UNIVERSITAT POLITÈCNICA DE VALÈNCIA

Escuela Técnica Superior de Ingeniería del Diseño

DEVELOPMENT OF PHOTOVOLTAIC AND ENERGY EFFICIENY SOLUTIONS VIA INK-JET PRINTING ON CERAMIC SUBSTRATES

FINAL DISERTATION OF: Degree in Electrical Engineering

DONE BY: Ián Fausto Zanchetta Chittka

TUTORISED BY: Javier Orozco Messana & Ronan Daly

DATE: September 2019

INDEX

1. Abstract 3

2. Objectives 4

3. Introduction 5

3.1. Present of ceramic tile industry 5

3.1.1. Ceramic tile sector in the international market 5

3.1.2. Ceramic tile sector in Spain 8

3.1.3. Inkjet printers in the ceramic tile industry 11

3.2. Innovations in ceramic tile industry 16

3.2.1. Ceramic tiles as energy efficient solutions in edification 18

3.3. Development of new applications for ceramic tiles via inkjet printing of conductive materials 25

4. Scientific foundations 27

4.1. Porcelain stoneware tiles 27

4.1.1. Characteristics and properties of porcelain stoneware tiles 27

4.1.2. Composition of porcelain stoneware tiles 30

4.1.3. Production process of porcelain stoneware tiles 38

4.2. Inkjet printing technology systems 44

4.2.1. Working principles 44

4.2.2. Characteristics and types of inks 48

5. Experimental procedure 57

5.1. Preparation, pressing, sintering and characterisation of porcelain stoneware substrates 59

5.1.1. Preparation and pressing of the ceramic porcelain stoneware substrate 61

5.1.2. Characterisation of porcelain stoneware substrates 69

5.2. Printing of inks over green porcelain stoneware substrates with an inkjet technology printer and characterisation 70

5.2.1. Printing of water-based inks 71

5.2.2. Printing of solvent-based inks 76

6. Analysis of results and discussion 78

6.1. Analysis of ceramic substrate 78

6.2. Analysis of printed water-based inks on the substrate 85

6.2.1. Analysis of spreading and penetration of water glycerol dye ink printed patterns 85

6.2.2. Analysis of spreading, penetration and conductivity of graphene water-based ink printed patterns 93

6.3. Analysis of printed solvent-based inks on the substrate 98

6.3.1. Analysis of spreading, penetration and conductivity of silver solvent-based printed patterns 98

7. Conclusions 122

8. References 125

1. Abstract

The ceramic tile industry has become a very competitive market. Europe, which in the past was the leader in ceramic tile production, is now challenged by the expansion of other ceramic industries all over the world, such as China, India, Brazil, Turkey and Vietnam. This rivalry between countries all around the world, has been stimulating the development of new technological advancements in such industry over the last twenty years.

One of the latest and most important technological advancements has been the introduction of digital inkjet printers into the production chains of ceramic tile industries, which has been revolutionising the ceramic decoration sector ever since its introduction during the beginning of the 20th century, with Spain and Italy as pioneers. Moreover, inkjet printers have also proved their suitability and efficiency for production of printed electronics and printing of functional materials. This kind of technological developments and the integration of functionalities onto ceramics is becoming key for tile producers as will be shown later.

Thus, the aim of this project is to incorporate and embed conductive patterns in porcelain stoneware tiles by using a drop-on-demand inkjet printer, in order to design solutions to facilitate the integration of photovoltaic, energy storage and energy efficiency technologies in ceramic tiles. In order to control and analyse spreading and penetration of the ink on the substrate, the optimal inks for the purpose will be selected in order to achieve optimal results and initiate the industrial validation process later.

This is a first step that when achieved will foster different new applications and possibilities for the development of ceramic tiles with technological added value in the ceramic tile industry in Valencia (Spain).

2. Objectives

In pursuance of the development of such solutions for the integration of functionalities such as photovoltaic generation and energy storage in ceramic substrates, specific objectives were set so as to establish an organised approach towards the buildout of such solutions:

- Production of ceramic substrates with a quality similar to porcelain stoneware ceramic tiles found in the ceramic industry, formed by dry pressing of an atomised ceramic powder and subsequent sintering.

- Printing of good quality patterns and embedding of functional materials such as conductive inks with an ink-jet printer for the production of embedded electrodes, conductive tracks and even micro-capacitors within the ceramic structure.

- Analysis and evaluation of ink/substrate interaction processes such as spreading and penetration and comparison of results between the different utilised inks.

- Analysis of the effect that sintering process of the ceramic substrate has over the integrity and conductivity of printed and embedded materials via inkjet printing.

3. Introduction

3.1. Present of ceramic tile industry

3.1.1. Ceramic tile sector in the international market

The ceramic sector, as every other industrial sector is submitted to great global challenges and risks. Between the main risks and uncertainties that ceramic companies and corporations have to deal with, the most significant ones are the increase of the cost of raw materials, the cost of labour and energy as well as the transport and provision of materials and components, the difficulty to respond efficiently to the constant technological changes, the intense competence in the global market and different legal and environmental impacts derived from national regulations, as well as a generalised increasing public awareness and increasing social and governmental demand for environmental sustainability. **[1]**

In order to overcome these, the ceramic sector is consequently forced to develop certain strategies to deal with the different necessities in the areas of industry dimension, innovation and global market. Therefore, over time, companies in the sector have invested in the areas of sales, distribution and logistics, as well as invested on the growth of companies in order to increase the production capability. Moreover, another common strategy is for companies to secure the presence and growth in specific markets, both local and international by investing in new plants or investing in the modernization of already existing plants in such markets. However, investment in innovation and efficiency upturn has become a critical strategy, since product price and quality are the main elements which define the competitivity in the global market.

Thus, it is possible to see how the ceramic sector is attached to a complex array of factors, the development of which determines the evolution of the industries in the global market.

Ceramic tile production per country					
Country	**2013 (mill. m2)**	**2014 (mill. m2)**	**2015 (mill. m2)**	**2016 (mill. m2)**	**Global production in 2016 (%)**
1. China	5700	6000	5970	6495	49,7
2. India	750	825	850	955	7,3
3. Brasil	871	903	899	792	6,1
4. Spain	420	425	440	492	3,8
5. Vietnam	300	360	440	485	3,7
6. Italy	363	382	395	416	3,2
7. Indonesia	390	420	370	360	2,8
8. Turkey	340	315	320	340	2,6
9. Iran	500	410	300	330	2,5
10. México	230	230	242	267	2,0
Rest of the world	2094	2103	2129	2124	16,3
Total	11958	12373	12355	13056	100

Table 1: Ceramic tile production per country from 2013 until 2016. Note: adapted from "El sector del azulejo", p. 20, 2018. [Online] Available: https://www.kpmg.es

In 2016, the global economy expanded a 2,2% as the lowest growth rate since 2009. This slow growth rate is due mostly to the low prices of raw materials and the geopolitical conflict and problems which have been taking place for the past years.

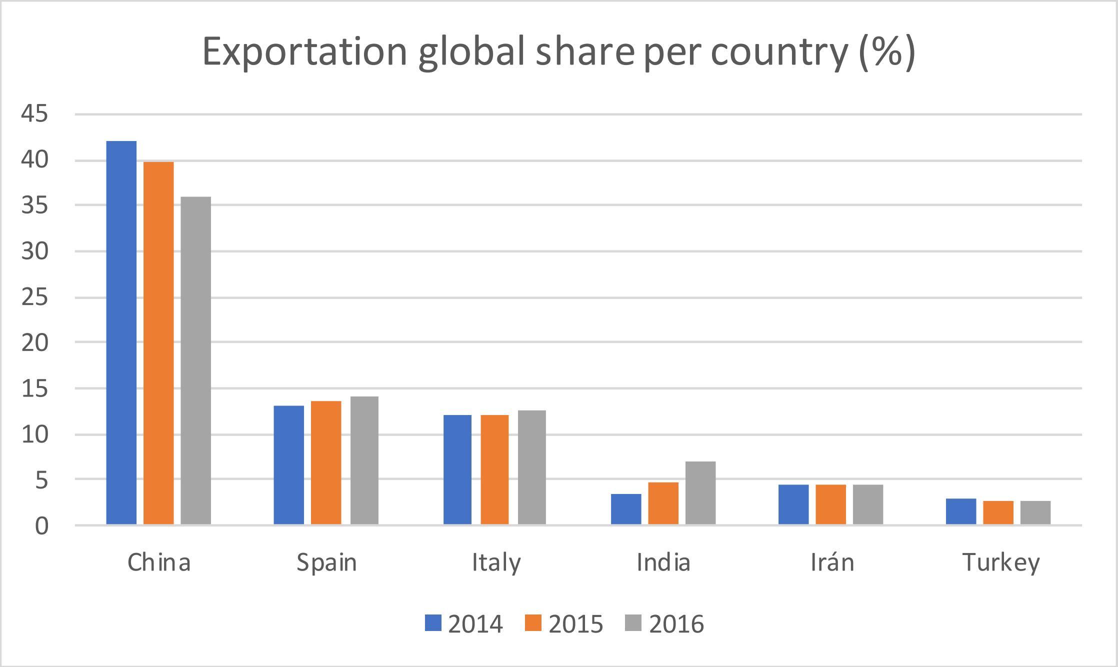


Table 2: Exportation global share per country. Note: adapted from "El sector del azulejo", p. 22, 2018. [Online] Available: https://www.kpmg.es

On the other hand, as it can be seen in ***table 1*** the global production in the ceramic sector increased a 5,7% in 2016. From the overall production, Spain lays in the 4th place with a 3,8% and China lays as the leader with a 49,7% of the production. In total, Asia was responsible for 71,5% of the global production. In relation to consumption, Asia represented a 69% of the global consumption with an of 8% respect the year before, being the consumption concentrated mostly in China, India and Vietnam.

Lastly, in the area of exportations and as shown in ***table 2***, the ceramic sector experimented a growth of 2,2%. Asia was responsible for a 54,2% of the global exportations with a 36,7% of it corresponding to China, whose exportations suffered a decrease of 5,9%. In comparison, the European Union was responsible for 37,6% of the total exportations, with a 14,2% corresponding to Spain and 11,7% corresponding to Italy with a total annual growth of the sector in the UE of 5,5%, positioning it as the geographical zone with the highest growth rate.

As a synthesis, we find a global market in which Asian countries have been experimenting an enormous growth in production, such that the ratio between Asian and European production has evolved from a 3 to 1 ratio in 2008 to a 7 to 1 ratio today. With China as the lead producer in the Asian sector, we can also see how it is not only the largest producer and exporter, but also the largest exporter. On the other side, African countries are the ones which show the highest growth rates in the global market and in Europe, even though China is expanding its reach around the world, Spain and Italy are still maintain leading positions in certain markets in which they have traditionally been the main sellers.

3.1.2. Ceramic tile sector in Spain

In Spain, ceramics have been developing since the 13th century, with the arrival of Islamism to the peninsula. Since then, the production of ceramics started to move towards the Valencian Community and in the 15th century, the Spanish ceramic products originating from this zone (particularly from Manises) were already famous around various parts of the world, exporting to countries such as Egypt, Turkey, Syria and Venice and even providing ceramics for the pavement of the Papacy. This was the beginning and consolidation of the bases for the ceramic sector in Spain; during the next 500 years this industry gradually extended its production, whilst improving the quality of the materials and processes, mostly during modern times, with the introduction of more efficient, cheaper, less contaminant and bigger systems for the sintering of ceramics, boosting a constant economic growth until today. Traditionally, ceramic production in Spain has been mainly located in the east coast, and mostly concentrated in the province of Castellón; 80% of the enterprises in this sector are located here, accounting around 90% of the overall production in the country. Such concentration has led to the formation over the years of an important cluster of ceramic companies with very similar characteristics which also count with the support of nearby auxiliary industries and organizations. These last mentioned include from suppliers of materials, components and machinery, which reduces costs in transport and provisioning for example, to public and private organizations such as universities, investigation centers and other institutions, facilitating technical services and driving the introduction of new technologies to the production system **[2]**.

This is the case for instance of the Instituto de Tecnología Cerámica (ITC), born in the 60s due to an agreement between the University of Jaume I of Castellón and the Association of Investigation of the Ceramic Industries, which has been the main reason for the development and innovation in the ceramic sector, acting as a linkage between the university and the enterprises and leading different processes of investigation, innovation and solving of appearing problems in the industry during the last 50 years.

The ITC has served as a support for the industry, promoting the competition of all the different enterprises located in the cluster, offering technical services to facilitate the development of solutions and innovations by introducing them to designs of new industrial procedures and equipments and providing technological and quality counselling. This could otherwise not be done, since most of the enterprises don't naturally count with the equipment and facilities necessary to direct and perform such processes. The institution also provides the necessary information to the enterprises in relation to the evolution of the market, designing tendencies and environmental necessities and transmitting the generated knowledge to these for them to have a certain scientific advantage to provide products that respond and adapt to the developing market **[4].**

It is then possible to see how, the success and growth of the ceramic industry in Spain, has always been linked to the integration of new developments to differentiate their products by offering a better quality and features than products of competitors, both national and foreign. This is why most of the efforts put into the industry nowadays, are to deliver products with better characteristics and even better functionalities.

Also, this coexistence of a great variety of enterprises in such a small geographic area favours the competition between them, which is also directly linked with the development and innovations in the sector. So, one can see how the formation of such a cluster is one of the most determining in the efficiency of the Spanish ceramic sector to compete with other countries in the global market.

During the first years of the 21st century, the Spanish ceramic sector was gradually growing, with annual growths of between 5-6% and even higher in years such as 2007 with a 9%. Then, with the beginning of the crisis in 2008, the ceramic sector in Spain started to suffer a serious reduction in profits, mostly in the area of national sales, with annual losses of around 3%, since the construction industry was one of the industries most affected by this crisis and consequently having a major impact on the production of the ceramic sector **[2, p 5].**

Total sales (mill. Eur)	Italy			Spain		
	Year 2016	Year 2015	Variation 2015/2016 (%)	Year 2016	Year 2015	Variation 2015/2016 (%)
National sales	835	807	3,5	746	647	15,3
Exportations	4.588	4.318	6,3	2.570	2.453	4,8
Total	5.423	5.125	5,8	3.316	3.100	7,0

Table 3: Total sales in the ceramic tile sector of Italy and Spain in millions of euros counting both national sales and exportations form years 2015 and 2016. Note: adapted from "El sector del azulejo", p. 25 2018. [Online] Available: https://www.kpmg.es

However, the described efficiency and adaptability to new tendencies and situations that the Spanish ceramic sector has, allowed the industry to readjust and overcome such crisis and from 2013 on, the sales in the national market began to recover once again, absorbing part of the overall growth of the sector. By the year 2016, Spanish ceramic sector was classified as the first European productor followed by Italy and second exporter in the world, with a variation of total national sales of 15'3% and a variation of total exportations of 4,8% in relation to the year before.

This sudden increase of national sales was due primarily to the improvement and investments in the construction sector. This variation is also reflected on the total percentage of exportations of 78% in 2016, which even if still high, was considerably lower in comparison to the percentage of exportations in relation to the total sales during previous years, since exportations have typically been higher than 80%. This capability for product exportation that this sector shows is also the reason for it being one of the principal exporting industries in Spain and the second industry that provides the biggest surplus for the Spanish market **[1, p 25].**

3.1.3. Inkjet printers in the ceramic tile industry

Earlier, it was mentioned how the use of inkjet printers has been revolutionizing the ceramic tile industry over the past twenty years in. During the 1980s and 1990s, the surface of ceramic tiles was being processed and decorated with printing technologies such as flat screen printing at first and then rotatory screen printing, rotogravure decoration and flexography as the latest improvements **[4]**. At the same time, inkjet technology had already shown and proven its potential as an automatic and additive manufacturing technology with application in industry. It started to be subject of investigation for its integration in ceramic tile decoration systems and soon it was seen how the introduction of such technology into the production chains could be technically and economically feasible, which made it an even more interesting option, given the high profitability that its adoption in the industry seemed to promise.

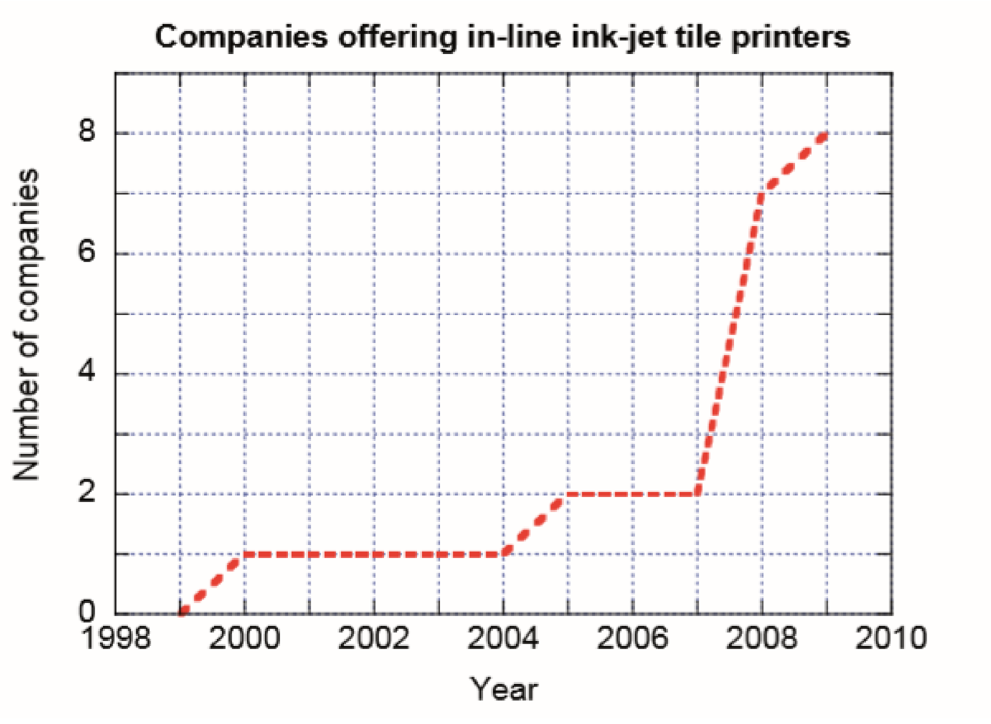


Figure 1: Evolution over the years of companies which offer in-line ink-jet printers for ceramic tile decoration. Note: Adapted from "Ink-jet printing for the decoration of ceramic tiles: technology and opportunities", by Hutchhings. I, 2010, Qualicer 10', p. 2.

Then, after the presentation of the first inkjet printer destined for decoration of ceramic tiles by KERAjet company in the year 2000, industry started to make a bigger effort in solving the remaining issues, mostly related to ink compatibility, composition and viscosity and also issues related to costs of the different components, in order to transform the integration of inkjet printers in ceramic tile decoration industry into a reality.

Short time after, during the early 21st century, this technology began to gradually be integrated in production chains for the decoration of ceramic tiles, being Spain and Italy the pioneers in this form of production. ***Figure 1*** above shows how ever since the public release of the first in-line ceramic tile inkjet printers, company which offer such technologies have gradually grown in number.

Figure 2: Ink-jet printer from EFI™ Cretaprint® for decoration of ceramic tiles. [Online] Available: https://www.efi.es

The introduction of inkjet printers in ceramic tile decoration systems has been a fundamental step taken in ceramic industry, mostly when analysing the situation of ceramic tile production in Europe with Spain and Italy as leaders. It allowed for a whole new business strategy to be created, based on the added value inkjet technology conferred to the ceramic products, providing these industries and advantage over emerging ceramic tile industries such as China, Brazil, India, Turkey and other countries, as mentioned already in **section 3.1.1. “Ceramic tile sector in the international market”.**

Figure 3: Xaar 1002 printhead (top left corner) and porcelain stoneware tiles with different surface finishing and textures. [Online] Available: https://www.xaar.com

Inkjet printing systems are currently used in systems for surface finishing and glazing of ceramic products. It is possible to use inks with different pigments and enamels, to decorate the tiles generating high quality digital images and it allows the generation of different textures and surfaces textures in a very efficient way.

In ***figure 3,*** a Xaar 1002 inkjet printing printhead is shown, the technical features of which allow the generation of great quality surface finishing, with a wide variety of colours and textures, which can be seen in the top-right corner and bottom corners of ***figure 3***. Nowadays, there exist various companies which offer printheads for inkjet printing and for their adaptation to digital printing systems. For instance, Xaar printheads as the one shown in ***figure 3*** are installed in digital printers for ceramic tile decoration, which is the case for instance of the EFI™ Cretaprint® digital printer seen in ***figure 2.***

Figure 4: In-line Kerajet ink-jet printers for ceramic tile decoration. [Online] Available: https://www.kerajet.com

In general, decoration of ceramic tiles using inkjet technology digital printers is done in a "single-pass" system, in which the tiles pass through the printer one only time. In the printer, several printheads can be installed, each of which will be in charge of printing a specific coloured ink and specific amount, in order to obtain a specific distribution and colour intensity.

However, as seen in ***figure 4***, it is also common to install various printers in a row, in order to print several layers and even achieve different kinds of textures. Thus, it is essential that there exists a coordination between all of the different components in the system, such as synchronicity between tile transportation and motion with the print head movements, ink supply into the printer, data feed etc. The different features of inkjet printer performance, as well as the types and characteristics of inks are explained in detail in **section 4.2. "Inkjet printing technology systems".**

By combining and coordinating all of the mentioned components with the production chains of ceramic tiles, robust, efficient and cost-effective inkjet printing tile decoration systems were born and have been revolutionising in ceramic tile decoration due to all the technical enhancements it has introduced in the decoration systems such as:

- Non-contact decoration
- High image quality and definition,
- process flexibility
- Easy customization and variation of designs
- 100% ceramic surface decoration or “edge-to-edge decoration”
- High capability four colour printing
- Minimum waste generation
- Faster and cheaper set-up of printing system
- Rapid payback and many other advantages **[5]**.

Thus, it has been proven, after many challenging years, how inkjet printing technology systems characteristics are optimal for the decoration of ceramic tiles, allowing the production of cost-effective tiles with an outstanding print quality, which are the main protagonists of the ceramic sector in global market. Moreover, inkjet printers for ceramic applications have also shown to have a great potential for a variety of developments which will most likely take place in the next few years, introducing ceramic tiles into a new world of modern technologies. This will be discussed in the following **section 3.2. “Innovations in ceramic tile industry”.**

3.2. Innovations in ceramic tile industry

As mentioned before, the ceramic tile sector in Spain is going through a critical stage, pressured by the increasing competitivity in the global market and pressured by gradually more demanding social, legal and environmental situations. It is in times as the ones described, when industries tend to make a greater investment in strategies as the ones previously described. Particularly, the ceramic tile sector in Spain, has always been characterised for being an innovative industry, which has traditionally given this sector an advantage over competing companies around the world.

Anyhow, since the area of technological development is also more demanding, it is necessary for the ceramic tile sector to put a bigger effort into innovation and added value, to be able to maintain the exclusiveness that has typically been related to the Spanish ceramic product. In recent years there has been various technological improvements in the sector, such as physical vapour deposition technology, laser firing technology and decoration by inkjet printing, as it has already been described in **section 3.1.3. "Inkjet printers in the ceramic tile industry".**

The combination of these new technological developments and the higher demand of more efficient and innovative products has led to the designing of ceramics with functional properties such as higher resolution decoration, heating and energy saving ceramics, air cleaning and hygienic tiles, products with increased mechanical properties etc. For instance, lasers have been developed for the use in kilns for tile firing and research is being done in relation to air cleaning, thermal, anti-slip, anti-electrostatic and photoluminescent tiles by doping glazes with certain compounds, bactericidal tiles, tiles with integrated sensors and even photovoltaic tiles **[6].**

Development of photovoltaic tiles is one of the most relevant developments and a big percentage of the research which is being done in relation to innovation in ceramic tile production is focused on this application. Integration of solar cells on ceramic tiles would allow to functionalize the surfaces of such ceramic tiles for the production of energy via a renewable source. Moreover, by combining the idea of photovoltaic tiles with other ceramic tile applications such as tiles for building linings, the concept of building linings which can have a huge impact over household energy consumption and which at the same time can produce energy is born. Such innovation entails not only a reduction in material costs and wastes, but also provides a solution to reduce humanity's environmental impact and a solution for a more efficient and clean way of both consuming and producing energy, which at the same time are critical factors directly linked with climate change. Progress and tendencies related to the development of ceramic tiles as energy efficient solutions in edification are discussed in the following section.

3.2.1. Ceramic tiles as energy efficient solutions in edification

For a long time ceramic porcelain stoneware tiles have been destined for their use in interiors. However, during the last 30 years, porcelain stoneware has gained its position as one of the best options for the covering of internal and external surfaces in architecture. Such coverings have been the result of the need to create a climatic separation between the interior and exterior infrastructures, with an energy efficient and economic material. Even though commonly temperature regulation of interiors has mostly relied on the installation of heating and cooling systems, building coverings offer an interesting and efficient solution for temperature regulation, whilst eliminating important factors attributed to typical heating and cooling systems, such as high energy consumption and environmental impact.

Figure 5: Top images shows the headquarters of the Botín Foundation in Santander (Spain). Bottom images show ceramic tiles which cover the façade and roof of the headquarters. From: "Iridescent Techniques in Ceramics: Physico-Chemical Analysis and Colorimetric Characterization of the Headquarters of the Botín Foundation in Santander" by Víctor Echarri-Iribarren et. al., Appl. Sci. 2019, 9, 1521.

Building covering is not a new concept or idea, but it had never had an important role in architecture until quite recently and little by little, by the realization that porcelain stoneware is a very versatile material, it is being re-introduced in the world of construction and design, since it allows to establish a harmonious relation between aesthetics and common technical and economic factors. For instance, in ***figure 5*** above a recent development of a building porcelain stoneware covering is shown, in which porcelain stoneware spherical caps have been produced to cover the façade of the headquarters of the Botín Foundation in Santander (Spain) **[7].** This caps are not only destined to protect and cover the façade, but also play an important aesthetical role, transforming the headquarters into a building that meshes and integrates with the environment by making use of chromatic effects originated from the coating of the porcelain stoneware caps with a specific iridescent coating.

Furthermore, building covering is not useful only for aesthetical reasons. By carefully selecting the materials and characteristics of building coverings, it is possible to reduce thermal losses during winter and reduce energy consumption during summer by designing coverings to cover those surfaces which are not transparent, and which represent over 80% of surfaces with heat transfer processes. If installations of this kind are efficiently applied, a reduction of up to 30% of heat losses can be accomplished **[8, p 97].**

As described in a project from the European Comission, “buildings consume large amounts of energy in the form of heating and cooling, giving rise 36% of the EU’s CO2 emissions and accounting for 40% of its energy consumption. EU legislation sets minimum energy performance requirements for new buildings, for major renovation of buildings and for the replacement or retrofit of building elements” **[9].**

Between the most common solutions, we can find the lining of buildings with highly insulating materials and the lining of buildings by installing what is known by the name of “ventilated façade”.

Figure 6: Ventilated façade in a unifamilial building in Prishtina (Kosovo). [Online] Available: https://www. grespania.com

Ventilated façades don't only protect and insulate the building but, by creating a space for air to flow between the ventilated façade structure and the building's façade, as seen in the left image of ***figure 6***, it also provides aid against problems with humidity, heat transfer and even soundproofing. Even though ventilated façades have a higher cost and require a slightly bigger volume to be occupied by the installation, one of the advantages it also provides is that they can be easily mounted over existing façades that have no historical value and can be legally modified, which is the case of most of the buildings constructed after the 1950s in peripheric areas of cities around Europe **[8, p 98].**

A great variety of materials can be used for such purpose. However, ceramics have played a huge part in the design of building linings during the past and in the past decades porcelain stoneware has been as the most suitable for such application, since it's a material with many advantages such as a great flexibility in relation to product size and shape, excellent mechanical and thermal properties and long material lifespan. In the right image ***figure 6*****,** the installation of a ventilated façade with porcelain tiles is shown, where it can be seen how, besides increasing the buildings general energetical efficiency, it also provides a nice aesthetic solution for the buildings design.

On another hand, since the 1990s the industry has been integrating photovoltaic technology in construction for their use in façades and roofs, in order to tackle the same energetical efficiency issues in buildings mentioned above related to the energetical consumption of these. Moreover, renewable energies have been one of the main targeted areas of development during the last years, due to the high consternations in relation to climate change and the targets the EU has settled in order to fight it. Between all the different available renewable energies, photovoltaics has been regarded as one of the most promising ones, mostly due to its feasible integration in various systems.

Figure 7: BIPV's installed in the façade of a building (left) and in a rooftop (right). [Online] Available: https://www.glassonweb.com (left image), https://www.skoltech.ru (right image).

Such integration has led to the invention of different kinds of BIPVs (Building Integrated Photovoltaics) and application in various infrastructures, combining and integrating photovoltaic modules in construction elements, such as in glass windows or roof tiles. For example, the first ever BIPV installation was done in Aachen (Germany) in 1991 **[10]**. In this installation, solar cells were stacked between layers of isolating glass to create an insulating glass element for the covering of the façade.

Since then, various installations with BIPV systems have been accomplished; lots of them in the form of BIPV modules integrated in glass façades or rooftops, as it can be seen ***figure 7***, but also ventilated façades with PV modules or PV modules integrated in structures for shade generation.

