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MINERALOGICAL AND CHEMICAL CHARACTERIZATION OF CDW AS FUNCTION OF PARTICLE SIZE AND THERMAL TREATMENTS FOR POTENTIAL RECYCLING

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ABSTRACT

Construction and Demolition Waste (CDW) originating from the rubble produced by the 2016 seismic events in the Marche Region (Central Italy) has been studied, focusing on its mineralogical and chemical characteristics, to investigate its recycling potentials as a component for eco-sustainable building material or in the glass industry. The aim was to obtain a full characterization of the behaviour of this material at high T in order to determine the most advantageous conditions for vitrification, considered as an effective process for volume reduction as well as for immobilization of potentially hazardous elements. Vitrification experiments, carried out with thermal treatments as function of temperature/duration/particle size and aimed at amorphization, were carried out under atmospheric conditions, at different temperatures (1000-1250°C) and durations (2-8 hours). The study demonstrated that mineralogical composition remains homogeneous for grainsize <4 mm, thus suggesting that no sieving is necessary for recycling of the fine fractions, which are the most difficult to treat. Vitrification, although not achieved for the CDW sample up to 1250°C, due to high-Ca and low-Si contents, demonstrated that this CDW can produce an interesting refractory material and a porous/insulating material. However, experiments showed that full vitrification can be easily achieved by mixing urban waste glass and CDW, suggesting applications in the glass industry. Based on the chemical and mineralogical features of the products, other significant upgrading alternatives of recycling the CDW in different fields of applications are highlighted.

1. INTRODUCTION

The EU Waste Framework Directive 2008/98/EC (European Commission, 2008) states that all EU members should take all necessary measures in order to achieve at least 70% of re-use, recycling or other recovery of non-hazardous Construction and Demolition Waste (CDW) by 2020 (Whittaker et al., 2019 and references therein). Construction and Demolition Waste (CDW), in fact, has been identified as a priority waste stream covering about the 30% of total waste generation in EU (approx. 800 million metric tons; European Commission, 2016a, 2016b).

The composition of CDW varies strongly between the different member states and geographical areas, making an uniform approach and recovery strategy difficult. CDW is, in fact, highly heterogeneous, depending on the geological availability of lithotypes, construction locations and building styles. Concrete, bricks, rocks, sanitary ware, ceramic tiles, roof tiles, plaster, wood, glass, metals, plastic as well as hazardous waste like asbestos, are commonly present in CDW. Often, the main option for recycling this waste type is still downgrading applications, as aggregates for road construction or backfilling (DG ENV, 2011) and, with limitations due to diminished mechanical performances, as recycled aggregates in concrete (Pacheco-Torgal et al., 2013 and references therein). Due to the low economic costs of landfilling, lack of incentives and sometimes dated regulations, still virgin aggregates are preferred over the recycled aggregates (Pacheco-Torgal and Jalali, 2011; Marie and Quiasrawi, 2012). However, a few studies already deal with the possible incorporation of CDW in new high-grade construction materials, as for example in terrazzo tiles (Favaretto et al.,2017; Ansaloni et al., 2017; Whittaker et al., 2019; Stabile et al., 2021), interesting for the environmental advantages in terms of saving of geo-resources and energy over ceramic tiles production.

It is noteworthy though that up-grading applications of CDW in the construction sector are still difficult to achieve. In 2019, the European Commission produced a

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comprehensive report entitled ‘On the Implementation of the Circular Economy Action Plan’ (European Commission, 2019; Whittaker et al., 2019). The report proposes the development of reliable strategies and new technologies to: a) increase the percentage of CDW-derived materials in new residential construction, b) increase the technical and economic value of CDW-derived materials, c) minimize the future production of CDW from the next generation of buildings, d) increase building energy efficiency. All these points should encourage studies in this field. In view of the overall latest environmental norms, a strong effort has been devoted to the elaboration of treatment processes in order to transform CDW into recycled eco-friendly products. Recent studies deal with different techniques able to meet these requirements, including solidification within concrete, leaching with acids and other solvents, sintering, and vitrification (Haugsten and Gustavson, 2000; Jung et al., 2005 and references therein). Vitrification as the preferred treatment is supported by studies that indicate it represents the most promising waste management technique that: a) produces a stable vitreous material, b) can provide chemical stability, c) immobilizes toxic elements (e.g. cadmium, nickel, etc.) in glass structure and d) decomposes dioxins (Kavouras et al., 2003; Jung et al., 2005; Stabile et al., 2019).

Here a full chemical and mineralogical characterization of CDW, before and after thermal treatments is presented, carried out to investigate the effects of composition, grainsize, experimental temperature and duration on the vitrification process. The aim of the work is also to explore possible alternatives to landfilling, investigating the recycling potential, based on compositional/mineralogical characterization of CDW and its derived products.

2. MATERIAL AND METHODS

The main methodological steps carried out in this study for the full characterization and thermal treatments of the CDW sample and products are summarized in Figure 1 and presented in details in the results section.

2.1 Sample collection and sorting

The CDW used in this study was obtained from the centralized processing plant (COSMARI, in Macerata, Italy) which, after the 2016 seismic crisis that hit four Regions in Central Italy, is in charge of collecting, separating and distributing all the earthquake rubble of the entire Marche Region. The CDW is preliminarily removed of health- or environmentally-concerned materials like cement-asbestos, lead and electronic waste, as well as of all other recyclable metals. Wood, plastic, glass, gypsum are separated, while large rock blocks, if reusable as building materials, are left in storage for reuse.

The CDW, acquired by local processing plants, is then made available to buyers in the desired grainsize range. The CDW material used here has been first sieved in order to assess the grain size distribution below. This range is mostly unwanted by buyers interested to backfilling because too fine, and therefore not recyclable, hence usually destined to landfilling. The grainsize separation carried out has been used also to verify possible variations of CDW composition as a function of granulometry.

