CO-UTILIZATION OF MARINE SEDIMENTS AND CONSTRUCTION/DEMOLITION WASTES FOR THE SYNTHESIS OF GEOPOLYMERS

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ABSTRACT

In the present experimental study the geopolymerization potential of marine sediments collected from the Greek ports of Souda in Chania, Crete and Patras in Peloponnese as well as their co-utilization with construction/demolition wastes (CDW) is studied. The effect of the molarity of alkaline activating solution (2-10 M KOH) as well as of mixing CDW components with 10 or 30 % w/w of each sediment on the compressive strength of the final products was investigated.

Geopolymers were synthesized by mixing raw materials, namely marine sediments and the three main components of CDW (concrete, bricks and tiles) with the activating solution. The solution was prepared by dissolving pellets of KOH in distilled water and adding sodium silicate solution. Then, the pulp was cast in moulds and heated at 80 °C for 7 days to produce geopolymers which were subjected to compressive strength testing. Analytical techniques, including Fourier Transform Infrared Spectroscopy (FTIR) and Scanning Electron Microscopy (SEM) were used for the identification of the morphology and structure of the final products. Results have shown that only marine sediments collected from Patras port can be successfully geopolymerized, while both sediments can be co-utilized with bricks or tiles for the production of geopolymers using 8 M KOH as alkali activator.

Keywords: geopolymer, compressive strength, marine sediments, construction and demolition wastes

1. Introduction

Geopolymers are formed by the alkali activation of alumino-silicates and are characterized of partially or fully amorphous polymeric structure consisting of Si–O–Al bonds. The unique properties of geopolymers such as high early strength, thermal stability and corrosion resistance, depend strongly on the properties of the raw materials used for their synthesis (Davidovits, 1994). The geopolymerization potential of sediments and construction/demolition wastes (CDW) has been investigated so far by a limited number of studies. Alkali activation has been used for the production of construction materials from sediments of the Yellow River in China by Li *et al.* (2014). Lightweight aggregates for building purposes have been prepared with the use of water reservoir sediments and NaOH by Liao *et al.* (2013). The possibility of utilizing waste bricks, tiles and concrete for the production of geopolymers as well as the optimization of alkali-activation conditions has been investigated by Allahverdi and Kani (2009) and Komnitsas *et al.* (2014).

The present experimental study aims at the synthesis and characterization of geopolymers produced from dredged marine sediments collected from two Greek ports and used either alone or after mixing them with tiles, bricks and concrete. FTIR and SEM were used for the elucidation of the morphology of the final products.

2. Materials and methodology

Marine sediments were collected from the Greek ports of Souda in Chania, Crete and Patras in Peloponnese. CDW including concrete, bricks and tiles were collected from various demolished buildings. Both sediments and CDW components were pulverized using a FRITSCH-BICO Pulverizer (Germany) and homogenized. A Mastersizer S (Malvern Instruments) particle size analyzer was used for particle size analysis (Table 1). Table 2 shows the chemical composition of each component of CDW and sediments, as derived from an X-ray fluorescence energy dispersive spectrometer (Bruker-AXS S2Range). Loss of ignition (LOI) was determined by heating at 1050 ^oC for 4h.

Table 1: Particle size of the raw materials

μm	Tiles (T)	Bricks (B)	Concrete (C)	Souda sediments (SS)	Patras sediments (PS)
size	<140	<140	<190	<120	<120
d_{50}	14	7	10	9	8

Table 2: Chemical composition (% w/w) of the raw materials

	SiO_2	Al_2O_3	CaO	Fe_2O_3	Na_2O	MgO	K_2O	MnO	P_2O_5	SO_3	TiO_2	LOI	SUM
T	70.54	9.80	8.78	5.39	-	4.46	1.37	0.06	-	-	0.77	0.23	101.41
B	57.79	14.95	8.79	6.00	1.03	4.75	2.80	0.05	0.23	-	0.85	1.89	99.12
C	5.81	1.49	65.42	0.75	0.57	4.21	1.26	0.01	0.73	0.82	0.03	21.59	102.68
SS	29.10	6.49	24.50	3.62	0.09	1.34	0.68	0.03	0.31	1.10	0.38	29.20	96.80
PS	37.10	4.97	21.30	2.63	1.16	1.55	1.41	0.10	0.09	0.62	0.34	27.34	98.61