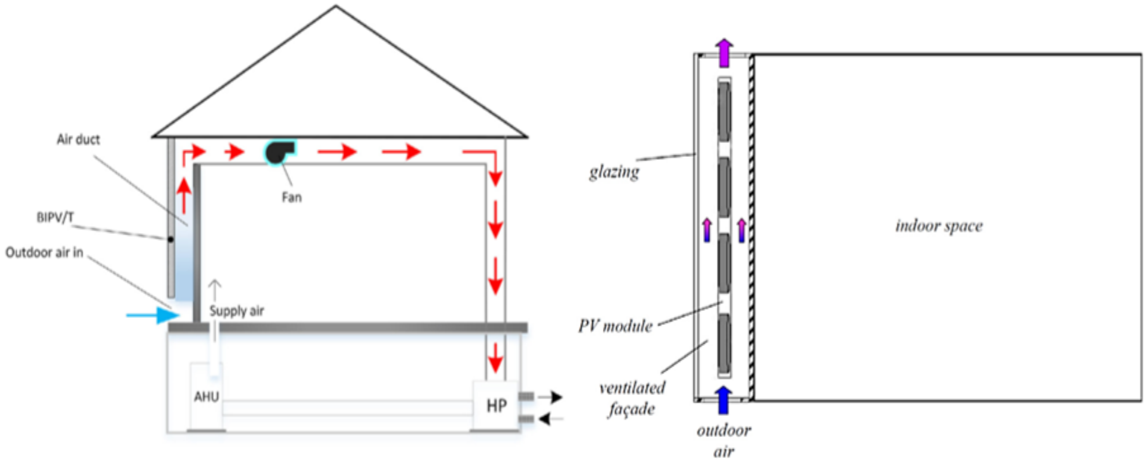


Figure 8: BIPV installed as a ventilated façade with a forced air current for temperature regulation (left) and BIPV installed as a ventilated façade with temperature regulation by natural air flow (right). From: A key review of building integrated photovoltaic (BIPV) systems by Biyik.E et. al., Engineering Science and Technology, an International Journal, Volume 20, Issue 3, pp 838-858.

Over the time this had led to the marriage of BIPV systems and ventilated façades, as a solution to the various energetical and economic need previously mentioned. Two schematic images are shown in ***figure 8*** above, where different photovoltaic systems have been coupled with ventilated façades in order to assess needs such as efficient electrical consumption and thermal insulation **[11][12].** Even though not all of the BIPV designed over the past years are cost effective, progress has been quite fast during the last 20 years, a noticeable market has appeared and by following the evolution of the integration and development of such systems it can be seen that great progress will be done during the next few years **[13].**

Furthermore, as it has been previously mentioned, a big effort has been and is being put into research for ceramics with functional surfaces. Most of the works in relation to the functionalization of ceramic surfaces for energy production consist in the production of thin film solar cells over the ceramic substrate. Thin film solar cells are an alternative to the traditional monocrystalline and polycrystalline solar cells which are currently under development. There has already been works that have accomplished thin film solar cells with efficiencies of up to 20%, which a remarkable result **[14].**

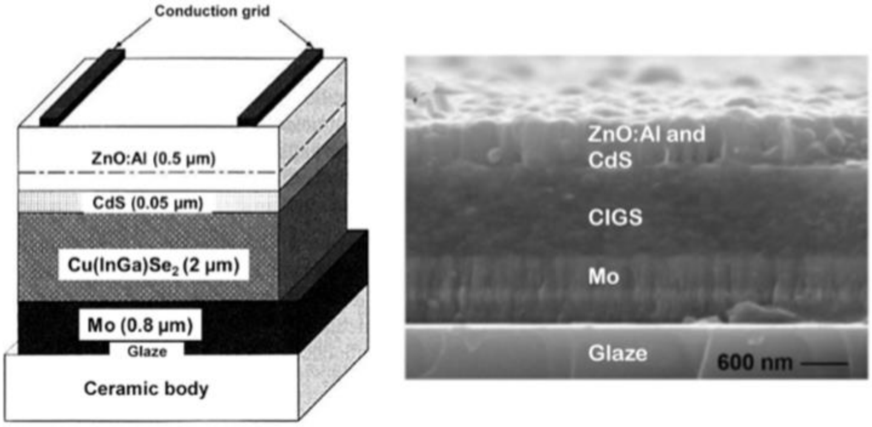


Figure 9: CIGS thin film photovoltaic cell produced over a ceramic substrate. From: The Ceramic Industry in Spain: Challenges and Opportunities in Times of Crisis by J.Llop et. al., Qualicer 14', p 9

The ***figures 9 and 10*** above show a series of ceramic substrate upon which different layers have been deposited (conductive, semi conductive, buffer and transparent layers) creating a thin film solar cell that is fully integrated in the ceramic body and that allows sunlight to reach directly to the active part of the solar cell, obtaining efficiencies of up to 4% **[15].**

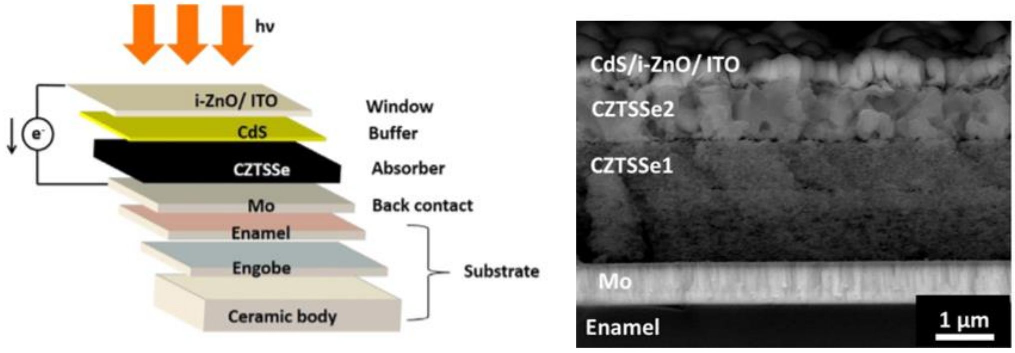


Figure 10: CZTSSe thin film photovoltaic cell produced on a ceramic substrate. From: Development of photovoltaic ceramic tile based on CZTSSe absorber by I. Calvet et. al., Materials Letters 161, 2015, pp 636-639

Moreover, there are projects in the field of photonics have developed and accomplished the integration of solid-state lighting and sensors in ceramic tiles and subsequently creating LED luminous tiles which can also sense movements in the nearby environment, which could also revolutionise the world of ceramic tile applications since it can be used for floorings, walls and even outer surfaces.

On another hand, porcelain stoneware is also being subject of investigation for other applications related to energy efficiency such as ceramic phase change ceramic tiles formed by combining phase changer materials with the ceramic mass in order to produce a tile which can regulate the temperature by absorbing and releasing heat from the nearby environment due to chemical phase transformation reactions which occur in it **[6, p 6].** There are studies which have evaluated the effect that the integration of phase change materials could have and stated that both energetical consumption in buildings and environmental impact could be reduced **[16].**

With this kind of developments taking place, it is possible to see how BIPVs could be applied in infrastructures in the shape of PV ceramic tiles, which can be installed in various surfaces such as the different described building linings.

3.3. Development of new applications for ceramic tiles via inkjet printing of conductive materials

As it is possible to see from what has been explained in sections **3.2. “Innovations in ceramic tile industry”** and **3.2.1. “Ceramic tiles as energy efficient solutions in edification”,** there exists many possible technological applications for ceramic tiles, mostly related to energy efficiency, which are currently under development phase.

Thus, as previously introduced, the aim of this work is to facilitate the integration of such technological applications and electronics with ceramic tiles, with a technology such as inkjet printing which is already present in ceramic tile production chains.

By accomplishing the printing and/or embedding of conductive materials in ceramic tiles, conductive tracks and electrodes could be integrated for instance, to aid the electrical connections needed in a photovoltaic tile, to feed sensors which are coupled to tiles, to feed LED panels integrated on ceramic tile surfaces and many other applications which would require electricity to be conducted.

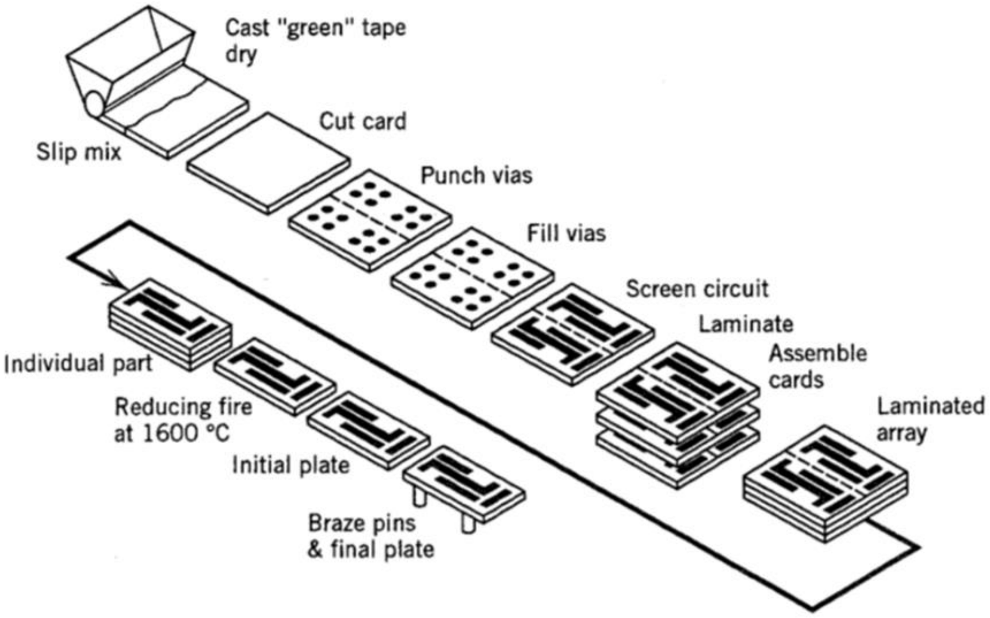


Figure 11: Schematic representation of a typical production process for multilevel ceramics with electronic structures. From: M. Bennet et al, Fabrication of multilevel ceramic microeletronic structures, United States Patent Office, Patented 1970

In order to embed such conductive tracks and conductive structures within the ceramic tile, the main idea is to utilise a “layer by layer” process, which in a way imitates the process followed for the production of multilevel and microelectronic ceramic structures, with integrated connections and conductive paths.

As it can be seen in ***figure 11***, thin tapes or layers of green ceramic can be formed (to which a binder is normally added for better adhesion between layers and for a higher flexibility in green state) on which vias/ holes are perforated with a punch or on which conductive patterns are typically screen printed. Subsequently, by stacking various layers of ceramic with vias and conductive paths and posterior sintering in reducing atmospheres (in order to prevent oxidation of the conductive material), ceramic bodies can be formed for electronic applications.

However, it is important to highlight the fact that this process is not utilised for the production of ceramic tiles, but rather for the production of thin ceramic substrates composed of ceramic materials such as alumina (production of printed circuit boards for example). Thus, this methodology will be taken as an important reference when designing and figuring out a way to produce ceramic tiles with integrated conductive patterns by means of inkjet printing.

4. Scientific foundations

4.1. Porcelain stoneware tiles

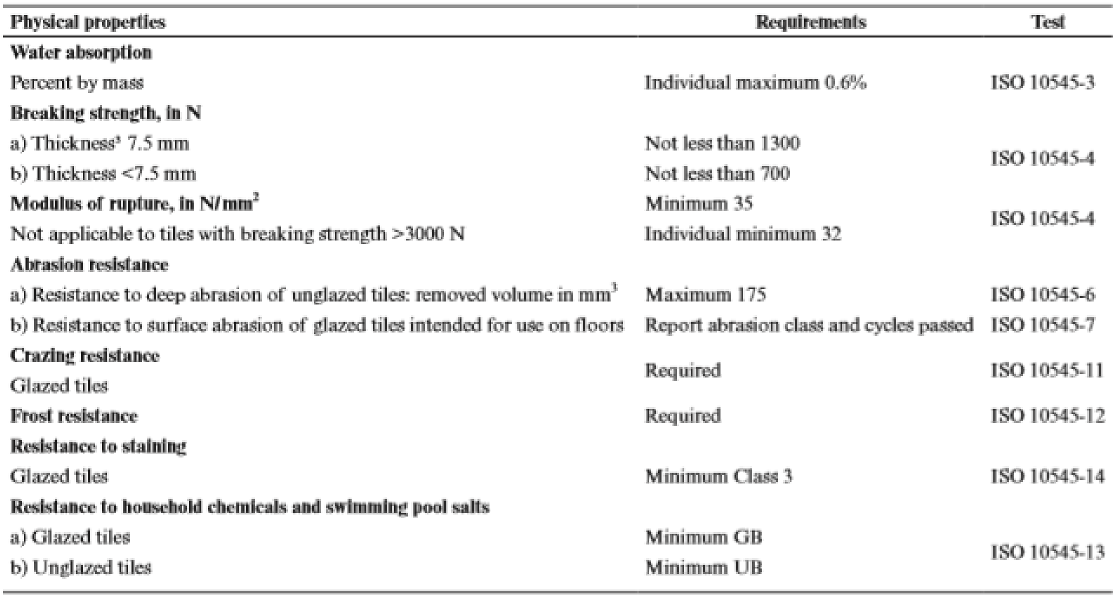
4.1.1. Characteristics and properties of porcelain stoneware tiles

Porcelain stoneware tiles are characterised for being low porosity ceramic products with excellent mechanical, thermal, chemical and electrical properties. Furthermore, it's chemical composition can be modified by changing the ratio of the different compounds which are used for its production or also by the addition of compounds which are not typically present in traditional porcelain stoneware products, in order to optimize the materials properties and adapt them for specific applications. This converts porcelain stoneware in a very versatile material with various technical features and benefits, since it can be destined for the production of not only different types of ceramic tiles, but also for the production of other ceramic products.

Products produced by ceramic powder processing	
Electronics	Advanced structural materials
Substrates, chip carriers, electronic packaging, capacitors, inductors, resistors, electrical insulation, transducers, servisors, electrodes, motor magnets, spark plug insulators, igniters	Cutting tools, wear-resistant inserts, engine components, resistent coatings, dental and orthopedic prostheses, high efficiency lamps
Chemical processing components	Refractory structures
ion exchange media, emission control components, catalyst supports, liquid and gas filters	Refractory lining in furnaces, thermal insulations, kiln furniture, recuperators, regenerators, crucibles, metal-processing materials, filters, molds, heating elements
Construction materials	Institutional and domestic products
Tiles, structural clay products, cement, concrete	Cookware, hotel china and dinnerware, bathroom fixtures, decorative fixtures and household items

Table 4: List of different products produced by the pressing of a ceramic powder. From: Principles of Ceramic Processing by S.R. James, Wiley-Interscience, 1995, p 7

In ***table 4*** above, a list of a great variety of applications for ceramic materials is shown, being porcelain stoneware ceramics utilised for lots of them, from construction and domestic products to electronics and advanced materials. However, since the aim of this work is to combine inkjet printing with common ceramic tiles for the production of a product suitable for electronic applications, we will centre on the properties and characteristics of common porcelain stoneware tiles and not on other ceramic products which might have similarities with these, but have sufficient variations in the chemical composition for them to have different and substantial physical and chemical properties.



Physical properties	Requirements	Test
Water absorption		
Percent by mass	Individual maximum 0.6%	ISO 10545-3
Breaking strength, in N		
a) Thickness^3 7.5 mm	Not less than 1300	ISO 10545-4
b) Thickness <7.5 mm	Not less than 700	
Modulus of rupture, in N/mm^2	Minimum 35	ISO 10545-4
Not applicable to tiles with breaking strength >3000 N	Individual minimum 32	
Abrasion resistance		
a) Resistance to deep abrasion of unglazed tiles: removed volume in mm^3	Maximum 175	ISO 10545-6
b) Resistance to surface abrasion of glazed tiles intended for use on floors	Report abrasion class and cycles passed	ISO 10545-7
Crazing resistance	Required	ISO 10545-11
Glazed tiles		
Frost resistance	Required	ISO 10545-12
Resistance to staining		
Glazed tiles	Minimum Class 3	ISO 10545-14
Resistance to household chemicals and swimming pool salts		
a) Glazed tiles	Minimum GB	ISO 10545-13
b) Unglazed tiles	Minimum UB	

Table 5: Physical properties, technical requirements and normalised tests for a dry-pressed porcelain stoneware tile. From: Relation between the microstructure and technological properties of porcelain stoneware. A review by M.Romero & J.M.Pérez, Materiales de Construcción,65, 2015, p 4

On one hand, porcelain stoneware has high abrasion and flection resistance, as well as high impermeability and good thermal expansion coefficient, thus making porcelain stoneware a strong and long-lasting material, with a good resistance to abrupt changes in temperature without the formation of cracks in its structure.

Also, due to its chemical composition and atomic structure it's a highly inert material, therefore it doesn't react with most of materials with which it enters in contact, making it also a very hygienic and chemically resilient material with good resistance to staining. Thus, this make this also makes this ceramic material easy to clean and maintain. Another important propriety is its high resistance to UV rays, reason for the material to suffer minimal degradation from exposure to ambient conditions.

Furthermore, it is possible to obtain porcelain stoneware tiles with excellent aesthetic appearance, due to the technological development that has taken place mostly in Europe since the 1980s, such as fast firing, wet grinding with spray drying and new decorating systems allowing the production of tiles with various types of glazing and polishing, complex decorations and large sizes. The requirements and normalised ISO tests for porcelain stoneware products is shown in ***table 5*** above for all of the different physical properties previously defined.

Putting all this together, it makes porcelain stoneware tiles suitable for numerous applications and in a great variety of surfaces from rooftops, facades and pavements to surfaces of common household furniture where once installed, it can last for a very long time.

4.1.2. Composition of porcelain stoneware tiles

The chemical composition of every porcelain stoneware product and of ceramic products traditionally, has been defined through a long process of trials, until the optimal combination is found. However, development in characterisation technologies has led to a more precise and scientific approach towards classifying, producing and utilizing all of the different materials with intervene in the production of porcelain stoneware products **[17, p 13].**

Porcelain stoneware tiles are composed by the combination of different raw materials which form a ceramic mass constituted by a variety of oxides, such as SiO_2, Al_2O_3, TiO_2, ZrO_2, Fe_2O_3, MnO, MgO, CaO, Na_2O and K_2O, in the form of different crystalline phases immersed in a vitreous matrix once the ceramic mass has been sintered**. [18, pp 75- 78].**

All these raw materials can be classified in three main groups by their composition and mineralogical structure and in relation to the specific function they perform: clays, silica minerals and feldspars.

Argillaceous minerals	
Mineral	Ideal Chemical Formula
Kaolinite	$Al_2(Si_2O_5)(OH)_4$
Halloysite	$Al_2(Si_2O_5)(OH)_4 \cdot 2H_2O$
Pyrophyllite	$Al_2(Si_2O_5)_2(OH)_2$
Montmorillonite	$(Al_{1,67}Na_{0,33}Mg_{0,33})(Si_2O_5)_2(OH)_2$
Mica	$Al_2K(Si_{1,5}Al_{0,5}O_5)_2(OH)_2$
Illite	$Al_{2-x}Mg_xK_{1-x-y}(Si_{1,5-y}Al_{0,5+y}O_5)_2(OH)_2$

Table 6: Ideal chemical formula of the most common argillaceous minerals found in porcelain stoneware tiles.

- Clays are formed by various argillaceous materials or minerals which confer plasticity and mechanical strength to the ceramic body both in green and sintered state and contain high percentages of Si and Al with minor contents of Ca, Fe and Ti. The most common argillaceous minerals present in porcelain stoneware clays are kaolinite, illite, montmorillonite, chlorite, mica, pyrophyllite and halloysite. In ***table 6***, the molecular structure of the main argillaceous minerals is shown. Normally, different kinds of argillaceous raw materials are used, as well as fusing minerals, depending on their individual chemical composition and depending on the reactivity between them. For instance, whilst clays are in charge of providing plasticity and mechanical strength to the ceramic body in its green and dry state, some varieties of clays are added to complement this function but at the same time, added to increase the alumina content of the ceramic product.

- Feldspars are aluminosilicate minerals which contain Na, Ca and K and the most common feldspars found in porcelain stoneware bodies are albite ($NaAlSi_3O_8$), anorthite ($CaAl_2Si_2O_8$) and microcline ($KAlSi_3O_8$). They act as fusing minerals and are crucial in the sintering process promoting the generation of vitreous liquid phases, which are responsible for the low closed and open porosity values of the fired ceramic product.

- Silica (SiO_2) can be present in various different crystalline forms, of which quartz is the most commonly found in ceramic powders. Depending on the temperature quarts is submitted to, it can also transform into polyforms of silica such as tridymite or cristobalite and amorphous phases, which is seen in porcelain stoneware products after the firing process. Quartz acts as a balancer of viscosity and vitreous flow when fusing with feldspar, but also conforms the base of the crystalline structure once the ceramic body has been fired and provides thermal and structural stability during and after the sintering process

- Lastly, there exists other materials such as inert materials which are employed to achieve the desired contents of different oxides, mostly Si, Ca and Mg oxides, carbonate compounds and additive materials which are used in minimal quantities in order to improve the rheology of aqueous suspensions or change the colour of the porcelain stoneware tile **[19, p59-137].**

As a brief description, the main functions of each of the common oxides in the production of the ceramic tiles are the following:

- Al_2O_3 acts as a refractory and plasticising compound
- SiO_2 has structural and fusing functions
- Fe_2O_3 and TiO_2 provide colour and smell and sometimes act as fusing agents
- CaO and MgO control de contraction of the ceramic body during firing
- K_2O and Na_2O act as fusing agents

The total composition and ratio of raw materials in porcelain stoneware products can be varied and depends on different factors, such as the firing method and the application or required final product properties. Even though long firing processes are no longer in use, its comparison with the current fast firing processes used in the industry allows for a better comprehension of the consequences that variations in the composition or in the production process can have over the final product.

For example, for a long firing process of up to 50 hours, a typical composition could be 35-45% China Clay, 12-18% Plastic Clay, 27-32% Feldspar and 12-18% quartz. On the other hand, for a fast firing process of about 60-90 min, the composition would need to be modified to a composition of 12-18% China Clay, 27-32% Plastic Clay, 42-48% Feldspar, 5-10% Quartz and 0-3% Talc **[19, p 330].** Therefore, it is also possible to group porcelain stoneware tiles according to the percentage of each compound contained in the ceramic mass.

On the other hand, porcelain stoneware tiles are also differentiated and classified according to their microstructure after forming and firing processes. When the tiles are submitted to this firing process for the sintering of the composing materials, different and complex physiochemical transformations occur in the ceramic body, altering its microstructure and providing the product the specific properties and characteristics previously mentioned. Such transformations involve the decomposition of clays, partial melting of quartz and feldspar eutectics formation and solution of mullite and gradual dissolution of quartz in the liquid phase **[20].**

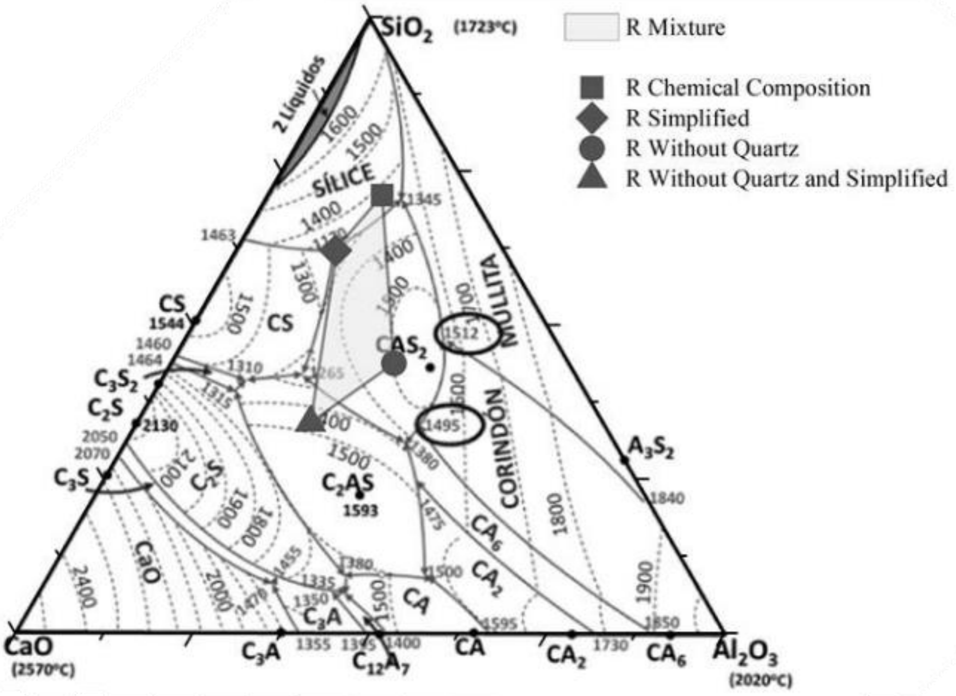


Figure 12: Ternary diagram of the SiO_2/CaO/ Al_2O_3 system. From: R.J. Galán-Arboledas et. al., Ternary diagrams as a tool for developing ceramic materials fromwaste. Relationship between technological properties and microstructure, 2019, p 7.

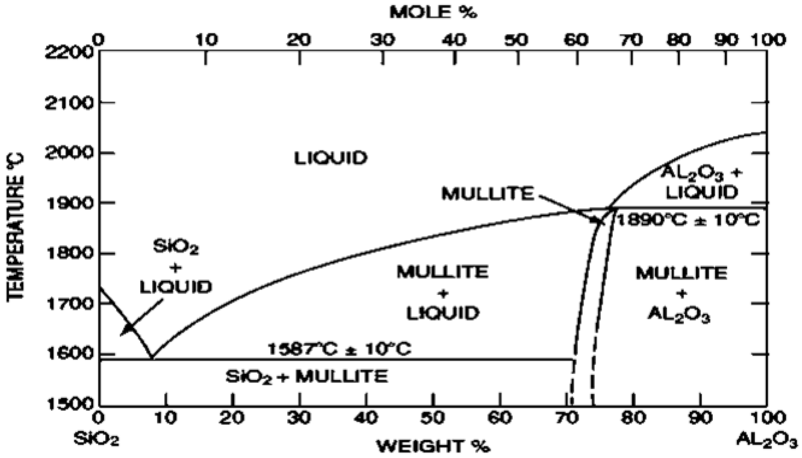


Figure 13: Binary diagram of the SiO_2/Al_2O_3 system. From: : F. J. Klug, S. Prochazka, and R. H. Doremus, "Alumina-Silica Phase Diagram in the Mullite Region," J. Am. Ceram. Soc., 70, no. 10, 1987, pp. 750–759.

On one hand, kaolinite begins its transformation to metakaolinite by the loss of the hydroxyl groups (which are shown in the molecular formula in the table) at 500 °C and is practically complete at 800 °C **[21].** At the same time, at temperatures near 1000 °C, these metakaolinite structures transform and give birth to mullite crystals but, depending on the overall composition and ratio of materials in the porcelain stoneware body, the transformations can occur at higher temperatures around 1100 °C, 1200°C and even higher **[22][23].** Albite and microcline minerals on the other hand are present in a partially molten phase until 1100 °C and melt completely at around 1200 °C as constituents of the liquid phase generated within the ceramic mass, whilst solid quartz particles are present during the entire sintering process **[24, p 3],** but begin to decrease in number after 1100 °C due to the partial dissolution in the aforementioned liquid phase **[21].**

All these transformations can be described by using general chemical reactions, but as highlighted in **[24, p 3],** "the former reactions are not exactly balanced as they are not totally stoichiometric. Moreover, impurities in the starting ceramic paste could result in the development of a liquid phase during firing, which could vary both the temperature of formation and the percentage of the different phases".

Another critical factor in relation to the composition of the porcelain stoneware body is the presence of water. On one hand, water is already present in the primary raw materials from which the ceramic powder is produced, since most of them are of sedimentary origin. Moreover, lots of the phase transformations previously described are due to the action of water contained in the molecular structure of different minerals. Then on the other hand, water is also added to the initial ceramic powder for the production of slurries and is also present in atomised powders, to which it confers a certain degree of plasticity, which allows the dry pressing of the atomised powder, into solid ceramic bodies with good mechanical strength **[19, pp 186-189]**. Nevertheless, it is of extreme importance to control the amount of water during the various processes, since an excess or lack of water can have negative effects over the integrity of the final product. For instance, for each type of forming process, dry or wet, an amount of water between specific values is needed, which vary from 3-6% in dry pressing to 20-25% in plastic casting. On the other hand, before the porcelain stoneware tiles are fired and sintered to their final state, water must be removed by drying, which is a very important process and can be quite complex in those cases were water content is high, since an uncontrolled drying can cause cracks, deformations and other problems in the ceramic body.

In order to produce a ceramic paste with a specific ratio of each of the previously defined compounds, so as to obtain a final product with the desired properties, it is necessary to study and characterize the different raw materials.

- Firstly, it is very important to know the mineralogical nature of the argillaceous materials, since it will provide the necessary information to be able to foresee possible advantages or technical problems during its use. Depending on the atomic structure, the catchment of H_2O in the structure or the catchment of fusing elements such as Na^+ or K^+ will vary. Knowing the mineralogical nature of fusing agents such as feldspars is also very important, since the mineralogical structure of these materials will influence on the temperature of vitreous phase formation and its viscosity.