2.2 Mineralogical composition

The mineralogical composition was determined on the starting material and the different granulometries, as well as on the products obtained after the thermal treatments. Specifically, X-ray diffraction (XRD) data were collected with a Panalytical X’Pert powder diffractometer (Geology Division, University of Camerino), using Cu Kα radiation (λ=1.5418Å) and an applied voltage and current of 40 kV and 25 mA, respectively. Acquisition range is from 5° to 70°, step size of 0.02° and an acquisition time of 1 sec/step was used. After the thermal treatments, all products were checked for the presence of glass and/or crystals by both optical polarizing microscope and Electron Microprobe (EMP) and then were analysed by XRD, which allowed identifying the crystalline phases and evaluation of the quantity of amorphous materials vs. the degree of crystallinity of the products. The Reference Intensity Ratio (RIR) method (Hubbard and Snyder, 1998) based upon scaling the sample diffraction data to the diffraction of standard reference materials (software Match! https://www.crystal-impact.com), was used to quantify the phases present and comparing the results of all the experiments.

2.3 Thermal treatments

The thermal treatments of CDW, towards vitrification, were carried out at ambient pressure in air using a chamber furnace (Carbolite RHF 14/3, ~3 litre internal volume). For the procedure used, 5g of CDW powder were loaded in a platinum crucible (15ml capacity) and placed in the constant temperature zone of the furnace. Samples were kept in a drying oven at 110°C overnight before the experiments. Temperature was recorded by a platinum-rhodium thermocouple, located in close proximity of the sample. The starting temperature of the experiments was 300°C, heating rate was set at 20°C/min up to the final temperature (either 1000°C, or 1250°C) and samples were kept at the desired temperature for 2 to 8 hours. After the treatment, the crucible was taken out of the furnace and rapidly quenched by immersion in a water bath.

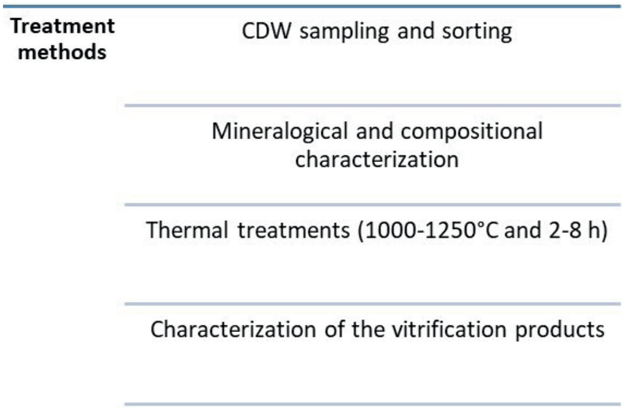

FIGURE 1: Methodological chart showing the sequence of treatments on CDW.

2.4 Chemical characterization

To determine the chemical compositions of the starting CDW sample, prior to thermal treatments, acid dissolution followed by ICP-MS analysis were employed in order to provide analyses of major, minor and trace elements. A lithium-borate fusion prior to acid dissolution was used for the major and more refractory elements, mainly major oxides and rare earth elements (REEs). The relative measurement uncertainties, validated on international standards, are 5% for trace elements and 10% for major elements.

Chemical analyses of the major elements in the samples treated at 1250°C and for the longest duration were obtained by electron micro-probe (EMP) using a CAMECA SX50 at the Consiglio Nazionale delle Ricerche (CNR)- Institute of Geosciences and Earth Resources (IGG) in Padova (Italy). Sample fragments obtained from the vitrification processes were embedded in 25.4 mm diameter epoxy plugs, polished to 1 µm quality, and then coated with an approximately 20 nm thick carbon layer for charge dissipation. The measurements were performed with an acceleration voltage of 20 keV, a beam current of 2nA for potassium, sodium, aluminium and silicon, all measured at first, and a beam current of 20 nA for all the other elements. All the analysis used a slightly defocused (ca. 10 µm) beam to minimize alkali volatility. The reference materials used for the analyses consisted of a range of silicate and oxide minerals of composition similar to the studied compositions, such as wollastonite, albite, orthoclase, TiO_2, Fe_2O_3, etc., following standard procedures. All measurements were made using wavelength-dispersive spectrometers. Sample compositions are given in oxides wt. % along with standard deviations in Table 1.

TABLE 1: Calcite and quartz proportions (wt.%) in CDW for different granulometries.

CDW sample grainsize (mm)	Calcite (wt. %)	Quartz (wt. %)
A6 <0.125	77.6	22.4
A5 0.125-0.257	76.3	23.7
A4 0.257-0.5	85.4	14.6
A3 0.5-1.0	86.3	13.7
A2 1-4	78.4	21.6
A1 >4	89.6	10.4
Average	82.3±5.5	17.9±5.7

Values obtained by Reference Intensity Ratio (RIR) method.

3. RESULTS AND DISCUSSION

3.1 Grain size distribution

The CDW sample before sieving is shown along with the cumulative grain size distribution in Figure 2 (a-b). CDW fractions divide almost equally between the grainsize range 1-4 mm (range of sand-gravel sizes), while the remaining fractions range from coarse to very fine sand (<1mm). This distribution reflects that the finest fractions (<2mm) can account for the majority of the CDW finer grainsize, compromising the use of CDW as backfilling materials towards final landfilling. This information therefore prompted us to investigate the possibility to use the finest grainsize as secondary raw material (SRM) in the ceramic or glass industry, by investigating their vitrification capacity in an attempt to find an upcycling application for CDW, which could be highly desirable, especially for the fine fractions for which there is a lack of effective recycling options.

