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Review article

Pomace from the wine industry as an additive in the production of traditional sustainable lightweight eco-bricks

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ABSTRACT

This research examines fired clay bricks made with waste pomace from the wine industry as an additive in brick production. To this end, we analyse and discuss the chemical, mineralogical, textural and physical-mechanical behaviour of fired bricks made with three concentrations of wine pomace (2.5, 5 and 10 wt%) and at three different firing temperatures (800, 950 and 1100 °C) and evaluate their durability to salt crystallization. Variations in colour were also examined. The firing process resulted in the decomposition of phyllosilicates and carbonates, the crystallization of Fe oxides and the appearance of high-temperature Ca- (and Mg-) silicates phases such as gehlenite, wollastonite, anorthite and diopside. The bricks made with added wine pomace had very similar mineralogy to the control samples made without it. The bricks made with added wine pomace were lighter than the control samples and underwent less linear shrinkage during the drying process. Particles in the wine pomace were consumed during firing, leading to the appearance of voids. The bricks made with this additive had higher levels of water absorption and poorer mechanical strength. The greatest colour differences were detected after increasing the amount of waste, which generally resulted in yellower bricks. The increase in firing temperature resulted in an improvement in mechanical resistance regardless of the composition of the bricks. However, bricks fired at 1100 °C made without additive are more resistant to damage caused by salts than those made with wine pomace.

1. Introduction

Vine cultivation is one of the most common, most widespread crops in Mediterranean countries and in the world in general (Barbieri et al., 2013; Fontana et al., 2013). In 2021, over 74 million tonnes of fresh grapes were obtained from approximately 7.4 Mha of plantations worldwide, from which 262 million hL of wine were produced (data from the International Organisation of Vine and Wine, OIV, www.oiv.int). This vast scale of production clearly generates a huge volume of waste, known as pomace. The countries with the highest worldwide production of wine pomace are Italy, France and Spain, with almost 1.4, 1.2 and 1 million tonnes respectively (OIV, www.oiv.int).

The chemical composition of wine pomace is affected by factors such as grape variety or climate (Kotsanopoulos et al., 2021; Aresta et al., 2020; Taladrid et al., 2019a; Bordiga et al., 2019). The presence of certain compounds, such as phenols (anthocyanins, flavan-3-ols, flavonols, hydroxybenzoic and hydroxycinnamic acids and stilbenes) (Monrad et al., 2010; Barcia et al., 2014; Fogliano et al., 2011; Lafka et al., 2007) could make disposing of the wine pomace in landfills or its incineration a threat to the environment, as it could lower the pH of the soil leading to oxygen depletion. It could also increase resistance to biological degradation (Fontana et al., 2013; Fogliano et al., 2011; Makris et al., 2007). According to Spanish Law 10/1998, these wastes must be treated before disposal to avoid environmental pollution. Wine companies that make unauthorised discharges of wastewater can be subject to heavy fines and waste disposal fees can be significant (Arvanitoyannis et al., 2006; Devesa-Rey et al., 2011). This regulation could encourage wine industries to investigate new waste treatment technologies or new ways of using these residues profitably and sustainably. However, small wine producers often choose not to comply with this law and dispose of wine pomace and winery sludge in landfills.

Traditionally, pomace is used as a fertiliser, animal feed or for the production of distillates (González-Paramás et al., 2006; Salinas et al., 2003; Meloni et al., 2015; Paradelo et al., 2011). Some researchers have also investigated its application as a biofuel, based on its high calorific value (Paradelo et al., 2013; Ye et al., 2016; Airado-Rodríguez et al.,

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2011; Maicas, 2020), and this seems to be the most promising sector for future research (Arya et al., 2022; Taladrid et al., 2019b).

Wine pomace is made up of grape skins, seeds and stems and wine lees (Perra et al., 2022). The proportions of each of the components of wine pomace vary, with some authors stating that seed content ranges between 38 and 52 wt% and skin content between 5 and 10 wt% (Bustamante et al., 2008; Nogales et al., 2005; Yu and Ahmedna, 2013; García-Lomillo and González-San José, 2017; Nardoia et al., 2017). Sulphur dioxide is often added to the grape must during winemaking to inhibit wild yeasts and control microorganisms such as bacteria and moulds (Makris et al., 2007), which explains why it can also be found in wine waste products. As regards the possible use of wine pomace in the brick industry, certain types of residues (both organic and inorganic) have been found to increase porosity in fired bricks, so reducing their thermal conductivity (Guardia et al., 2018; La Rubia-García et al., 2012; Eliche-Quesada et al., 2017; Cultrone and Sebastián, 2009). When it comes to forming pores, organic wastes are generally cheaper than inorganic ones and also have the advantage of contributing to the heat required during the firing process (Perra et al., 2022; Nardoia et al., 2017). However, the amount of residue that can be added is limited by the fact that it can impair the mechanical properties of the bricks (Cultrone et al., 2020). In addition, residues can have negative effects on the plasticity of the clayey material, causing an increase in the amount of water required during the moulding process (Anjum et al., 2020). Another drawback of organic wastes is that CO_2 emission during firing is usually higher than when inorganic wastes are used.

At the same time, the widespread exploitation of clayey soils for brickmaking is leading to the depletion of these non-renewable natural resources (Anjum et al., 2020). Clays are essential for making bricks in a process which briefly involves: the extraction of the raw materials, their crushing, sieving and, in some cases, mixing with other clays or additives, kneading with water and shaping the samples. After drying, the bricks are fired at temperatures that cause mineralogical and physical transformations. The composition of the raw material and the firing temperature are the two main factors that affect the final characteristics of the bricks (Demir, 2008). This paper aims to investigate the recycling of a winemaking by-product, pomace, by using it as an additive to make quality bricks for use in the construction industry, so reducing the amount of clay used and preventing its depletion. By using this waste material in the production of bricks, we could reduce the amount of wine pomace that is dumped in landfills and perhaps also make savings in production costs.

In this paper, we investigate the effects of the addition in different proportions (2.5, 5 and 10 wt%) of wine pomace to a mix of two different clayey materials to produce lightweight bricks fired at three different temperatures (800, 950 and 1100 °C). The main objectives are to find out more about the properties of the wine pomace, to determine the optimum amount to use in the brick-making process, and to evaluate the quality and durability of the resulting bricks. The percentages of waste were chosen in view of the promising results obtained in previous research into wine pomace (Guardia et al., 2018) and other organic wastes (Cultrone, 2001). On this question, Coletti et al., (Monteiro and Vieira, 2014) recently observed that the addition of grape stalks increases the porosity and thermal insulation properties of the bricks. However, high percentages of pomace seem inadvisable. In fact, Monteiro and Vieira (Cultrone, 2001) and Muñoz et al. (Coletti et al., 2023) found that amounts of over 10 wt% would produce excessively brittle bricks from a mechanical point of view.

2. Materials and method

2.1. Geological context of the clayey materials

The raw materials used to make the bricks come from Viznar and Guadix (Granada, Spain). The Viznar clay formation is part of the Granada basin, while the clay from Guadix belongs to the Guadix basin. Both basins are part of the central area of the Betic Cordillera.

Table 1
Reference and firing temperatures of brick samples made with (W samples) and without (Mi samples) added wine pomace.

Firing temperature (°C)	Control	Wine pomace (wt%)		
		2.5	5	10
800	Mi800	W800/2.5	W800/5	W800/10
950	Mi950	W950/2.5	W950/5	W950/10
1100	Mi1100	W1100/2.5	W1100/5	W1100/10

The clay from Viznar was deposited during the late Turolian in a lacustrine environment, with alluvial sediments (conglomerates and sands), deltaic sediments, small calcarenitic platforms and other materials from the Sierra Nevada and Sierra Arana (Muñoz et al., 2014).

The clay from Guadix was deposited in the Middle-Late Pleistocene during the last stages of basin infilling (García-Alix et al., 2008; Braga et al., 2003), mainly in small lagoons and marshes that appeared temporarily on the banks of braided rivers draining from the nearby Sierra Nevada (García-Alix et al., 2008; Braga et al., 2003; Pérez-Peña et al., 2009).

