The LOI is expressed in weight percent of the dry matter (EN 15169:2007 (E)). The mass of the sample was  $5 \pm 0.1$  g.

### 2.2.2 X-ray powder diffraction and Rietveld analysis

The diffractograms of studied materials were recorded using a Bruker D8 Advance X-ray powder diffractometer, equipped with LynxEye detector. The machine was operated with an accelerating voltage of 40 kV and an X-ray beam current of 40 mA. The X-ray source was a Cu-tube working with characteristic Cu-K $\alpha$  wavelength of 1.54060 Å. The samples were scanned varying the 2-theta angles between 10° and 70°. For quantitative phase analysis, standard reference material (alumina,  $\text{Al}_2\text{O}_3$ , NIST Standard Reference Material 676a) was added and blend was subsequently mixed for about 2 minutes. Phase identification was performed using Bruker Eva 4.2 software and appropriate databases. Rietveld quantitative phase analysis was performed using Bruker Topas 5.1 software.

### 2.2.3 Acid-soluble chlorides and water-soluble sulfates

The *acid-soluble chlorides* were obtained by acid dissolution using nitric acid (6 mol/l) according to EN 1744-5. The material was dried in an oven at 105 °C for 24 h. Samples of approximately 20 grams were used for analysis. Typically, the sample was weighed into a 250 ml beaker in which 100 ml of 6M nitric acid was added subsequently. The mixture was shaken manually for 30 s followed by heating until boiling and boiled for about 5 min under continuous magnetic stirring. After cooling down, the mixture was vacuum filtered using a Buchner filter with a medium grade filter paper 110. The residue on the filter paper was rinsed 4 times with deionized water and 10 ml 1M nitric acid to ensure that all ions had been rinsed. The filtrate was transferred from the filter flask into a volumetric flask. The solution in the volumetric flask was filled up with deionized water to 500 ml. Then 100 ml solution was pipetted into a clean glass cup. Acid-soluble chloride salts content was further determined following Volhard method as described in EN 1744-5. The solid residue left on the filter paper was dried in an oven at 105 °C for 24 h. This allowed determination of the cement paste content by subtracting the weight of insoluble substances from the initial weight of the oven-dried material.

The *water-soluble sulfate content* in the fRCA was determined according to EN 1744-1. The sample consisting of 25 g of sand (crushed below 4 mm) was mixed with 1 l of water at 65 °C under stirring to extract water-soluble sulfate ions. A neat sample is filtered using a Buchner filter with a medium grade filter paper 110, and the filtrate is analyzed by Metrohm 850 ion chromatography system. Sulfate ion was resolved on an anion exchange column and detected by a conductivity detector. Quantification was performed by linear regression analysis of peak areas from the standard sulfate calibration curve containing five points.

## 3. RESULTS AND DISCUSSION

### 3.1 Chemical composition

The chemical composition of the investigated primary natural sand (A) and fRCA (B, C, D) fractions (0-0.25 mm, 0.25-4mm, 0-4 mm) is shown in Table 1. As expected, the natural sand is composed mainly of SiO<sub>2</sub> and minor CaO, Al<sub>2</sub>O<sub>3</sub>, MgO, K<sub>2</sub>O, Fe<sub>2</sub>O<sub>3</sub>, SO<sub>3</sub>. In comparison to natural sand, the fRCA contain lower amounts of SiO<sub>2</sub> and higher amounts of CaO, Al<sub>2</sub>O<sub>3</sub>, MgO, K<sub>2</sub>O, Fe<sub>2</sub>O<sub>3</sub>, SO<sub>3</sub>. This is due to presence of cement paste in fRCA, which can be either adhered to original sand particles or form individual grains. The chemical composition of the fRCA is made up mainly by SiO<sub>2</sub> (62-76%), CaO (14-23%), Al<sub>2</sub>O<sub>3</sub> (6-10%) and Fe<sub>2</sub>O<sub>3</sub> (1.6-3.3%). The chemical composition of fraction D 0-4 mm is very similar to the composition of fraction 0-4 mm studied by Lotfi and Rem [7], which was obtained from recycled concrete based on the use of CEM III/B cement. However, the obtained results in this study are different than that reported by Gomes et al. [2] who reported much lower values for CaO and much higher values for Na<sub>2</sub>O and K<sub>2</sub>O. On the other hand, the obtained values for CaO are much lower than that reported by Florea et al. [8].