3.2 CDW mineralogical and chemical characteristics

Six samples, with grainsize between <4 and <0.125mm (A1 to A6 in Figure 3) were analysed by XRD to identify the

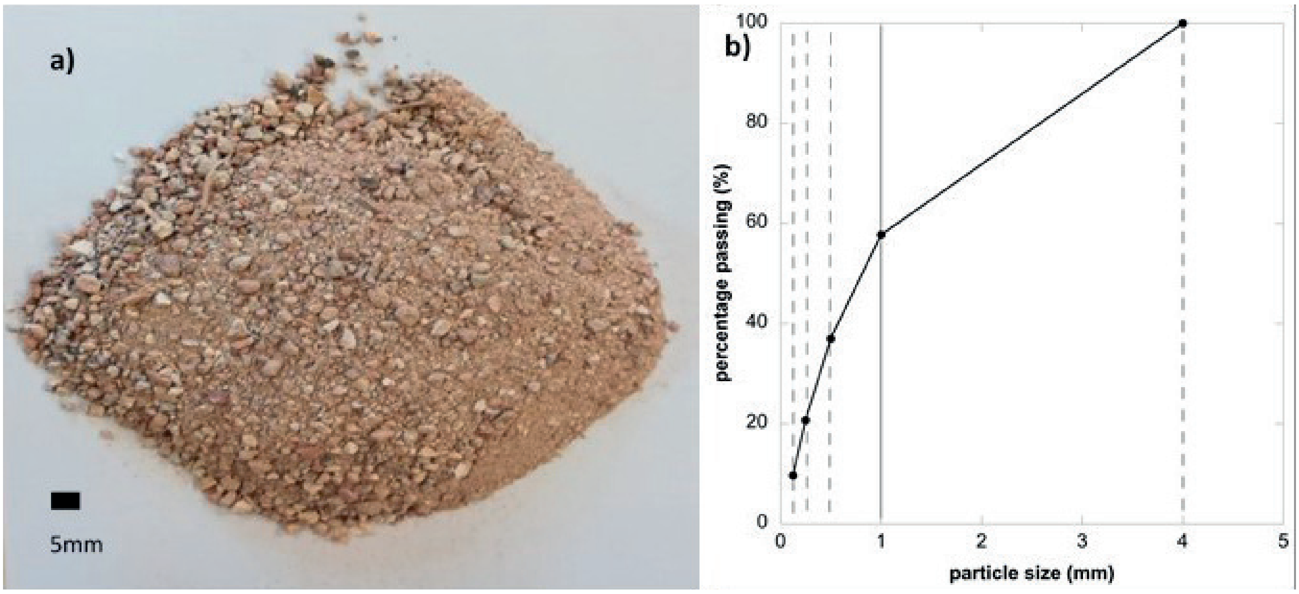

FIGURE 2: (a) CDW sample before sieving; (b) Rosin Rammler particle size distribution.

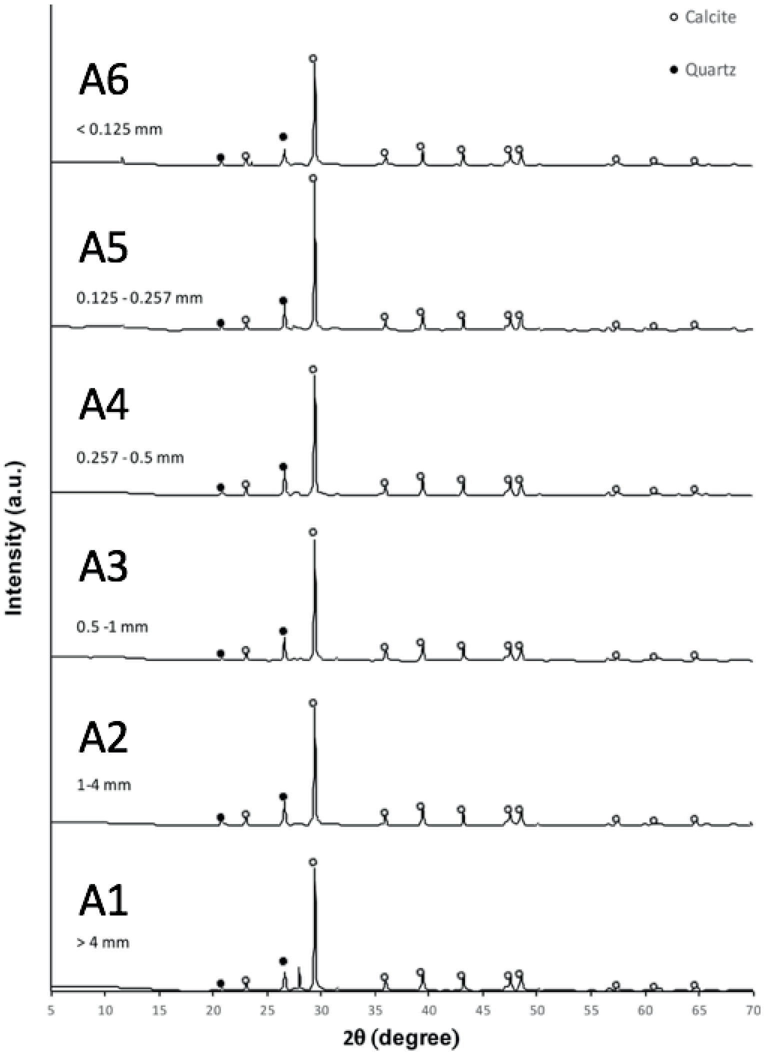

FIGURE 3: XRD mineralogical composition of CDW different granulometries. Notes: full circles are Quartz; empty circles are Calcite; grain-size intervals in mm are reported.

