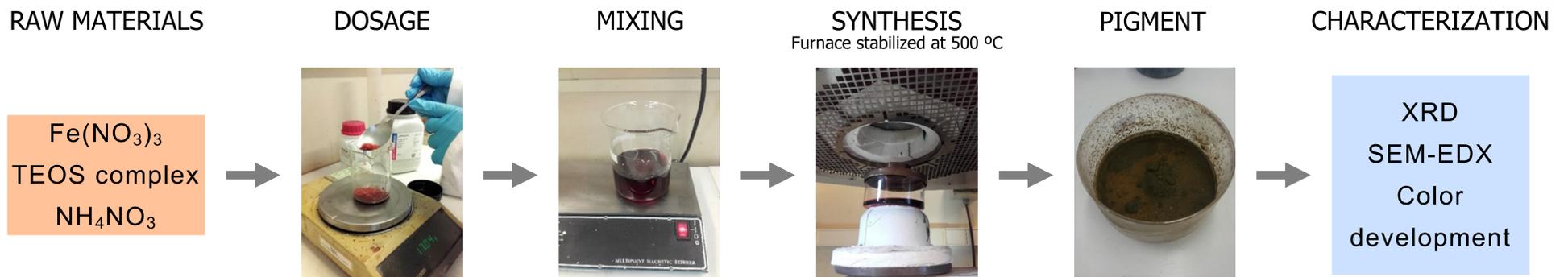


## Introduction

The synthesis of ceramic pigments is an energy-intensive process due to the high maximum temperatures required, as well as the long residence times involved in the reactions between solids. Therefore, alternative methods have been sought to synthesise pigments at lower temperatures or using shorter times. Solution combustion synthesis (SCD) is a technique that allows the synthesis of ceramic materials from an aqueous solution of precursors (typically nitrates) and a fuel (urea, glycine, etc.), in very short times (typically minutes) and with a moderate starting temperature of the process (300-500 °C)<sup>1</sup>.

Grès de Thiviers is a natural pigment used to impart reddish colours to ceramics. Nowadays a synthetic analogue is used to colour porcelanized stoneware. This synthetic pigment is obtained by thermal treatment of a mixture of iron oxide and a silica precursor<sup>2</sup>. In this case, the analogue has been synthesized by SCD from an aqueous solution of iron nitrate, a complex of TEOS with an organic ligand and ammonium nitrate as oxidiser. Four reddish pigments were obtained with iron/silicon molar relations ( $\psi$ ) between 0,05 and 0,20.

## Experimental



## Results

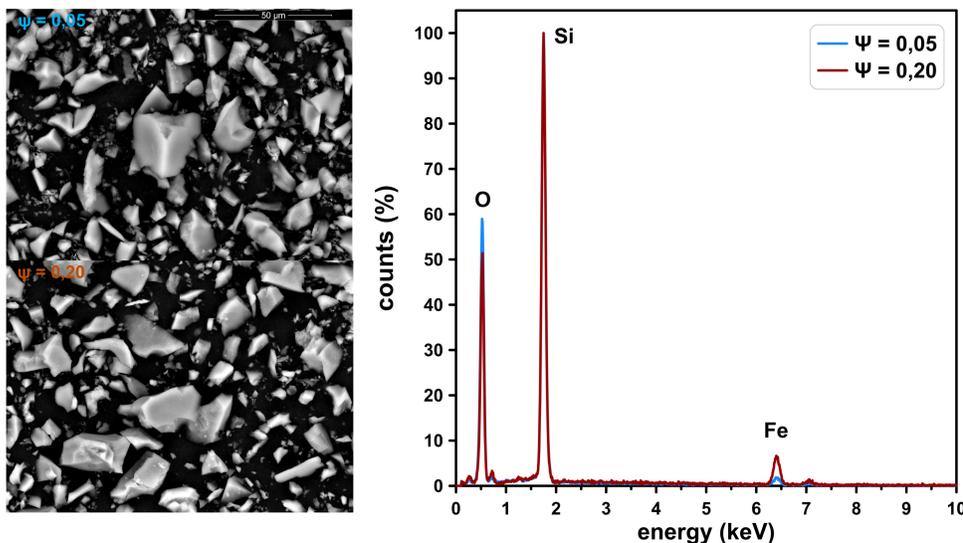


Figure 1: SEM images of the pigments with  $\psi = 0,05$  and  $\psi = 0,20$  and EDX analysis of them.