- Secondly, determining and defining the granulometric distribution and particle size is also a critical factor, since the reaction between solid particles which don't fuse is key for the structural integrity of the sintered final ceramic product. By controlling the size of solid and fusing particles and increasing the contact surface area between them it is possible to optimize the sintering process and therefore the mechanical properties.

There exist different techniques, which most of times are combined, to try and determine with maximum certainty and detail the chemical composition, mineralogical structure and granulometric distribution, such as X-ray fluorescence, atomic spectroscopy, crystallographic analysis (X-ray diffraction) and electron microscopy (SEM) to determine the different phases, structures and microstructures. Other techniques such as thermal and chemical analysis are also used to analyse the effect that changes in temperature or atmosphere have on the composition and structure of the ceramic body. Gaining insight/knowledge in relation to the characteristics of the raw materials allows a more precise selection and control of such materials, which will have a direct impact on the final quality of the fired ceramic tile **[17, p 78].**

Moreover, there exists other techniques which are also utilised to study and design the composition for a specific ceramic product and to determine and predict the presence of certain phases. For instance, different phase diagrams such as binary or ternary phase diagrams, shown in ***figures 12 and 13*** above, can be used to try and predict with good precision the apparition of different phases in the ceramic body, depending on the weight percentage of each of the compounds defined in the diagram and depending on the evolution of the temperature **[25].** Such diagrams represent the complex system formed by all of the different phase transformations which normally occur in ceramic bodies and have been designed from information gathered by many years of empirical processes and characterisation of ceramic materials.

The chemical composition is not the only factor that influences the final characteristics of the product; depending on the techniques and treatments followed during the production process and the technological parameters of the ceramic mass in its green state both before and after pressing, porcelain stoneware masses with similar chemical composition can have very different technical properties:

- The grinding grade of the ceramic paste defines how good the vitrification and densification are during the sintering process, thus it is necessary to reach an optimal particle size in order to increase the specific surface area of the particles in contact and consequently enhance the reactivity between them.

- The density of the ceramic body in its green state once it has been pressed needs to reach a certain minimum for good cohesion of the ceramic mass particles, which normally corresponds with a minimum specific conformation pressure of between 350-450 kg/cm^2. However, depending on the chemical composition and physical structure, this pressure can even reach values of 600 kg/cm^2.

- In order to obtain a fully vitrified ceramic body with low porosity, time and temperature of the sintering process must be carefully defined to allow the different needed reactions to take place. In the fast firing processes that are currently used in industry, these values are generally around 60 min of sintering at a temperature between 1200 to 1230 °C.

4.1.3. Production process of porcelain stoneware tiles

In general, the production process followed for different ceramic products is relatively similar. However, the technology and techniques utilized during each main stage or process can vary significantly, deriving in different product final characteristics.

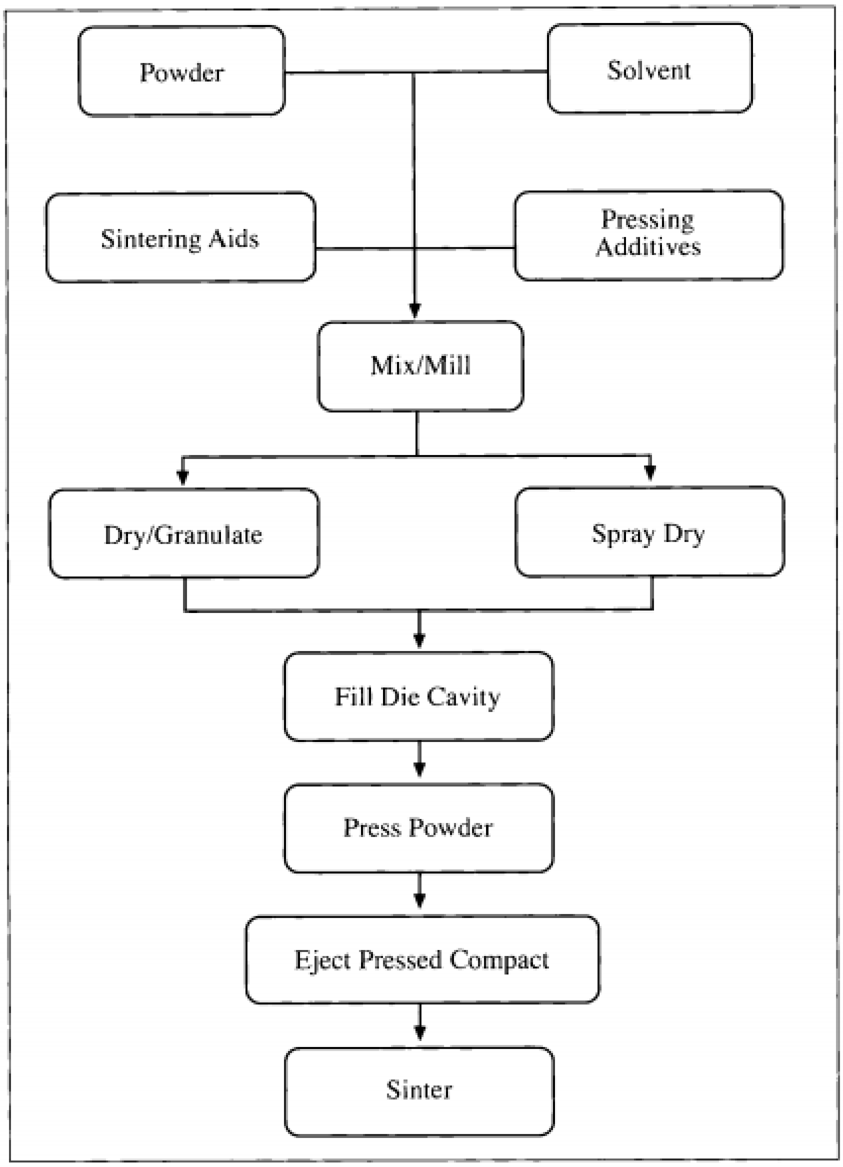


Figure 14: Schematic representation of the steps and processes for the dry pressing of stoneware ceramic tiles. From: James. S. Reed. From batch to pressed tile: mechanics and system microstructure changes, Qualicer, 2000, pp 23-42

The main stages common in the production process of ceramic products are: batching, dosage, milling, forming, drying, coating and firing. However, for some products, some steps are not required, or further treatments are needed. In the case of porcelain stoneware tiles, they are generally formed by dry pressing of atomised powder, as seen in ***figure 14*** and the main processes are the following:

- Dosage: Dosage of the different raw materials which have previously been treated and prepared for the formation of the ceramic paste. Unlike processes for other kinds of ceramics, in this stage colouring powders can be added to the ceramic mass.

- Milling: Wet milling of the ceramic mass is performed with a continuous grinder for preparation of the base slip/slurry, since wet milling allows obtaining smaller particle sizes than those obtained by dry milling. At the end of the milling process, sieves are installed to eliminate any possible residue and to filter and prepare the slip for the atomization process. The residues of the sieves are recirculated and recycled in the same production process. Also, it is also common for coloured slip with a high concentration of pigments to be added at this stage.

- Atomization: The atomization process is responsible for the drying of the slip, obtaining a powder of porcelain stoneware which has a specific humidity content. Typically, humidity is reduced from a 30-45% in slip state to between 3% and 6% humidity in the ceramic powder. The drying process by atomization consists in the pumping and spraying of the slip/slurry into a warm drying medium, normally air or some other gas. As the pulverized droplets come into contact with the air, they quickly start to dry by heat transfer. Due to fast evaporation starting at the droplet surface and slow capillary flow within the droplet, the outer part of the droplet solidifies while the rapid heating causes the formation of a vapor bubble at the core of the droplet, which derives in the expansion of the forming particle. As a result, the droplet dries in form of spherical granulates or even donut shaped particles **[17, p 384].**

- Regranulation: Depending on the application and the particle/granulate size desired a regranulation process follows, for the purpose of increasing the particles dimensions. Atomised powder granulates have diameters from 0,1mm to 0,8mm, whilst re-granulated powder can have particle sizes between 2 to 8mm.

- Pressing: The ceramic powder is poured into a mould and pressed in a hydraulic press. By reaching the specific pressure defined for each particular porcelain stoneware powder, low porosity is ensured for the sintered product as well as a minimisation of the contraction and good mechanical resilience. However, this pressure has a limit, since it must allow the oxidation of organic materials and the exit of generated gases in the ceramic body during the sintering process. Pressing is one of the most utilized forming techniques in industry for its productivity and ability to produce ceramic bodies in a great variety of shapes and sizes and with a minimal drying shrinkage.

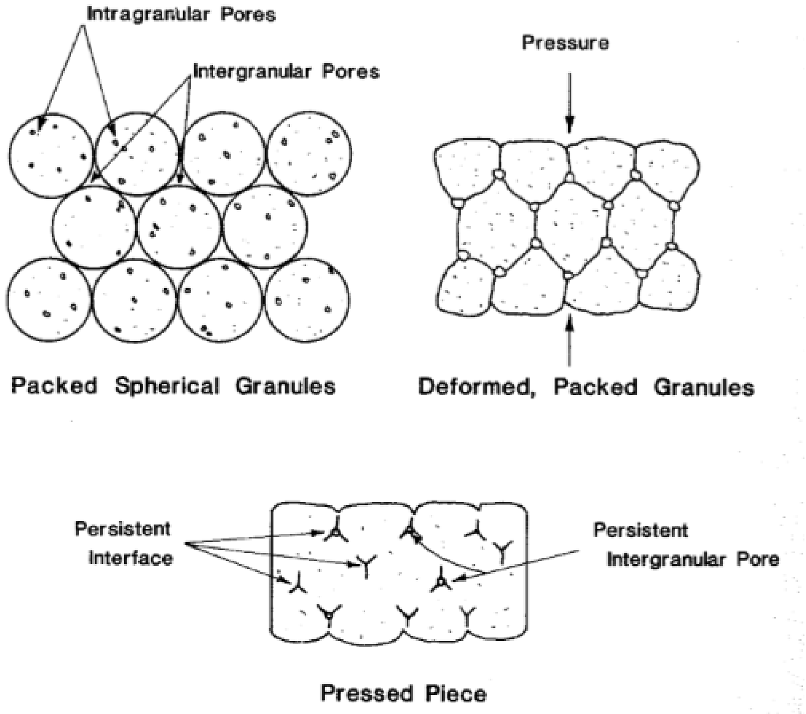


Figure 15: Packing of ceramic particles an variation of porosity during pressing process of a ceramic powder. From: Principles of Ceramic Processing by S.R. James, Wiley-Interscience, 1995, p 428.

As it can be seen in the ***figure 15***, porosity in porcelain stoneware substrates produced by the pressing of a ceramic atomised powder is present in the form of intergranular and intragranular pores. Even after the pressing of the powder and compaction of the ceramic particles, both types of pore are still present. This reflects how, there must exist a minimum pressure which is needed to be applied in order to obtain minimal porosity values. If such pressure is reduced, then the number of pores both intergranular and intragranular will be higher.

- Drying: The process of drying in porcelain stoneware tiles and in ceramic products in general is performed in order to reduce up to a minimum the content of water present in the ceramic mass by evaporation. In the case of porcelain stoneware tiles, after the atomization process, a percentage of water between 3% and 6% remains in the ceramic mass. Furthermore, during decoration and coating of the ceramic surface, the percentage of water present in the porcelain body might slightly increase. For this reason, drying of the porcelain stoneware tiles in dryers can take place more than one time. In the case of a tile which will be decorated or glazed, there exists one drying process before decoration and another drying process once the tile has been decorated but before it is fired and sintered to its final state.

- Coating and decoration: Once the tiles have been formed and dried, a vitrifying slip or a glaze can be applied over the surface of the ceramic tile. Vitrifying sips are typically applied to improve surface quality and to prevent issues during degasification and to avoid contact of contaminants on the surface with the glaze. Over the untouched surface or over the deposited slip, a glaze can be applied for aesthetic and protection purposes. Glazes are water solutions of different types of salts and oxides. Decoration of the tiles can be done by applying inks or pastes with different techniques such as plane and rotative serigraphy, with airbrushes or even, as mentioned in the previous section with ink-jet printers. These inks are applied over the glazed surface and consist of a solvent vehicle, normally glycols and ethylene glycols, which transport pigments and salts that vitrify with the glaze during sintering. After decoration, tiles are dried once again for stabilisation of the decorating substances **[26, pp 177-205].**

- Firing and sintering: The firing of the ceramic tile is done for the activation of reactions between the different argillaceous materials and for the vitrification and sintering of the ceramic body. For the production of ceramic tiles, continuous belt or roller hearth kilns are used and heating of the kiln chamber is commonly heated by gas combustion and even sometimes by electric heating. Being combustion gas heating the most common process, the heating of the ceramic product can be done in a muffle kiln, insulated from the combustion gases or in a kiln in which the atmosphere contains the combustion gas products.

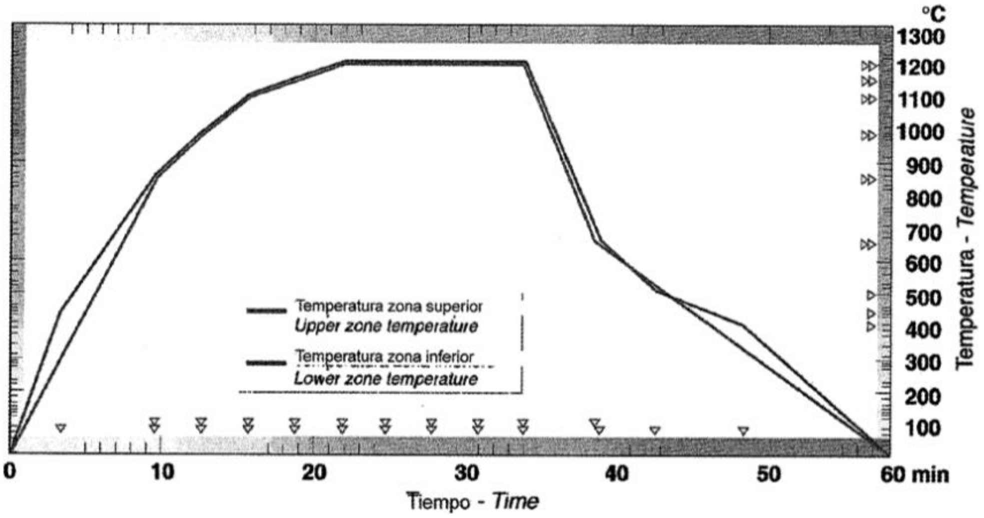


Figure 16: Typical heating curve for a fast-firing sintering process of a ceramic porcelain stoneware tile. From: SACMI: Spanish Asotiation of Ceramic Technicians, Tecnología Ceramica Aplicada, Faenza Editrice Ibérica, 2004, p 343.

In relation to the sintering process, it does not normally begin until high temperatures are reached, around ½ or 2/3 of the melting temperature. The grade and quality of this sintering process depend on the technical factors aforementioned, such as the grade of milling, conformation pressure and time-temperature curve that is applied. During the firing process, before sintering of the ceramic mass begins, different pre-sintering processes take place. The most important of these processes are drying, decomposition of organics, vaporization of chemically bound water, pyrolysis of organic granulates introduces by contamination or with raw materials and decomposition of carbonates and sulfates introduced in the mass as additives or with raw materials.

At the same time, the atmosphere in the kiln will also influence on the reactions which take place inside the ceramic tile. For instance, the porosity will vary, since gas bubbles can easily remain trapped inside the pores and depending on the gas and its solubility, it will allow or not for pores to disappear from the ceramic structure. Moreover, the amount of oxygen in the atmosphere can also influence in oxidation and reduction process which naturally take place in the ceramic body.

For all of the different reactions and processes to take place, specific and minimum times and temperatures must be reached. For a fast firing process of porcelain stoneware tiles, which is shown in ***figure 16*** above, typical sintering temperatures are around 1200 °C, but both higher and lower values can also be used and sintering is performed during intervals of time of 45 to 90 minutes "cold-to-cold". Fast-firing processes are the most common firing processes nowadays, since they have proven more effective and energy efficient than traditional long-firing processes. It is also important to mention that porcelain stoneware tiles can be submitted to several firings at different temperatures. However, the tendency of the ceramic tile industry is to work with one-firing processes in order to minimise costs related to the energy consumption of industrial kilns.

4.2. Inkjet printing technology systems

4.2.1. Working principles

Inkjet printers have been utilised since the 1950s and in the 1970s they were already commercialised worldwide. This technology emerged as an alternative to traditional printers that used printing plates to print on paper and other substrates. However, it hasn't been until the present days in which its technological impact in industry has been acknowledged.

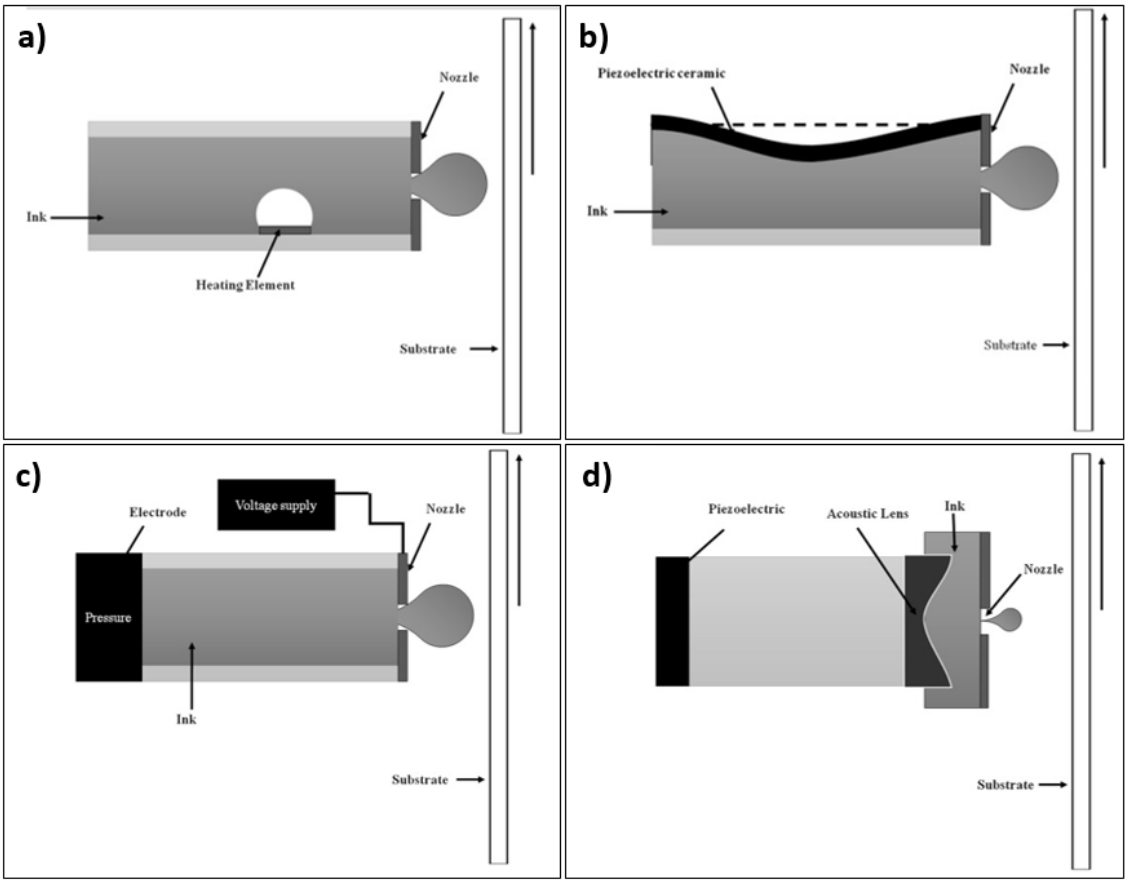


Figure 17: Schematic representation of the four main DOD inkjet printing technologies: Thermal (a), piezoelectric (b), electrostatic (c) and acoustic (d). Adapted from: Atasheh.S., Printing on polymers: Fundamentals and Applications, 2016, p 231-246.

Typically, inkjet printers are differentiated between Continuous Inkjet (CIJ) printers and Drop-on-Demand (DOD) printers. Whilst CIJ printers have a more traditional use and are less controllable (since they jet a continuous stream of drops at high frequency), DOD printers are the commonly used printers for more complex applications in industry and research. At the same time, DOD inkjet printers can be classified as thermal, electrostatic, acoustic or piezoelectric printers. In ***figure 17*** above a schematic representation of the drop ejection process for each of the DOD printers is represented.

We will centre in the performance and characteristics of piezoelectric inkjet printers, since they are widely used in research nowadays and since this kind of printer will be the utilised printer for the development of the project.

Piezoelectric inkjet technology printers are digital printers based on the ejection of microdroplets of ink through the action of a piezoelectric transducer. These electrical transducers are usually formed by crystals such as quartz or ferroelectric materials such as lithium nitrate or lithium tantalate and their main characteristic is that they deform due to the appearance of internal forces when subjected to an electric field.

By applying voltage to the piezoelectric it deforms, and pressure is generated on a chamber/reservoir to which the piezoelectric is coupled, and which contains the ink. This pressure propagates through it in the form of acoustic waves, causing the ink to come out of the nozzle or injector. Then, if voltage is lowered to a certain level and applied at the right moment, a negative pressure is generated inside the chamber, since the piezoelectric will now deform in the opposite direction, returning to the initial state and resulting in a process of suction of the ink. If this combination of pressure and suction processes is coordinated correctly, this stretching of the fluid will allow drops with diameters in the micron range to be generated, at frequencies typically between 1 and 20 kHz.

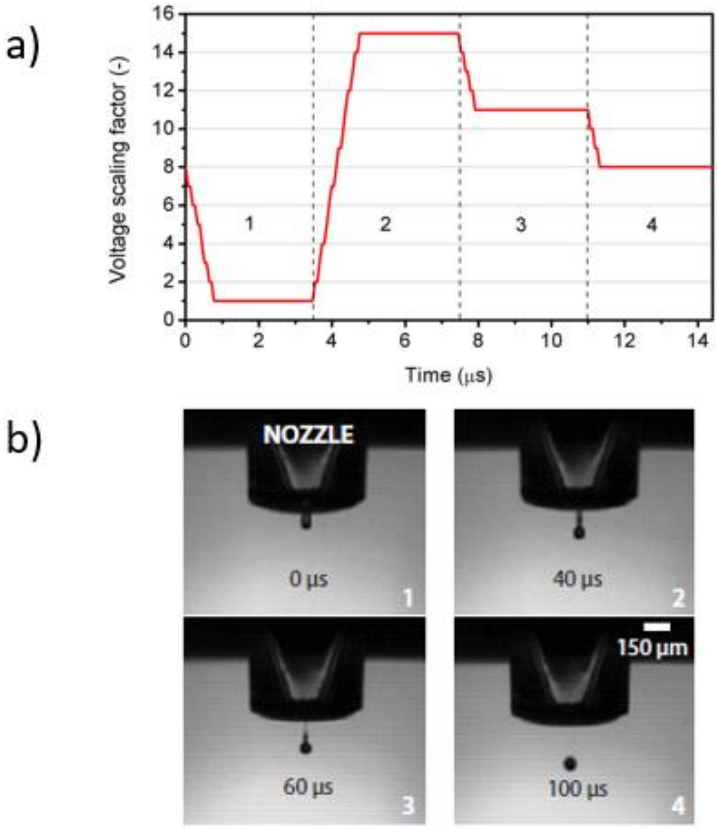


Figure 18: Representation of the different stages in the applied waveform (a) and the jetting of a droplet (b) during ink-jet printing with a piezoelectric digital ink-jet printer.

To achieve this process in this type of printers, a waveform is usually designed in which the voltage level to be applied, the duration during which it is applied and the ramps between voltage levels are controlled. This voltage wave is modifiable, and its modification is carried out to optimize the printing of different inks since, depending on their physical characteristics such as surface tension and viscosity, the voltage and frequency levels will be different.

For example, a simplification of a voltage wave for the ejection of a given ink is shown in the figure. When printing is not taking place, piezoelectric is submitted to a voltage level which is not zero, thus the piezoelectric is generating pressure over the chamber. The first interval corresponds to the filling process of the camera. Here, voltage is lowered, in order to generate the relaxation of the piezoelectric to its normal state, consequently allowing ink to fill in the chamber by increasing the volume of it (interval 1 shown in ***figure 18*** a)). Then, during the second interval, the ejection of the ink takes place applying a higher positive voltage, which is maintained for a determined time. The slew rate between voltage level from interval 1 and voltage level of the current interval will determine how the ink ejects and the shape it will have (interval 2 shown in ***figure 18*** a)). Then in the third interval the voltage is reduced to an intermediate level in order to generate a slight suction effect inside the chamber, which causes a force on the fluid ejected in the opposite direction to the ejection, giving rise to the complete separation of fluid to the nozzle (interval 3 shown in ***figure 18*** a)). Finally, interval 4, the relaxation of the piezoelectric is carried back to the initial state and is maintained for a time, so that possible disturbances within the chamber before the next ejection process can disappear (interval 4 shown in ***figure 18*** a)).

This kind of inkjet printers have a few advantages in comparison to other DOD printers. On one hand, since the amount of ink that is jetted depends on the applied voltage, it is possible to precisely control the droplet size, which allows great printing definition and accuracy. On another hand, by not relying on thermal energy, inks don’t need to be designed to withstand high temperatures, which at the same time allows a bigger flexibility in relation to the tailoring of inks.

Other main advantages of its introduction in industry are that the printer does not come into contact with the substrate in question, it is easy to adapt to industrial level in different applications, the consumption of ink and material waste are minimal and can be printed forms and complex prints with great ease, precision and very good control.

4.2.2. Characteristics and types of inks

Inkjet printing process is very complicated and requires delicate and precise tailoring of the chemical and physicochemical properties of inks. All of the different properties and parameters which can be modified affect over different factors such as ink storage stability, jetting performance, colour quality and wetting, spreading, penetration and adhesion phenomena.

In general, inkjet inks can be differentiated in four main groups: solvent based inks, water-based inks, UV curable inks and phase-change inks. However, in the end most of the inks which are commercialised consist in combinations of these different types of inks. Commonly, inkjet inks are composed by a liquid vehicle (water, solvents, cross-linkable monomers) which accounts most part of the inks mass, additives to modify ink properties (surfactants, preservatives, photo initiators), functional molecules and particles and polymers for the binding of these molecules and particles to the substrate. Preparation of inks is often quite complex, since inkjet printers typically require specific values or ranges of ink characteristics such as surface tension, viscosity and are very sensible to the composition of such inks, most of all in relation to the volatility of ink components and size of the functional material particles in the case of some inks. There are many variables in relation to ink properties which affect and influence on the overall performance of inkjet printers. However, the main factors that need to be considered when tailoring and manipulating inkjet inks have been thoroughly studied **[27]** and they are the following:

- Ink surface tension: Surface tension of the ink influences both over drop formation during the printing process and over wetting, spreading and penetration of the droplet once it has entered in contact with the substrate. Each printer requires certain values of surface tension for a good printing performance. Ink surface tension can be result of the composition of the ink medium like solvent composition and concentration for instance, or by adding a surfactant; this last technique is very common. Normally, surfactants are added in very low concentration of around 1% in weight or even values of 0,1% in weight, meaning that minute variations in surfactant addition are highly influential over ink performance. When adding surfactants, dynamic surface tension should also be studied, since it will not be constant in those processes of new surface formation such as drop formation and spreading on substrate, since surfactant takes a certain amount of time to diffuse to the interface. Moreover, sometimes with surfactant addition foaming occurs, so the further addition of defoamers is needed.

- Ink viscosity: Viscosity influences on the performance during ink jetting and spreading and penetration on the substrate **[27, p 254]**. Ink viscosity is mostly affected by concentration of polymers and binders which are added to the ink, surfactants, solvent composition, flocculation of the contained particles and evaporation of the carrier fluid. Since inks have low viscosity, size and density of particles influence heavily on viscosity due to sedimentation and aggregation. Therefore, a big effort is put into controlling and reducing particle size to a minimum.