mineralogical content of the samples and verify if the particle size could show different mineralogical compositions, affecting therefore the products obtained upon the thermal treatment. The XRD data of the CDW samples indicate that the principal mineral species is Calcite, followed by Quartz and by trace amounts of phyllosilicates, visible only in the finest grainsize samples. Calcite is always strongly predominant in all the different granulometries analyzed (Figure 3, Table 1), averaging 82.3±5.5 wt.% for Calcite vs. 17.9±5.7 wt.% for Quartz, as determined via the RIR method. The samples are rather homogeneous in mineralogical composition and all very enriched in $CaCO_3$, as originating from a CDW composed predominantly by building rocks like limestones and travertines, or sandstones rich in the calcareous component, all common in the area, as well as occasional ornamental rocks like marbles and granites. XRD data show that there is no strong variation in composition between the different grainsize categories, apart the limited variability of Calcite and Quartz contents, all reflecting the building materials and architectural styles of the rubble provenance area. The building materials composing the CDW are in fact directly connected to the geological characteristics and availability of lithologies in the area. These are mostly used locally and have been extracted for centuries, as evidenced by the many historical buildings, some also affected by the earthquake. Some stone quarries are still in operation now. On the other hand, in the area there is also a long-term tradition of exploitation of clays deposits for the ceramic industry, which produced an established use of bricks/roof tiles as major building materials in constructions, since the XIV century. All these materials are therefore expected to contribute to the bulk composition of CDW from the area, as well as others like concrete or metakaolin from sanitary waste and limited plaster although it should be separated from CDW before crushing.

The contribution of all materials to CDW composition is evidenced by the bulk chemical data. The XRD data agree well with the chemical composition (Table 2) showing that this CDW is very low in silica, with Si coming mainly from

TABLE 2: Major oxide composition (wt%) of starting CDW and CDW treated at the highest melting temperature for 8 hrs (CDW-1250) reported along with literature CDW data and other comparable compositions.

	This study		Other CDW compositions			Other compositions	
Wt%	CDW-bulk	CDW-1250	Volpintesta (2019)	Favaretto et al. (2017)	Bianchini et al. (2005)	CR1 Concrete	FC1 Clay bricks
SiO_2	32.89	27.33 (1.51)	33.26	85.50	51.90	38.03	63.00
Al_2O_3	6.42	24.08 (2.11)	9.65	3.69	12.48	5.01	15.14
CaO	54.43	39.14 (0.42)	47.07	7.12	22.64	39.88	8.52
FeO*	2.79	5.64 (1.66)	4.16	1.41	5.17	1.80	5.03
MgO	1.60	2.85 (0.67)	2.87	1.34	4.45	12.21	3.22
Na_2O	0.58	0.64 (0.23)	1.05	n.d.	1.79	0.74	1.00
K_2O	1.29	0.32 (0.16)	1.52	0.92	2.17	1.06	2.57
Total	100	100	100	100	100	99	98.48

Notes: Microprobe analyses for CDW-1250 are based on 10 measurements, using analysis conditions as described in text. Measurement's uncertainty for CDW-bulk is 10 %, while standard deviations for CDW-1250 are reported into parenthesis. Totals have been normalized to 100%; FeO refers to total Fe expressed as FeO. CDW composition from Bianchini et al. (2015) corresponds to an average value; CR1 Concrete and FC1 clay bricks compositions are taken from Panizza et al. (2018).*

Quartz grains from sand and cement, or from clays constituting the ceramic components like mixed bricks, tiles and roof tiles. It contains abundant Ca, reflecting the presence of both cement/concrete and limestones or sandstones. In particular, major oxides are represented by CaO (54.3 wt%), SiO_2 (32.8 wt%), and Al_2O_3 (6.4 wt%), followed by other oxides in minor amounts (Table 2). Table 3 reports also the minor elements, including REEs, determined in the CDW sample, in total accounting for about 0.1 wt.%. In particular, elements such as Pb or other heavy metals, for instance, are considered to be harmful species that are not permissible for direct disposal or reutilization, although in this CDW sample they are well below allowed environmental protection limits. The chemical characterization, however, is particularly important for the impact CDW can have on the environment when recycled, to quantify the release of possible harmful elements with time, carried out using leaching tests (Kida et al., 1996; Kosson et al., 2002). The leaching properties of trace elements are determinant to learn about their chemical speciation and to gather information about the chemical properties of the waste before its eventual disposal into the environment or recycling into new waste-based products. Though, leaching tests are commonly widely used for other different waste materials, more hazardous than CDW, as for instance municipal solid waste bottom ash, that are notably richer than CDW in harmful elements (e.g. As, Cu, Cd, Cr, Hg, Ni, Pb and Zn; Li et al., 2004), which represent a significant risk for contamination of groundwater resources and surrounding soils via weathering.

TABLE 3: Minor elements (ppm by weight), including REEs, in the starting CDW of this study.

Minor elements (ppm)	CDW-bulk	Minor elements (ppm)	CDW-bulk
Sr	812	U	1.47
W	82	Er	1.24
V	49	Yb	1.19
Pb	40.7	Eu	0.52
Ce	25.9	Ta	0.40
La	15.4	Ho	0.40
Y	13.50	Tb	0.33
Nd	13.2	Lu	0.17
Th	4.66	Tm	0.12
Sn	4.00		
Pr	3.40		
Gd	2.34		
Sm	2.32		
Dy	2.10		

Notes: ICP-MS and acid dissolution have been employed with a relative measurement's uncertainty, validated on international standards, of 5%. Elements are reported in descending order of abundance.