2.2. Traditional brick production

The bricks for this study were made by mixing the raw materials from Viznar and Guadix in proportions of 3/5 and 2/5 by weight, respectively, following the same proportions as those used by a brick manufacturer from Viznar (Granada, Spain), who provided the raw materials. The wine pomace was provided by a wine manufacturer from Valdepeñas (Ciudad Real, Spain). In order to remove all residual moisture, the pomace was dried at 60 °C in an electric oven for 8 h to avoid degradation of the polyphenols during the drying process. The clayey materials were sieved and fragments of over 1.5 mm in size were discarded, while the wine pomace was mechanically crushed to a particle size of up to 3 mm in size. The clayey material, wine pomace and water were mixed together to form a kneadable paste. Once enough plasticity had been achieved, the clayey paste was placed in moistened wooden moulds of 15 × 20 × 4 cm. After one hour, the moulds were removed and the clayey pastes were cut into ~4 cm edge cubes using a stretched cotton thread and left to dry. When the bricks were dry, they were fired in a Herotec CR-35 electric oven at 800 °C, 950 °C and 1100 °C. Table 1 summarizes the samples analysed in this paper. The samples were preheated for 1 h at 100 °C so as to eliminate any residual moisture that might still be present inside them. Then, the temperature was increased at a rate of 2 °C/min. Once the maximum temperature was reached, it was maintained for the dwell time of 3 h. Finally, the oven was turned off and the samples were left to cool slowly until the next day, so as to prevent fissures from developing due to the β-to-α quartz transition at 573 °C. After removal from the oven, the bricks were immersed in water for about 1 h so as to prevent possible “lime blowing” due to the presence of lime grains (Vera and Rodríguez Fernández, 1988).

2.3. Analytical techniques

2.3.1. Chemical, mineralogical and textural study

Elemental analysis of the wine pomace was conducted using a Thermo Scientific Elemental Analyser CHSN TM FlashSmart and its calorific value was determined using a calorimetric pump IKA Werke model C5003. The grain size of the raw material and the wine pomace were measured separately using a Galai CIS-1 laser gauge. X-ray fluorescence (XRF) was used to determine the major elements in the clayey material with a PANalytical Zetium compact spectrometer. 3 g of each sample was ground to powder prior to its analysis. The mineralogical composition of the raw sample and fired bricks was determined by powder X-ray diffraction (PXRD) using a PANalytical X’Pert PRO diffractometer. The samples were milled with an agate mortar to a particle size less than 53 μmand then analysed. The working conditions were as follows: CuKα radiation, 45 kV voltage, 40 mA current, 3 to 70° 2θ exploration range, 0.1 2θ s^{-1} goniometer speed. The mineral phases were identified using the PANalytical X'Pert Highscore Plus 3.0 software.

The thermal decomposition of the raw material up to 950 °C was determined using a METTLER-TOLEDO TGA/DSC1 thermogravimetric analyser coupled with differential scanning calorimetry. The sample was deposited on an Al crucible and analysed in a flowing air atmosphere (50 ml/min) at a heating rate of 20 °C/min up to 950 °C. The petrographic features (mineralogy and texture) of the fired samples were observed under plane- and cross-polarized light by means of polarized optical microscopy (POM) using a Carl Zeiss Jenapol-U microscope equipped with a Nikon D7000 digital camera. A high-resolution Carl Zeiss SMT (AURIGA series) field emission scanning electron microscope (FESEM) coupled with X-ray energy dispersive analysis (EDS) was used to observe the texture and porosity of the samples in more detail.

2.3.2. Pore system

Hydric and porosimetric tests were carried out in order to analyse the pore system of the bricks and how it is altered by the addition of wine pomace. Free (Ab, at atmospheric pressure) and forced (Af, under vacuum) water absorption, drying (Di) and capillarity tests (C) were carried out according to UNE-EN 13755 (Laird and Worcester, 1956), NORMAL 29/88 (UNE-EN 13755, 2008) and UNE-EN 1926 (NORMAL 29/88, 1988) standards, respectively. These tests enabled us to determine the saturation coefficient (S), the apparent (ρ_a) and real (ρ_r) densities, and the open porosity (P_o). Hydric tests were performed under controlled thermo-hygrometric conditions (20 °C and 60% relative humidity) using deionized water. Three samples per brick group were analysed.

The pore system of the bricks within a range of 0.002 to 200 μm was analysed by mercury intrusion porosimetry (MIP) using a Micromeritics Autopore IV 9500 porosimeter. Samples of about 1 g were dried in a ventilated oven for 48 h at 30 °C prior to analysis. Specific surface area (SSA), apparent and real densities (ρ_{aMIP} and ρ_{rMIP}) and open porosity (Po_{MIP}) were calculated.

2.3.3. Physical-mechanical properties

Ultrasound was used to determine the compactness of the bricks. Measurements were performed using a Control 58-E4800 ultrasonic pulse velocity tester with transducers of 54 kHz and a circular surface of 27 mm in diameter. A water-based eco-gel was used to enable homogeneous contact between the transducers and the brick. The measurements were carried out on three samples per brick type. P-wave propagation was measured in m/s according to the ASTM D2845 (UNE-EN 1926, 2007) standard.

The compressive strength (CS) was measured using a Matest E181 hydraulic press with double frame 25 kN/300 kN, according to the UNE-EN1926 (ASTM Committee D-18 on Soil and Rock, 2008) standard. CS was measured perpendicular to the compaction plane of the clayey mass and was calculated in MPa on three samples per brick type according to the following Eq. 1:

$$CS = \frac{F}{A} \quad (1)$$

Where F is the breaking load (in N) and A is the cross-sectional area in m^2.

2.3.4. Colour

Colour measurements were carried out to quantify the lightness (L*) and chromaticity (a* and b*) of the fired bricks. A Konica Minolta CM-700d spectrophotometer was used following the UNE-EN 15886 (UNE-EN 1925, 1999) standard. Illuminant D65, 10° observer angle and 8 mm measurement area were used. Nine measurements per sample were performed. The total colour variation (ΔE) between bricks without additive and with added wine pomace was calculated as follows (Eq.2):

$$\Delta E = [(\Delta L^*)^2 + (\Delta a^*)^2 + (\Delta b^*)^2]^{(1/2)} \quad (2).$$

Table 2
Elemental analysis (in %) of wine pomace.

N	C	H	S
2.39	50.77	6.11	0.00

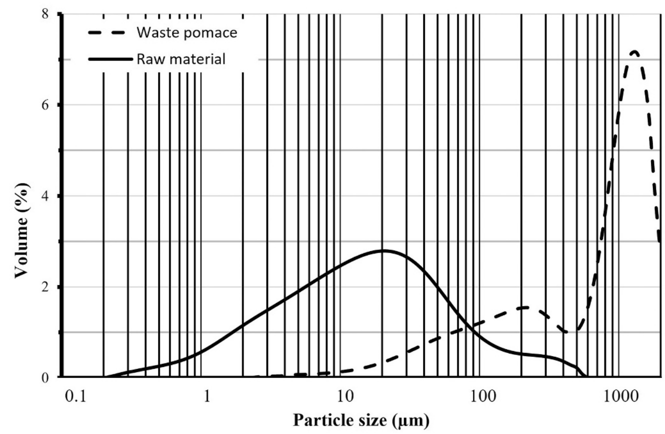

Fig. 1. Grain size distribution of the raw material and waste pomace.

2.3.5. Salt crystallization test

Fifteen salt crystallization cycles were performed to observe a theoretical degradation that could affect the lifetime of the bricks (made with and without wine pomace) according to the UNE-EN 12370 (UNE-EN 15886, 2011). The salt crystallization test reproduces the deterioration that the bricks may undergo due to the dissolution and recrystallization of soluble salts within their porous systems.

3. Results and discussion

3.1. Characterization of the raw material and the wine pomace

Table 2 shows the elemental composition (in %) of the wine pomace used for the production of the bricks. It is clearly very high in C and it is interesting to note the absence of S, given that sulphur is widely used to prevent biological attacks on vines, as mentioned in the introduction section.

The calorific value of wine pomace is 19.2 kJ/g. Compared to the calorific value of other wastes such as avocado peel (14.7 kJ/g) or olive pits (18.4 kJ/g), which have also been investigated for their possible use in the production of lightweight bricks (UNE-EN 12370, 2002; Alami, 2013; José et al., 2021), waste pomace could save a little more energy during brick firing due to its higher calorific value.

The granulometric analysis shows that the raw material has unimodal particle size distribution while the wine pomace is bimodal (Fig. 1). The raw material curve is quite symmetrical with a maximum at around 20 μm. In contrast, the wine pomace curve has larger particle sizes with a main curve that peaks at 1345 μm and a less intense second peak at 276 μm.