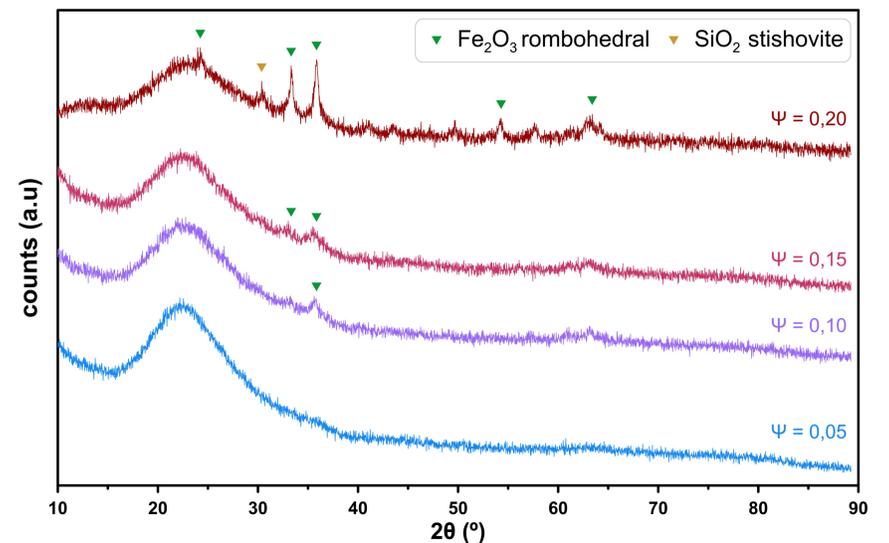


Figure 2: Diffractograms of the four pigments, which are mainly non-crystalline materials.

The pigment particles have the aspect of a broken glass, with signs of conchoidal fracture, a fact that points to an amorphous structure. In fact, the homogeneous aspect of the particles points to a good homogeneity in the chemical composition. There are no significant changes in aspect between the samples with  $\psi = 0,05$  and  $\psi = 0,20$  which implies that a separate iron-rich phase is not formed. However, the EDX demonstrates a clear difference in the iron content between the two samples.

XRD confirmed the mostly non-crystalline nature of the pigments as the amorphous silica band is their main feature. Some weak reflections of crystalline phases appear as the pigments are progressively richer in iron. Those reflections have been tentatively assigned to a rombohedral form of  $\text{Fe}_2\text{O}_3$  and to a stishovite (high pressure form of silica) as they are very few and weak to obtain a conclusive identification