The fraction below 0.25 mm represents between 5% (B) and 17% (C, D) of the total weight of fraction 0-4 mm. This fraction has a different composition compared to 0.25-4 and 0-4 mm with a reduced SiO<sub>2</sub> content (59–67%) and increased CaO (19–27%). The LOI was 8 - 11%.

It is clear that sands are SiO<sub>2</sub>-rich material, corroborated with XRD analysis, where it was found that quartz is the main phase in all batches (~60 wt. % material). This was expected, since

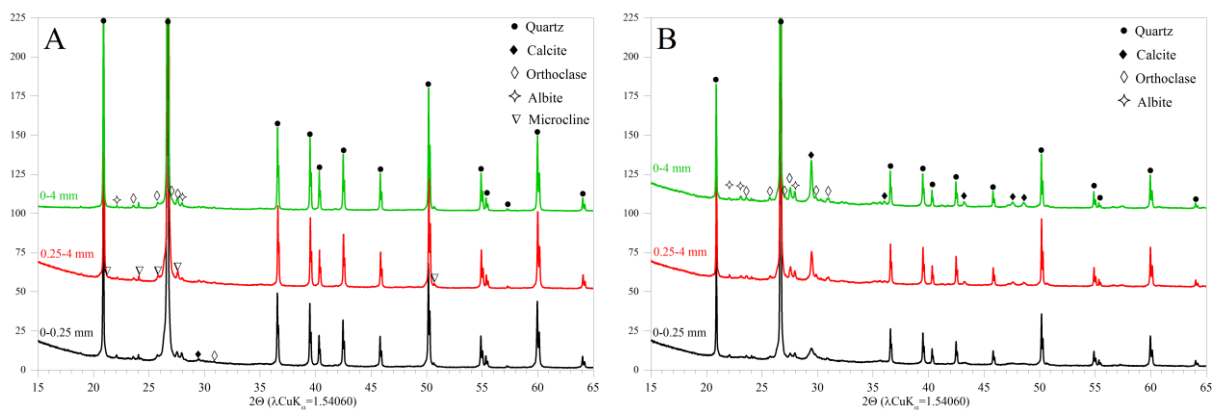
river sand, and, therefore, quartz, is a widely used sand type in the Netherlands. The CaO, Al<sub>2</sub>O<sub>3</sub>, Fe<sub>2</sub>O<sub>3</sub> originate from cement which was used in parent concrete. Their contents in studied fractions are much lower than of that of typical cements used in the Netherlands.

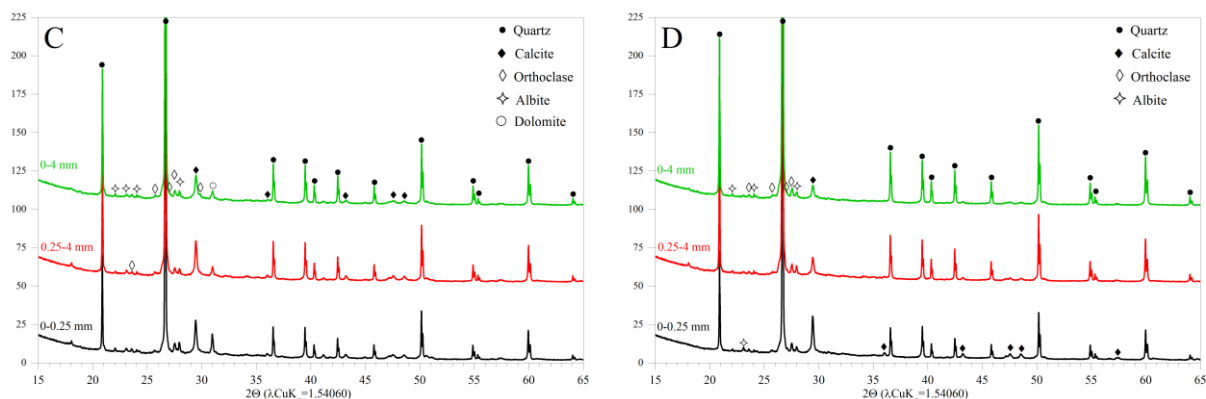
**Table 1: Chemical composition of different fractions of natural and recycled sands**