Table 3 shows the chemistry of the mixed clayey sample. It is rich in SiO_2 and has high Al_2O_3 and Fe_2O_3 contents. The presence of CaO (9.23%) and MgO (2.82%) is a sign of its carbonate content and it can be classified as calcareous according to Maniatis and Tite (Limami et al., 2021) and Tite (El Boukili et al., 2022).

PXRD analysis reveals that the clay is rich in quartz (Fig. 2), so confirming the high SiO_2 content detected by XRF. Various phyllosilicates were encountered including illite, paragonite, smectite, chlorite and kaolinite while the carbonates consist of calcite and dolomite.

Table 3
XRF results (in %) for the raw material used to manufacture the bricks.

SiO_2	Al_2O_3	Fe_2O_3	MnO	MgO	CaO	Na_2O	K_2O	TiO_2	P_2O_5	LOI
47.98	14.95	5.69	0.07	2.82	9.23	1.25	2.66	0.84	0.15	12.33

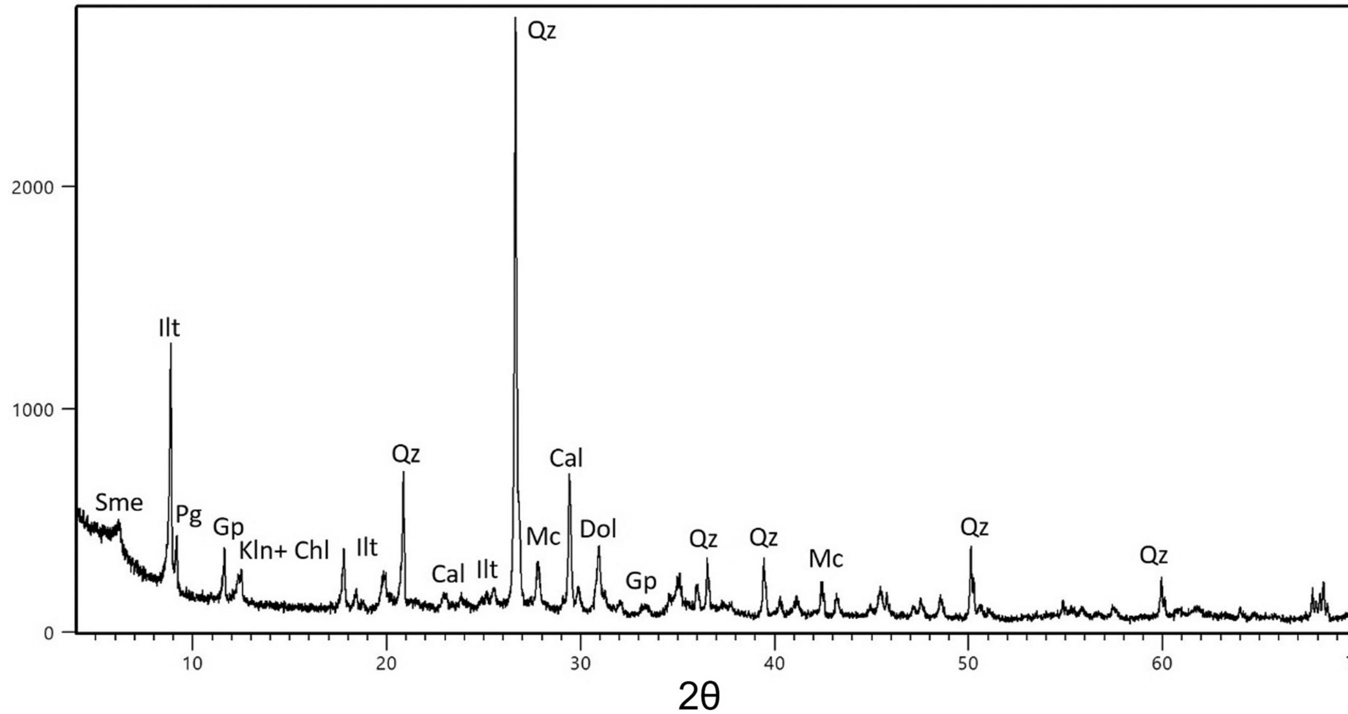

Fig. 2. X-ray diffraction pattern of the raw material. Legend according to Whitney and Evans (Torres et al., 2020): Qz = quartz; Cal = calcite; Gp: Gypsum; Dol = dolomite; Ilt = illite; Pg = paragonite; Kln = kaolinite; Chl = chlorite; Sme = smectite; Mc = microcline.

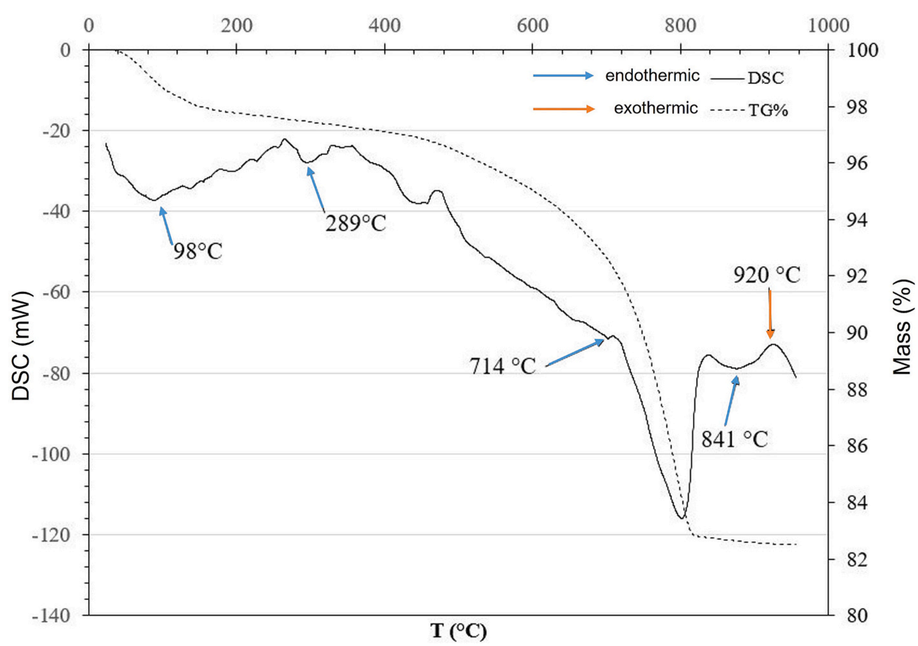

Fig. 3. TG-DSC analysis of the raw material. The abscissa represents the temperature (in °C) and the two ordinates represent the weight loss (right ordinate, in %) and the differential scanning calorimetry (left ordinate, in mW).

Table 4
Lightness (L*), chromatic coordinates (a*, b*) and colour change (ΔE) values in fired bricks. σ is the standard deviation of nine measurements per brick.

	L*		a*		b*		ΔE
	$\bar{x}$	σ	$\bar{x}$	σ	$\bar{x}$	Σ	
Mi800	56.85	2.60	18.76	1.13	24.40	0.73	–
W800/2.5	60.68	1.41	16.17	0.85	23.60	1.07	1.48
W800/5	63.01	2.43	14.24	2.02	23.83	1.47	2.04
W800/10	63.51	2.11	9.64	2.29	18.76	1.63	2.69
Mi950	59.75	3.21	16.30	1.04	22.90	1.53	–
W950/2.5	60.28	2.19	13.51	1.18	20.15	1.64	1.68
W950/5	67.95	3.44	8.95	1.50	22.91	2.27	2.15
W950/10	63.22	2.15	6.55	1.38	18.71	2.11	2.79
Mi1100	67.30	4.69	7.66	1.70	23.12	0.86	–
W1100/2.5	76.13	3.00	4.11	0.90	23.45	1.76	1.74
W1100/5	76.10	3.01	4.08	0.46	22.22	1.11	2.55
W1100/10	72.74	4.41	3.56	0.59	23.39	1.67	2.75

Gypsum and K-feldspar (microcline) were also detected. Paragonite is very common in the internal areas of the Betic Cordillera (Maniatis and Tite, 1981; Tite, 1975), an area from which part of the clay (Guadix) used to make the bricks was obtained. For its part, the clay from Viznar is made up above all of carbonates and gypsum, common features of the different geological formations that make up the Granada Depression (Ramos et al., 1989; López and Cruz, 2016; Ruiz-Bustos et al., 1992).