- Pigment and functional particle sizes: When functional particles or pigments are contained in an ink, they must be added below the solubility limit, so as to avoid precipitation of the ink due to slight variations of conditions during storage. Normally, pigments added to inks for colouring present no issues in relation to size. However, dye containing inks are more stable than inks with pigments since they are both kinetically and thermodynamically stable. On the other hand, when functional particles are added to an ink, reduction of size is critical. Such particles typically have size between 200 and 300 nanometres and to ensure a good jetting performance, particle size should be 100 times smaller than the nozzle diameter **[27, p 34],** in order to prevent ink from clogging. By reducing particle size to the nano scale, surface contact between printed particles is improved thus affecting positively to the formation of continuous patterns during the sintering process. Still, the percentage of particles or pigments contained in the ink must be carefully controlled, since an increase in particle/pigment concentration also increases the possibility of aggregation, which is an undesired phenomenon **[27, p 40].**

- Evaporation and drying of ink: Evaporation is one of the key processes during ink printing, to not say the most important, since it affects over many of the ink properties and printing stages. On one hand, in particle and pigment containing inks, evaporation of the carrier fluid leads to a decrease in solubility and increase in particle/pigment concentration, thus also increasing the chances of precipitation and aggregation and subsequent crust formation and nozzle blocking and increasing the local viscosity of the ink near the nozzle, inhibiting the jetting of the fluid. On the other hand, once the ink drops have been jetted, they are submitted to evaporation by both contact with the gas around it and by contact with the substrate. When evaporation occurs in a printed drop, it's properties vary with time, thus originating surface tension gradients in the fluid and changes in viscosity, which directly affects on wetting, spreading and penetration processes **[27, p 61]** as it has been previously mentioned and which can typically lead to the formation of ring structures, known in the scientific community as the "coffee stain effect**" [27, p 63].**

- Latency: Latency is described as the maximum time an ink can remain in the nozzle of a printer without being jetted and at the same time without experimenting changes in its physicochemical properties which can affect the printing performance **[27, p 31].**

- Compatibility of ink with printer components: When designing an ink, it must be tested with all the individual parts which compose the printer and with which the ink will enter in contact. Possible chemical interactions that can occur can be between metal parts and inks with low or high pH or between plastic parts and organic solvents **[27, p 37].**

As one can see, tailoring of inkjet inks can be quite a difficult task and the relation between all of the ink properties and printing factors can be very complex; none of the controllable parameters can be modified without taking into account it's influence over the rest of parameters, since each component of the system has an effect on the ink performance and on the environment and health of the users.

In relation to the carrier fluid employed in inkjet inks, inks which are mainly used are either solvent-based or water-based.

Overview of typical inkjet components	
Component	**Purpose**
Water	Primary solvent, carrier fluid
Colorants (0,5-10%)	Production of vibrant and long-lasting images
Pigment dyes	
Co-solvents (5-50%)	Prevent nozzle drying, enhance ink formation and modify physiochemical properties
Surfactants (0-2%)	Improve wetting of ink on media, reduce "puddling" of ink on print head, reduce resitor deposits
Polymeric binders (0-10%)	Improve durability and adherence of prints on substrate, improve gloss of prints
Other additives Biocides	Prevent growth of microorganisms
Chelatting agents	React with free metals
Anti-corrosion additives	Prevent corrosion

Table 7: Overview of typical inkjet ink components. Adapted from: Magdassi.S, Chemistry of inkjet inks, World Scientific, 2010, p.12

Most solvent inks are those in which solvent carrier evaporates or is driven off by a process subsequent to printing, with the objective to deliver a functional material unto a substrate. Solvent based inks have been used for a great variety of applications for many years due to the print quality they provide, durability, rapid evaporation and compatibility with various substrates. Between the most common used solvents we can find ethylene glycol ethers, propylene glycol ethers and esters of these two ethers **[27, p 155].** Solvents have another advantage, which is that they are inexpensive. Nevertheless, they also have important drawbacks related to environmental issues and maintenance due to the high volatility they have. This is why, ink development is trying to aim towards the use of less harmful solvents and the design of solutions with water-based inks.

Water based inks on the other hand, are environmentally friendly. Most of inkjet printers, including home and business printers mainly use water-based inks, mostly due to the fact that they usually require less maintenance than solvent based inks and due to the fact that these inks are more suitable for printing over porous substrates such as paper. In fact, water-based inks typically have a bad adherence to non-porous substrates.

Even though water composes the main part of water-based inks, different components are added in order to obtain the necessary values for all the parameters, stablishing a suitable balance between them. An overview of the various components which can be added is shown in ***table 7***.

However, most water-based inks are dye or pigment-based, for their use in the packaging and ticketing industry. Because of characteristics such as evaporation rate, wetting and adhesion, they are not suitable for printing and delivering of most of functional materials which industries are aiming for.

Lastly, we will introduce the world of conductive inks, which compose on of the main parts of this project. The development of conductive inkjet inks has risen from the production expansion and growing interest related to organic and printed electronics **[11]** and also due to the promise that inkjet technology represents as a cost-effective technique for the production of efficient and good quality printed electronics. Between the main advantages this technology provides we can find the fact that it is easily automatable, it can operate in ranges from microns to millimetres with no variations in the system needed depending on the desired range and it reduces greatly the amount of material waste generation, which is a common factor in conventional processes for the elaboration of electronics. Inkjet printing of conductive materials is adequate for production of sensors, transistors, LCD and plasma displays and touch screens. Recent developments have proved how inkjet printers will probably play a big role in the photovoltaic market and OLED market for the printing of electrodes and semiconductors. Recent research shows that “the total market for printed, flexible and organic electronics will grow from $31.7 Billion in 2018 to $77.3 billion in 2029. The majority of that is OLEDs (organic but not mainly made by printing); printed biosensors; and printed conductive ink (used for a wide range of applications, but predominately PV)” **[28].**

Commonly, until recent times, photolithography has been the predominant technological process destined for the production of printed circuit boards. It allows for very precise and complex patterns to be produced, with a high quality and resolution. Still, it’s a process which involves many steps such as etching, masking and electroplating during which various corrosive and harmful chemicals are employed. Furthermore, it consists in a “subtractive” method which involves generation of a considerable amount of waste and most of the processes involved are time consuming and relatively expensive, mainly due to the necessary and subsequent treatment of these chemical residues. But as it has already been mentioned before, inkjet printing market is continuously growing and improving year after year, allowing the printing of precise, complex and good quality patterns in a great variety of substrates and solving some of the main issues related to current technologies.

The main difficulty conductive inkjet inks are facing at the present is related to pricing. Most of screen printing inks which are commercialised are based on silver o silver alloy particles, but the size of such particles is much bigger than the minimum required for the printing with inkjet printers, since particles in the range of nanometres are necessary to avoid clogging of the ink. At the same time, the development of silver nanoparticle inks for inkjet involves complex processes, reason why the price of inkjet inks can reach values up to 2 and even 3 times of those used in other printing techniques. Actually, it’s because of this that many universities and research institutions are quite reluctant to using these inks, since they are still not scalable to an industrial level and the evolution of conductive inks is still quite slow at the moment.

As with other inkjet inks, conductive inks consist on a carrier fluid, either a solvent or water, which transports the functional conductive material. However, when we talking about this type of inks, besides the common requirements which have been previously explained, such as printability, adhesion to substrate, resolution and minimal maintenance, conductive inks must retain a certain value of conductivity after printing, with or without further sintering, and must be protected against ambient conditions and must be compatible with the substrate. Between the most common functional materials that are added to conductive inks in order to provide conductivity, we can find metal and metal oxide nanoparticles **[29-32]**, metal precursors **[33]**, conductive polymers **[34]** and organometallic compounds.

When evaluating the use conductive inks, it is interesting to consider all the options available, since depending on the application and substrate, some inks will be more suitable than others.

On one hand, metal and metal oxide nanoparticle inks are the most conductive inks, but metal precursors have the advantage to be prepared in solutions, rather than particle dispersions. Polymers conductive materials have higher resistivity but are suitable for flexible electronics and compatible with a great variety of materials and applications. On the other hand, Nanoparticle ink dispersions have the advantage that particle size has been tailored for optimal for printing and they are feasible to produce in high quantities and can be prepared in high concentrations, thus improving the electrical properties and having the highest conductivity values from all the conductive inks available. From all the metals currently available for nanoparticle ink production, silver and gold are the ones which are mainly used, since they present lower resistivity values, low oxidation when exposed to ambient conditions and good chemical stability, since other materials such as copper or nickel tend to oxidize and their respective inks are less stable in ambient conditions. However, coated copper nanoparticle inks and other metal nanoparticles inks are already in development in order to provide solutions to oxidation and chemical stability **[29-31].**

As with all types of inkjet printing inks, there are various factors to take into account and that will highly influence on the quality of the printed patterns and the conductivity of the final product such as dynamic ink-substrate interaction, which has already been previously introduced, ink-substrate chemical interaction, relation between thermal coefficient of both substrate and ink and sintering of the printed patterns.

Dynamic ink-substrate interaction factors which should be considered will be the same for all or practically all of inkjet inks, such as drop impact, wetting, spreading, ink penetration, solvent evaporation rate etc.

In relation to both dynamic and chemical ink-substrate interaction, substrates which have been typically used for printing of conductive inks are polymeric materials, glass or silicon **[12][33][35].** Furthermore, surface treatment is also a very common procedure. Surface can be pre-patterned to form channels where the ink can be printed, chemically treated, corona treated and even coated with a protective layer or a porous layer.

Subsequent to printing, conductive inks have to be cured or sintered in order to obtain a continuous printed pattern. In the case of metal nanoparticle inks, this sintering process allows the coalescence of printed nanoparticles, establishing a better contact between them and eliminating grain boundaries, reducing the number of pores in the printed patterns **[36-37]**. In common industrial processes, sintering of materials such as metals and ceramics is done at temperatures below their melting point, which have relatively high values. However, when working with nanoparticles of these materials, temperatures required for sintering are further reduced down to values between 200-500ºC, since nanoparticles don’t have the same chemical properties in relation to the bulk values oh the material. There are different techniques which are currently used for the sintering of inkjet-printed conductive patterns, such as thermal treatment, plasma treatment, laser technology, photo-irradiation or microwave radiation. Moreover, during the sintering process, there are important parameters to take into account and which will have a direct impact on the conductivity of the patterns such as temperature, duration of the process, particle size and shape or thickness of the printed pattern.

5. Experimental procedure

As it has been already mentioned, the aim of this project was to integrate and embed conductive patterns in porcelain stoneware tiles by using a drop-on-demand inkjet printer.

In order to control and analyse spreading and penetration of the ink on the substrate, two different types of inks were utilised, water-based and solvent-based inks, since they are the two main types of ink which are industrially produced and because of their individual physiochemical properties, their interaction with the substrate was expected to be different.

By utilising different types of ink, parameters such as ink viscosity, surface tension and particle size of the material contained in the ink were varied, thus altering the interaction substrate-ink.

Firstly, porcelain stoneware substrates were prepared by pressing with a mould we designed for such purpose. Substrates formed under different values of applied pressure were prepared and characterised with a micro CT scanner and their apparent density was measured by an X-ray diffraction technique **[38].**

Further on, porcelain stoneware substrates were prepared and fired at two different temperatures of 1100 ºC and 1200 °C, so as to analyse the microstructure of the samples with an SEM equipment and in order to evaluate changes in such microstructure by decreasing the temperature during the firing process.

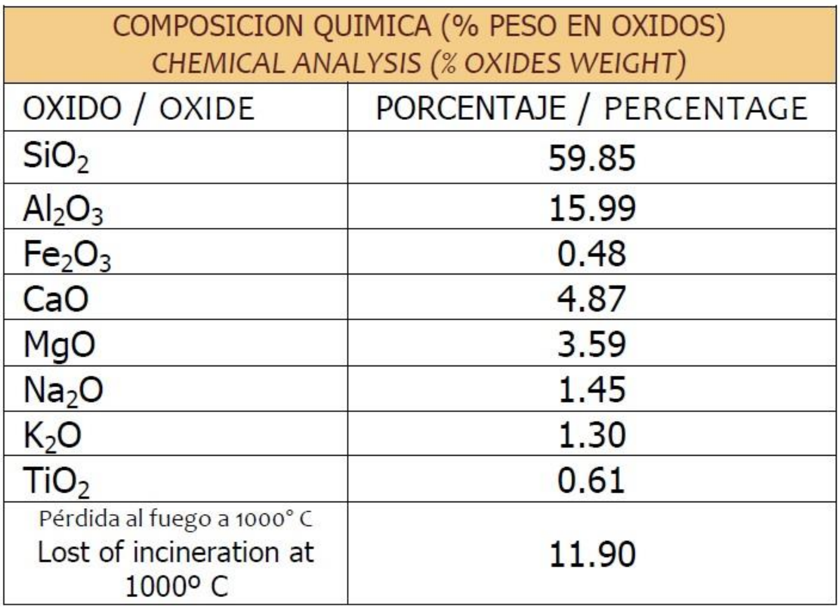
Secondly, since drop-substrate interaction such as wetting, spreading and penetration are complex phenomena which are difficult to quantify and predict via mathematical models, we continued by printing with a water-based pink glycerol dye, in order to analyse optically spreading and penetration of water-based inks. This information would then be used as a base to evaluate the printing of a conductive graphene water-based ink.

Then lastly, a silver solvent-based ink was printed over porcelain stoneware substrates and once again, the printed lines were optically analysed.

Substrates on which graphene ink and silver ink had been printed were then fired in order to sinter both the ceramic substrate and the inks and analyse the effect firing process had over the adhesion and integrity of the printed lines and their interaction with the substrate during such process. In those samples where line integrity remained after firing process had taken place, conductivity measurements were taken.

5.1. Preparation, pressing, sintering and characterisation of porcelain stoneware substrates

For the production of the porcelain stoneware substrates we used a ceramic atomised powder provided by company Euroatomizado, which is formulated for the production of porcelain stoneware ceramic tiles at an industrial level.



COMPOSICION QUIMICA (% PESO EN OXIDOS) *CHEMICAL ANALYSIS (% OXIDES WEIGHT)*	
OXIDO / OXIDE	PORCENTAJE / PERCENTAGE
SiO_2	59.85
Al_2O_3	15.99
Fe_2O_3	0.48
CaO	4.87
MgO	3.59
Na_2O	1.45
K_2O	1.30
TiO_2	0.61
Pérdida al fuego a 1000° C Lost of incineration at 1000° C	11.90

Table 8: Chemical composition of the porcelain stoneware ceramic powder used for the production of the ceramic substrates. Note: data provided by Euroatomizado S.A.

In ***table 8*** is listed the proportion of the different oxides present in the ceramic powder. Even though these compounds are commonly present in all of the different porcelain stoneware products existing in the ceramic industry, as well as some other oxides like P_2O_5 and ZrO_2 which can also be added, the proportion of each oxide in the total ceramic mass is tailored and designed by each company depending on the application which the ceramic product is meant for. Thus, the chemical reactions which occur in the ceramic body during sintering and consequently the mechanical properties and appearance will vary from one porcelain stoneware product to another. From the 11,90% indicated as a loss of incineration at 1000 °C, approximately 5-7% is composed by water contained in the ceramic mass in the green state, which is gradually eliminated during the sintering process. The rest of the mass percentage is composed by organic material present in the form of different compounds and which burns during the firing of the ceramic substrate.

Initial characteristics		Characteristics of pressed sample	
Mass residue (45u)	5,5%	Pressing humidity	6,0%
Plasticity (Pfefferkorn)	20,4 und	Specific pressure	380 kg/cm2
Calcimetry	0,7%	Apparent density in green state	2,08 g/cm3
Organic carbon	0,03%	Post-pressing expansion	0,6%
		Mechanical resistance in dry state	44 kg/cm2

Table 9: Fundamental characteristics of the porcelain stoneware ceramic powder before and after pressing.

In the ***table 8*** above, a list of the fundamental characteristics of our porcelain stoneware product is listed. From all of the characteristics available, the most important to take into account during the preparation of the porcelain stoneware samples is the specific pressure, which basically defines the minimum pressure required to be applied during pressing of the powder, in order for the ceramic body to have optimal mechanical properties. This specific pressure will as well define the overall load to be applied during pressing, depending on the desired size of the ceramic sample/substrate.

5.1.1. Preparation and pressing of the ceramic porcelain stoneware substrate

For the conformation of the substrates via pressing of the powder, we designed an AISI 316L steel mould which allowed us to produce rectangular samples of 50x15 mm and with different thicknesses up to 8 mm, depending on the amount of powder introduced in the mould before the pressing.

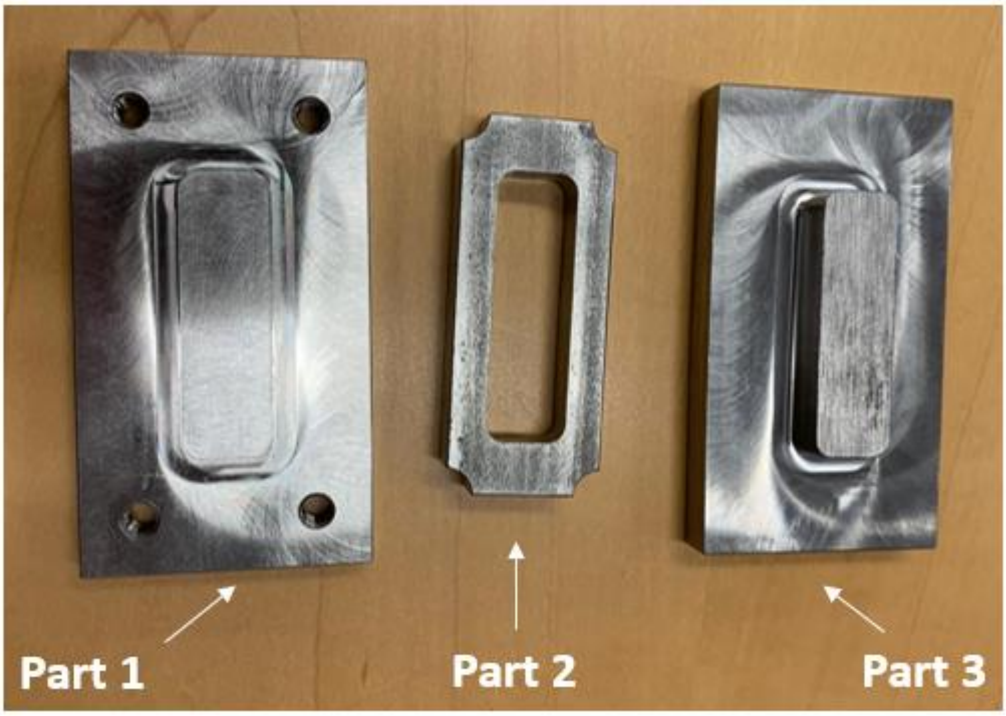


Figure 19: Steel ceramic mould used for the pressing and forming of the porcelain stoneware ceramic substrate used in the work.

As it is possible to see in ***figure 19,*** the mould is composed by three steel parts which fit together with minimum tolerance, in order to contain the powder nicely and avoiding it to get into the joints of the different parts of the mould. Also, all of the fitting-corners were rounded in order to facilitate the extraction of the ceramic substrate without it breaking, which can easily happen with sharp edges since they are spots which concentrate high forces during compression processes.

On the other hand, the load for the pressing process was applied by using a hydraulic press. The pressing mechanism consisted in two steel plates of 250x250 mm; the upper plate was fixed whilst the lower plate was the plate manually actioned with a lever and where the mould was placed. The press had a maximum working load of 20.000 kg. However, when the mould was designed, dimensions were calculated in order to ensure that the press worked below such limit. The process for the conformation of the porcelain stoneware substrates is the following:

- Firstly, all of the metallic surfaces of the mould which enter in contact when fitting the three parts together must be lubricated by applying some lithium stearate powder. This powder is commonly used in metallurgy and in our case, it prevents the pieces from jamming, since the whole is submitted to great compression forces, which combined with the minute tolerance between the different parts, can easily lead to such jamming.

- Secondly, the first part of the mould (part 1) is laid over the working table. The middle part (part 2) fits on top of it and its function is to contain sideways the ceramic powder once it’s poured into the mould.

- Thirdly, the ceramic mass must be poured into the mould and once this is done, the mould must be gently shaken in order to get a homogeneous distribution of the powder. The ideal case is that the top surface of the poured powder is in level with the mould to ensure an even thickness throughout the substrate.

- In fourth place, the last and top part of the mould (part 3) must be fitted on top of the previously fitted middle part and which will act as the punch that will transmit the pressure onto the top area of the powder. It is important that this last part is also fitted in level with the rest of the mould, since fitting it in an inclined or crooked position can also lead to jamming of the mould.

- Next, the powder-loaded mould is laid on the steel plate of the press, putting in between both a 0,2mm thick aluminium plate to protect the steel surfaces of both the press plate and the mould; another aluminium plate is also laid on top of the mould for the same reason. After this is done, pressing process can be started manually by using a lever which activates the hydraulic mechanism of the press. The lever must be operated gently until the analogic load indicator is marking the desired load; once this load is reached, the plates can be released by operating a crank which stops the hydraulic system from working and causes the steel plate to lower back to its position. Once the press has returned to its original state, mould can be removed.

- Lastly, the three parts of the mould can be separated, but the high compression forces the substrate to stick to the sides of the middle part and therefore it must be pressed out of it. For this, the third part which had previously been fitted on the top of the mould will now be laid flat over a surface, with the punch pointing upwards. Over the punch the middle part will be fitted and over this one, two separators will be placed on the sides of the steel piece; these separators will need to be taller than the height of the substrate. Subsequently, the whole will be again placed in the press, following the same previous steps. This time, the compression will force the middle part to slide through the punch while this one will also stop the substrate from sliding together with the middle part, consequently freeing the substrate from it. Finally, after the mould has been removed from the press, the substrate will ready to be extracted.

The process for the conformation of the porcelain stoneware substrates is simple but must be thoroughly followed in order to not damage any of the intervening components and in order to obtain a good quality substrate. The resulting ceramic sample will have enough mechanical resistance in its green state to be manipulated with a set of tweezers, but it will still be fragile to scratches and impacts. As explained previously in the chapter, one of the main factors to take into account for the production of the ceramic substrates is the specific pressure of the atomised powder. Knowing the surface area that our substrates have and knowing this specific pressure, the value for the need load to be applied can be easily calculated with the following formula:

$$p_{pressing} = p_{specific} \cdot S = 380 \cdot 5 \cdot 1{,}5 \approx 2850\ kg$$

However, this load value of 2850 kg will be round out to 3000 kg, since the analogic indicator of the press has a precision of 500 kg and this variation won't have a negative effect over the substrates, but it will actually influence positively due to the fact that an increase in conformation pressure increases the mechanical strength of the ceramic body both in green and sintered state and can also slightly decrease the temperature needed for complete sintering of it. For those experiments in which the interaction between ink and substrate was studied, the same process previously described was followed for the production of 4 different types of substrate, which differed from each other in the pressure applied during pressing process. The first of the substrates was prepared by applying the 3000 kg load (Substrate A) necessary for optimal green state apparent density. Next, the other substrates were prepared by applying a load of 1500 kg (Substrate B) which is ½ times the optimal load, 500 kg (Substrate C) which is 1/6 times the optimal load and 5000 kg (Substrate D) which is 5/3 times the optimal load. The preparation of different substrates is done in order to have substrates with different porosity values, which is accomplished by altering the conformation pressure, as explained in **section 4.1.2. "Composition of porcelain stoneware tiles".** At the same time, we decided to establish and maintain a sample thickness of approximately 3 mm. Mathematically, the amount of powder which needs to be poured in the mould to obtain samples 3mm thick after pressing can be calculated using the apparent density in green state provided in the table. Accordingly, since the sample volume in green state can be now defined as 50x15x3 mm^3, knowing the apparent density, the total amount of powder needed is:

$$m_{powder} = V \cdot \rho_{ap.green\,state} = 5 \cdot 1{,}5 \cdot 0{,}3 \cdot 2{,}08 = 4{,}68 \approx 4{,}7\ g$$

5.1.2. Sintering of the ceramic porcelain stoneware substrates

Before beginning the different printing experiments, porcelain stoneware substrates were prepared and fired in a conventional box furnace, which didn't allow atmosphere control nor temperature ramp setting. Consequently, the sintering of this first samples wasn't done by applying a defined temperature curve. However, temperature evolution was estimated by measuring the evolution of temperature values over time.

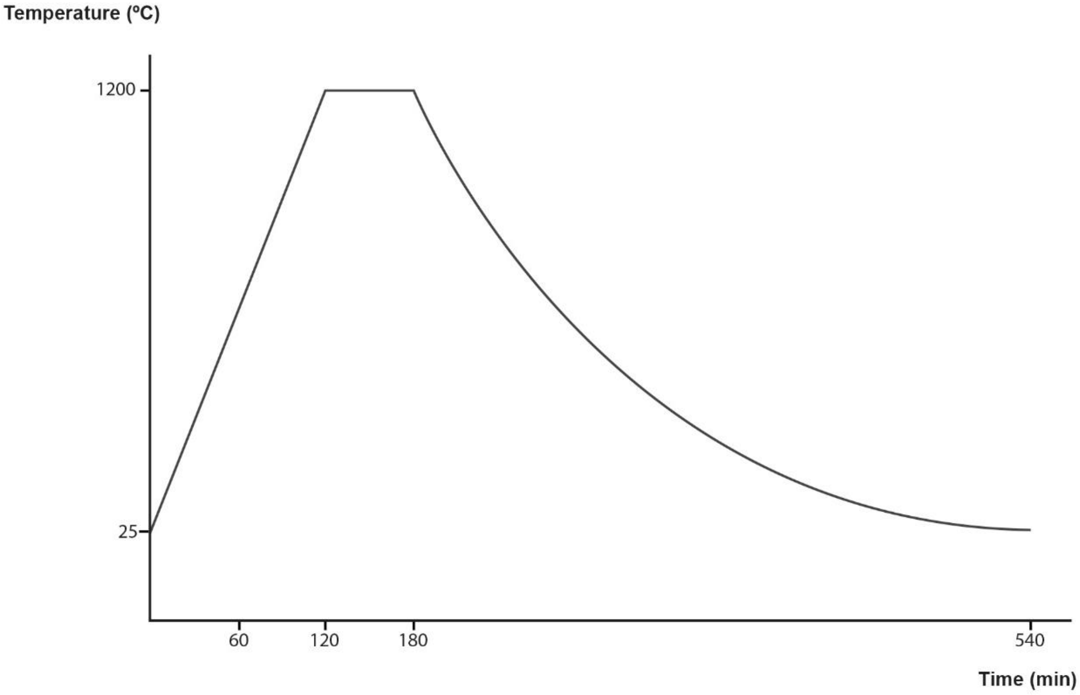


Figure 20: Heating curve applied for the sintering/firing process of the porcelain stoneware substrates in a conventional box furnace.

The approximate heating curve applied for the sintering of the porcelain stoneware samples is shown in ***figure 20***. The heating ramp up to 1200 °C, was of approximately of 10 °C/min taking a total of 2 hours to reach the nominal temperature. Then, nominal sintering temperature was maintained for 1 hour to ensure full sintering of the ceramic mass and furnace was powered off, since cooling-down could not be controlled. Cooling process from 1200 °C to ambient temperature was around 6 hours. This process would not actually correspond to a fast-firing technique. Nowadays, in industry strict and fixed temperature curves are designed and utilised for the fast-sintering of porcelain stoneware products whilst ensuring that all of the different physicochemical processes take place in the ceramic body and have enough time to be fully completed, as it has already been explained in chapter 4. However, in theory as long as the sintering temperature is reached and maintained for long enough, sintering of the porcelain stoneware product will be of good quality, as it has been already described in **section 4.1.3. "Production process of porcelain stoneware tiles".**

Two different batches of ceramic substrates were fired for sintering; one batch reaching 1200 °C which is the necessary sintering temperature for the porcelain stoneware in use, and another batch at 1100 °C, to compare both results and analyse the effect of temperature reduction over the microstructure of our sintered ceramic body. This was also done anticipating the fact that probably, the furnaces to be used for future experiments wouldn't be able to reach 1200 °C, thus obtaining data that would be useful to have as a reference for those possible samples sintered at lower temperatures.

Figure 21: Tube furnace utilised for the sintering of porcelain stoneware substrates.

Two different batches of ceramic substrates were fired for sintering; one batch reaching 1200 °C which is the necessary sintering temperature for the porcelain stoneware in use, and another batch at 1100 °C, to compare both results and analyse the effect of temperature reduction over the microstructure of our sintered ceramic body. This was also done anticipating the fact that probably, the furnaces to be used for future experiments wouldn't all be able to reach 1200 °C, thus obtaining data that would be useful to have as a reference for those possible samples sintered at lower temperatures.

On the other hand, after the printing experiments which will be defined in the next section, substrates on which conductive inks were printed were sintered in the tube furnace shown in ***figure 21***, in which both atmosphere and temperature curve could be controlled. Atmosphere control was performed in order to avoid the oxidation of the conductive materials deposited on the substrates during the sintering process. In particular, we used a helium gas flow to create an inert atmosphere for the porcelain substrates to be sintered in. Once the substrates had been introduced in the quartz tube and system was set up, helium flow was activated at 650 sccm for 4 minutes to remove the air present in the tube.