If compared to other CDW analyses from the literature (Table 2), CaO is strongly predominant in this CDW, whereas SiO_2 and Al_2O_3, are considerably depleted, showing that the CDW compositional range is highly variable both in oxide abundances and proportions among them, depending on the different nature of the waste and provenance. Also, although CDW represents a problem in waste management and recycling on a global scale, it is worthwhile noticing that literature studies are still lacking of CDW chemical composition data, in spite of the importance of this information which can negatively affect industrial applications. For a better evaluation of the available sources, CDW data were compared using the $CaO–Al_2O_3–SiO_2$ ternary diagram (Figure 4), where the composition of mineral phases typically recognised in cements and ceramic materials were also reported. Raw material compositions required for ce-

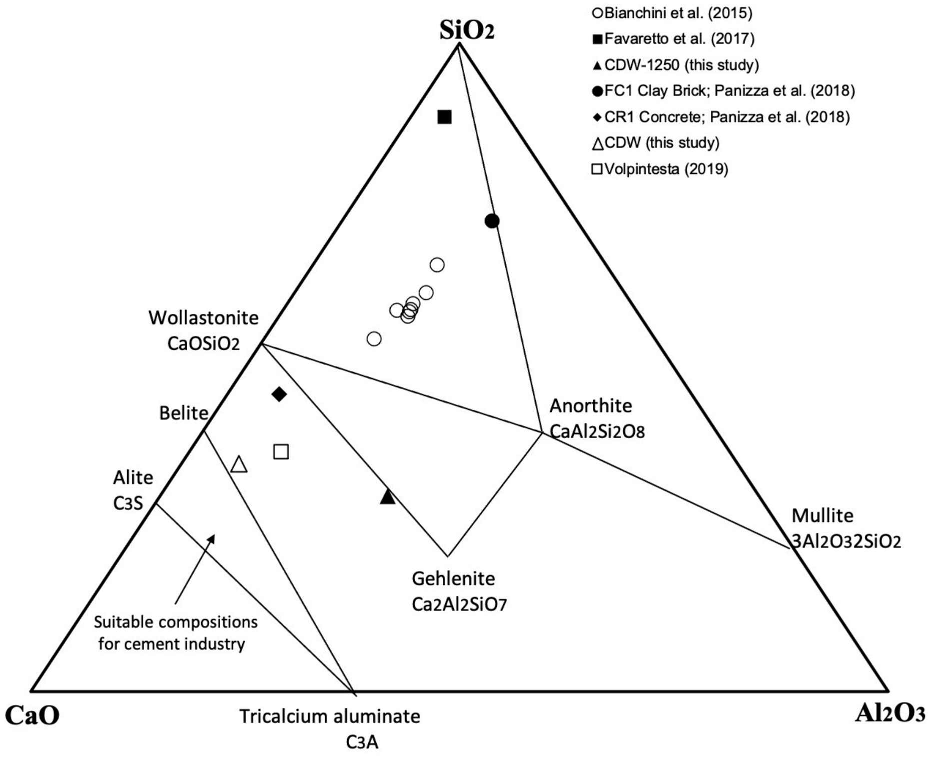

FIGURE 4: Ternary diagram describing the system CaO–Al2O3–SiO2 (wt%). Triangles are our CDW study composition (empty starting material, full after thermal treatment at 1250°C, circles are data from Bianchini et al. (2015) and full square from Favaretto et al. (2017). A clay brick and a concrete composition (Panizza et al. 2018) are reported as comparison.

ment preparation are usually included in the sub-triangle tricalcium silicate (alite; C_3S) - dicalcium silicate (belite; C_2S) - tricalcium aluminate (C_3A) (Manning, 1995). Components that could be suitable as secondary raw materials for the ceramic industry can be considered in the same diagram (Bianchini et al., 2005). In Figure 4, the CDW composition used in this study (empty triangle) shows a silica content considerably lower than the literature data of both CDW compositions from Favaretto et al. (2017) and Bianchini et al. (2005). Moreover, CDW (this study) composition is also far from CDW-1250 (full triangle in the Triplot), because the latter corresponds to a residual melt composition (Tab. 2) of the treated CDW_1250 sample with ca. 50% xls. Data from this study and from Volpintesta (2019) are more similar to each other, falling close to the sub-triangle containing compounds suitable for cement industry. Moreover, if we consider the Basicity Ratio (BR) of the different CDW materials, as a parameter expressed as the ratio between the CaO/SiO_2 oxides wt% or C/S (data from Table 2), the CDW of this study has a BR of ca. 0.6 compared to the literature C/S values that reach values strongly higher than the unity, up to an average value of 2.2 (as for Bianchini et al. 2015), or even 12 as for Favaretto et al. (2017) samples. This reflects a composition with a high proportion of concrete, limestone and ceramic components able to produce a CaO-rich and SiO_2-poor CDW. This information is useful for a better comparison between materials and suggests a possible recycling application of this CDW in the cement industry.

3.3 Thermally-treated CDW

The samples used as starting materials for the thermal experiments were selected from two different gransizes: sample A6 (<0.125 mm), the finest and most interesting fraction for recycling this CDW in a non-conventional way, and A1 (>4 mm), the largest size, which contains the least amount of Quartz of all the sample series.

The experiments were carried out on sample A6 in the temperature range 1000-1250°C for 2 hours at each T step. The XRD data were collected after each step in the same analytical conditions. Figure 5(a) shows that Quartz decomposes rapidly going from the experimental run at 1000°C to 1100°C and it is completely absent at 1200°C. At 1000°C Gehlenite and Larnite, both Ca-bearing silicate species, are already forming thanks to the decomposition of Calcite and to the availability of silicon and aluminium.

Calcite, in fact, is known to start decomposing slowly at 700°C, more rapidly at 750°C, to complete decomposition by 800°C (Karunadasa et al., 2019), releasing CO_2 (Trinidade et al., 2009) and forming lime, CaO. Portlandite, $Ca(OH)_2$ present in the 1200°C XRD pattern, formed as a secondary phase after CaO. The hydration and carbohydration processes are expected to occur after thermal treatment, although some Calcite is still evident at 1000°C, due to the fast recarbonatation of CaO in the sample holder during the XRD analysis, without indication, however, of significant volume changes (Setién et al., 2009). In contrast, the carbohydration processes of periclase (MgO), which could provoke a significant volume increase jeopardizing