Thermal analysis (TG-DTA) of the clayey material (Fig. 3) shows a weight loss of 5% at 98 °C due to the loss of hygroscopic water (Santamaría-López et al., 2022; Whitney and Evans, 2010). At 289 °C there is an inflection in the curve corresponding to the combustion of organic matter (Maritan et al., 2006; Nieto et al., 2008; Geng and Sun, 2018). At around 500 °C, a gradual dehydroxylation of the phyllosilicates begins to occur which continues until just below 714 °C (Touch et al., 2019; Achik et al., 2021; Eberhart, 1963). Between this temperature and 800 °C, the main weight loss of around 15% occurs, a value very similar to that detected by XRF (LOI, Table 4) and linked to the decomposition of carbonates and the release of CO_2 (Cultrone et al., 2001; Heller-Kallai and Lapides, 2015). The sample starts losing weight again at 841 °C, probably due to further dehydroxylation of the phyllosilicates (Rodriguez-Navarro et al., 2009; Rodriguez-Navarro et al., 2012; Cultrone et al., 2004). Finally, an exothermic peak is observed at 920 °C due to the formation of new crystalline phases (Dubacq et al., 2010; Hirono and Tanikawa, 2011; Eliche-Quesada et al., 2012a; Eliche-Quesada et al., 2012b), which will be described later by PXRD.

3.2. *Chemistry, mineralogy and texture of fired bricks*

3.2.1. *Weight difference and linear shrinkage*

Figure S1 shows the relationship between weight difference and linear shrinkage after firing. All samples show a shift downwards and to the right that is related to their composition.

Bricks without additives show a decrease in weight (from 4 to 6%) as the firing temperature increases. This trend is not observed in the bricks with added wine residues (Fig. S1). The bricks made with 2.5 wt% pomace are clearly lighter (approximately 10.5% lighter at all three firing temperatures) than the Mi bricks. This trend continues as the amount of additive is increased. Those made with 5 wt% wine pomace were up to 18% lighter than the control samples, while those made with 10 wt% pomace were 22–24% lighter. This weight reduction could represent an advantage for the construction industry in terms of cost savings, in that lighter bricks are cheaper to transport.

As regards linear shrinkage, all the bricks become shorter (Fig. S1). The control bricks show the least linear shrinkage and this is mainly due to the loss of the hygroscopic water still present in the samples and the dehydroxylation of phyllosilicates during firing (Taurino et al., 2019; Rodriguez-Navarro et al., 2003; Velasco et al., 2015). This is why the bricks fired at 1100 °C (−1.80 mm) shrink more than those fired at 800 °C (−1.07 mm). The shrinkage of the bricks that contain wine pomace is directly related to the amount of waste added to the clay

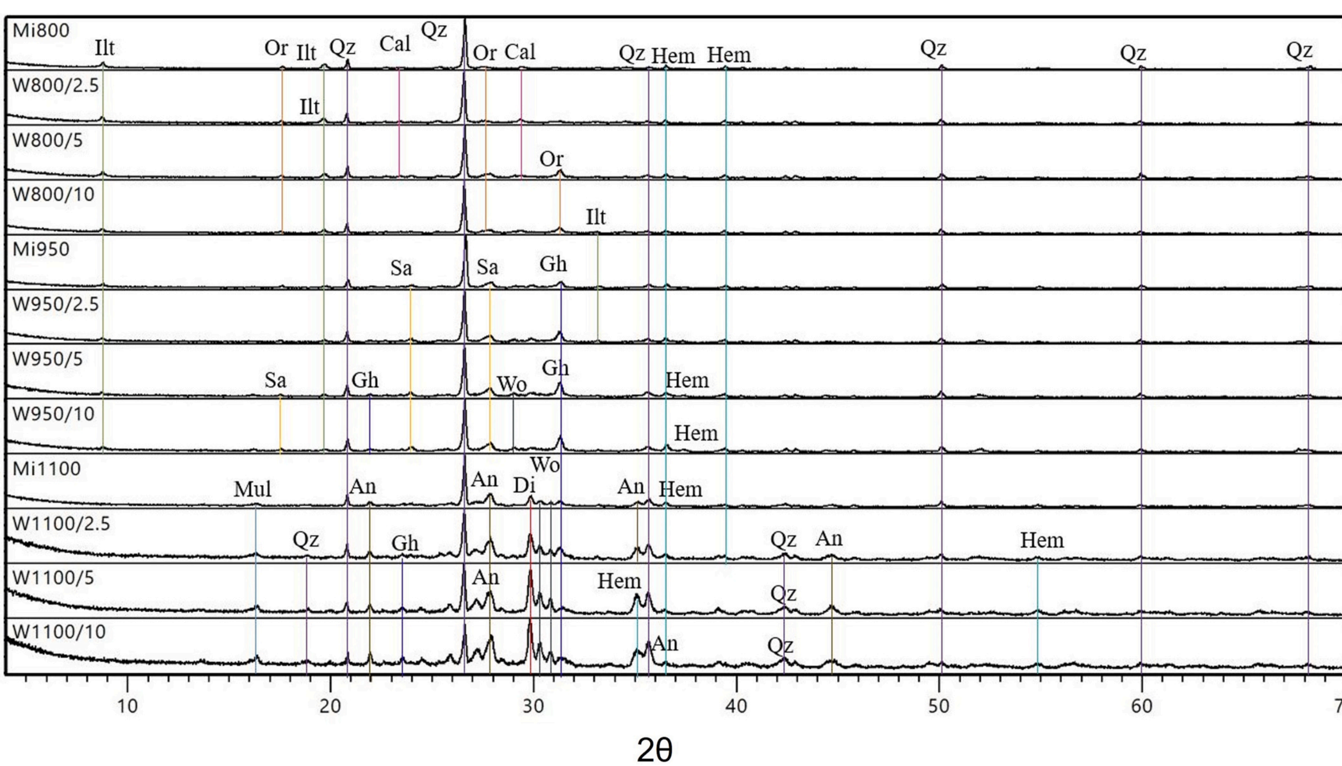

Fig. 4. PDRX patterns for control bricks (Mi) and bricks with added wine pomace (W) fired at 800, 950 and 1100 °C. Legend according to Whitney and Evans (Torres et al., 2020): Qz = quartz; Cal = calcite; Ilt = illite; Hem = hematite; Or = orthoclase; Sa = sanidine; An = anorthite; Gh = gehlenite; Di = diopside; Wo = wollastonite; Mul = mullite.

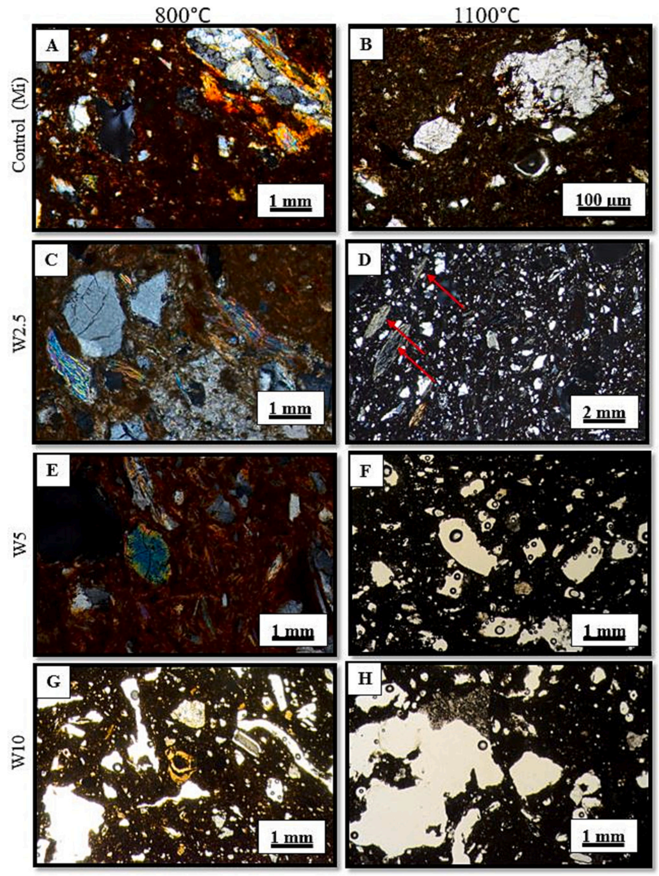

Fig. 5. Bricks with and without added wine pomace fired at 800 and 1100 °C. Abbreviation: PPL = plane-polarized light; PPX = cross-polarized light. A) matrix of sample Mi800 (PPX); B) detailed image of extended vitrification in the matrix of Mi1100 (PPL); C) phyllosilicate grains with a preferential orientation (PPX); D) muscovite-type crystals with a whitish colour (red arrows, sample W1100/2.5, PPX); E) unaltered phyllosilicates in W800/2.5 sample (PPX); F) ellipsoidal-to-rounded pores and darker matrix in W1100/5(PPL);G) decomposed carbonate grain in W10/800 sample (PPL); H) very large and rounded pores in W10/1100 sample (PPL). (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