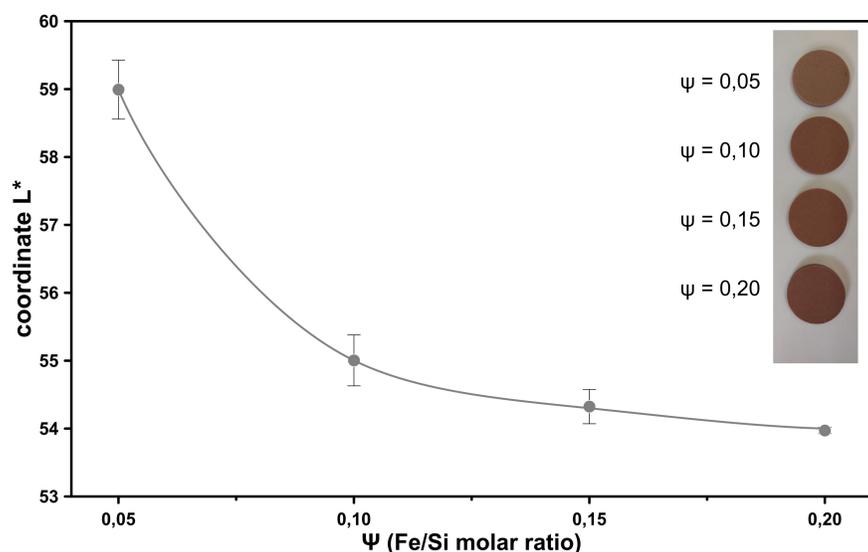


Figure 3: Evolution of chromatic coordinate  $L^*$  (luminosity) of the fired porcelanized stoneware samples as a function of Fe/Si molar ratio in the incorporated pigment. An image of the samples is included.

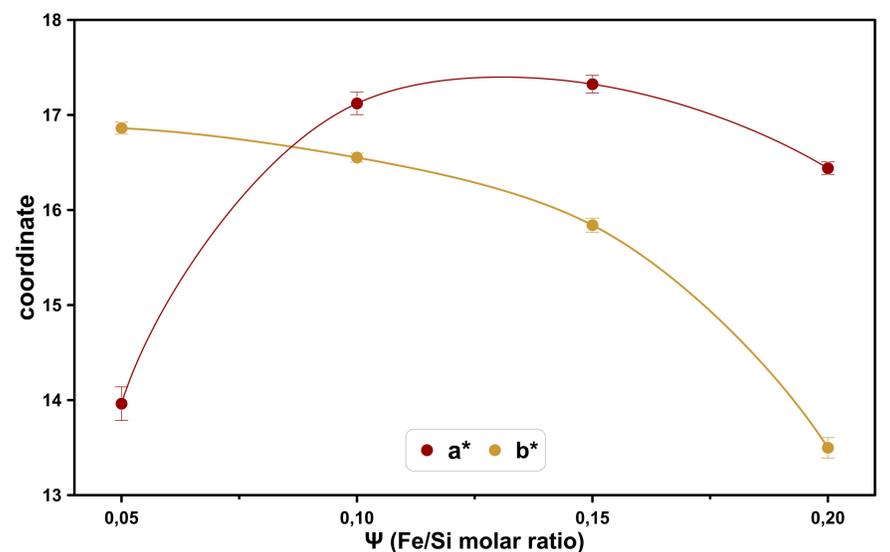


Figure 4: Evolution of chromatic coordinates  $a^*$  (red) and  $b^*$  (yellow) the fired porcelanized stoneware samples as a function of Fe/Si molar ratio in the incorporated pigment.

The incorporation of pigments into porcelanized stoneware generated a palette of reddish colours as expected. As the proportion of Fe increases, luminosity initially decreases significantly, but a trend towards stabilization is detected for molar relations higher than  $\psi = 0,10$ .

The coordinate  $a^*$  increases with iron content until it reaches a maximum around  $\psi = 0,15$ . By contrast,  $b^*$  coordinate decreases with iron content, but the trend is more pronounced for higher iron contents. As a result, the highest red coordinate value is obtained for  $\psi = 0,15$  but the highest red/yellow coordinate ratio corresponds to  $\psi = 0,20$ .

## Conclusions

- An analogue of the “Grès de Thiviers” pigment has been obtained by solution combustion synthesis from an aqueous solution of precursors.
- The pigments are mostly amorphous and show a homogeneous distribution of iron.
- The pigments show a high colouring power in porcelanized stoneware, generating reddish colours.
- The most intense colours are obtained for iron contents corresponding to  $\psi = 0,15-0,20$

## References

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2. V. Bagán et al. Pigmentos con base de sílice y óxido de hierro, y método para su producción. EP1182234 A1 (27.02.2002).

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