	SiO <sub>2</sub>	CaO	Al <sub>2</sub> O <sub>3</sub>	MgO	Na <sub>2</sub> O	K <sub>2</sub> O	TiO <sub>2</sub>	Fe <sub>2</sub> O <sub>3</sub>	SO <sub>3</sub>	Cl
<b>A</b>										
0-0.25	93.60	1.08	2.49	0.18	0.49	0.86	0.23	0.88	0.042	0.013
0.25-4	95.60	0.92	1.71	0.12	0.21	0.68	0.06	0.46	0.084	0.007
0-4	96.00	0.46	1.77	0.10	0.22	0.74	0.07	0.49	0.047	0.000
<b>B</b>										
0-0.25	67.80	19.10	5.19	1.20	0.64	1.34	0.37	3.08	0.97	0.03
0.25-4	70.30	17.10	5.09	1.35	0.56	1.33	0.38	2.60	0.98	0.03
0-4	62.80	22.50	5.76	1.54	0.61	1.49	0.47	3.26	1.16	0.03
<b>C</b>										
0-0.25	58.60	27.50	5.14	2.10	0.58	1.47	0.36	2.35	1.32	0.1
0.25-4	62.70	25.80	4.09	1.47	0.42	1.25	0.34	2.38	1.00	0.09
0-4	68.20	20.40	4.44	1.62	0.51	1.24	0.28	2.02	0.91	0.07
<b>D</b>										
0-0.25	59.50	26.70	5.80	1.26	0.46	1.46	0.43	2.36	1.56	0.060
0.25-4	71.70	17.30	4.75	1.06	0.41	1.08	0.30	1.95	1.12	0.043
0-4	75.80	14.40	4.26	0.91	0.41	1.06	0.27	1.67	0.89	0.042

### 3.2 Phase analysis

Figure 2 shows the X-ray diffractograms of investigated primary natural sand and fRCA, while Table 2 gives an overview of the phases combined with quantification using Rietveld refinement method.





**Figure 2: X-ray diffractograms of the natural sand (A) and fRCA (B, C, D).**

It is apparent that total fraction and subfractions within each batch contain the same phases. The main phases of fRCA are quartz and calcite. Besides quartz and calcite, albite, orthoclase and microcline are present in all aggregates; quartz makes up 60%. Besides dolomite which is also observed in batch C, there were no other phases present in the fRCA. The amount of quartz is significantly less in the fRCA (B, C, D) compared to natural sand (A) in Figure 2. Each of the phases, their origin and content, is discussed below.

**Table 2: Phase quantification by Rietveld refinement method (wt.%).**

Phase	Quartz	Albite	Orthoclase	Microcline	Calcite	Dolomite	Amorphous
<b>A</b>							
0-0.25 mm	91.10	2.90	1.30	3.90	0.00	0.00	0.90
0.25-4 mm	95.30	2.50	1.70	0.00	0.00	0.00	0.50
0-4 mm	94.10	1.51	0.84	3.20	0.00	0.00	0.40
<b>B</b>							
0-0.25 mm	58.80	3.50	3.70	0.00	8.58	0.00	25.30
0.25-4 mm	58.20	2.55	5.00	0.00	6.99	0.00	27.30
0-4 mm	57.70	3.63	4.90	0.00	8.70	0.00	25.10
<b>C</b>							
0-0.25 mm	48.50	4.05	4.06	0.00	9.58	3.40	30.40
0.25-4 mm	55.30	2.25	3.50	0.00	10.71	1.81	26.50
0-4 mm	62.70	3.03	4.70	0.00	7.60	0.00	21.90
<b>D</b>							
0-0.25 mm	50.10	3.15	3.12	0.00	9.81	0.00	33.80
0.25-4 mm	62.70	2.45	2.67	0.00	5.05	0.00	27.10
0-4 mm	72.10	2.43	2.62	0.00	3.82	0.00	19.00

**Quartz** The most common mineral found in all three batches in high quantities is quartz, meaning that origin of fRCA is mainly river sand.