mixture. The more the additive, the greater the shrinkage, which reaches a maximum value of −4.6 mm in samples with 10 wt% waste. These results are in line with those of other authors such as Barbieri et al. (Barbieri et al., 2013), Demir (Anjum et al., 2020) and Eliche-Quesada et al. (Hirono and Tanikawa, 2011), who reported that linear shrinkage depends more on the amount of residue used in the mix than on the firing temperature (Ngon et al., 2012). Our bricks all had shrinkage values of less than 8%, the maximum shrinkage value for producing good quality bricks, according to Laita et al. (Saenz et al., 2019).

3.2.2. *Mineralogical composition of fired bricks*

The evolution of the mineralogy of the bricks during the firing process determined by powder X-ray diffraction (PXRD) can be seen in Fig. 4. No substantial differences can be observed in the bricks fired at 800 and 950 °C. However, at 1100 °C an increase in background noise is detected, probably due to the development of amorphous phase (i.e. vitrification of the samples) and the crystallization of high temperature phases, which increase in concentration in line with the increase in the amount of additive used. This indicates that the calorific value of the wine pomace plays a key role in the reaction between the mineral phases to promote further development of new silicates.

At the three firing temperatures studied (800, 950 and 1100 °C), quartz (as the main crystalline phase) and feldspars *s.l.* are present in all the samples regardless of the amount of wine pomace added. At 800 °C, all the phyllosilicates have disappeared with the exception of a dehydroxylated illite, which can still be detected at 950 °C. Calcite is detected in very small amounts at 800 °C, but not at the higher temperatures. According to Rodríguez-Navarro et al. (Cultrone et al., 2001), calcite starts to decompose at 600 °C and disappears completely at 850 °C.

As for K-feldspar, the microcline detected in the raw material converts into orthoclase at 800 °C and sanidine at 950 °C and 1100 °C (Achik et al., 2021). Hematite, which was absent in the raw material, starts to appear in traces at 800 °C and increases in concentration as the firing temperature augments. It probably forms due to the decomposition of phyllosilicates, which favour Fe recrystallization (Eliche-Quesada et al., 2017). The decomposition of carbonates and their reactions with quartz and other silicates lead to the appearance of new Ca- (and Mg-) silicates such as gehlenite at 950 °C and wollastonite, anorthite and diopside at 1100 °C (Fig. 4). The presence of gehlenite in the bricks fired at 950 °C could explain the appearance of the exothermic peak detected in the DSC curve at 920 °C (Fig. 3).

At 1100 °C, gehlenite content falls because it is involved in the formation of anorthite and wollastonite (Achik et al., 2021). Another new phase, mullite, is identified. This phase replaces illite, with which it shares certain specific crystallographic orientations (Eliche-Quesada et al., 2012b).

3.2.3. *Structure of the fired bricks*

Polarized optical microscope (POM) observation of the samples fired at 800 °C revealed the presence of fragments of metamorphic rocks (quartz grains with undulose extinction, mica-schists and gneiss, Fig. 5A) of about 1 mm in length in an orange-to-brown matrix. As expected, higher porosity can be observed when residues with irregularly-shaped pores are added and it increases in line with the amount of residue added to the clay (compare Figs. 5A and B with Figs. 5C to G). Phyllosilicates and elongated fragments often show a preferential orientation due to the pressure exerted on the raw material during the kneading process (Fig. 5C). Phyllosilicates are composed of muscovite-type crystals and appear unaltered reaching second-order interference colour (Fig. 5C and E). The carbonate grains are partially decomposed and have lost their typical high interference colour (Fig. 5G). At 1100 °C, due to the high firing temperature, the pores become ellipsoidal-to-rounded in shape and the matrix becomes darker (Fig. 5B, D, F and H). Muscovite-type crystals have lost their birefringence and have a whitish colour (Fig. 5D, red arrows). According to Rodríguez Navarro et al. (Eliche-Quesada et al., 2012b) and the PXRD results (Fig. 4), this phyllosilicate has probably been replaced by mullite.

3.2.4. *Microstructure of fired bricks*

FESEM observations were carried out on the bricks fired at 800 °C (Fig, 6) and 1100 °C (Fig. 7) with and without 5 wt% wine pomace in order to highlight any textural differences between them.

Figure 6A (Mi800) shows a dense structure with lower porosity than Fig. 6B (W800/5) in which large pores with irregular shapes can be observed. These are due to the imprints left by the wine pomace particles (grape seeds, stems and skins) present in the clay mixture before firing. A detailed observation of the bricks made without (Fig. 6C) and with 5 wt % wine pomace (Fig. 6D) shows that they are compositionally very similar, which corroborates the previous XRF and PXRD analyses. K-feldspar (Fig. 6C) and quartz fragments (Fig. 6D) have been detected by EDS analysis. Fig. 6E is a zoomed version of Fig. 6B, in which we have recreated the imprint left by an elongated, cylindrical stem after firing of the brick.

Figure 7A (Mi1100) shows an even more compact structure than in Fig. 7A (Mi800) due to the vitrification process after firing the samples at 1100 °C, thus confirming the POM observations (see section 3.2.3.). Fig. 7B (W1100/5) shows the same level of vitrification level as in Fig. 7A (Mi1100), although the morphology of the surface is quite

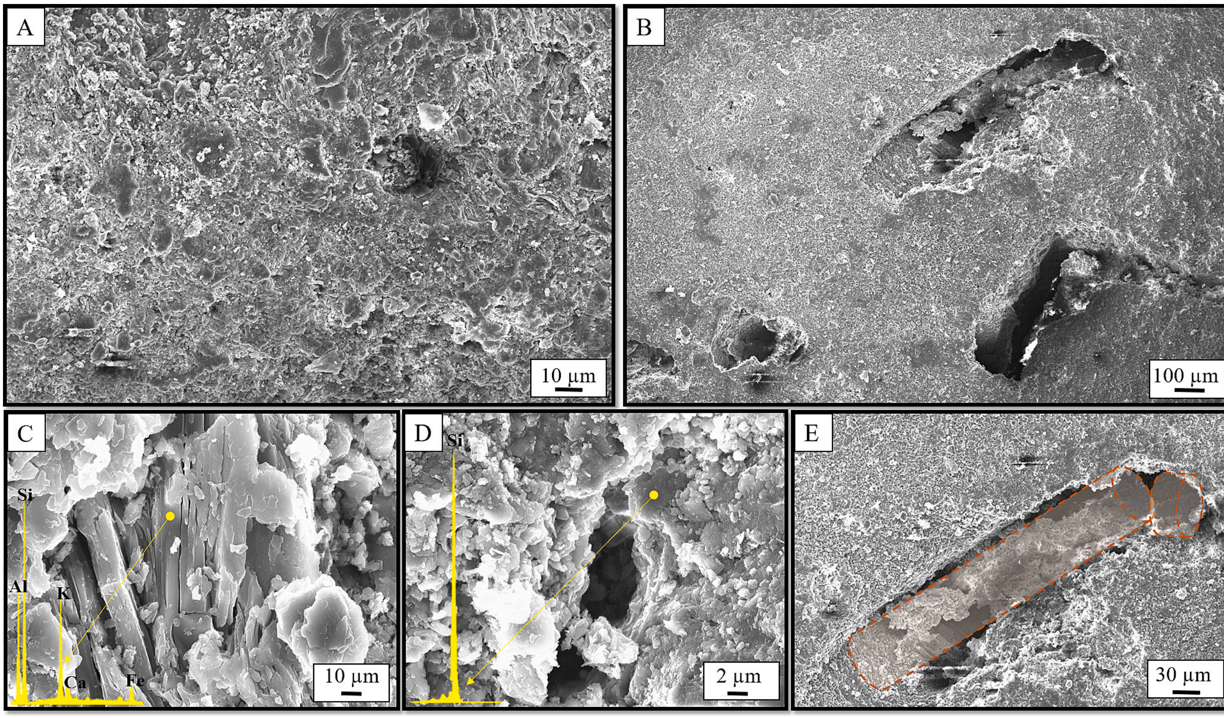

Fig. 6. FESEM images of bricks fired at 800 °C without additives (A and C) and with wine pomace (B, D and E). EDS spectra of some of the mineral phases have been included.