T: tiles, B: bricks, C: concrete, SS: Souda sediments, PS: Patras sediments

Geopolymers were synthesized by mixing raw materials, namely marine sediments from Souda or Patras port or the three main components of CDW (concrete, bricks and tiles) or their combinations (CDW mixed with 10 or 30% w/w of each sediment), with the activating solution. The solution was prepared by dissolving pellets of KOH in distilled water and adding sodium silicate solution (Na_2SiO_3, Merck, Na_2O=7.5-8.5%, SiO_2=25.5-28.5%). The morphology and structure of the final products was studied using Fourier Transform Infrared Spectroscopy (FTIR) and Scanning Electron Microscopy (SEM). The experimental methodology is described in detail in Komnitsas *et al.* (2014).

3. Results and discussion

3.1. Compressive strength of geopolymers

Figure 1 shows the evolution of the compressive strength of geopolymers produced from Souda sediments, Patras sediments and CDW components (tiles, bricks and concrete) vs KOH concentration. Tiles exhibit the best geopolymerization potential and under the optimum activating solution molarity (10 M KOH) their compressive strength reached 55 MPa. A similar behaviour is shown for brick-based geopolymers reaching though substantially lower strength (up to 27 MPa). For both tile- and brick-based geopolymers, the strength increase is related to the increase of KOH molarity which enhances dissolution of Si and Al from the raw materials and acceleration of geopolymeric reactions. The compressive strength of Patras sediments increases sharply from 8.5 to 19 MPa when KOH molarity increases from 2 to 4 M while further increase of KOH molarity (6-10 M) has no beneficial effect. Souda sediments are practically not geopolymerized (max compressive strength 5 MPa) while concrete exhibits low geopolymerization potential (max compressive strength 10 MPa). The main reasons for the development of low strength are the low content of SiO_2 and Al_2O_3 in concrete (5.81% and 1.49%, respectively), as well as the high content of CaO in concrete (65.42%) and Souda sediments (24.5%) which may consume KOH rendering it unavailable for the dissolution of aluminosilicates from the raw materials.

The compressive strength of the produced geopolymers when tiles, concrete and bricks were mixed with 10 or 30% w/w of Souda (SS) or Patras (PS) sediments, as well as of the control geopolymers prepared by each raw material alone, is shown in Figure 2. Geopolymers were prepared with 8 M KOH based on the results of Figure 1. Table 3 shows the molar ratios of the oxides present in the initial paste.

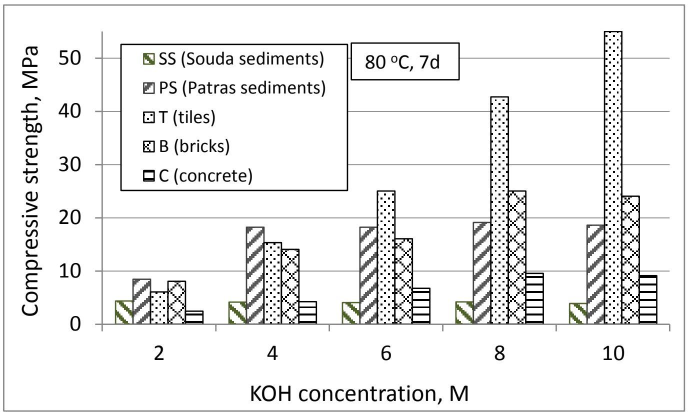


Figure 1: Evolution of the compressive strength of geopolymers produced from Souda sediments, Patras sediments, tiles, bricks and concrete vs KOH concentration

When tiles, concrete and bricks are mixed with 10% w/w Souda sediments, geopolymers produced show a slightly decreased compressive strength compared to the respective control geopolymers prepared from each CDW component (Figure 2a). A noticeable further decrease in strength is shown when the SS addition percentage increases to 30% w/w. This behaviour can be explained by the decrease of SiO_2/Al_2O_3 and $SiO_2/(Al_2O_3+CaO)$ ratios in the initial CDW component – sediment mixture. For example when tiles are mixed with 30% w/w sediments (SST column in Table 3) these ratios become 11.43 and 2.91, respectively, while when tiles are only used as raw materials the ratios are higher (12.57 and 4.78, respectively). A similar trend is shown for brick- and cement-based geopolymers.