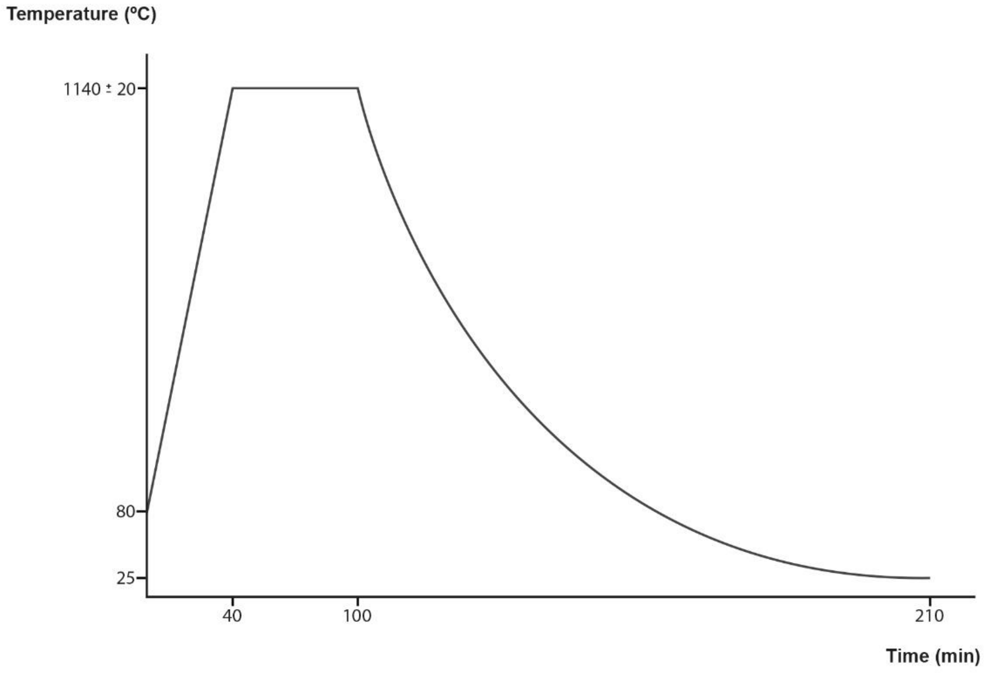


Figure 22: Heating curve applied for the sintering/firing process of the porcelain stoneware substrates in a tube furnace.

Then, temperature was increased until 1140 °C (which is the maximum temperature this furnace could reach with an error of ±20 °C) by applying a temperature ramp between of 30 °C/min approximately. Next, nominal temperature of 1140ºC ±20 °C was maintained for 1 hour. Finally, cooling process took place, taking an average of 3 ½ hours to reach ambient temperature. The heating applied for this sintering process is shown in ***figure 22***.

It is important to mention that, as mentioned in **section 4.1.3**, for both of the applied heating curves, shown in ***figures 21 and 22,*** once the nominal temperature had been reached, furnaces were maintained at such temperature of about an hour in order to allow the necessary physiochemical transformations to take place and subsequently ensuring the proper sintering of the ceramic mass.

5.1.3. Characterisation of porcelain stoneware substrates

Imaging and microstructure analysis of both types of sintered porcelain stoneware substrate was done by scanning electron microscopy (SEM) at 5 kV and with a working distance between 5-8 mm. For this purpose, substrates were cut in pieces to reveal the internal microstructure, which were subsequently sonicated in distilled water for 5 min and an pressure air gun was used in order to eliminate dirt that could have entered in contact with the substrate during post-sonication manipulation. Later on, samples were left to dry overnight in an oven at 80 °C. During the following morning, samples were taken for sputtering of the cross-section with Au-Pd using a sputter equipment.

On another hand, since we had a Micro CT Scanning equipment available and the SEM equipment didn’t allow the characterization of ceramic samples in their green state (due to the fact that the release of particles from the unfired substrate during vacuum process can damage components in the SEM chamber) we utilised it in order to analyse microstructural changes derived from variations in the applied conformation pressure of the four different substrates defined in **section 5.1.2. “Sintering of the ceramic porcelain stoneware substrates”.**

CT scanning was ran at 140 kV and 10 W to obtain a transmission of up to 60% and a sufficient emission of X-rays to obtain a good image. For each substrate we obtained between 500 and 1000 images.

Lastly, as mentioned in section **5. “Experimental procedure”,** apparent density in green state of the different ceramic substrates was measured by utilising a patented non-destructive technique based on X-ray absorption **[38].**

5.2. Printing of inks over green porcelain stoneware substrates with an inkjet technology printer and characterisation

Printing of the different inks used in the project was done with a Dimatix DMP 2800 Series inkjet printer. This a very versatile printer with which a great variety of inks can be printed, since it permits to modify many of the printing parameters by using a very intuitive software.

On one hand, it allows to set the working temperature of the printing head and printing bed. For each ink a waveform can be designed in which different voltage levels can be set, as well as time-maintenance for each voltage level and slew rates between different voltage levels. The purpose of each of the voltage levels has been explained in **section 4.2.1. "Working principles of inkjet printers".**

For the tailoring of each of the waveforms, we parted from a default one and by modifying the various parameters whilst printing, we were able to obtain after some time a suitable waveform which allowed the printing of good quality lines.

Since our printed patterns consisted in various layers, printer was adjusted to perform cleaning cycles every few layers (depending on the ink in use) in order to avoid clogging of the nozzles and subsequent ununiform printing. Furthermore, once in a while printer had to be re-calibrated, since it is usual for printers like the one in use to lose calibration when working during long periods of time and at the same time being manipulated by different users which utilise different printer settings. Calibration of the printer is important in order for it to precisely print the desired lines in the desired locations.

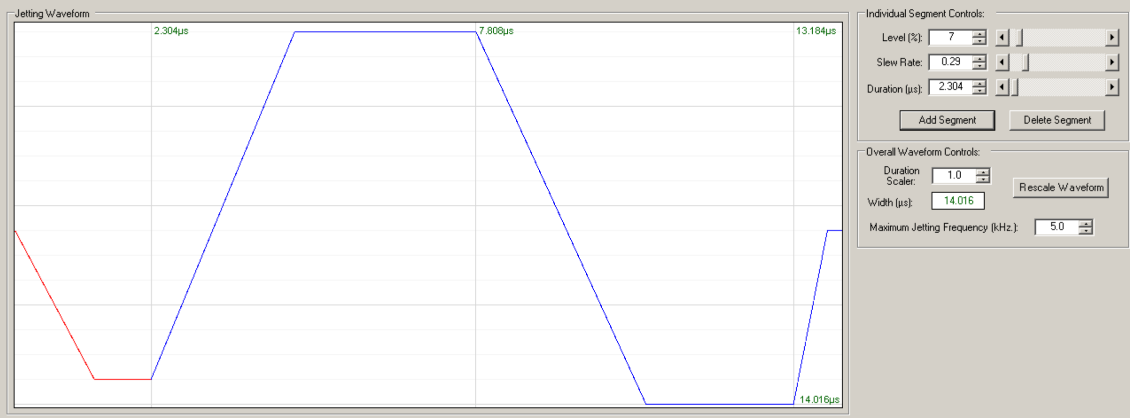
One last important general factor to take into account when printing with solvent inks is the flash point of the solvents present in the formulation of such inks. Flash point of a solvent is the minimum temperature at which a solvent can vaporize into an ignitable vapor. In order to print under safe conditions, temperature of the laboratory where the printing was performed was set between 21-24 °C and when using solvents, nozzle temperature and printing bed temperature parameters were deactivated.

5.2.1. Printing of water-based inks

5.2.1.1. Printing of water-glycerol dye ink

Once the method for the preparation of the substrates was defined, we continued by printing a water-glycerol dye ink. This ink was prepared by preparing a solution 50 wt. % of a commercial pink food dye and 50 wt. % water.

We decided to use this ink because it's an easy ink to print with an inkjet printer and because its intense pink colour allows optical characterisation with a microscope of the printed patterns on the substrate, without the need of performing further processes or using more complex equipment. Moreover, since the characterisation of this substrates will be done in their green state, it has sense to use such an ink; if the aim would be to characterise the substrates after firing, another ink should be utilised since the organic dye printed on the substrate would burn off during such process and the patterns would most likely not be able to be visualized.



Level (%): 7

Slew Rate: 0.29

Duration (µs): 2.304

Duration Scaler: 1.0

Width (µs): 14.016

Maximum Jetting Frequency (kHz.): 5.0

Figure 23: Designed and applied waveform in for the jetting of water-glycerol pink dye ink droplets via ink-jet printing with a Dimatix DMP Series printer.

Before starting to print, the waveform had to be modified until we were able to print good quality lines. The final designed waveform utilised for the printing of the water-glycerol pink dye ink is shown in ***figure 23*** above. The first experiments which were conducted were done in order to evaluate the behaviour of the ink when printed onto the surface of different green porcelain stoneware substrates which were prepared by pressing at different loads. Of the four types of substrate described in **section 5.1. “Preparation, pressing and sintering of porcelain stoneware tiles”**, three different substrates were utilised, substrates A, B and C with pressed at loads of 3000 kg, 1500 kg and 500 kg respectively. This was done to analyse the effect that changes in substrate porosity due to variations in conformation pressure, might have over ink spreading and penetration processes.

Thereby, over the surface of each of every three substrates, 12x0,1 mm lines were printed with a drop spacing between droplets of 10 um. Subsequently, each layer was composed by the printing of 1201 droplets in the X axis and 10 droplets in the Y axis. Thus, by setting the number of layers and knowing that each droplet has a volume of 10 pL (given by the Dimatix inkjet printer) the total printed volume can be determined by applying the following equation:

$$V_{printed} = droplets_{X-axis} \cdot droplets_{Y-axis} \cdot N_{layers} \cdot \ V_{droplet}$$

Over each substrate seven different lines were printed gradually increasing the number of layers per line, from 1 to 5, 10, 15, 20, 40, 60 layers. Once the lines were printed, samples were cross sectioned. Surface and cross-section of the three substrates were characterised with a microscope in order to quantify spreading and penetration by measuring over the taken images.

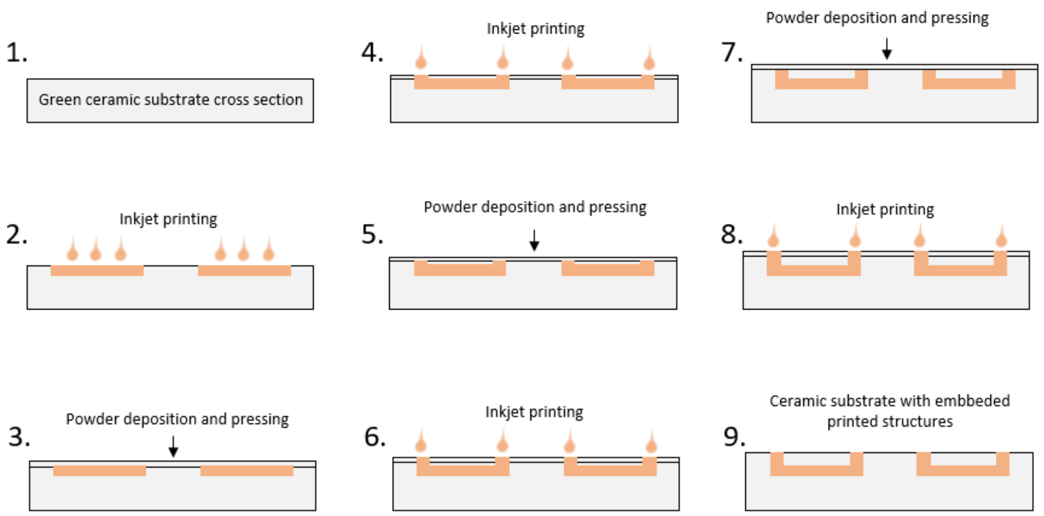


Figure 24: "Schematic representation and simplification of the "layer by layer" process performed for the production of ceramic substrates with integrated printed structures.

Next, following the steps 1 to 3 form the detailed procedure shown in ***figure 24***, two 20 layered lines were printed over the three new substrates and later another layer of powder was pressed over the printed lines, consequently "encapsulating" the ink in a ceramic matrix.

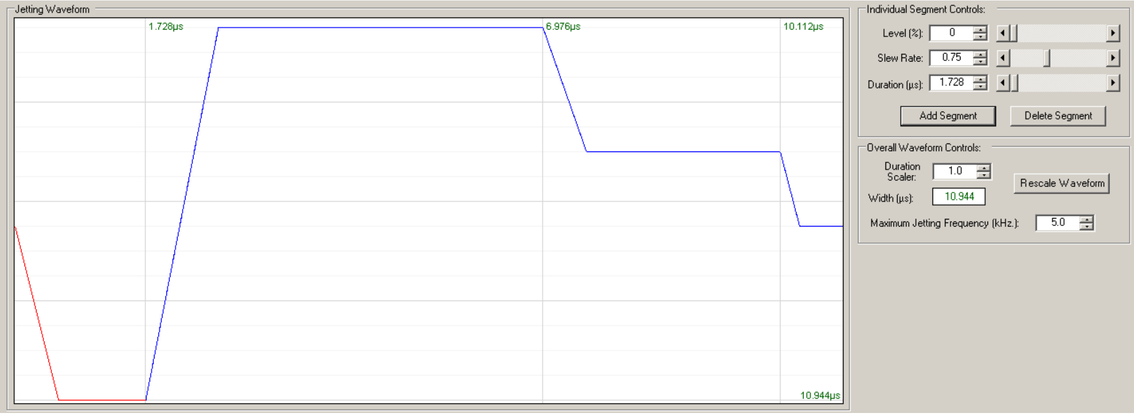
Lastly, following the whole procedure detailed in ***figure 24,*** 20 layered ink lines and dots were printed over the substrate in order to form a "U" shaped pattern, establishing a contact between the ink on the surface of the sample and ink which is embedded in it.

For both of this last two procedures, the substrate which has already been pressed had to be re-introduced in the mould in order to press another layer of porcelain stoneware powder over the printed lines. This process is a very delicate one, since pressed samples tend to expand once they've been extracted from the mould. In this manner, when substrates which have been printed were attempted to be re-introduced in the mould, they happened to be slightly bigger than the chambers in which the powder is poured. So, substrate had to be laid on the base piece of the mould and the middle piece had to be slowly and gently fitted around the already pressed sample.

5.2.1.2. Printing of water-based graphene ink and conductivity measurements

Further on, printing experiments were done using a graphene water-based ink purchased from Sigma Aldrich, which had a concentration of <0,1 wt. % of solids in water and 1 cP viscosity. Graphene is present in the form of exfoliated flakes with sizes between 80-500 nm. This was one of the only available water-based conductive inks meant for inkjet printing found in the market, reason why we decided to purchase it and use it to try a conductive water-based ink.

As well as with the water-glycerol dye ink, water-graphene ink was printed over three different kinds of substrates, pressed once again at 3000 kg, 15000 kg and 500 kg. Some of the substrates were meant for cross-sectioning and analysis of both spreading and penetration as with the water glycerol-dye ink.



Individual Segment Controls:
Level (%): 0
Slew Rate: 0.75
Duration (µs): 1.728

Overall Waveform Controls:
Duration Scaler: 1.0
Width (µs): 10.944
Maximum Jetting Frequency (kHz.): 5.0

Figure 25: Designed and applied waveform in for the jetting of water-based graphene ink droplets via ink-jet printing with a Dimatix DMP Series printer.

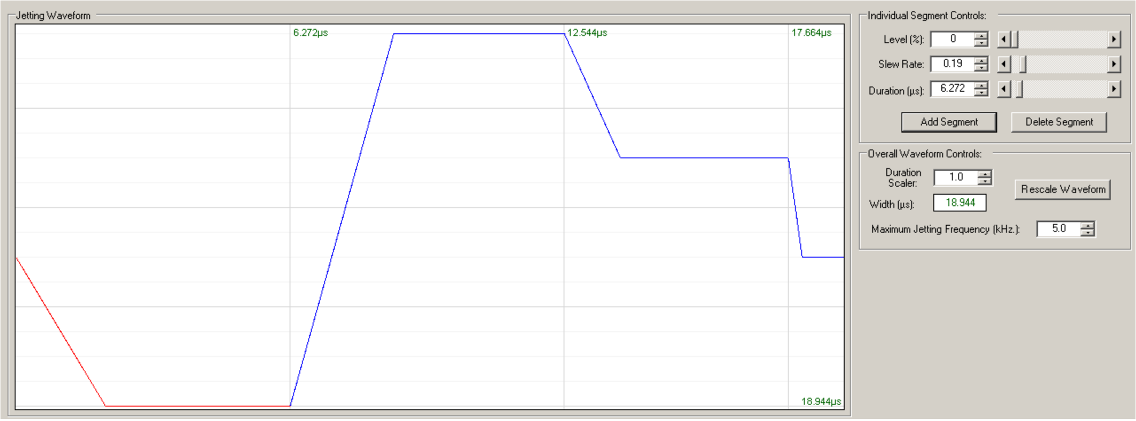
This time, we first printed lines of 40x0,1 mm and a drop spacing of 15 µm with 1, 3, 5, 9, 12 and 15 layers of ink. Then, since the solid concentration in the graphene ink was very low and in order to make an efficient use of the ink we had available, we decided to also print the lines with a higher number of layers. Thus, 20, 30, 40 and 60 layered 40x0,1 mm lines were printed over the three types of substrate, with a drop space of 15 µm, since we found that with this drop spacing, printed line quality was the best. Subsequently, each of the printed layers was composed by 2667 droplets in the X-axis and 7 droplets in the Y-axis. By using the equation described in section 5.2.1.1. total ink printed volume can be calculated. The waveform designed for the graphene water-based ink is shown in ***figure 25*****.**

On another hand, some of the samples were submitted to a sintering process in the tube furnace for posterior conductivity measurements of the lines. Conductivity measurement of the samples was done by using a traditional two probe multimeter.

5.2.2. Printing of solvent-based inks

5.2.2.1. Printing of silver solvent-based ink

Solvent-based silver ink was a Sicrys^{TM} I50TM-119 purchased from PV Nanocell, which is based on silver nanoparticles suspended in triethylene glycol monomethyl ether (TGME) designed for inkjet printing. Metal loading of silver in the ink is 50 wt. % and particle size is between 85-120 nm. Ink viscosity is 34 cP and surface tension 30 dyne/cm.



Level (%): 0
Slew Rate: 0.19
Duration (µs): 6.272
Duration Scaler: 1.0
Width (µs): 18.944
Maximum Jetting Frequency (kHz.): 5.0

Figure 26: Designed and applied waveform in for the jetting of solvent-based silver ink droplets via ink-jet printing with a Dimatix DMP Series printer.

First, over the same three different types of substrate utilised for the other printing experiments, seven 40x0,05 mm lines were printed over each substrate, with different number of layers, varying from 1 to 3, 6, 9, 12, 15 and 18 layers and with a 20 um drop spacing. Subsequently, each layer was composed by 2000 droplets in the X-axis and 3 droplets in the Y-axis.

Then, more samples were prepared by printing four 40x0,05 mm lines over each substrate, increasing the number of layers per line to 30, 40, 50 and 60 layers. Moreover, drop spacing was reduced to 15 um in order to optimize printed line quality to its maximum. Subsequently, droplet amount per layer varied to 2667 droplets in the

X-axis and 4 droplets in the Y-axis. By using the equation described in **section 5.2.1.1. "Printing of water-glycerol dye ink"**, total ink printed volume can be calculated. The waveform designed for the silver solvent-based ink is shown in ***figure 26***.

Lastly, over some of the samples with silver printed lines of 30, 40, 50 and 60 layers, powder was deposited over the surface and pressed in order to encapsulate the printed line in the ceramic sample, following the same procedure as described in **section 5.2.1.1**. **"Printing of water-glycerol dye ink".** The same procedure was also performed over samples with three printed lines of 100 layers.

As it was done with all of the samples on which conductive inks were printed on, some of the samples with silver ink were submitted to a sintering process in the tube furnace for posterior conductivity measurements of the lines. Conductivity measurement of the samples was done by using a traditional two probe multimeter.

6. Analysis of results and discussion

6.1. Analysis of ceramic substrate

Characterisation of the ceramic substrate was performed in order to analyse the microstructure and quality of the substrate after sintering and to analyse the microstructure and porosity of substrates in their green state. Sintering process at 1200°C confers the ceramic body a white or light-yellow colour, depending on the conditions of the sintering process, with smooth and shiny/glassy appearance and an already noticeable hardness.

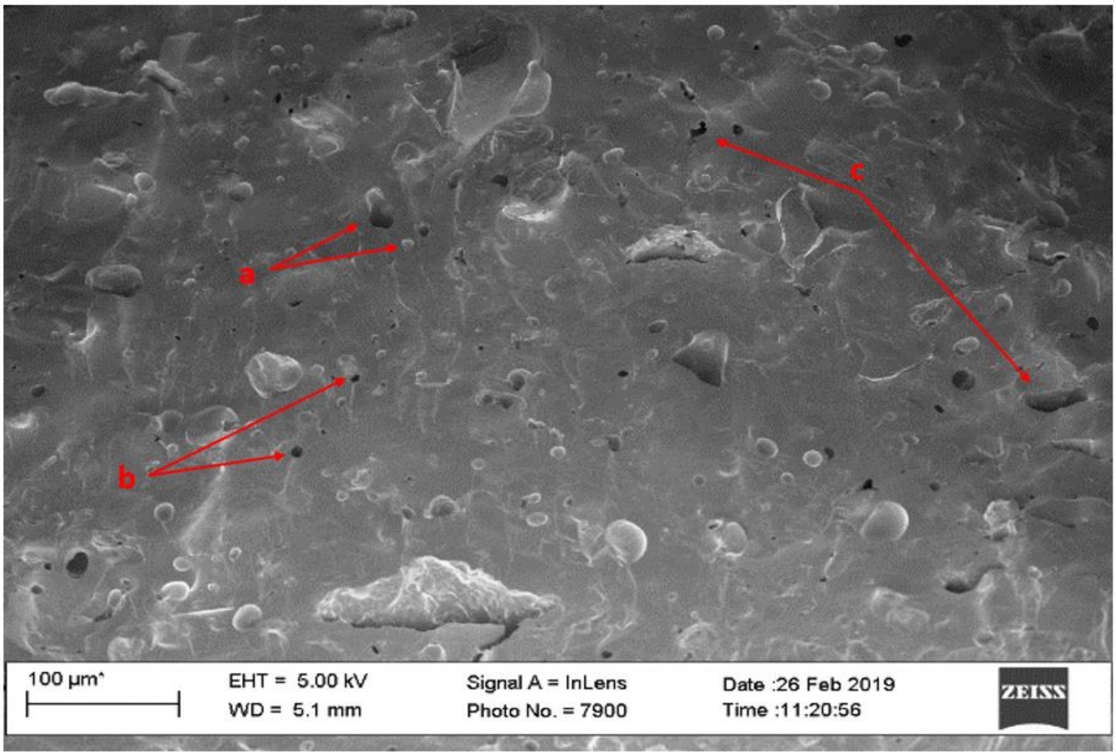


Figure 27: SEM image of a porcelain stoneware substrate fired at 1200ºC. Closed porosity ((a) and (b)) and minimal interconnected porosity (c) are indicated with arrows

SEM image shown in ***figure 27*** of the sample prepared and fired at 1200ºC as described in section 5.1, reveals that the general crystalline structure of our ceramic substrate is adequate, and that interconnected porosity is minimal, which also indicates that the substrate has been sintered at the needed temperature and during a sufficient amount of time. In the substrate we can mainly distinguish fine closed porosity and a lower presence of coarser porosity, with barely apparent interconnected porosity, corresponding to porosity analysed for porcelain stoneware samples in other works **[39].** This suggests that the substrate has been sintered correctly, since the aim is to obtain a ceramic body with a low percentage of closed porosity (<10%) and minimal percentage of open porosity (<0,5%).

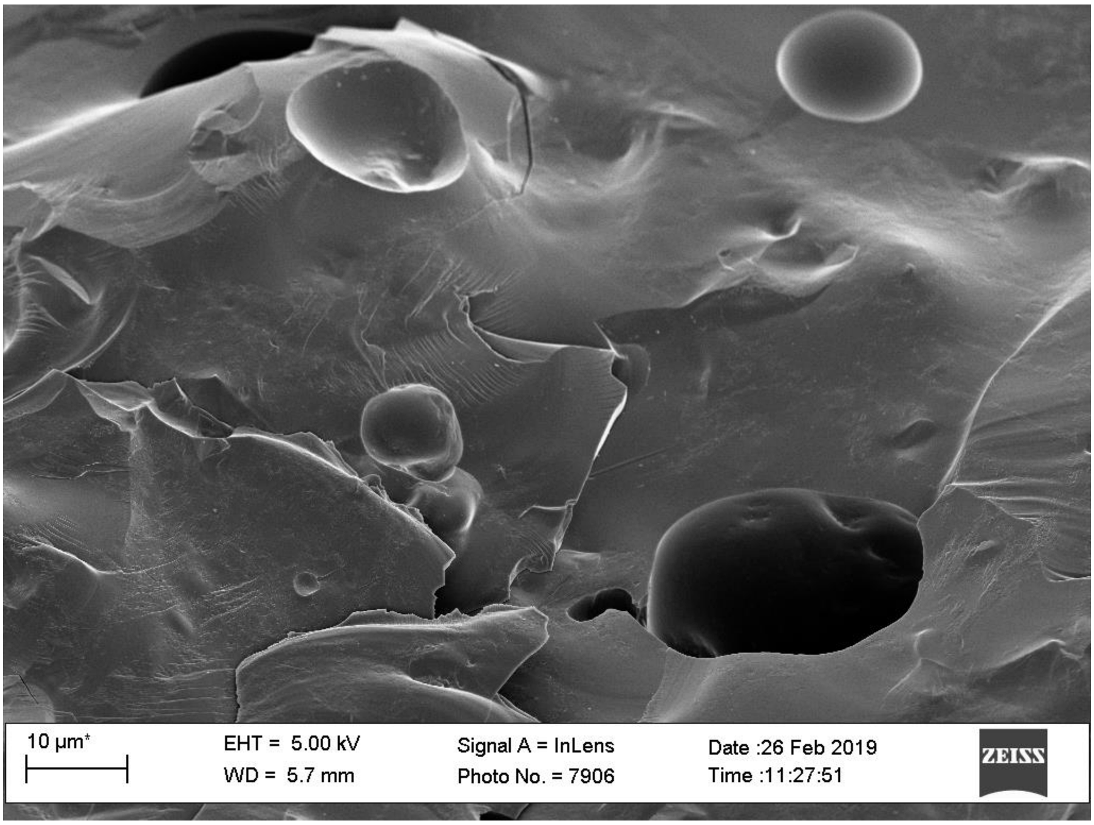


Figure 28: SEM image of porcelain stoneware substrate fired at 1200ºC

In ***figure 28*** also corresponding to the substrate fired at 1200 °C, glass phase is predominant, with few remaining raw material particles. In comparison with microstructure analysed in other works **[40]** in which for a sintering temperature of 1200ºC the microstructure consists on a rougher ceramic matrix in which different particles can be differentiated, we find in our case a more homogeneous glassy phase in which mostly closed pores can be identified.

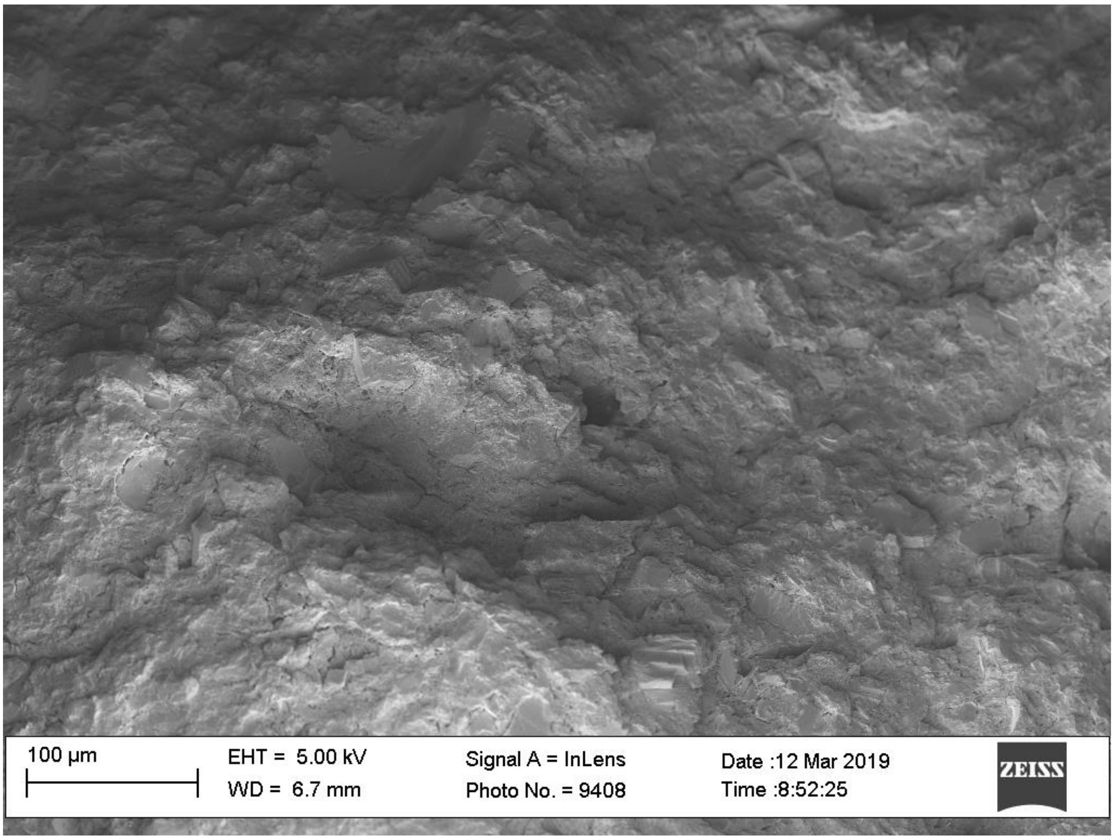


Figure 29: SEM image of porcelain stoneware substrate fired at 1100ºC.