**Calcite** Potentially, there are four different sources of carbonates:

- from limestone aggregates;
- from limestone filler;
- from carbonation of Ca-rich phases (calcium silicate hydrate gel,  $\text{Ca}(\text{OH})_2$ , ettringite) during concrete service life;
- from carbonation of Ca-rich phases (calcium silicate hydrate gel,  $\text{Ca}(\text{OH})_2$ , ettringite) after crushing of concrete due to storage and weathering.

**Amorphous phase** Amorphous phases originate from amorphous hydrated phases (e.g. C-S-H-) and unreacted material in amorphous form in cement paste which is usually adhered to fRCA. The amorphous content originating from the raw material (such as unreacted blast furnace slag) can be an indicator about the potential reactivity of the cement.

**Anhydrous cement compounds** The residual anhydrous cement components (clinkers) were not identified within the XRD detection limit, in agreement with some studies [2, 9, 10] and in disagreement with study of Bordy et al. [11].

### 3.3 Chlorides, sulfates and cement paste content

Table 3 lists cement paste content, chlorides and sulfates in different fractions. Content of old cement paste adhered to the fRCA ranges from 14.% to 29.8%, depending on the batch (B, C, D) and on particle size range (0-0.25 mm, 0.25-4 mm, 0-4mm). These values are similar to cement paste content estimated by HCl selective dissolution, being between 16.1% and 24.6% for recycled coarse and fine concrete aggregates, respectively [3]. The cement paste concentrates in the finer fraction (0-0.25 mm), in agreement with [12].

**Table 3: Cement paste content, acid soluble  $\text{Cl}^-$  and water soluble  $\text{SO}_4^{2-}$  in fRCA.**

	Cement paste	Acid soluble $\text{Cl}^-$	Water soluble $\text{SO}_4^{2-}$
	[sand wt.%]	[sand wt.%]	[sand wt.%]
<b>A</b>			
0-0.25 mm	0.00	0.00	0.01
0.25-4 mm	0.00	0.00	0.00
0-4 mm	0.00	0.00	0.00
<b>B</b>			
0-0.25 mm	28.91	0.04	0.37
0.25-4 mm	17.86	0.04	0.14
0-4 mm	19.03	0.04	0.16
<b>C</b>			
0-0.25 mm	29.81	0.06	0.18
0.25-4 mm	21.43	0.05	0.09
0-4 mm	25.84	0.04	0.14
<b>D</b>			
0-0.25 mm	22.72	0.04	0.24
0.25-4 mm	14.72	0.04	0.08
0-4 mm	16.16	0.04	0.10

Compared to the primary natural sand (A), in which no chlorides and sulfates are present, fRCA can be a chloride and sulfate source in a concrete mix. The chlorides from fRCA should be considered in total concrete mix design calculations (as is traditionally done for all concrete components) since there is no consensus on the value of the critical chloride content allowed in recycled concrete aggregates. The  $\text{SO}_4^{2-}$  content in the fRCA is below standard limit value 0.2% (m/m) (EN 12620) for all samples, except for B 0-0.25 mm. The high water soluble  $\text{SO}_4^{2-}$  of fRCA B 0-0.25 mm and D 0-0.25 mm, might be a result of ettringite dissolution due to carbonated cement paste in these fractions. Brocken and Nijland [13] showed that when ettringite breaks down during carbonation, sulfur is increasing especially in the pore solution.