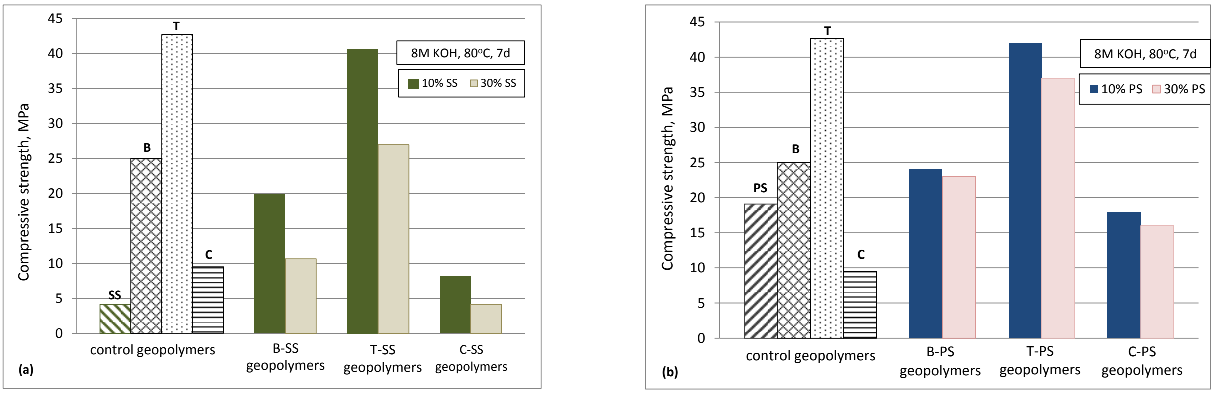


Figure 2: Compressive strength of tile-, concrete- and brick- based geopolymers when 10 or 30% w/w of (a) Souda (SS) or (b) Patras (PS) sediments are added

Table 3. Molar ratios of oxides of the initial paste of selected geopolymers (8 M KOH)

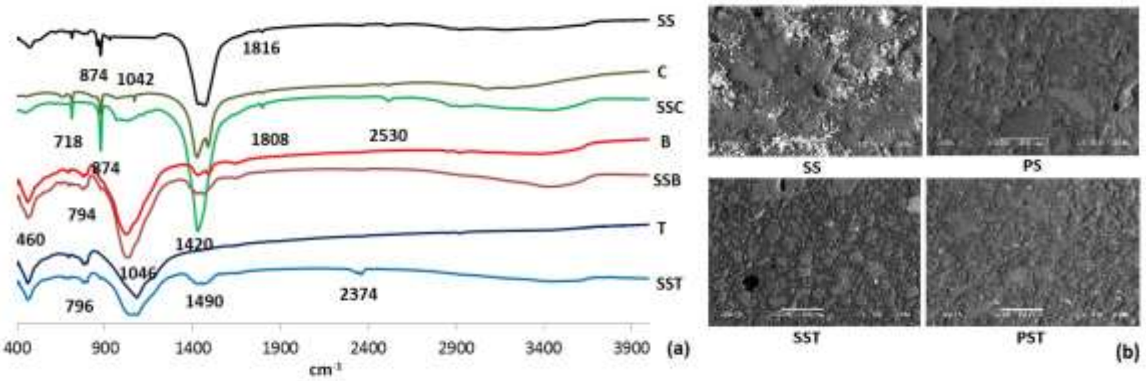
	T	B	C	SS	PS	SST	SSB	SSC	PST	PSB	PSC
SiO_2/Al_2O_3	12.57	6.83	9.01	5.85	13.47	11.43	6.74	7.47	12.40	7.42	11.37
$(Na_2O+K_2O)/Al_2O_3$	1.0	0.98	7.53	2.15	2.62	1.10	0.91	5.08	1.21	0.85	5.42
$(Na_2O+K_2O)/SiO_2$	0.08	0.14	0.84	0.37	0.19	0.10	1.15	0.68	0.10	1.08	0.48
$SiO_2/(Al_2O_3+CaO)$	4.78	3.30	0.11	0.56	1.53	2.91	0.17	0.18	3.68	0.14	0.25
$SiO_2/(Al_2O_3+Fe_2O_3)$	9.31	5.44	6.82	5.85	13.47	8.46	2.22	5.59	5.87	2.77	8.57
$H_2O/(Na_2O+K_2O)$	10.42	8.30	9.76	9.59	9.08	10.05	5.32	10.06	10.08	5.87	9.80