On the other hand, in ***figures 29 and 30*** corresponding to the substrate fired at 1100 °C a rougher and more irregular microstructure is visible, which is possibly due to the fact that amorphous or liquid phases haven't taken place yet. Typically, the glass phases start to have a notable presence from 1100 °C upwards, partially filling in the pores in the ceramic structure and dissolving some of the bigger raw material particles. Before this process takes place, underfired and high interconnected porosity structures are common in temperature ranges of approximately 500-1000 °C, which can also be seen in the figure. Visually, such difference in the sintering temperature is easily noticeable, since the porcelain stoneware substrate fired at 1100 °C losses its characteristic shininess and vitreous appearance and it appears more brittle to the touch. Ideally, sintering temperature is not a parameter which should be varied, at least not below the nominal temperature, which is 1200 °C in our case, since it will define the physiochemical processes that take place in the ceramic body and subsequently it will define the mechanical and aesthetical quality of the substrate. However, it is still interesting to analyse the microstructural variations of the porcelain stoneware ceramic mass to have a reference and comparison for future results.

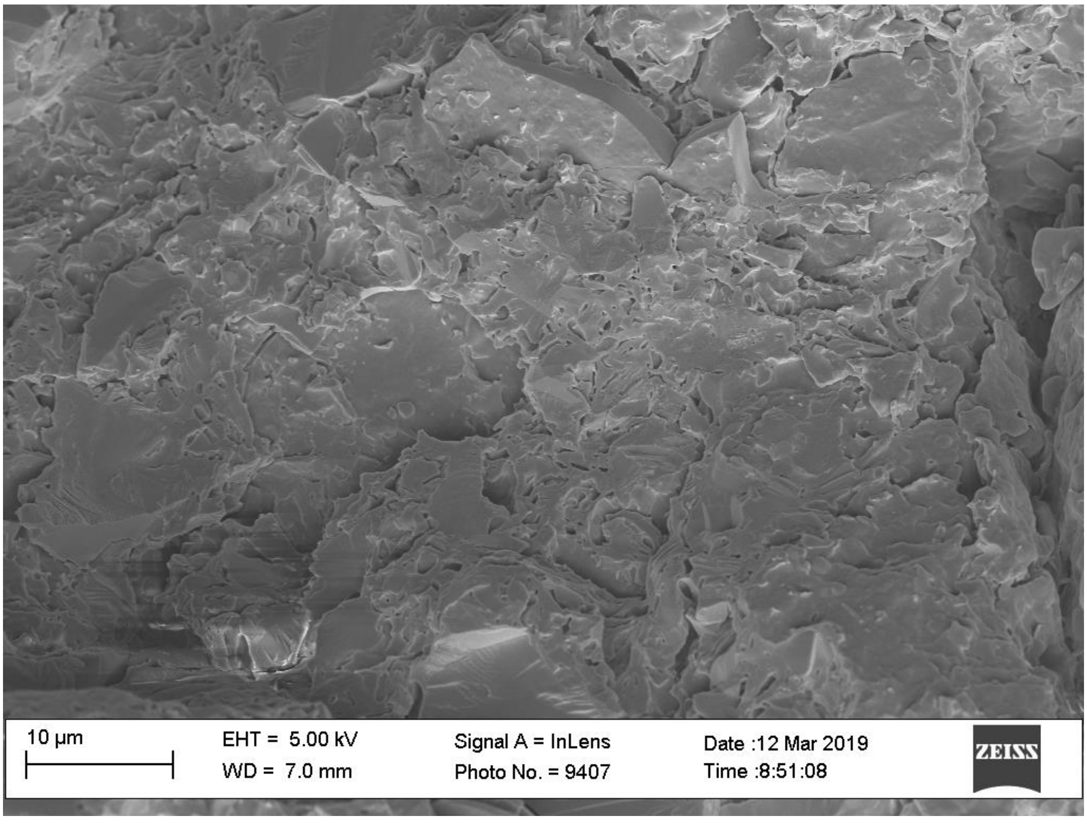


Figure 30: SEM image of porcelain stoneware substrate fired at 1100ºC.

One of the main differences that the optical characterisation we performed has with characterisation done with SEM equipment in some of the cited articles is that commonly, surface of the samples is treated previous to sputtering and visualization, either by polishing of the surface which is going to be analysed or doing and etching process with solutions such as hydrofluoric acid. Nevertheless, the laboratories in which the project was developed weren't used to working with dangerous chemicals such as HF and we considered neither etching or polishing were necessary, since we were looking for qualitative data to evaluate our ceramic sample rather than quantitative data.

As it has just been mentioned, sintering temperature is of crucial relevance in the final characteristics of the ceramic substrate and should not be modified below the nominal limit. Nevertheless, conformation pressure can be varied up to a certain limit as long as the interconnected porosity is low enough and the ceramic body has the necessary mechanical strength in its green state.

Apparent density in green state, which has been introduce in **section 5.1. "Preparation, pressing and sintering of porcelain stoneware substrates"** and which is one of the main characteristics of the ceramic product, is a direct reflection of the quality of the ceramic body after the pressing process and it is used in industry to evaluate this, since a decrease in apparent density is linked to an increase in porosity or increase of defects within the ceramic structure.

By analysing the substrates with the mentioned X-ray absorption technique **[38],** the values of apparent density in green state of the substrates was measured, which gives information about the structure integrity and compaction of the ceramic particles after the pressing process, which at the same time is related to the porosity of the substrates. Thus, the values of apparent density in green state are 2071 kg/m^3 for substrate D, 2047 kg/m^3 for substrate A, 2018 kg/m3 for substrate B and 1932 kg/m^3 for substrate C. The optimal value of apparent density should be around 2080 kg/m^3, according to the specifications of the provided ceramic powder. Thus we can see how substrates A, B and D have values relatively near the optimal value, but substrate C is much lower than the required, indicating that the structural integrity of the sample both before and after sintering will be of bad quality.

Figure 30 shows a section obtained by micro CT scanning of each of the four substrates prepared according to the method described in **section 5.1. "Preparation, pressing and sintering of porcelain stoneware substrates".** As it can be seen in the different images of the figure, porosity increases substantially and gradually from images a) to d) when decreasing the pressure/load applied during pressing of the porcelain stoneware powder. Furthermore, in images c) and d), inter-granulate limits can also begin to be observed. This occurs because, when decreasing the applied pressure from the optimal value, it begins to be insufficient for compaction of the ceramic particles, which are mostly particles shaped as hollow spheres due to the atomisation process.

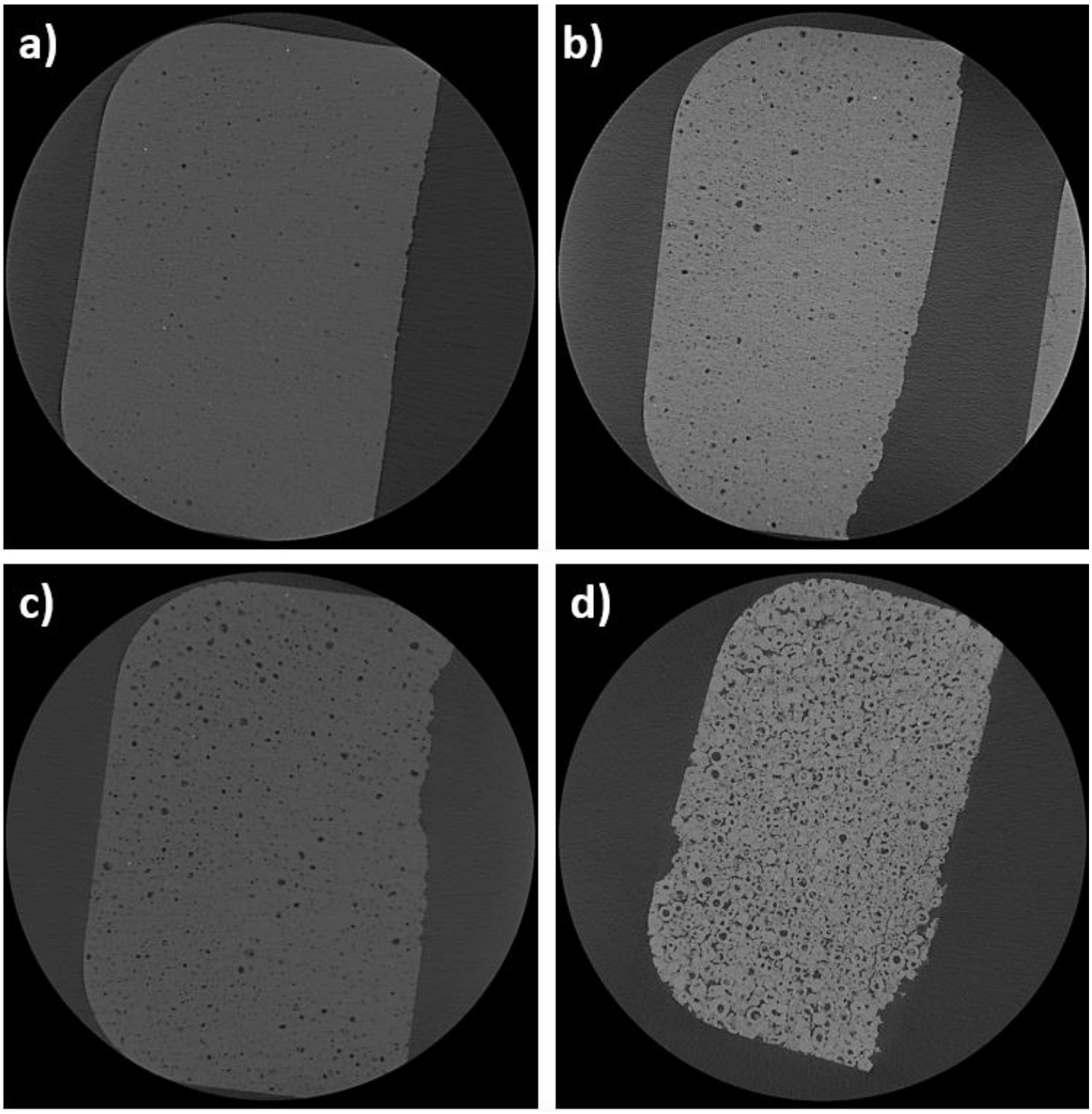


Figure 31: Images obtained via CT Scanning of different porcelain stoneware substrates. Images corresponds to: substrate pressed at 5000 kg load (a), 3000 kg load (b), 1500 kg load (c) and 500 kg load (d).

Moreover, for this same reason it is difficult to differentiate between interconnected porosity (in the form of micro-channels) and apparent pores which are actually the empty cores of such spherical particles, which have not been destroyed during the pressing process; as it is indicated in the figure, many of the visible apparent pores actually are these undestroyed particle cores.

In relation to the conformation and pressing process of ceramic products, this is totally undesirable, since the presence of these particle cores and the presence of inter-particle limits will make the ceramic body mechanically weak. From the first and second images of the figure, it can be seen how, by performing a goof pressing process, practically all the spherical particles are destroyed and compressed into the ceramic matrix and interconnected porosity is minimal. Then, by looking at the following images it can be seen how the porosity begins to increase while the conformation pressure of the samples is decreased, thus also decreasing the apparent density of the ceramic body.

By conducting this scan, we are able to see how the internal structure in the ceramic varies with the applied pressure and the particle distribution is in the ceramic powder, which can be useful when drawing conclusions. However, the images by their own are not sufficient to quantify substrate porosity and should be analysed with some kind of image-processing software such as FIJI or VG Studio Max **[41].**

Overall, these initial experiments allowed us to have a first look and have a first impression of the porcelain stoneware samples, which were going to be used as substrate for the printing of ink, so as to obtain basic information to compare with results of the future experiments, confirming at the same time its adequacy for the elaboration of the project.

6.2. Analysis of printed water-based inks on the substrate

6.2.1. Analysis of spreading and penetration of water glycerol dye ink printed patterns

The first experiments which were conducted were done in order to evaluate the behaviour of the water-glycerol dye ink when printed onto the surface of different green porcelain stoneware substrates which were prepared by pressing at different loads. As described in **section 5.1. "Preparation, pressing and sintering of porcelain stoneware substrates"**, four different substrates were prepared, but for these experiments only three of them were utilised, pressed with loads of 3000 kg (Substrate A), 1500 kg (Substrate B) and 500 kg (Substrate C) respectively.

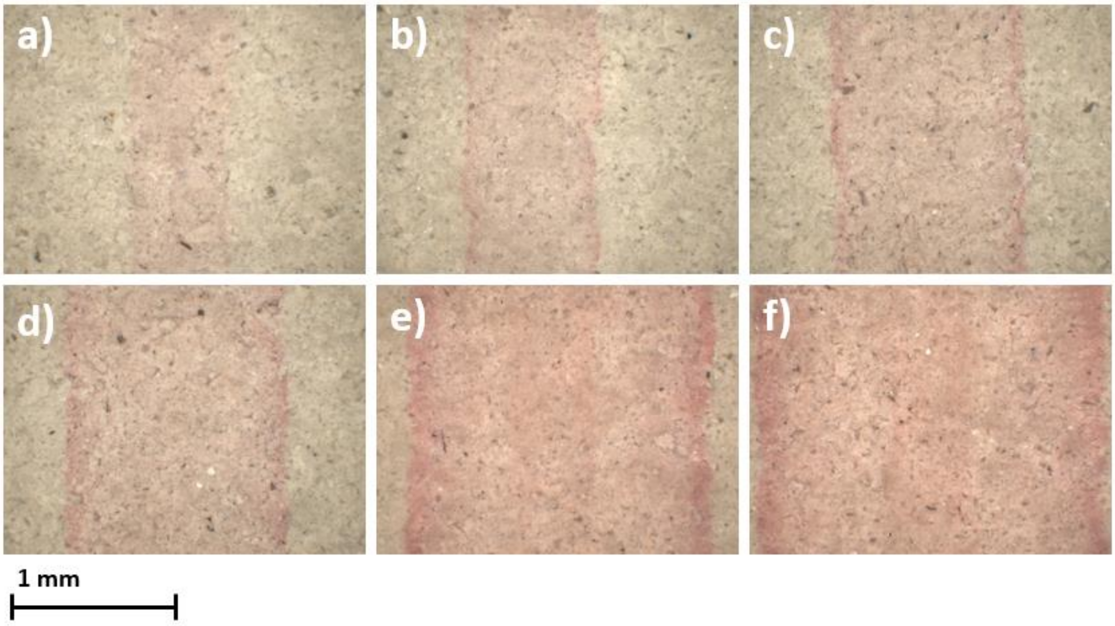


Figure 32: Lines of 5, 10, 15, 20, 40 and 60 layers of water-glycerol pink dye ink printed on substrate A pressed at 3000 kg, from a) to f) respectively.

Following the process defined in **section 5.2.1.1. “Printing of water-glycerol dye ink”**, seven lines with different number of layers were printed over each of the three substrates. This was done to analyse the effect that changes in fundamental conditions of the ceramic body such as substrate porosity, pore distance and particle size might have over ink spreading and penetration processes due to variations in conformation pressure.

By applying the equation described in **section 5.2.1.1. “Printing of water-glycerol dye ink”**, the total volume of water-based ink deposited in each line was calculated, which allows to compare quantitatively the difference between the different printed lines. These calculations are simple, since the increase in printed volume is directly proportional to the number of layers.

Number of layers	1	5	10	15	20	40	60
Printed ink volume (µL)	0,1201	0,6005	1,201	1,802	2,402	4,804	7,206

Table 10: Printed ink volume of water-glycerol pink dye ink in relation to the number of printed layers

Table 10 shown on top represents the value of printed ink volume for each of number of layers printed on each line. As it can be seen, the increase in printed ink volume is substantial. ***Figure 32*** shows images of different printed lines taken by analysing the substrate with an optical microscope. These images were taken for all the three substrates for analysis of ink spreading on the ceramic.

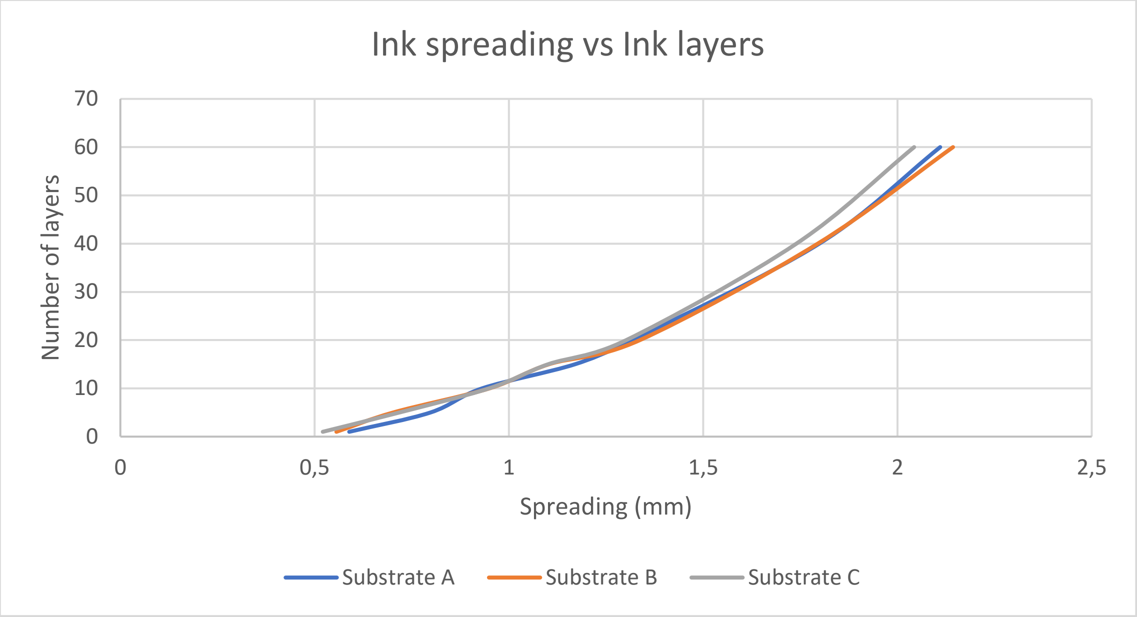


Figure 33: Plot in which the relation between the number of printed layers and the spreading of the ink is represented for substrates A, B and C.

From each image, spreading was measured with the microscope software and plotted in the ***figure 33*** shown on top, in order to evaluate the variation of spreading in relation to the variation in the structure of the three substrates. From both the figure and the plot, various conclusions can be drawn.

First of all, printed lines appear of good quality and homogeneous spreading, with no visible agglomeration or clogging of ink along the lines. It is clearly visible how the variation in spreading exponentially grows with the increase of printed ink volume. Already in lines with one layer of ink, line width has values of over 0,5 mm, being up to five time higher than the theoretical line width defined in the Dimatix printer software which was of 0,1 mm. This clearly shows the affinity our porcelain stoneware substrate has for water-based fluids.

Then, on the other hand, slight differences can be seen in spreading depending on the substrate used for printing. By analysing the values represented in the plot, it can be seen how in general, water-glycerol dye ink has a tendency to spread more in higher-pressed substrates in comparison to less-pressed substrates, which is more noticeable in lines with higher amount of layers, where spreading in less-pressed samples is between 3-5% lower than in higher-pressed substrates. Between 5 and 15 layers some values appear to be higher for the 500 kg pressed sample. However, this can be due to irregularities in the substrates or in the printing process.

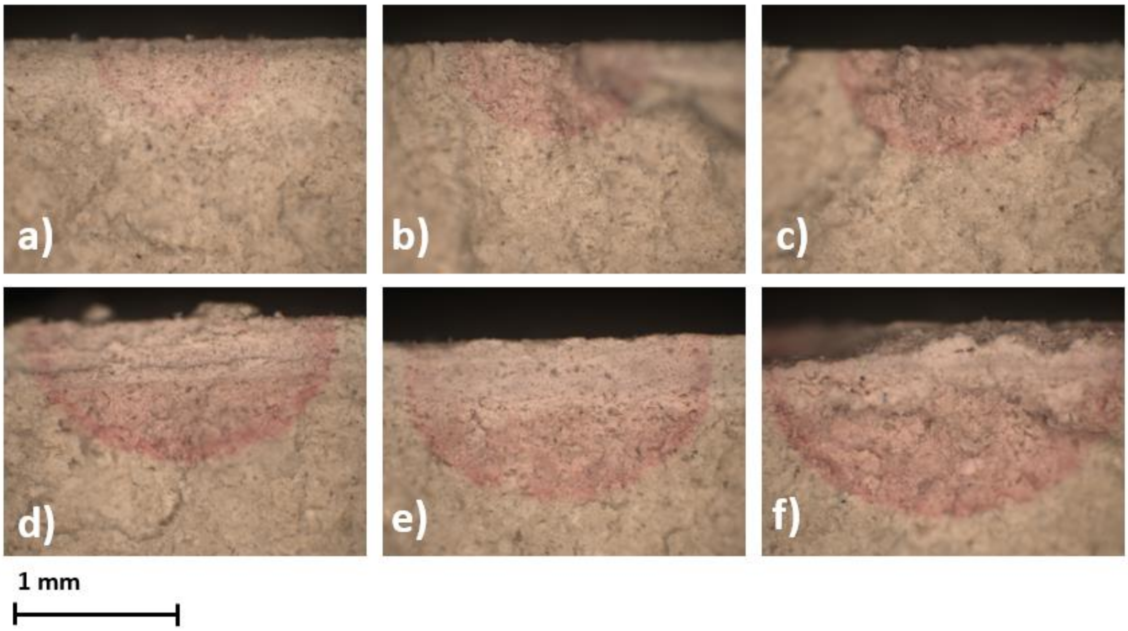


Figure 34: Cross section of lines with 5, 10, 15, 20, 40 and 60 layers of water-glycerol pink dye ink printed on substrate A pressed at 3000 kg.

On the other hand, once the lines were printed, samples were cross sectioned in order to also analyse ink penetration on the three substrates by once again using the optical microscope. In ***figure 34*** the cross section of different lines is shown.

As with the images taken for spreading analysis, cross section of the lines was measured with the microscope software and plotted in the plot which can be seen above. As with ink spreading, ink penetration appears to gradually increase with the increase of printed ink volume.

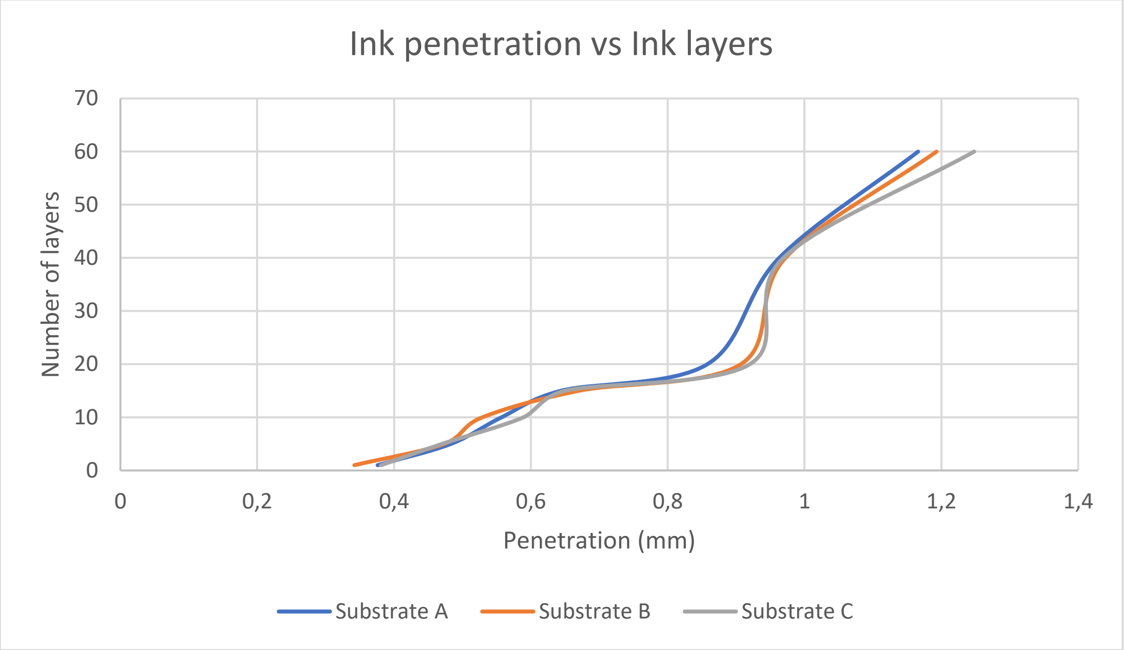


Figure 35: Plot in which the relation between the number of printed layers and the penetration of the ink is represented for substrates A, B and C.

As with the images taken for spreading analysis, cross section of the lines was measured with the microscope software and plotted in the plot which can be seen in ***figure 35*** above. As with ink spreading, ink penetration appears to gradually increase with the increase of printed ink volume.

However, this time penetration tends to be higher for the more porous substrates. This phenomenon is more noticeable at higher printed volumes, where penetration in substrate C is between 3-8% higher than in substrates A and B.

This result actually makes sense and was expected, since it relates to the results obtained for ink spreading. Penetration and spreading seem to be correlated in a way that, for a fixed amount of printed ink, while spreading tends to decrease as porosity of the substrates increases, penetration tends to increase, since the proportion of ink which is not spreading sideways is directed downwards both by capillarity effect and gravitational pull.

This correlation and interaction between spreading and penetration has also been described as a complex system, in which the coupling between both phenomena was quantified and the maximum extension of the droplets could be mathematically predicted **[42].**

On the other hand, overall values of ink spreading always tend to be higher than the values of ink penetration for all of the different lines and in the three of the selected substrates, confirming that the printed water-glycerol dye ink has more tendency towards spreading on the surface of the substrate rather than penetration in the substrate's ceramic body. Nevertheless, in relation to the purpose of this project, it can be affirmed that variations in the porosity of the samples don't have a significant effect over the spreading and penetration of a water-based ink over the substrate. The amount of ink on another side, does signify bigger variations of these two parameters.

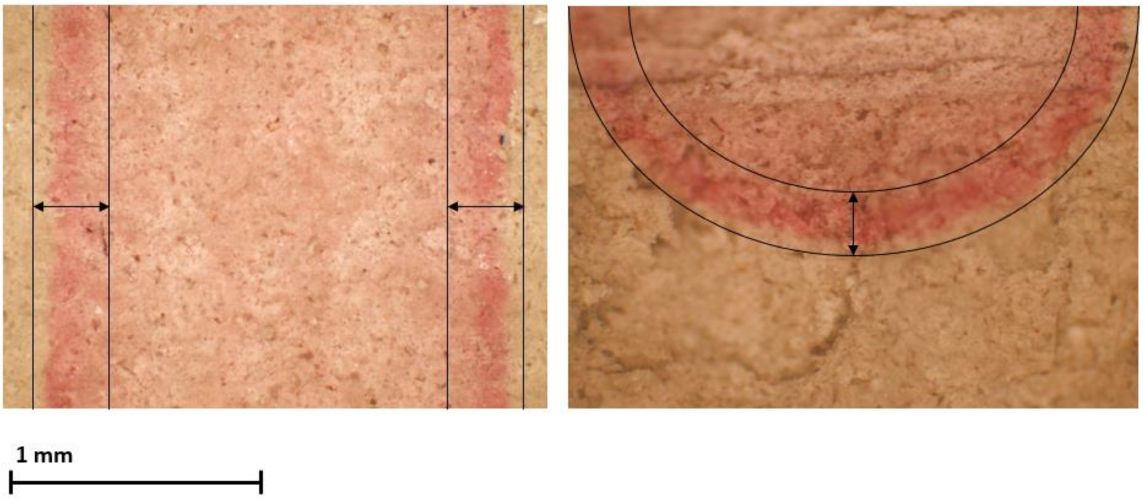


Figure 36: Coffee ring effect is indicated with arrows and lines on the ink printed on the surface of the substrate (left image) and on the cross-section of the printed ink (right image).

There's another important factor to take into account and analyse, which is the distribution of the dye particles once the ink has been printed on the substrate. As it can be noticed, mostly in those lines with a higher amount of ink, colour intensity of the ink is higher towards the edges of the lines. This relates to a higher concentration of dye particles at the edge of the lines in comparison to the central zone of the lines. Furthermore, this difference in colour intensity or dye concentration doesn’t have a gradual variation from the centre of the lines towards the edge, but rather a clearer and more defined limit is present. This effect is shown in ***figure 36*** above, where the edge of the lines both from the surface and cross-section are highlighted. In the scientific communion this is phenomenon is known by the name of “coffee-ring” or “coffee-stain” effect, which was already introduced in the **section 4.2.2. “Characteristics and types of inks”** when describing ink characteristics.

This particular distribution occurs due to the apparition of differential evaporation rates across the fluid; while the fluid at the edge of a deposited drop or “puddle” evaporates it is replenished by a capillary flow originated at the centre of such drop or “puddle”, subsequently carrying those particles suspended in the fluid and increasing the concentration of particles at the edge. This flow actually takes place due to a complex relation between the wetting of the fluid, its surface tension, capillary flows and contact line pinning **[5].** Coffee ring effect is an undesired phenomenon and should be solved if conductive materials want to be printed on our porcelain stoneware substrates, since ideally lines have to be as homogeneous as possible in order to have a continuous conductive printed pattern and establishing good contact between particles to have electrical conductivity. There exist different solutions to this problem, some more suitable than others depending on the applications, such as modifying the shape of the particles in suspension, adding small amounts of surfactant or modifying the surface tension of the ink carrier fluid by partially adding another fluid with lower surface tension.