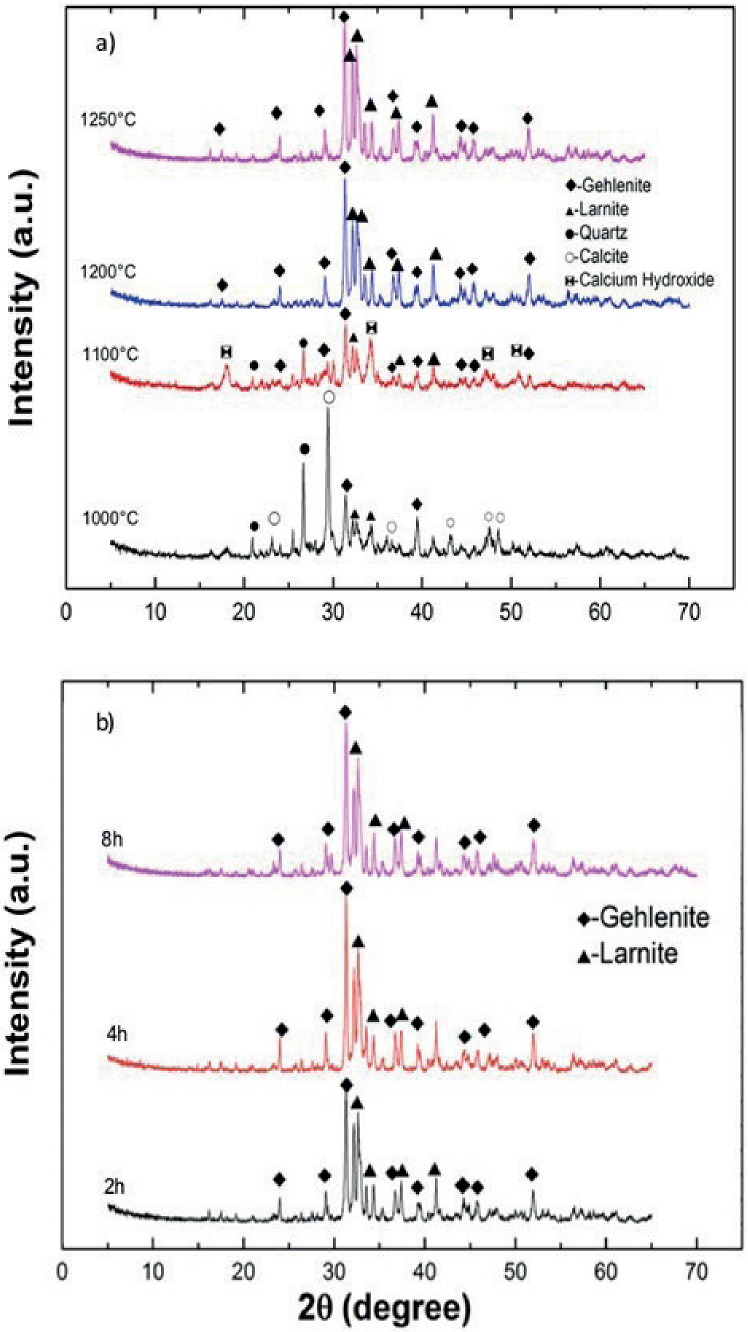

FIGURE 5: a) XRD analysis of CDW A6 sample treated at different temperature and same duration of 2 hours each; b) A6 at the highest temperature (1250°C) and different durations (2 to 8 h).

the use of this treated material in construction and building (Juckes, 2003), is however negligible because of the very low amount of Mg present in the CDW starting composition, which prevented the formation of MgO.

The newly formed species, Gehlenite and Larnite, already present in the experimental runs at 1000°C, at 1200°C are the only crystalline species present in the samples. They persist at increasing temperatures and are still present in the samples heated at 1250°C, independently from the duration of the thermal treatment, as shown in the runs lasting from 2 to 8 hours (Figure 5(b); Table 1), which indicate there is no significant variation in the XRD patterns, testifying that they are the only crystalline compounds present in the sample.

Figure 5(b) shows that there is no further variation of the mineralogical composition after experiments at 1250°C, even with increasing the experiment duration from 2 to 8 hours. Longer runs have been carried out (up to 16h) also with no difference in results. This means that the two phases are already stable even using the shortest experimental time of 2 hours, which could be interesting for the optimization of an industrial process.

Moreover, the comparison of XRD data between sample A6 (the finest) and A1 (the coarsest) collected from

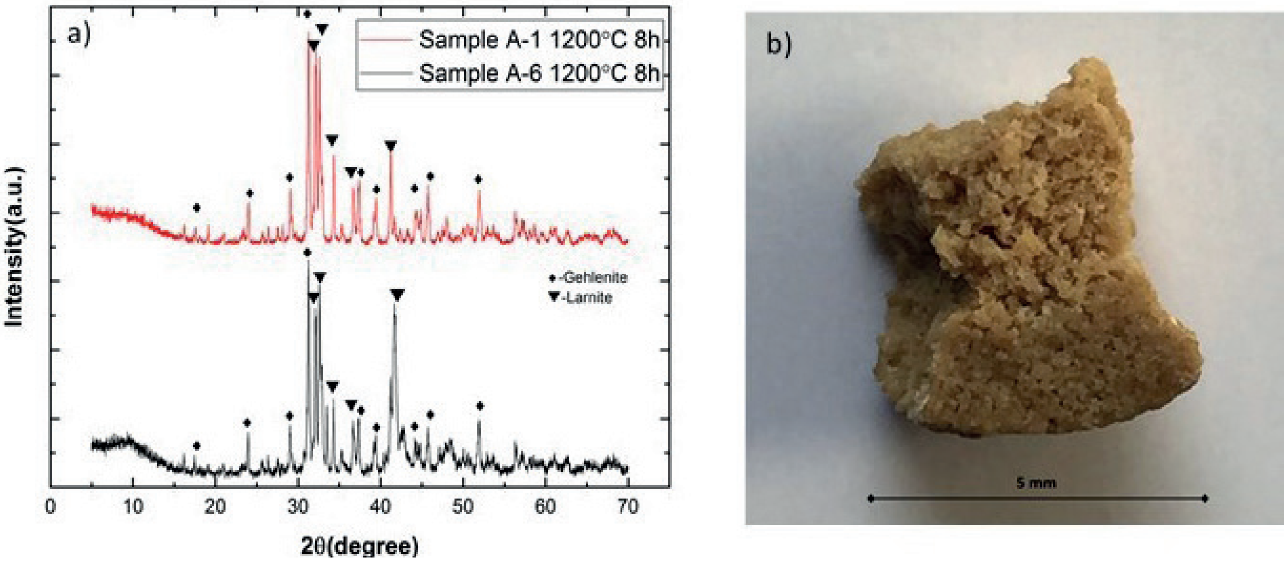

FIGURE 6: (a) Comparison of XRD data between the samples A1 and A6 after thermal treatment at the same temperature (1200°C) and duration (8h). (b) The porous material produced at high temperature from the CDW thermal treatment.