T: tiles, B: bricks, C: concrete, SS: Souda sediments, PS: Patras sediments, SST: T+30% w/w SS, SSB: B+30% w/w SS, SSC: C+30% w/w SS, PST: T+30% w/w PS, PSB: B+30% w/w PS, PSC: C+30% w/w PS

From Figure 2b, it is shown that geopolymers produced by mixing bricks or tiles with 10% w/w of Patras sediments (PS) acquire a slightly lower strength compared to brick and tile control geopolymers, respectively. When the PS addition percentage increases to 30% w/w strength further decreases but is as high as 23 and 37 MPa, for PSB and PST geopolymers, respectively. As shown in Table 3 the values of SiO_2/Al_2O_3 ratio for these geopolymers do not vary significantly, for example it is 12.57 for T geopolymer and 12.40 for PST geopolymer. When geopolymers are produced by mixing concrete and 10% w/w PS the strength is 18 MPa and is much higher than the strength of concrete-control specimen (9.5 MPa). When the PS addition percentage increases to 30% w/w a slight further decrease to 16 MPa is shown. This result is in accordance with SiO_2/Al_2O_3 ratio for PSC geopolymer compared to the concrete-control geopolymer (Table 3), which is 11.37 and 9.01, respectively.

3.2. Mineralogy and morphology of geopolymers

Figure 3a shows the FTIR spectra of selected geopolymers produced using Souda sediments and CDW. A similar behaviour is noticed for Patras sediments and CDW geopolymers (not shown). The small bands appeared in the region of 2300-2500 cm^{-1} and around 1800 cm^{-1} are assigned to stretching and bending H–O–H vibrations of bound water molecules. The doublet of peaks seen at 1490 and 1420 cm^{-1} for all geopolymers is due to atmospheric carbonation. The band at 1420 cm^{-1} is quite strong in SS, C and SSC geopolymers and is attributed to the modes of CO_3 contained in $CaCO_3$. The sharp peak at 874 cm^{-1} is also assigned to out of plane bending of CO_3 and shown only in these geopolymers that have a high $CaCO_3$ content. The broad peaks at around 1050 cm^{-1} are major fingerprints of the geopolymeric matrix and are attributed to Si–O stretching vibrations of SiO_4 and Si–O–Si or Al–O–Si asymmetric stretching vibrations during geopolymerization. This peak is barely shown in SS, C and SSC geopolymers that acquire strength lower than 10 MPa. The bands at around 460–800 cm^{-1} are due to Si–O, Al–O, Si–O–Si and O–Si–O vibrations.



T: tiles, B: bricks, C: concrete, SS: Souda sediments, PS: Patras sediments, SST: T+30% w/w SS, SSB: B+30% w/w SS, SSC: C+30% w/w SS, PST: T+30% w/w PS

Figure 3: (a) FTIR spectra and (b) SEM images of selected geopolymers produced using Souda or Patras sediments and CDW

In Figure 3b SEM images of selected geopolymers produced using Souda or Patras sediments and CDW are illustrated. The matrix of SST and PST geopolymers is more homogeneous compared to SS and PS geopolymers, respectively, indicating a sufficient reaction of the raw materials during alkali-activation. As also deduced from EDS analysis (not shown) in SST and PST geopolymers which acquire a strength of 27 and 37 MPa, respectively, the content in Si and Al that are the main elements required for geopolymerization is high. In SS geopolymer, Ca is the main component and Cl is detected in the white areas of Figure 3b, while Si and Al are found in smaller quantities.

4. Conclusions

Sediments collected from Patras port can be successfully geopolymerized (strength up to 20 MPa) for the production of building materials, while specimens produced using Souda sediments acquire strength lower than 5 MPa. However, both sediments can be co-utilized with bricks or tiles for the production of geopolymers with compressive strength up to 42 MPa using

8M KOH as alkali activator. The strongest geopolymeric bonds are developed when sufficient Si and Al are provided by the raw materials, as revealed by FTIR and SEM analysis.

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