Figure 37: Cross section of a "U" shaped pattern printed following the procedure defined in section 5.2.1.1.

Lastly, samples prepared by the procedure defined in the ***figure 24*** of **section 5.2.1.1**. **"Printing of water-glycerol dye ink"** were cross sectioned and imaged with a microscope. The images taken are shown in the ***figure 37*** above. As it is possible to see, a layer by layer printed "U" shaped structure was accomplished, establishing contact between ink printed on the surface with ink embedded in the interior of the porcelain stoneware substrate through "columns" of ink.

Here once again the "coffee-stain" effect can be seen; however, by performing the mentioned layer by layer process it has been proven that complex structures can be printed with an ink jet printer by printing a water-based ink over a ceramic substrate.

After printing with the water-glycerol pink dye ink, printing with a graphene water-based was performed as described in the next section. This was done in order to print with a water-based ink with functional conductive material, in order to analyse if conductive tracks could be printed and also in order to analyse the effect that variations in the size and shape of the particles contained in the ink can have over spreading and penetration processes.

6.2.2. Analysis of spreading, penetration and conductivity of graphene water-based ink printed patterns

As with the water glycerol dye ink, graphene ink was printed over three different types of substrates, substrates A, B and C. Printing with the graphene water-based ink was a much more complex process than with the water glycerol dye ink. Viscosity of the graphene ink was substantially lower and surface tension higher, which hindered the printing of the ink. On one hand, nozzles tended to clog very easily, which caused the print head to stop jetting ink during the printing process without us noticing, thus creating an uncertainty in relation to the amount of ink printed. On another hand, if nozzles didn't get blocked, quality of drop formation would sometimes suddenly worsen, jetting drops with satellites and even causing the deviation of the droplets from the printing trajectory.

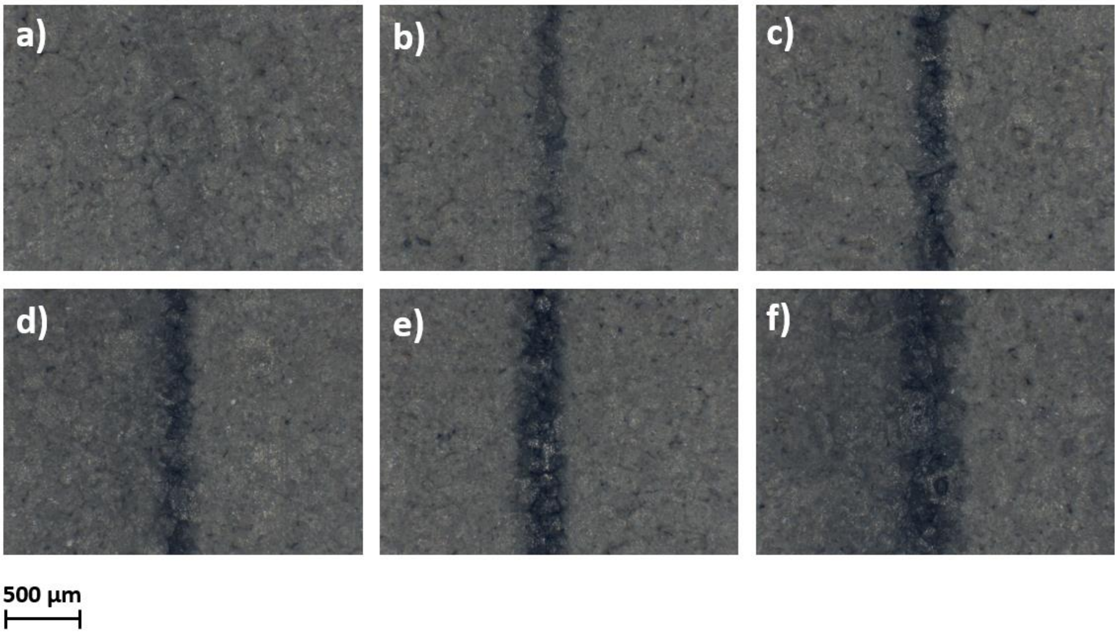


Figure 38: Lines of graphene water-based ink with 1, 3, 5, 9, 12 and 15 layers (from image a) to f) respectively) printed on the surface of the porcelain stoneware substrate A.

These phenomena might take place due to the size of the graphene flakes and due to electrostatic processes, causing the graphene flakes to agglomerate easily and interact between each other or the environment.

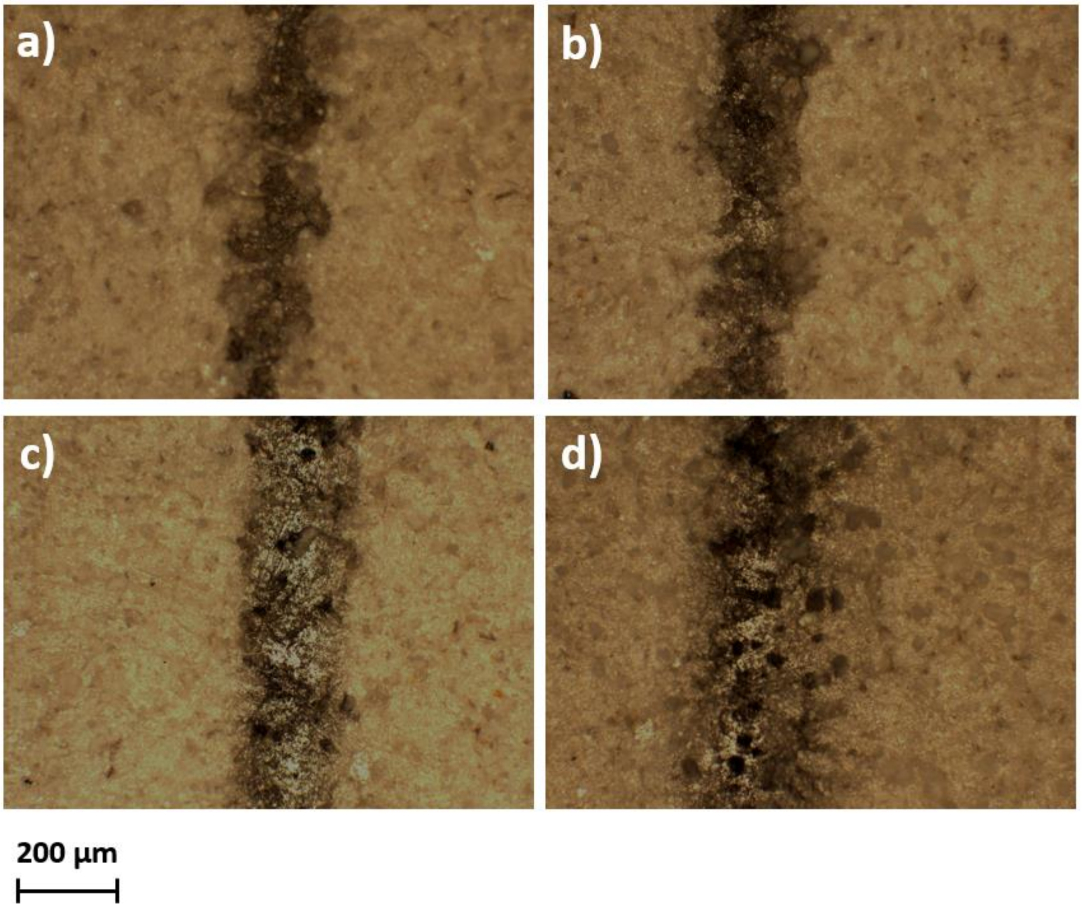


Figure 39: Lines of graphene water-based ink with 20, 30, 40 and 60 layers (from image a) to f) respectively) printed on the surface of the porcelain stoneware substrate A.

However, by eventually modifying and correcting the waveform and by setting the printer to clean the print head frequently, we were able to print some graphene lines over the substrates with a decent quality. In the ***figures 38 and 39*** above, graphene lines of 1, 3, 5, 9, 12, 15, 20, 30, 40 and 60 layers which were successfully printed are shown. As it can already be seen, in comparison with the pink water-glycerol dye ink, the distribution and spreading of the graphene flakes over the substrates surface is much more homogenous. Coffee ring effect is no longer visible and lines also show much less spreading than the water-glycerol ink printed lines.

These six lines presented continuous spreading values between 0,2 and 0,4 mm. However, by analysing different batches, we came to the conclusion that most of the cases in which higher values of spreading around 0,4 mm were due to misbehaviours of the printer, since these values were present in a random manner, sometimes at lines with a high number of layers and some other times present at lines with low number of layers. When comparing with the pink water-glycerol dye ink, lines of 20 layers of printed graphene ink spread up to three times less than lines of pink water-glycerol ink for the same amount of layers (and consequently same amount of printed volume) and for those lines with 60 layers of ink, graphene ink lines typically spread almost up to ten times less than lines of pink water-glycerol dye.

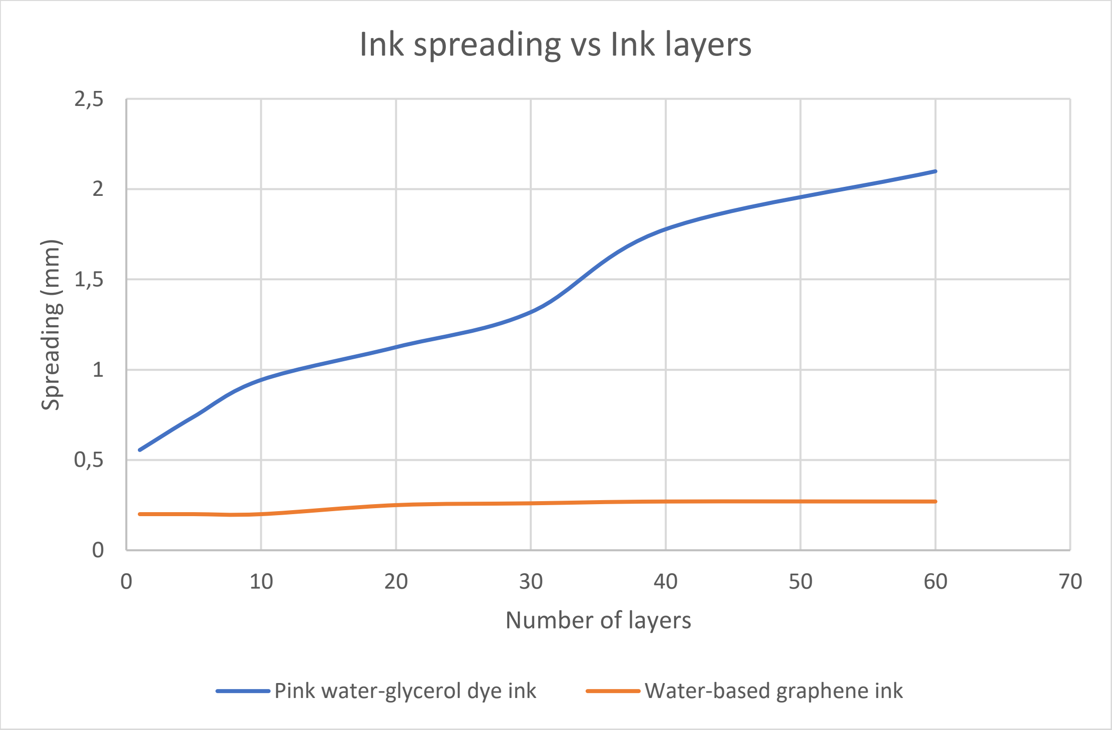


Figure 40: Plot which represents the variation of the spreading of ink in relation to the number of layers for both the water-glycerol pink dye ink and the graphene water-based ink.

As it is possible to see in the figures and as represented in the figure above, spreading of the printed graphene ink lines doesn’t seem to be influenced much by the amount of ink printed (Number of printed layers). After microscope visualization and analysis, it is possible to see how the deposition and distribution of the graphene flakes once printed on the surface is much more stable and uniform than in the case of the dye particles contained in the water-glycerol ink. This decrease in spreading values of the graphene ink in comparison to the pink water-glycerol dye ink (represented in ***figure 40***) is due to the shape of the solid graphene. As it has been previously described in **section 6.2.1. "Characterisation of spreading and penetration of water-glycerol dye ink printed patterns"**, distribution of the solid particles contained in any ink is highly influenced by the shape of such solids; actually, modifying the shape of the solid particles is one of the most common procedures done in order to solve "coffee-ring" effect issues. Particles which are shaped in the form of fibres and flakes have more difficulty to be driven by internal fluid flows towards the edges of the printed fluid, thus they have less tendency to accumulate in specific regions and "coffee-ring" effect is not typically present.

This is perfectly reflected in the case of our work, when comparing the particle distribution of the pink water-glycerol dye ink and the graphene ink. Being both water-based inks, spherical dye particles in the water-glycerol ink are easily driven towards the edges of the deposited fluid by the apparition of internal flows in the fluid, whilst graphene flakes, due to their shape are not strongly affected by such flows.

At the same time, due to the shape of the graphene flakes contained in the ink, penetration of the graphene flakes in the substrate happened to be apparently null or minimal when analysing the cross section of the samples. Black deposition of graphene flakes as seen on the surface of the substrate is not seen in the cross section. This is due to the fact that the shape of the flakes doesn't allow them to penetrate the ceramic substrate by flowing through the present pores, but they rather get stuck in the pores and prevent other particles to penetrate the substrate. Thus, graphene flakes are mostly concentrated on the surface of the substrate.

Once again, by applying the equation described in **section 5.2.1.1. "Printing of water-glycerol dye ink"**, the total volume of water-based ink deposited in each line was calculated, which allows to compare quantitatively the difference between the different printed lines. Knowing the number of droplets printed in each layer of ink, we can calculate the total printed ink volume and consequently, with the data provided in the material data sheet of the graphene water-based ink, we can also calculate the deposited graphene mass per line:

$$m_{printed-graphene} = V_{printed} * \rho_{ink} * m_{graphene\,w/w}$$

Subsequently, the total printed volume of graphene water-based ink was calculated, as well as the graphene deposited mass in each line.

Number of layers	1	3	6	9	12	15	20	30	40	60
Printed ink volume (µL)	0,18669	0,56007	1,12014	1,68021	2,24028	2,80035	3,7338	5,6007	7,4676	11,2014
Printed graphene mass (g)	1,8669E-06	5,6007E-06	1,1201E-05	1,6802E-05	2,2403E-05	2,8004E-05	3,7338E-05	5,6007E-05	7,4676E-05	0,00011201

Table 11: Printed volume of graphene water-based ink and deposited graphene mass in each line with different number of layers.

Then after sintering of the substrates on which the graphene ink was printed on top by following the procedure described in **section 5.1.2. “Sintering of the ceramic porcelain stoneware substrates”**, conductivity measurements of the printed lines were taken. However, even though the printed lines were of good quality and graphene deposition was uniform and even though sintering was performed under an inert atmosphere in order to avoid oxidation, none of the printed lines showed any conductivity. Even though it has been proven that conductive graphene can be produced at high temperatures of up to 2000 °C **[43],** the sintering atmosphere in which the material es heated must be precisely controlled. Carbon materials such as graphene are very sensible to high temperatures and to oxidation. Thus, it is possible that the graphene, which is normally formed from a reduction of graphene oxide **[44],** even though being sintered in an inert atmosphere, has oxidised due to the presence of water and oxygen present in the ceramic substrate and which are normally released during the firing process, as a consequence of the chemical transformation which occurs in the ceramic mass during sintering.

6.3. Analysis of printed solvent-based inks on the substrate

6.3.1. Analysis of spreading, penetration and conductivity of silver solvent-based printed patterns

After printing with the water-based inks, we decided to print with some solvent-based inks. As we were able to see with the water-based inks, our porcelain stoneware sample has great affinity for water-based fluids. However, with the water glycerol dye ink on one hand, "coffee-ring" effect was present, which is undesirable for our application. With the graphene water-based ink on the other hand, even though "coffee-ring" effect was not as perceivable as with the dye ink, conductivity after sintering process was non-existing.

Thus, we decided to try some solvent-based inks, starting with the silver ink. Silver nanoparticle inks as well as gold nanoparticle solvent inks are the two main metal nanoparticle inks which are currently used in ink jet applications, so they are relatively easy to get hand on. As we already knew, this solvent ink would have a greater viscosity than both water-based inks and surface tension would be quite lower.

Figure 41: Pressed porcelain stoneware substrates cut in half (left of the image) and pressed porcelain stoneware substrates cut in half with silver printed lines of 1, 3, 5, 9, 12, 15 and 18 layers of ink.

The reflection of such variations was immediately seen during the first printing processes, since ink didn't appear to be penetrating the substrate whilst printing and ink tended to simply deposit on the surface of the substrate. However, since the printing of successive layers was done at a normal speed, each ink layer had time to set and start drying, so ink over-flowing or "puddle" formation didn't occur.

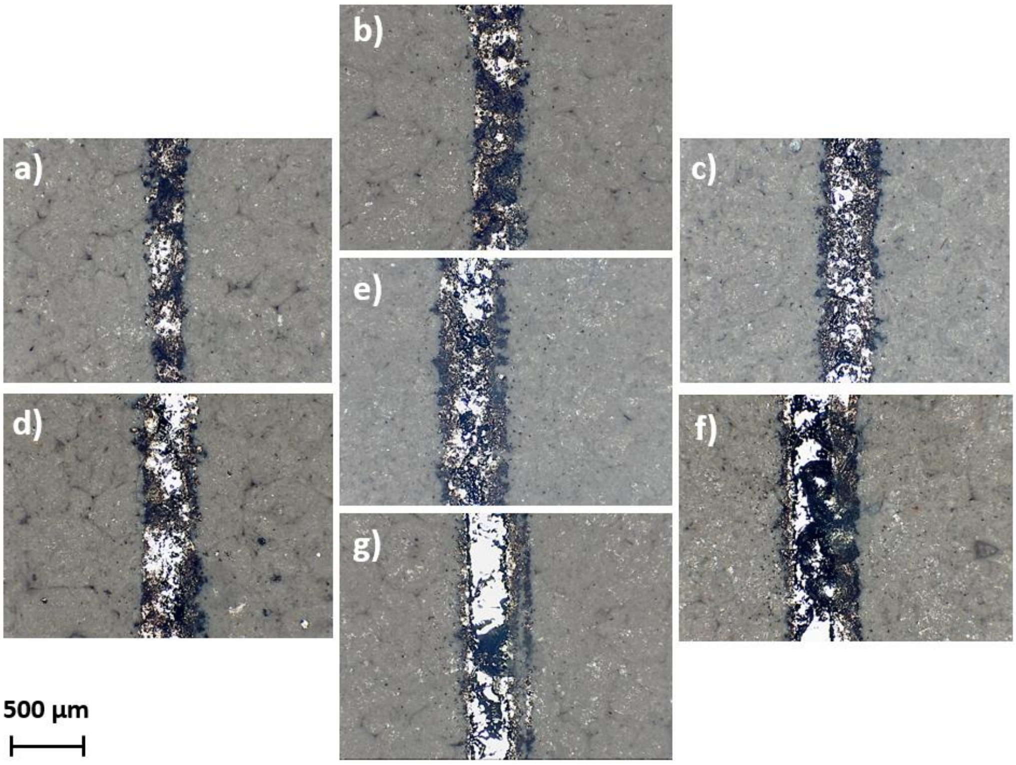


Figure 42: Microscope images of silver ink lines of 1, 3, 5, 9, 12, 15 and 18 layers (images a) to g) respectively) printed over the porcelain stoneware substrate A pressed with a 3000 kg load.

Over the first samples, lines with 1, 3, 6, 9, 12, 15 and 18 layers were printed over the substrates A, B and C, which can be seen in ***figure 41***. We started printing with low number of layers because theoretically, the silver ink we purchased is meant for "one-pass" printing patterns, meaning the printing of patterns with one layer of ink. Nevertheless, since the ink is also meant for flat and smooth surfaces such as PET, ITO or glass, we decided to increase the number of layers, supposing that integrity and contact between deposited particles would be worse and to compare how ink addition might affect conductivity measurements. We also wanted to print a relatively high amount of ink to evaluate the interaction with the substrate during sintering.

In ***figure 42*** the seven different printed lines over substrate A are shown. In general, performance of the silver ink was of good character during the printing process. However, we were never able to print with the 16 nozzles the printer head counts with and we tended to print using between 4-6 nozzles at the time, since the printing was more reliable this way.

From the optical analysis, it can be seen how the lines do have a tendency to spread over the surface. The majority of the printed lines were of good quality, but sometimes they did show a more irregular or non-straight shape, which lead us to think that the printed ink droplets were not coalescing well enough. Drop coalescence **[45]** is defined mainly by the drop spacing utilised during printing. Typically, there exists an optimal drop spacing for each, above which the contact between drops is not good enough and irregular and bellow which drops begin to accumulate and form bulges that lead to non-straight and ununiform lines.

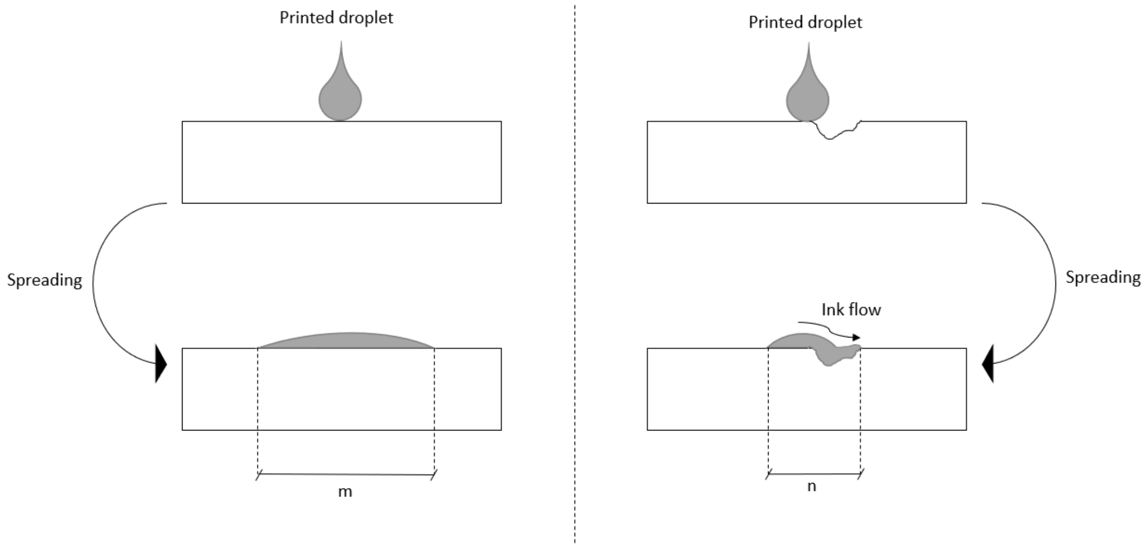


Figure 43: Schematic representation of spreading of ink over the substrate under normal conditions (left) and ununiform spreading when there exists presence of irregularities in the substrate surface.

The theoretical line width defined in the software was of 0,05 mm. However, for the lines with the least amount of ink (1 layer) the line width on the printed surface is around 0,2 mm, which is already four times the theoretical width and for the lines with the highest amount of ink (18 layers) the width increases up to values between 0,4 mm. Evolution of spreading in relation to the number of layers showed no consistency in occasions, since sometimes lines with a higher number of layers spread less than lines with less number of layers.

We attributed this phenomenon to the fact that the surface of the substrates is irregular and not homogenous throughout the entire sample. This phenomenon is also represented schematically in ***figure 43*** above**,** where it is possible to see that, for the same amount of ink, ink spreading also depends on the roughness of the zone in the substrate where the ink is being printed.

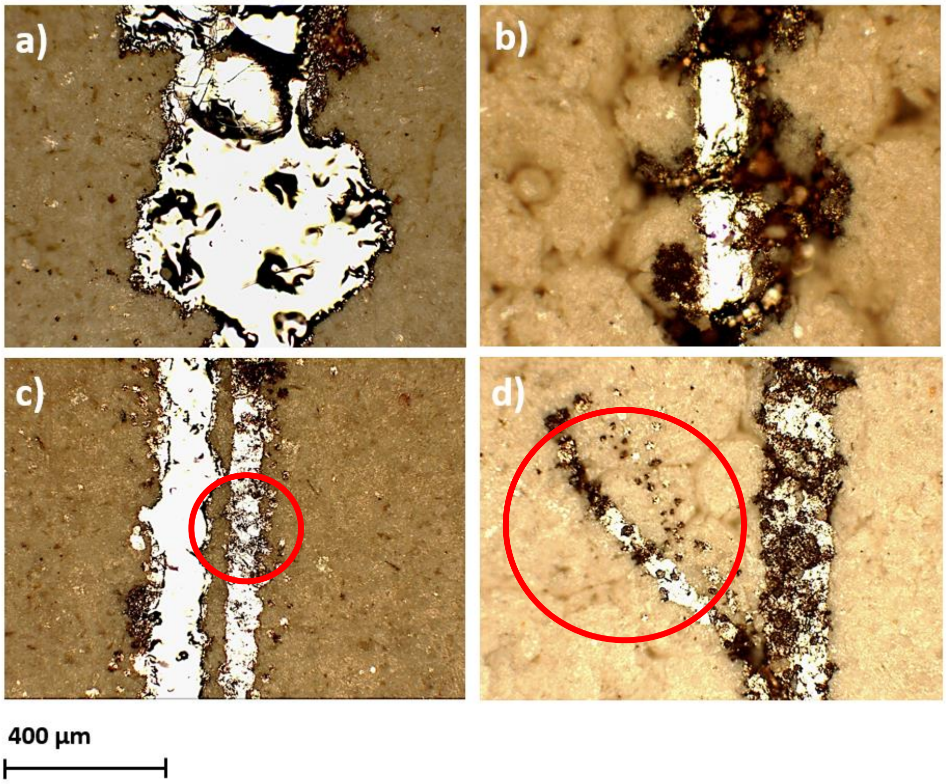


Figure 44: Issues present in printed silver ink lines: puddle formation (a), ununiform spreading (b) and spraying of ink droplets (c and d).

When irregularities are present in the nearby surface where the line is going printed in the shape of pores, interparticle limits or small cracks, ink can be deviated from the line driven by a flow towards these irregularities, as depicted in ***figure 43***. This reflects the need of controlling the porosity of the samples and that if pressure during pressing of the substrates is too low, printing quality over the substrate can be affected.

This effect can also be extrapolated to analyse the variation of spreading over the three different substrates. On those substrates that have been prepared under a lower pressure, ink appears to spread less due to the presence of more irregularities that exist because particles haven't been fully pressed and compacted with each other.

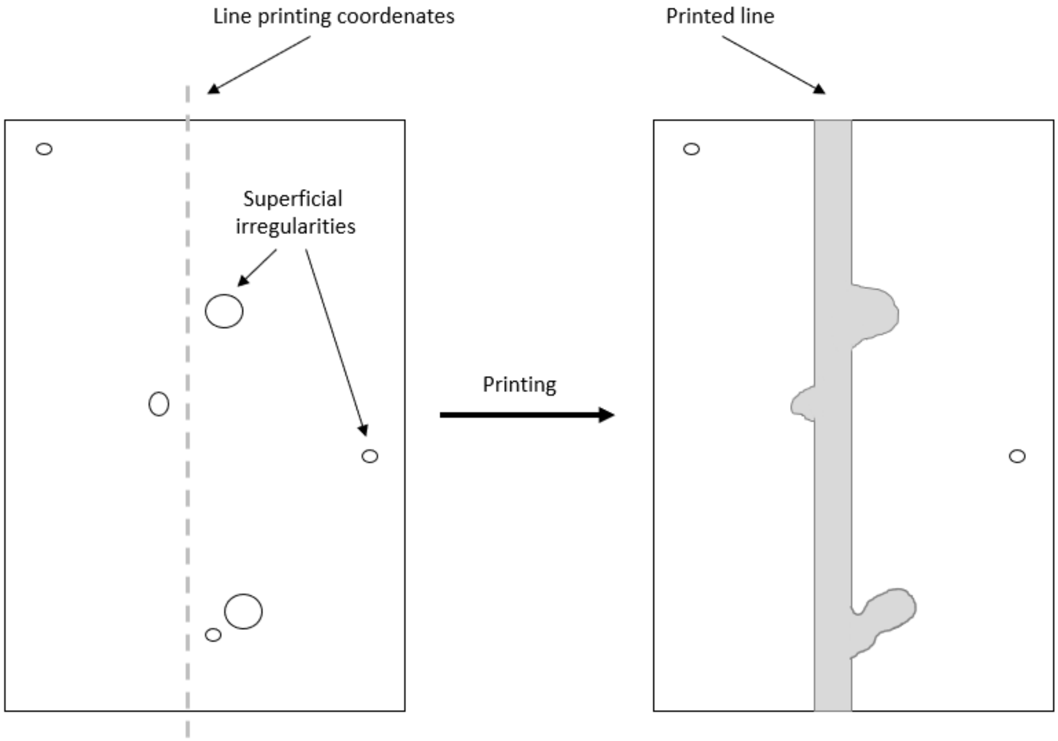


Figure 45: Schematic representation of irregular and uniform spreading of ink due to the presence of superficial irregularities.