experiments at same temperature and duration (1200°-8h runs) (Figure 6a) show that the samples reach the same mineralogical composition, without significant variation as a function of granulometry. This suggests that sieving this CDW below 4mm size does not affect the thermal treatment results, producing the same type of final product (Figure 6b).

Gehlenite and Larnite form, above 750°C and 570-670°C, (Gonzalez-Garcia et al., 1990) respectively, from the reaction between CaO, SiO_2 (and Al_2O_3 for Gehlenite), thanks to the decomposition of the original CDW components. The composition of the two species is reported, as an indication, in the ternary diagram CaO-Al_2O_3-SiO_2 (Figure 4). In particular, Gehlenite ($Ca_2Al(AlSiO_7)$) is the Ca and Al-rich end member of the Melilite binary system (Gehlenite-Åkermanite) where Åkermanite is the Mg and Si-rich end-member, $Ca_2Mg(Si_2O_7)$. Gehlenite is also a high temperature phase forming in ceramics and is common in heterogeneous waste materials after treatment at high temperature, like municipal solid waste bottom ash (e.g. Schollbach et al., 2016; Stabile et al. 2019). Pure Gehlenite melts at 1595°C at ambient pressure, well over the temperature of these experiments, accounting for the lack of melting of this CDW sample. The structure of Gehlenite can incorporate the Al present in CDW and can also include a substitution of Al by Fe^{3+}, even up to 18 wt.% at 1237°C (Huckenholz and Ott, 1978), suggesting that Gehlenite structure could allocate also the ferric iron present in the original CDW (Table 2). Also, other transition elements could possibly substitute in Gehlenite, suggesting it might serve as a possible confinement phase for other metals.

Larnite Ca_2SiO_4 is the natural mineral species whose structure corresponds to the synthetic β-Ca_2SiO_4, forming as belite in Portland cement. The name larnite is connected to a series of Ca_2SiO_4 polymorphs (γ, β, a in order of increasing temperature of stability) where β and α phases are characterized by reversible polymorphic transitions and α presents also a higher and a lower temperature phases (Yamnova et al. 2009), difficult to detect because of peak overlapping in the XRD patterns of quenched samples. The low temperature synthetic γ phase has its natural analogue in the Ca-olivine (γ- Ca_2SiO_4) the calcium end-member of the olivine group of minerals.

In the experimental runs (Figure 5), Larnite is present at 1000°C and with increasing temperature there is a progressive increase of larnite presence and also an increase of the crystallinity degree of the two species, Gehlenite and Larnite, from the early crystal nucleation up to the highest experimental temperature (1250°C). This is testified by the increased sharpness and intensity of the diffraction peaks and by the decrease of the amorphous components, as evidenced by the flattening of the XRD pattern background. The early formation of larger amounts of glass may reflect metastable melting, followed by delayed nucleation and growth of larnite and gehlenite. The minor presence or even the absence of amorphous material at high temperature reflects the highly refractory nature of this Si-poor, Ca-rich CDW compositions investigated.

Calcium silicates are interesting materials for CO_2 sequestration (Santos et al., 2009): this is possible because, for example, Larnite presents the highest carbonation reaction rate among the calcium silicate, with 64–67 wt.% of CaO, about 50% more than that of wollastonite (42-44wt.% of CaO), interesting therefore for acting as a possible CO_2 structural confinement (via Ca-carbonate formation). While here the process of decarbonation takes place by a high temperature treatment of CDW, it is however interesting that the calcium silicates, on the other hand, could possibly be recycled as CO_2 storage materials. The carbonation process is not well documented yet in Larnite, although its β-Ca_2SiO_4 phase Belite is a major constituent of Portland cement where carbonation is an important process capable to reduce its environmental impact, helping also decrease curing time and increasing materials strength (Santos et al., 2009). A different and peculiar aspect relates also larnite and its possible role in an acid-neutralizing effect produced after the Cretaceous/Tertiary meteoritic impact, where a mechanism producing larnite from the interaction between acid rain and the vapour plume produced from the Ca-rich target rocks at the impact site, able to neutralize acidity in a short time preventing the acidification of freshwater and preserving the living organism within (Maruoka & Koeberl, 2004).

3.4 Further considerations

3.4.1 Vitrification

The presence of crystalline phases and their persistence in the thermally treated samples implies that complete vitrification is not accomplished for the studied CDW sample, using this thermal process (maximum T=1250°C, 8 hrs). In the treated samples, newly formed phases like Gehlenite and Larnite can be observed and are stable up to at least 1250°C. Thus, it is clear that the amorphous proportion in the samples, when present at these temperatures, is nonetheless limited by the refractory, Si-poor and Ca-rich bulk composition.