#### 4. CONCLUSIONS

- Based on multi-level chemical characterization of the different fRCA, it was found that they are mainly made up by crystalline phases (> 70 wt.%), notably quartz (> 60 wt.%), originating from the primary natural sand. In addition, amorphous content varied among the fractions (20-35 wt.%).
- The fRCA (B, C, D) fractions (0-0.25 mm, 0.25-4mm, 0-4 mm) show differences in chemical composition, notably  $\text{SiO}_2$  and CaO contents.
- The content of sulfates was below the critical values adopted for aggregates for use in reinforced concrete, with exception for fine fraction 0-0.25 mm. Therefore, from the aspect of chemical properties, the fRCA show a good potential for sand replacement in new concrete.
- Finally, the present work provides new insights for better understanding of the variations among different fRCA batches toward their use in the new concrete mix design.
- In the further study of this project, these chemical results will be combined with the physical characterization and the significance of the results and variations between batches will be studied with respect to appropriate mix design and concrete performance.

#### ACKNOWLEDGEMENTS

Authors acknowledge funding provided by the Materials innovation institute M2i ([www.m2i.nl](http://www.m2i.nl)), Rijkswaterstaat, TweeR Recycling, AVG, Caron Recycling (CRH) and BRBS Recycling.

#### REFERENCES

- [1] Ministry of Infrastructure and the Environment and the Ministry of Economic Affairs in the Netherlands, 'A circular economy in the Netherlands by 2050.' 2016.
- [2] Gomes, P. C. C., Ulsen, C., Pereira, F. A., Quattrone, M., and Angulo, S. C. 'Comminution and sizing processes of concrete block waste as recycled aggregates.' *Waste Manage.* **45**(2015) 171-179.
- [3] Angulo, S. C., Ulsen, C., John, V. M., Kahn, H., and Cincotto, M. A. 'Chemical-mineralogical characterization of C&D waste recycled aggregates from São Paulo, Brazil.' *Waste Manage.* **29**(2)(2009) 721-730.
- [4] de Brito, J., F. Agrela, and R.V. Silva, 'Legal regulations of recycled aggregate concrete in buildings and roads.' in *New Trends in Eco-efficient and Recycled Concrete*, Elsevier. 2019, 509-526.

- [5] Nováková, I. and B.-A. Buyle. 'Sand Replacement by Fine Recycled Concrete Aggregates as an Approach for Sustainable Cementitious Materials.' in Proceedings of the International Conference of Sustainable Production and Use of Cement and Concrete. Springer. 2020.
- [6] Bouarroudj, M. E., Remond, S., Michel, F., Zhao, Z., Bulteel, D., and Courard, L. 'Use of a reference limestone fine aggregate to study the fresh and hard behavior of mortar made with recycled fine aggregate.' *Mater. Struct.* **52**(1)(2019) 18.
- [7] Lotfi, S. and P. Rem, 'Recycling of end of life concrete fines into hardened cement and clean sand.' *J. Environ. Prot. Ecol.* **7**(06)(2016) 934.
- [8] Florea, M. and H. Brouwers, 'Properties of various size fractions of crushed concrete related to process conditions and re-use.' *Cem. Concr. Res.* **52**(2013) 11-21.
- [9] Evangelista, L., Guedes, M., De Brito, J., Ferro, A. C., and Pereira, M. F. 'Physical, chemical and mineralogical properties of fine recycled aggregates made from concrete waste.' *Constr. Build. Mater.* **86**(2015) 178-188.
- [10] Oksri-Nelfia, L., Mahieux, P. Y., Amiri, O., Turcry, P., and Lux, J. 'Reuse of recycled crushed concrete fines as mineral addition in cementitious materials.' *Mater. Struct.* **49**(8)(2016) 3239-3251.
- [11] Bordy, A., Younsi, A., Aggoun, S., and Fiorio, B. 'Cement substitution by a recycled cement paste fine: Role of the residual anhydrous clinker.' *Constr. Build. Mater.* **132**(2017) 1-8.
- [12] Ulsen, C., Kahn, H., Hawlitschek, G., Masini, E. A., Angulo, S. C., and John, V. M. 'Production of recycled sand from construction and demolition waste.' *Constr. Build. Mater.* **40**(2013), 1168-1173.
- [13] Brocken, H. and T.G. Nijland, "White efflorescence on brick masonry and concrete masonry blocks, with special emphasis on sulfate efflorescence on concrete blocks." *Constr. Build. Mater.* **18**(5)( 2004) 315-323.