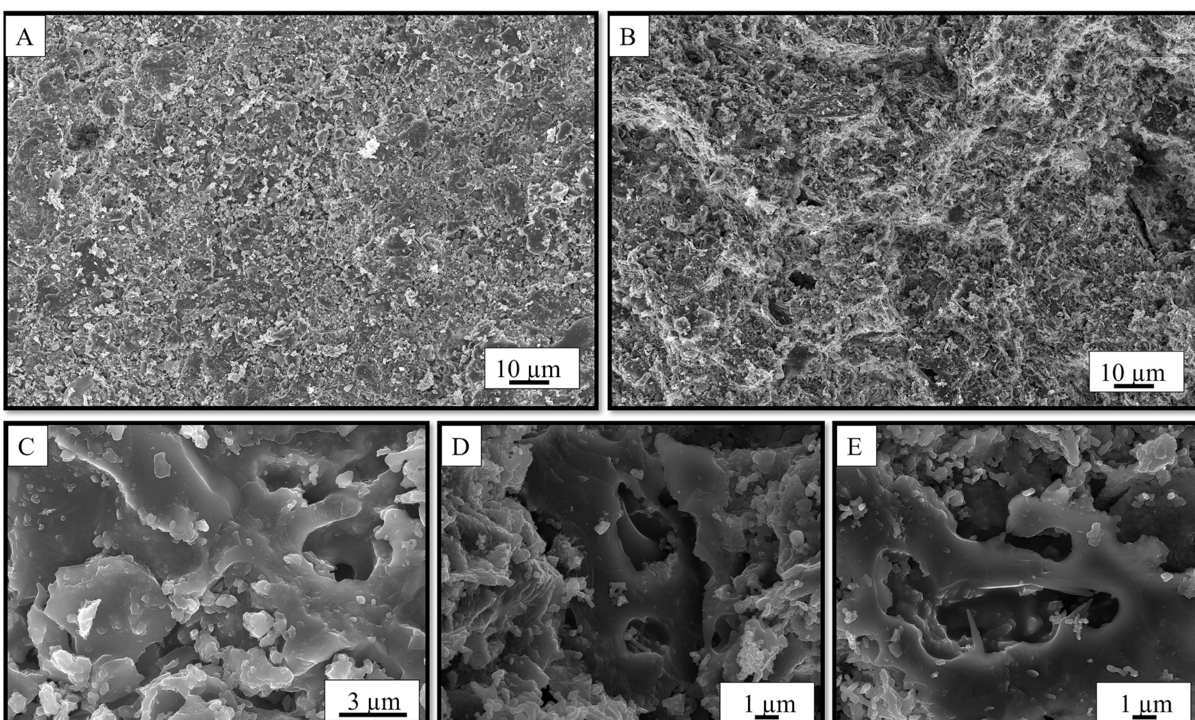

Fig. 7. FESEM images of bricks fired at 1100 °C made without (A and C) and with wine pomace (B, D and E).

irregular due to the presence of larger pores as a result of the addition of the wine pomace. Detailed images of the bricks fired at 1100 °C (Figs. 7C, D and E) highlight the presence of elongated and irregular-shaped pores, created by the vitrification of the matrix. Pores tend to coalesce forming larger pores and remain larger in the bricks with added wine pomace (Fig. 7D and E). The difference in the porosity of bricks made with and without wine pomace will be corroborated later by studying the pore system with hydric tests and MIP.

3.2.5. *Colour measurement of fired bricks*

The colour of bricks is mainly dependent on the composition of the raw material, the firing temperature and time, and the oxidant-redox

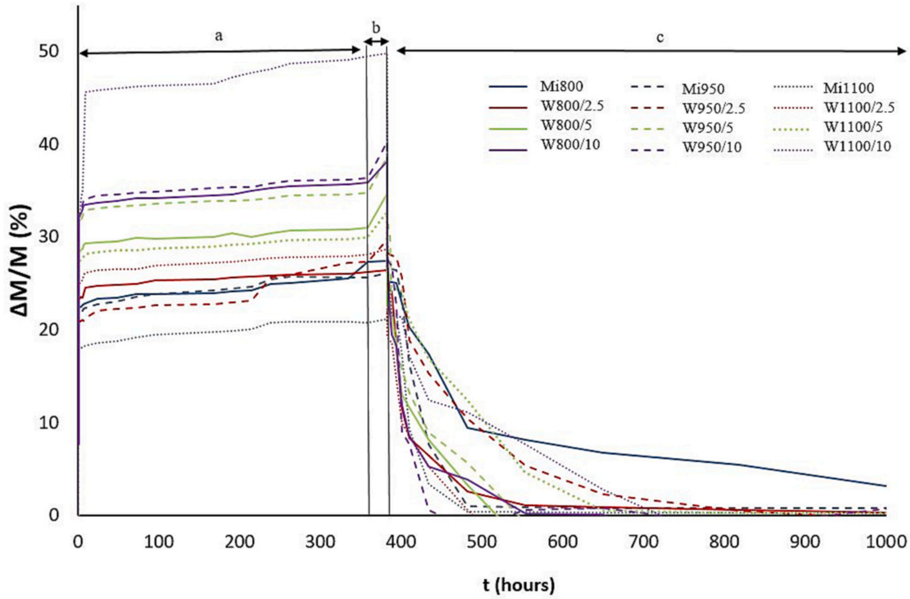

Fig. 8. Free (a) and forced water absorption (b) and drying curves (c) for bricks made without (Mi) and with wine pomace (W) fired at 800, 950 and 1100 °C.

Table 5
Hydric parameters of bricks. Ab: free water absorption (%); Af: forced water absorption (%); S: saturation coefficient (%); Di: drying index; P_o: open porosity (%); C: capillarity coefficient (g/m^2s^{05}); ρ_a: apparent density (g cm^{-3}); ρ_r: real density (g cm^{-3}). For sample acronyms, see Table 1.

	Ab	Af	S	Di	Po	C	ρ_a	ρ_r
Mi800	27.31	27.43	85.39	1.08	38.66	3.21	1.84	2.93
W2.5/800	26.18	26.40	84.05	1.49	40.95	3.34	1.71	2.88
W5/800	31.01	34.72	85.11	1.74	43.12	3.59	1.64	2.61
W10/800	35.87	38.10	88.94	1.96	44.41	3.66	1.52	2.50
Mi950	25.65	26.13	88.33	1.16	37.65	2.15	1.27	1.98
W2.5/950	27.29	29.71	74.78	1.19	38.96	2.28	1.20	1.74
W5/950	34.79	38.63	86.17	1.46	44.85	2.46	1.09	1.60
W10/950	36.42	40.27	85.97	1.87	48.28	2.71	0.98	1.57
Mi1100	20.81	21.14	88.97	1.57	30.73	2.09	1.59	2.61
W2.5/1100	28.10	28.76	91.93	1.64	37.94	2.15	1.42	2.54
W5/1100	29.94	32.60	87.49	1.74	42.97	2.54	1.25	2.36
W10/1100	49.47	49.74	92.59	1.93	52.64	2.69	1.04	2.75

environment inside the oven (Wang et al., 2020; Laita et al., 2021). The colour of bricks can also be modified by adding organic or inorganic compounds to the raw material (Weng et al., 2003; Bautista-Marín et al., 2021). In this research, the fired bricks are generally yellowish-red in colour, but there are certain differences between those made without additive and those made with (Fig.S2). The addition of wine pomace increases the lightness (L*) and decreases the chromatic coordinates (a*and b*) (Table 4). The results show that the increased lightness in samples with wine pomace appears to be linked to the increase in firing temperature. Conversely, the decrease in the values of the chromatic coordinates, especially in those linked to the red colour (a*) could be related to changes in the size of the crystallized hematite particles, which give the bricks their reddish hue (Rathossi and Pontikes, 2010; Ordieres and Cultrone, 2022; Crespo-López and Cultrone, 2022).