In fact, the CDW studied, although chemically belonging to the SiO_2-Al_2O_3-CaO system, does not contain amounts of network-forming elements in quantities that could facilitate the vitrification process by lowering liquidus temperatures. A silicate glassy material consists of a network of SiO_4 tetrahedra in which Si^{4+} can be partially replaced by other cations with similar ionic radius as network-formers; among these, Al_2O_3, TiO_2 or P_2O_5 usually act as glass forming oxides (Öveçoğlu, 1998; Colombo et al., 2003). On the other hand, other cations, such as alkali metals or alkaline earths, like CaO and MgO, are network modifiers and decrease the connectivity of the glass network (Schaffer et al., 2010). Therefore, if the starting chemical composition results lacking of network-formers, the formation of a glass phase can be expected only if more glass-forming oxides are added, preventing crystallization of high temperature-stable phases and lowering melting temperatures. Therefore, to reach vitrification at reasonable temperatures (<1300°C), a change of chemical composition of the starting CDW is necessary.

Although most wastes can vitrify without additions or fluxes (Neuville et al., 2017), the addition of a modest amount of glass cullet or other compounds (like quartz sand) can promote the vitrification, if such agents are not present in sufficient quantity. In fact, considering a glass-forming system, a wide range of elements can play a crucial role in stable and metastable phase separation processes, inhibiting nucleation and crystallization in response to a physical or chemical change (e.g. heating) (Galoisy 2006; Neuville et al., 2017). To overcome this problem and obtain higher amorphous contents, preliminary tests were carried out by combining CDW with silicate glass waste materials. In particular, special glasses, like borosilicate or lead-containing glasses, multilayer glasses (laminated glasses or windshields) or solar panel glasses, cannot be inserted in the normal waste streams, requiring special recycling techniques or missing recycling due to lack of applications or for the presence of contaminants which could be released in the environment. Thus, they are often destined to landfill if a separate recycling line is not available and can represent an important environmental issue (Barbieri et al., 2000; Colombo et al., 2003; Kavouras et al., 2003; Li et al., 2004; Stabile et al., 2019). In these tests, by mixing CDW with 30 wt.% of windshield glass, the amorphous proportion obtained in the thermally treated sample, determined by RIR method, reaches 58 wt.%, compared to 42 wt.% crystalline phases present. This value increases up to 75 wt.% if 50 wt.% of glass is added, making this process valuable for the production of a fully glassy materials by a mixing of wastes.

3.4.2 Applications

Apart from CDW recycling as a backfilling material, still the most used worldwide, other applications can be highlighted for the recycling of this CDW, which render useful this material, especially the finest unwanted grainsizes.

The vitrification data give us promising information about the propensity of this CDW materials for vitrification and suggests a procedure that could be adopted to improve recycling of low-quality waste materials as secondary materials in the glass industry, for example in the production of soda-lime glass (Na-silicate + CDW). Moreover, one possible application of vitrified CDW is contributing to the production of glass fibres (Scarinci et al., 2000), in alternative or in combination with other waste, such as bottom ashes from incinerators and milled glass fibres from the recycling of fiberglass insulation material (Lopez et al., 2012). On the other hand, this CDW proved to produce a refractory material when thermally treated, with a porous texture, possibly interesting as thermal insulator, and meriting further work concerning porosity evolution as a function of heat treatment conditions.

Other possible uses, some of which already mentioned before, can be proposed in view of the chemistry of this CDW, such as:

- as secondary raw material in the production of cement and concrete, depending not only on the composition, but also on the granulometry (Oliveira et al., 2020);
- for the production of geopolymers, incorporating CDW as either inert aggregates or partially reactive materials (Panizza et al., 2018);
- in acid correction in soil and freshwater in polluted areas, which can be of interest whenever, such as in this work, CDW is duly separated and characterized, while it encounters difficulties otherwise (Staunton et al., 2014), and providing that there is no presence of heavy metals;
- in mining areas of sulphide ore deposits, for the correction of Acid Mine Drainage (AMD), commonly carried out using limestones, which however could be partially substituted by CDW of similar composition due to its high Calcite content (Yilmaz et al., 2018).

Also, whenever CDW contains sufficient amounts of clay materials, the extraction from waste of nanoclays would represent an enhanced upgrading option, since nanoclay does have extensive use e.g., for the improvement of mechanical and wear properties of thermosetting polymer resins including those used in the construction sectors (Shettar et al., 2020).

4. CONCLUSIONS

The large differences among CDW samples of different provenance (and/or waste source) highlight the strong heterogeneity of CDWs coming from different regions or localities where they have been produced and collected. This observation suggests the need of a better characterization of CDW since the bulk chemical and mineralogical composition must be controls possibilities for finding novel upgrading industrial applications for this material.

From the mineralogical analysis, the CDW composition appears to be quite homogeneous and characterized by a strong predominant presence of Calcite over Quartz, independently of its granulometry. The results of this study show that a complete glassy state is not reached by the CDW samples, at the highest T used (1250°C) and despite even long experimental duration, producing a porous refractory material. This is due to the chemical composition of CDW, characterized by a lower amount of glass network-forming cations like silicon and aluminium in the sample composition, combined with a higher amount of calcium. However, mixing this CDW with a waste-glass component improves drastically the vitrification process, strongly promoting an increased amount of glass formation, thus opening a larger application field for this CDW.

Moreover, its chemical composition makes the studied CDW most likely suitable either for direct use as raw component or as a tool for compositional correction of other materials for the cement preparation and for the making of other cement-based building products. Additionally, CDW produced by vitrification shows a particular porous macro-appearance that may imply its possible application as filler in cement-based insulation materials.

The results obtained are in the view of reducing as much as possible the downgrading of CDW materials to proceed with their economically and structurally viable recycle. It needs to be suggested that, although EC 98/2008 directive indicated 70% of CDW to be recycled by 2020, this ambitious objective has proven difficult to be reached, due to the inconsistencies about the secondary raw materials supply and the consequent possibilities to recycle it in new materials for construction. Setting general rules, though necessary, led so often to dismiss the local situation about generated rubbles, their nature and inherent quality, together with their chemical composition and possible vitrification. This study is aimed at offering the evaluation of these characteristics to serve towards the fulfilment of circular economy goals by tailoring the treatment of local CDW to its effective recycling potential.

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