The differences in colour between the control samples and those made with wine pomace augment with the firing temperature, varying between 1.5 and 2.8 (ΔE, Table 4). According to Mokrzycki and Tatol (Wang et al., 2022), this means that bricks with added pomace fired at 800 °C can only be distinguished from those without additive by an experienced observer, while those fired at 950 and 1100 °C can also be recognized by inexperienced observers. These results are particularly important in the construction sector, as colour is an essential feature of the first impression that the consumer gains of any brick and can strongly influence their choice.

3.3. Hydric tests

As expected, the porosity and water absorption of the bricks increase in line with the amount of residue added (Fig. 8 and Table 5). This indicates that the addition of pomace has a more substantial effect on the hydric behaviour of the bricks than the firing temperature. In particular, control bricks (Mi) absorb less water (Ab decreases from 27.3% at 800 °C to about 21% at 1100 °C, Table 5) as the firing temperature increases. The same trend is observed when water absorption is forced under vacuum (Af, Table 5). The open porosity values also fall (Po, Table 5). This is due to a gradual vitrification of the matrix and, if we look at the curves for the Ab and Po values, it seems more pronounced from 950 to 1100 °C than from 800 to 950 °C. Other researchers found that in the raw materials that contain carbonates, the vitrification process does not occur at the same gradual rate throughout, but is slow at low firing temperatures (a stable structure is created) and then accelerates as high temperatures are reached (Rodriguez-Navarro et al., 2009; Wang et al., 2022; Clifford, 1984; Mokrzycki and Tatol, 2011). However, this does not happen when wine pomace is added. In fact, these bricks are more porous and absorb more water as firing temperature increases (Table 5). The large pores left by organic fibres in the wine pomace already observed under FESEM (Figs. 6 and 7) clearly affect the hydric properties of the bricks, not only by increasing their water absorption capacity, but also by improving water flow as the matrix sinters and vitrifies. The high calorific value of the residue used in this research may have favoured a partial fusion of the matrix around the fibres, so improving the connectivity between the capillaries. The observation that bricks made with and without additives have quite different hydric behaviour is confirmed by the drying index (Fig. 8). While the control bricks tend to dry more slowly as firing temperature increases (Di augments, Table 5), those made with wine pomace showed similar drying index values at all 3 firing temperatures, with a slight improvement at 950 °C (Table 5). As for capillarity (C, Table 5), the bricks tend to absorb water faster as the temperature increases and as the amount of wine pomace decreases. The control bricks have the highest C values. This is because the capillaries are larger in the bricks with added organic matter in which water rises more slowly (Tarvornpanich et al., 2008; Gliozzo, 2020). And the more organic matter added, the greater the proportion of larger capillaries in the bricks, and the slower the capillary rise. No clear trend is observed

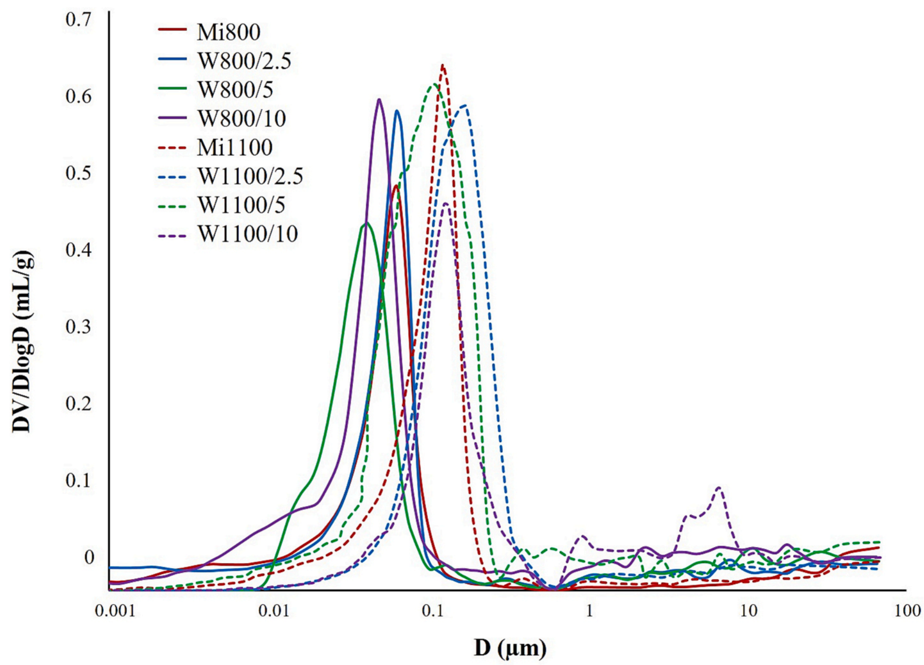

Fig. 9. MIP curves for bricks fired at 800, 950 and 1100 °C without additive (Mi, continuous line) and with added wine pomace (W, dashed line).

Table 6
MIP parameters for bricks without additive (Mi) and with added wine pomace (W) fired at 800 and 1100 °C. SSA = specific surface area (m^2/g); ρ_{aMIP} = apparent density ($g \cdot cm^{-3}$); ρ_{rMIP} = real density ($g \cdot cm^{-3}$); Po_{MIP} = open porosity (%).

	SSA	ρ_{aMIP}	ρ_{rMIP}	Po_{MIP}
Mi800	9.64	1.40	2.03	27.49
W800/2.5	1.21	1.11	2.11	36.60
W800/5	2.63	1.16	2.29	38.52
W800/10	2.11	1.34	1.98	41.43
Mi1100	7.21	1.45	2.55	36.65
W1100/2.5	1.04	1.36	2.40	39.67
W1100/5	0.84	1.22	2.36	46.53
W1100/10	0.84	1.14	1.93	51.61

Table 7
Average UPV ($\bar{x}$Vp, in m/s) and compressive strength (CS, in MPa) values for handmade bricks made without (Mi) additive and with added wine pomace (W). σ is the standard deviation of $\bar{x}$Vp and CS values.

	$\bar{x}$Vp	σ	CS	σ
Mi800	2534	2.31	7.8	4.52
W800/2.5	2447	6.47	6.2	2.50
W800/5	2164	7.89	3.0	1.14
W800/10	861	10.55	2.1	1.64
Mi950	2576	3.74	10.1	7.92
W950/2.5	2400	7.85	6.9	2.22
W950/5	2371	7.94	5.5	9.45
W950/10	1147	12.33	3.5	7.10
Mi1100	2823	4.11	15.2	7.22
W1100/2.5	2676	5.23	12.3	9.41
W1100/5	2500	6.93	9.5	1.52
W1100/10	1053	13.08	6.7	2.43

regarding the saturation coefficient (S, Table 5). It is quite similar in brick samples and ranges from 75 to 93% ca. The increase in the amount of wine pomace always leads to the reduction of apparent density (ρ_a, Table 5). Real density (ρ_r) also appears to be affected at least in part by the addition of this organic matter. At 800 and 950 °C, real density fell as the % of additive increased. However, this tendency was not observed at 1100 °C.

3.4. Mercury intrusion porosimetry (MIP)

The MIP analysis highlights the way the addition of wine pomace modifies the pore system of the bricks in terms of open porosity and pore size distribution. All bricks show unimodal pore size distribution at around 0.1 μm with the exception of W1100/10, where a second family of pores can be clearly observed in the 0.08–0.12 μm range (Fig. 9). This second group was made up of the voids left by the organic particles after firing, as revealed in FESEM observations (Figs. 6 and 7).

When comparing bricks fired at 800 and 1100 °C, the maximum peak always shifts towards larger pore sizes as the firing temperature increases. The porosity of the bricks increases with the percentage of wine pomace and also with the firing temperature (Po_{MIP}, Table 6), thus confirming the results of the hydric tests. This suggests that at 1100 °C, the small pores coalesce into new, larger ones, as the FESEM images showed (Figs. 7C, D and E). In fact, the specific surface area decreases at 1100 °C, above all in bricks with added wine pomace, reaching 0.84 m^2/g for the bricks with 5 and 10% (SSA, Table 6). These data confirm what was previously suggested in the hydric tests, i.e. that the combustion of the fibres in the wine pomace improves the connectivity between the pores. The porosity and density values measured by MIP are in line with those calculated in the hydric tests. Any differences between these two techniques are probably due to the use of two liquids with different intrusion pressures and different physical properties.

3.5. Ultrasonic pulse velocity (UPV) and compressive strength (CS)

Table 7 shows the average values for ultrasound velocities (Vp_1, Vp_2 and Vp_3) and compressive strength measured in bricks made with and without added wine pomace. It is commonly reported that UPV values in bricks increase in line with increasing firing temperature, so indicating a stronger structure due to vitrification and densification of the matrix (Cultrone et al., 2020; Achik et al., 2021). If we analyse the bricks with wine pomace, Vp decreases in line with increases in the percentage of additive, a logical result given the increased porosity of these bricks (see hydric and MIP values in Tables 5 and 6). The lowest Vp value was for the samples containing 10 wt% residue (Table 7). Note how the standard

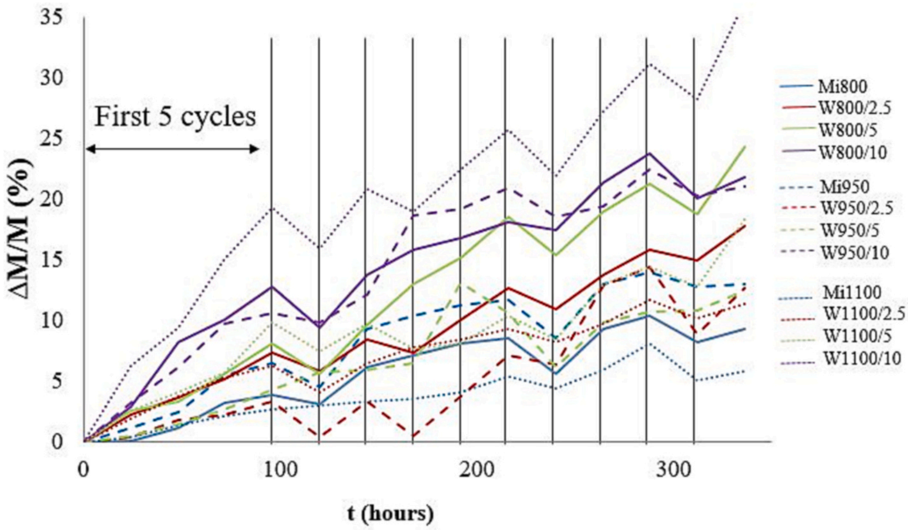

Fig. 10. Salt crystallization diagram for bricks made with and without wine pomace added and fired at 800, 950 and 1100 °C. Weight variation (ΔM/M) vs. time (in hours).

deviation (σ, Table 7) follows an opposite trend: σ increases in line with the amount of additive. This increase in σ is probably due to the fact that as the amount of wine pomace increases, mixing the pomace with the clayey material during the moulding process becomes more and more difficult. This leads to the appearance of more voids when the bricks are fired, which in turn cause greater standard deviation in the UPV values.

The bricks with the highest mechanical strength are the control bricks. This parameter increases in line with firing temperature reaching the highest value at 1100 °C (Mi1100 Table 7). The wine pomace reduces the strength of the bricks due to their increased porosity, such that the higher the residue content, the lower the mechanical resistance. The lowest compressive strength value is obtained by W10/800 (2.1 MPa, Table 7). According to the RL-88 (Dacuba et al., 2022) standard, the minimum strength value recommended for bricks for use in building work in Spain is 10 MPa. The only bricks that meet this requirement are those fired at 1100 °C and those without additives fired at 950 °C. However, according to the same standard, bricks with a compressive strength of at least 5 MPa may be used as lightweight bricks in construction. In this case, only the bricks fired at 800 °C with 5 and 10 wt% waste and those fired at 950 °C with 10 wt% should be excluded. If we compare the mechanical strength values of these bricks with those obtained in other studies in which organic matter was added (Cultrone and Sebastián, 2009; Eliche-Quesada et al., 2012a; Taurino et al., 2019; Bautista-Marín et al., 2021), our values are lower, especially at 800 and 950 °C. This means that lower concentrations of wine pomace or higher firing temperatures must be considered if we want to obtain mechanically stronger bricks.

4. Salt crystallization test

During the salt crystallization test, all the bricks show an increase in weight during the first five cycles, which is probably due to the deposition of sodium sulphate inside the pores (Fig. 10). This initial increase in weight varies depending on the type of bricks tested, in that the bricks with the highest amount of added residue (W800/10, W950/10 and W1100/10) show the greatest weight increase. This confirms the results of the hydric tests (see section 3.3) where the bricks without additives gained the least weight.

A decrease in weight can be observed in the following two cycles. This decrease can be attributed to the loss of brick fragments because of the crystallization of salt crystals in confined spaces. As the test progresses, continuous fluctuations of the curves can be observed with increases and losses in weight respectively linked to the crystallization of the salt in new fissures generated by the crystallization pressure and to the consequent loss of new fragments (Fig. 10). At the end of the test, the bricks with 10 wt% wine pomace are those that suffer the highest weight variation and weight increase.

5. Conclusions

In this paper, we assessed the physical-mechanical behaviour of lightweight bricks made with a clayey material rich in quartz and phyllosilicates and a smaller amount of carbonates, which was mixed with wine pomace at three percentages (2.5, 5 or 10 wt%). The samples were fired at 800, 950 and 1100 °C. The addition of the wine pomace did not affect the mineralogy of the brick samples. The wine pomace reduced the linear shrinkage of unfired samples and the samples were lighter after firing due to the consumption of this organic matter. The mineralogical changes that occur during firing were directly related to the composition of the raw material and were not affected by the addition of wine pomace.

In terms of texture, particles in the wine pomace were consumed during firing, which led to the appearance of voids. The bricks fired at 1100 °C are highly vitrified and have the highest compactness and lowest open porosity values. Conversely, the addition of wine pomace caused a fall in ultrasonic velocity. It also increased the water absorption capacity and open porosity of the bricks, while impairing their mechanical properties. The organic fibres in the wine pomace affected the hydric behaviour of the bricks, not only by increasing their water absorption capacity, but also by improving water flow within the pore system. The addition of wine pomace influenced the lightness and the chromatism of the bricks, which ranged from reddish to yellowish depending on the amount of additive added and the firing temperature. It also reduced the mechanical strength of the bricks, especially at low firing temperatures. Suitable resistance values for use in construction work in Spain (10 MPa) are only reached at 1100 °C, when the samples are highly vitrified. However, the same standard allows bricks with a compressive strength of at least 5 MPa to be used as lightweight bricks in the construction industry. Most of the bricks studied here would meet this requirement. In terms of durability, the bricks made with the largest amount of additive suffer the highest variation in weight due to salt crystallization. This means that when used in a building they would be more vulnerable to damage from salt attack.

The advantage of reusing wine pomace in the brick industry is demonstrated by analysing the data on bricks produced and wine pomace generated in Spain. In 2019 (latest available data from the

Geological and Mining Institute of Spain, IGME, https://www.igme.es/), 7.4 million tonnes of clay soils were extracted for the ceramic industry with an approximate value of 36.2 million euros. Of these clays, 4.3 million tonnes were destined for the manufacture of bricks, representing a value of 21 million euros. Regarding the amount of wine pomace generated per year (1 million tonnes, see Introduction section), the replacement of the clay material with up to 10% by weight of wine pomace would represent a maximum saving of 2 million euros and the use of 43% of this waste by the brick industry. The wine pomace is at no cost, so the only expense is the transportation of the waste to the brick factories. The vineyard area in Spain is almost 1 million hectares (www.oiv.int), the largest in the world, which extends mainly in the flat and hilly areas of the Iberian Peninsula. These are the same areas where the brick factories are located, so the approximate average distance between the wine factories and the 130 brick factories registered in 2022 (www.hspalyt.es) is estimated at 100 km. Thus, the cost of the fuel used to transport the waste would be relatively low, certainly lower than the benefit produced by making bricks with wine pomace. Therefore, this common waste in some countries, especially those in the Mediterranean area, can be efficiently used in brick production by combining it with local natural resources.

The research carried out here has shed more light on the possible use of wine pomace in the production of lightweight bricks for use in the construction industry. This could lead to environmental benefits by reducing the amount of clay required in brick production and by usefully disposing of the pomace, a waste product that might otherwise end up in landfills.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Data availability

Data will be made available on request.

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Appendix A. Supplementary data

Supplementary data to this article can be found online at https://doi.org/10.1016/j.clay.2023.107084.

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