As it can be seen in ***figure 44*** image (a) overflowing occurred in some sections of the printed lines. As it has been previously mentioned, if too many drops accumulate in one spot, a small puddle of ink is formed leading to an excessive spreading. Image (b) of ***figure 44***, shows how when printing over samples with high porosity and where particles, interparticle limits and surface defects are present, ink also tends to spread in a more uneven fashion. This is once again shown in the ***figure 45***, which based on the previous explanation of how irregularities and superficial defects affect spreading of the ink, represents how irregular lines are formed when such defects are present.

Moreover, as seen in images c) and d), printer also had the tendency to misbehave for short periods of time leading to "spraying" of the ink, process in which droplets are deviated from their normal trajectory and are also deposited unevenly over the substrate; this normally happens when ink starts to block the nozzles. However, we attributed both puddle formation and spraying to misbehaviours of the printer, since they only occurred at random times and in very seldom cases. So, as it is possible to see, over-coalescence of droplets, surface defects and irregularities and printer misbehaviours are the main reasons for the decrement in printed line quality and homogeneity.

By analysing the cross section, it could be seen how penetration on the other hand is null due to the high viscosity of the silver ink. Knowing the number of droplets printed in each layer of ink, we can calculate the total printed ink volume and consequently, with the data provided in the material data sheet of the silver ink, we can also calculate the deposited silver mass per line:

$$m_{printed-silver} = V_{printed} * \rho_{ink} * m_{Ag\ w/w}$$

Being the density of the silver ink of 1,9 g/mL and the metal loading of silver in the ink of 50% w/w, by applying the equation we can easily know the amount of silver printed in each line:

Number of layers	1	3	6	9	12	15	18
Printed ink volume (µL)	0,06	0,18	0,36	0,54	0,72	0,9	1,08
Printed silver mass (g)	0,000057	0,000171	0,000342	0,000513	0,000684	0,000855	0,001026

Table 12: Printed volume of silver solvent-based ink and deposited silver mass in each line with different number of layers.

After the substrates were optically characterised with the microscope, they were sintered in the tube furnace by following the procedure described in **section 5.1**. **"Preparation, pressing and sintering of porcelain stoneware substrates"**. It is important to mention that initially, another furnace was going to be used for the sintering of the samples, which consisted on a much bigger tube furnace with an alumina tube and which could reach temperatures up to 1300 °C approximately, functioning with argon gas flow.

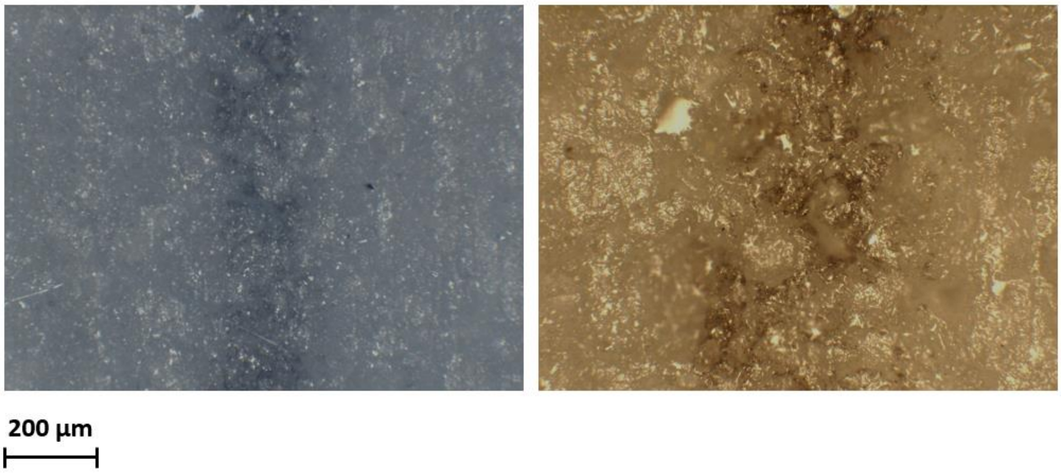


Figure 46: "Faded" silver lines after being submitted to the corresponding sintering process.

This furnace would have been ideal since we would not be limiting the sintering temperature. However, after some first initial tests we realised that the furnaced was contaminated with carbon fibre from previous experiments which hadn't been successfully eliminated from the system. This being so, we had to search for a suitable alternative, which was the tube furnace described in such procedure.

Once the substrates had been sintered, they were once again characterised with the optical images. From the images shown in ***figure 46*** above, it is possible to see how all of the ink seems to have "faded" away from the lines. Where the silver ink had been printed, only dark-grey lines stained on the surface can be seen with no solid metal remaining. This indicates that some of the ink must have penetrated the substrate and even oxidised, perhaps with the small amounts of oxygen present in the porcelain stoneware substrate, either in the form of oxygen trapped in the ceramic body or from the small percentage of water contained in the ceramic mass. Furthermore, the whole ceramic substrate had gained a darker colour during the sintering process, showing off a light grey colour instead of the white-light yellow usual colour, which was not expected.

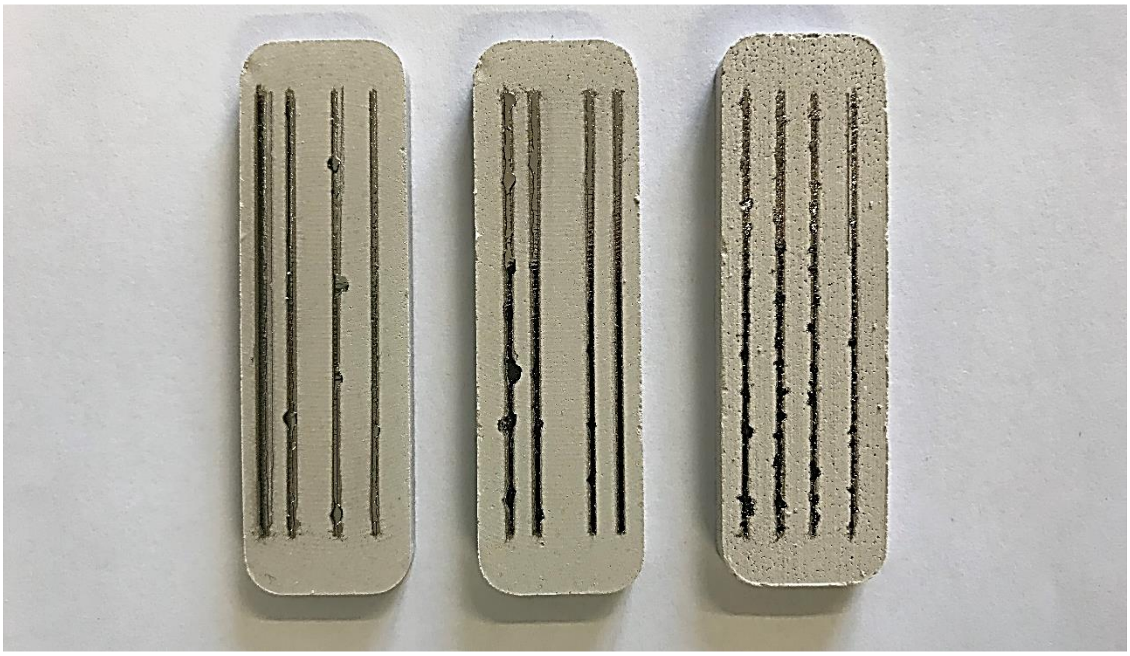


Figure 47: Substrates A, B and C (from left to right) with solvent-based silver ink printed lines of 30, 40, 50 and 60 layers.

After these initial results with the printed silver ink, we decided to increase the number of layers. Once again over samples A, B and C, we printed for lines of 30,40, 50 and 60 layers each, whilst also decreasing the drop spacing to 15 um, for printing optimising purposes, which can be seen in ***figure 47***. Printed lines were of good quality in general. However, the issues we had observed with the previous printing process were still present. In those lines with higher amount of ink, formation of puddles takes place, generating irregularities over the shape of the printed lines. This excessive accumulation is more susceptible to happen with higher amounts of ink and can also be due to irregularities on the substrates surface, which can cause uneven distribution of the ink.

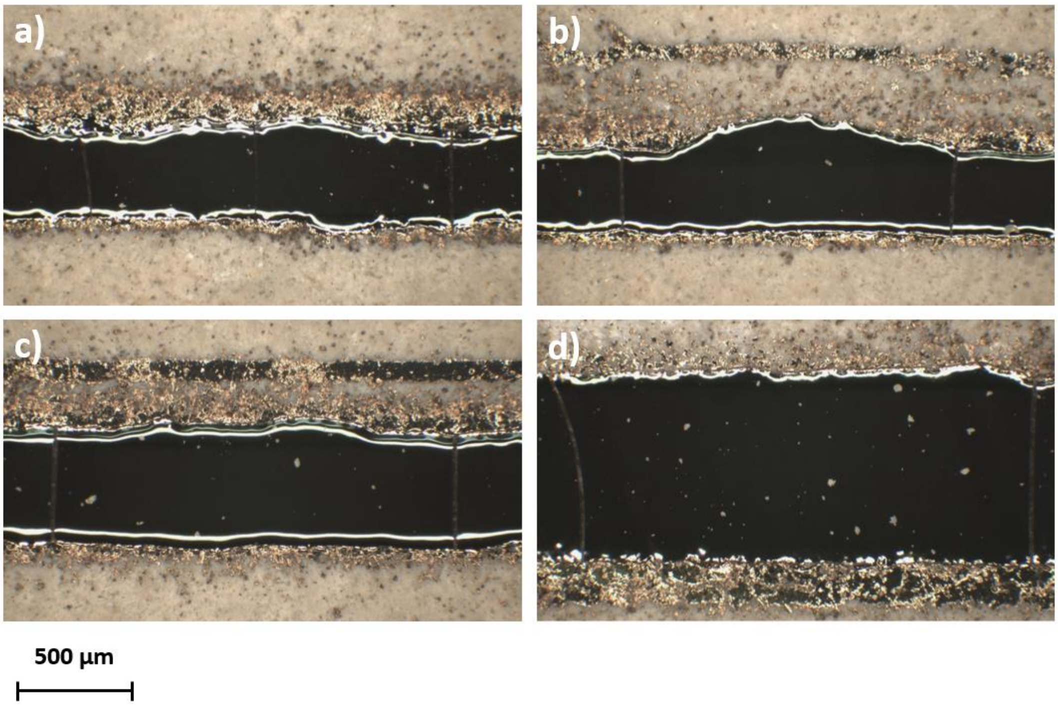


Figure 48: Microscope images of solvent-based silver ink lines of 30, 40, 50 and 60 layers printed over substrate A.

In ***figure 48***, the four printed lines are shown for the case of sample A. As it can be seen, the printed lines are quite regular and straight. Nevertheless, spraying effect which has already been previously is sometimes present and when it is not, small droplets still deviate from the printed trace. Ideally, all of the ink should be concentrated within the limits of the printed line in order to have a homogeneous distribution of the printed material. Moreover, in this case where higher amount of ink has been deposited on the substrate, once the ink has been left to dry at ambient conditions, cracks appear on the silver printed lines in direction of the line-width and in several places along the lines, which might be due to the apparition of forces from the combination between the shrinkage of the ink whilst drying and surface tension phenomena originated from the interaction between substrate and ink.In this case, following the same procedure as done for the previous experiments with the silver ink, the volume of ink printed and the mass of printed silver are the following:

Number of layers	30	40	50	60
Printed ink volume (µL)	4,0005	5,334	6,6675	8,001
Printed silver mass (g)	0,00380048	0,0050673	0,00633413	0,00760095

Table 13: Printed volume of silver solvent-based ink and deposited silver mass in each line with different number of layers.

Then, after the optical visualization of the new printed lines, samples were once again fired in the tube furnace, in order to analyse the behaviour and interaction of the ink with the substrate and analyse the integrity of the lines post-sintering.

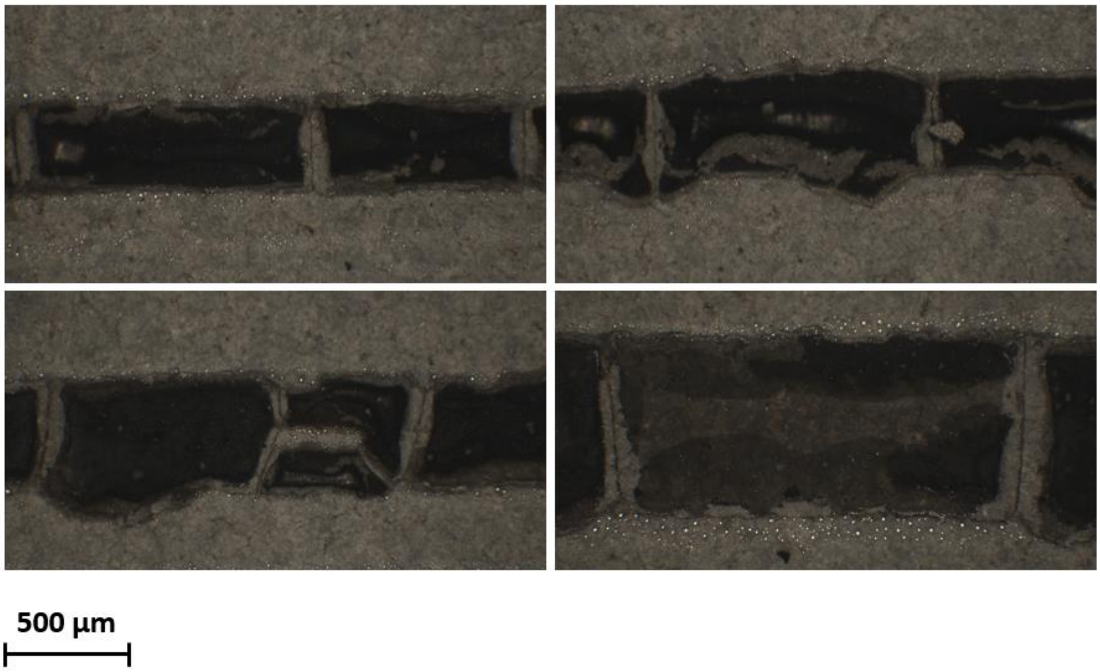


Figure 49: Microscope images of solvent-based silver lines with 30, 40, 50 and 60 layers printed on substrate A, after firing/sintering process in the tube furnace.

Figure 49 shows the result and effect that sintering of the porcelain stoneware substrate A had over the silver printed lines. Where before the ink had been printed, now only remains a black residue and some minute silver metallic particles.

Where before cracks could be seen on the surface of the printed ink, now it is revealed how those cracks are also present on the surface of the substrate in the same location as they could be seen on the ink. This indicates that the apparition of forces caused by the interaction between the ink and the substrate are strong enough to also affect the superficial structure of the it.

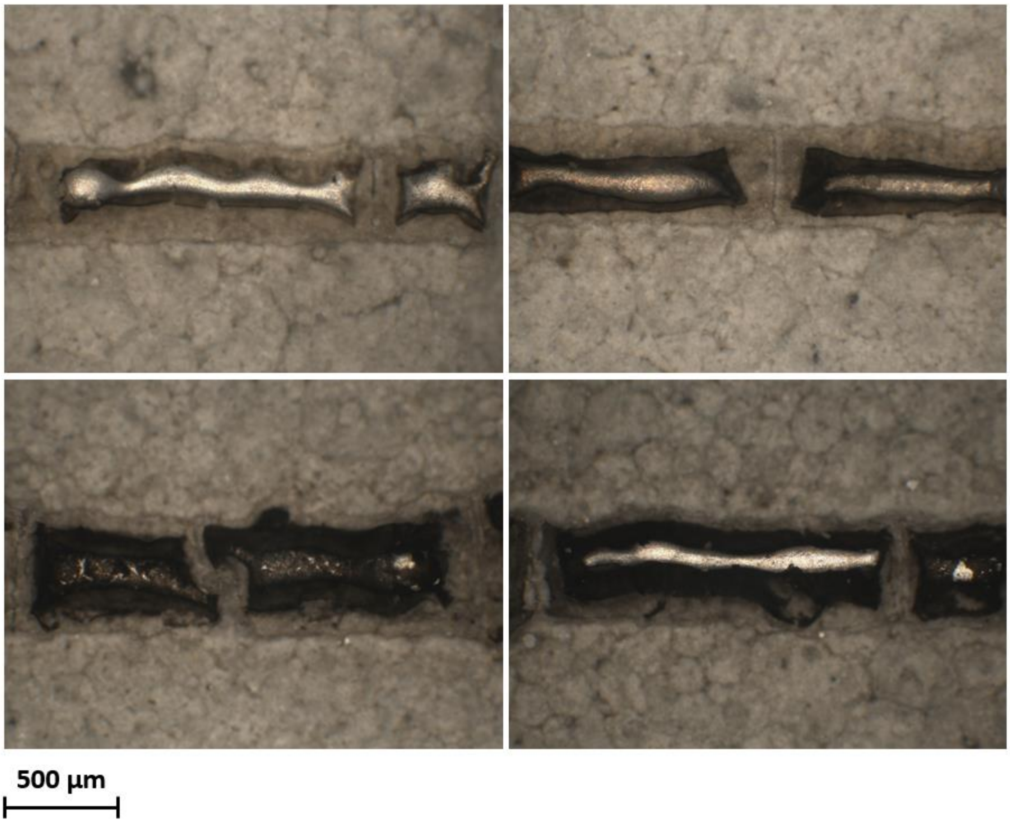


Figure 50: Microscope images of solvent-based silver lines with 30, 40, 50 and 60 layers printed on substrate B, after firing/sintering process in the tube furnace.

Then, as seen in ***figure 50,*** in substrate B the same black residue was still present. However, in this case, over the black residue remained a high amount of silver which had solidified in the form of short threads along the length of the previously printed line; the threads had "cut" or divided in the same spot where before the cracks on the surface of the ink could be seen. The formation of these threads also reflects the de-wetting of the material, meaning that the adherence between the silver ink and the substrate was not strong enough.

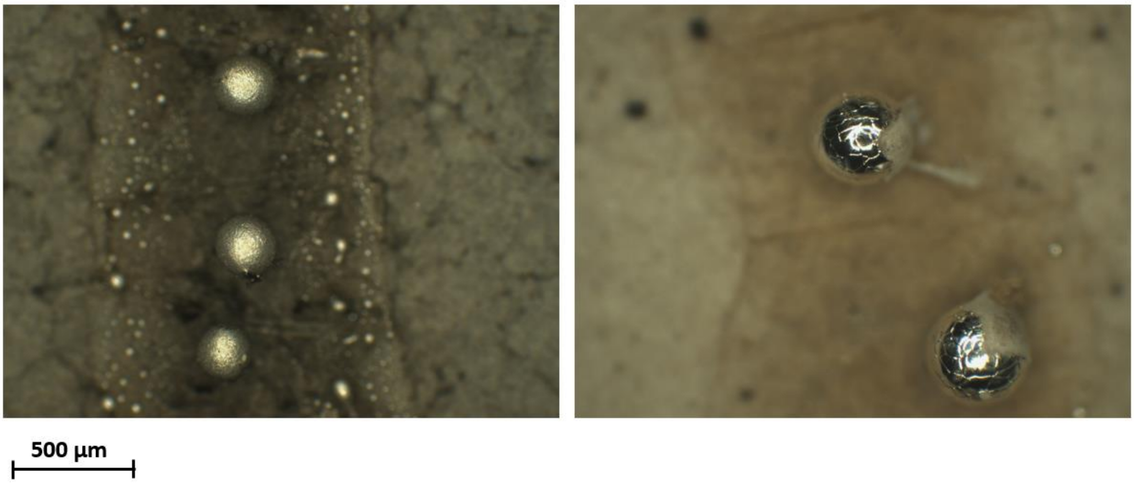


Figure 51: Microscope images of spherical silver particles present in the surface of the substrate after sintering process.

At the same time, in some other cases, the ink printed on the substrates de-wetted in the form of small spherical particles (shown in ***figure 51***) instead of longer threads, which also corresponded to those cases where the cracks that appeared on the surface of the printed ink were closer together.

As with the previous substrates, after the sintering process, samples had a darker and greyer colour, instead of the typical white/light yellow tone they should have. In addition, this different coloration of the samples was not homogeneous. Instead, the samples presented a gradual coloration in the direction of the gas flow in the tube.

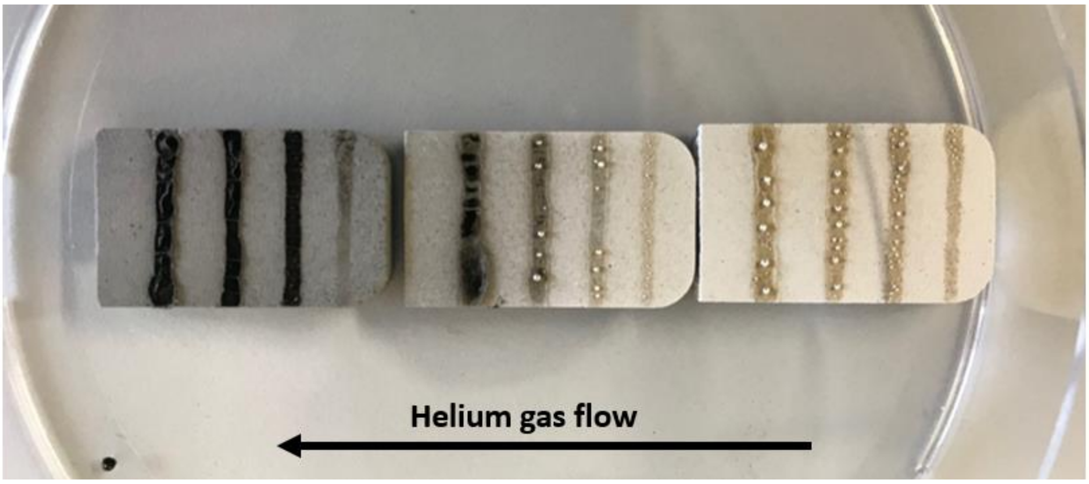


Figure 52: Substrates with silver printed lines after sintering process, in which change in coloration is visible.

The three samples were introduced in the tube aligned with each other as shown in the ***figure 52,*** in which the direction of the flow of helium gas is also represented**.** As it can be observed, the sample which was located near the tube end from which the gas flowed in shows no change in colour, while the middle sample shows a gradual coloration from white to grey and the last substrate located near the tub end where the gas flowed out presented a even darker grey coloration. In addition, in those zones of the samples were this dark coloration was not present or present in a lower degree, the solid silver particles and threads mentioned above can be seen. On the other hand, in those zones where the substrate presented a darker coloration, the black residue earlier described is present where the silver had been printed and practically no solid silver with metallic appearance is visible. In order to asses this change in the coloration of the samples, we fired a set of samples A, B and C without printing on their surface, to see if the change in the colour of the substrates might have been due to and external source which could be contaminating our samples. However, in this case the samples showed no change in coloration and instead they were white in colour as they should. This indicates that the dark coloration of the substrates must be related to the printed silver ink. When studying the effect the ink might have in relation to this phenomenon, it is important to consider the different components of it, which would in this case be the solvent carrier and the silver nanoparticles.

On one hand, we have considered the possibility that the dark coloration might be consequence of the reaction of the solvent contained in the ink with the ceramic substrate. In ceramic tile industry a variety of structural, superficial and aesthetic defects are known and have been studied **[26, pp 341-424].** Between the studied aesthetic defects, a phenomenon called “black-heart” causes changes in the coloration of the ceramic body to green and dark grey tones, originated from chemical reactions which occur during the firing process. The three main chemical reactions that are attributed to this phenomenon are the release of water and OH groups from the crystallisation of argillaceous materials and which contribute to other reduction reactions, the reduction of iron oxides and the decomposition of organic matter by pyrolysis between temperatures of 500 and 700 °C.

Firstly, the release of water and OH groups is inevitable and takes place due to changes in the molecular structure of the different argillaceous materials. The pyrolysis of organic matter between temperatures of 500 and 700 °C leads to the decomposition into organic products and H_2O and CO_2. Further on, at higher temperatures the following decomposition of the organic products can lead to the production of H_2 gas, which can consequently combine with other organic compounds and also producing H_2O. This production of H_2O, CO, CO_2 and H_2 gases can favour other reactions such as iron oxide reduction for instance, which combined with the decomposition of organic matter present in the ceramic body can cause changes in the coloration of the ceramic product. However, “black-heart” phenomena typically take place in those ceramic bodies in which the concentration of organic matter is higher than desired. In our case organic compounds in the form of solvent (as the silver ink carrier fluid) are only present on the surface of the substrate and in very small quantities, meaning that before even having the chance to react and decompose, they most likely evaporate and detach from the ceramic surface. Moreover, solvents as the one contained in the silver ink (triethylene glycol monomethyl ether) are commonly used in inks for the decoration of ceramic surfaces, having been their effect on ceramic substrates already tested **[26, pp 204-205] [27, p 155].**

On the other hand, we have also considered that the coloration issue might be related to the silver nanoparticles. Even though the porcelain stoneware substrates have been fired under a constant helium gas flow to prevent the oxidation of the silver lines, it is possible that the oxidation of the silver lines has taken place by the reaction with H_2O realised from the structure of the argillaceous materials contained in the ceramic mass during the different transformations taking place in their molecular structure. This can also be the reason for the uneven coloration of the three different porcelain stoneware substrates. Due to the presence of the helium gas flow, water vapor of the sample nearest to the end tube in which the gas flows in is dragged downstream and can enter in contact with the two other substrates.

At the same time, water vapour released from the middle sample will also be dragged downstream and enter in contact with the last substrate located at the end of the gas stream. This would mean that the last substrate would be in contact with a higher amount of water and that the first substrate would be the one which would enter in contact with the least amount of water vapour. This would also be a possible explanation for the gradual coloration of the substrates seen in the ***figure 52*****.** Additionally, it is also possible that the helium gas flow might have dragged the oxidised silver nanoparticles, which could combined with the dragging of water vapour could also explain the gradual coloration of the substrates, being the last sample the one with a higher concentration of silver oxide (both from oxidation of the silver lines printed on its surface and from oxidised silver nanoparticles dragged by the gas flow from the samples located upstream) and the first sample having the lowest concentration of silver oxide. Simultaneously, in those samples which have a darker coloration are the samples in which where the silver lines had been printed, now a dark and flaky deposit was visible. On the contrary, in those samples which haven't suffered much change in coloration, lines have not transformed into a black deposit but solid silver particles and threads are visible.

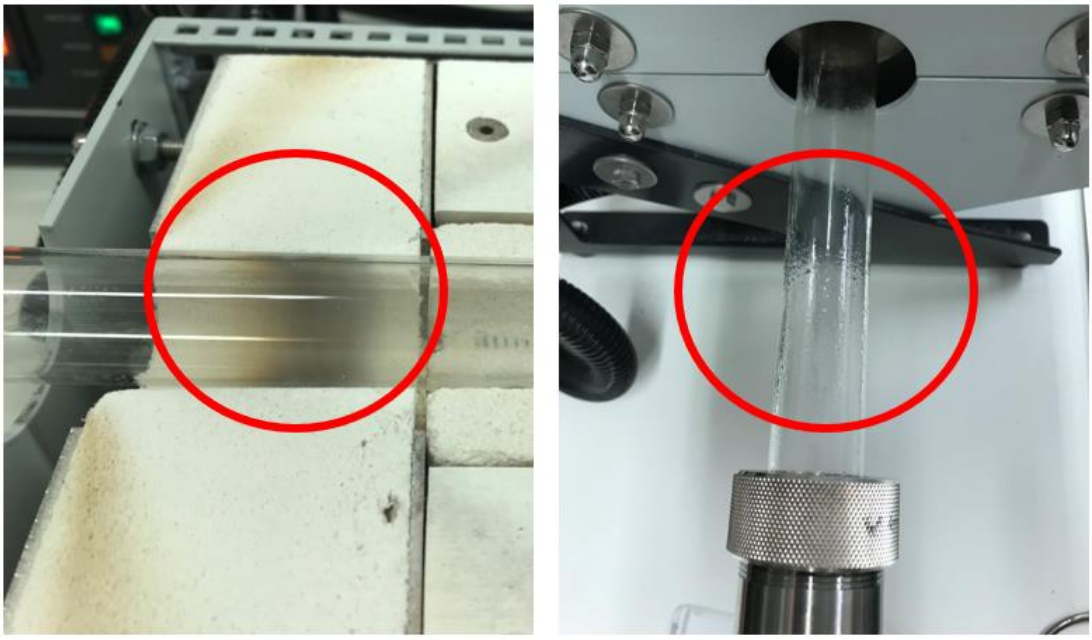


Figure 53: Black deposit (left image) and water condensation (right image) present in the quartz tube after the sintering of the porcelain stoneware substrates with printed silver lines.

This corroborates that the black residue present where the printed lines once where and the dark coloration of the samples might be due to the formation of silver oxide. Samples near the tube end in which the gas flows enters the tube have both less or no coloration and solid silver metal on the surface, whilst samples located at the opposite end have both dark coloration and transformation of the silver lines into black residue. In relation to this, silver oxide (Ag_2O) typically has a black-dark brown colour.

Furthermore, this last hypothesis could also be an explanation for the dark deposit and condensation of water observed in the inner wall of the quartz tube utilised in the furnace, which can be seen in the images of ***figure 53*****.** Both deposits were only present in the end of the tube through which the gas flows out and matches by also being the end of the tube near which samples have a darker coloration. This dark deposit is of black colour, which fades to browner tones towards the edge of the deposit, which also coincides with the colour of Ag_2O.

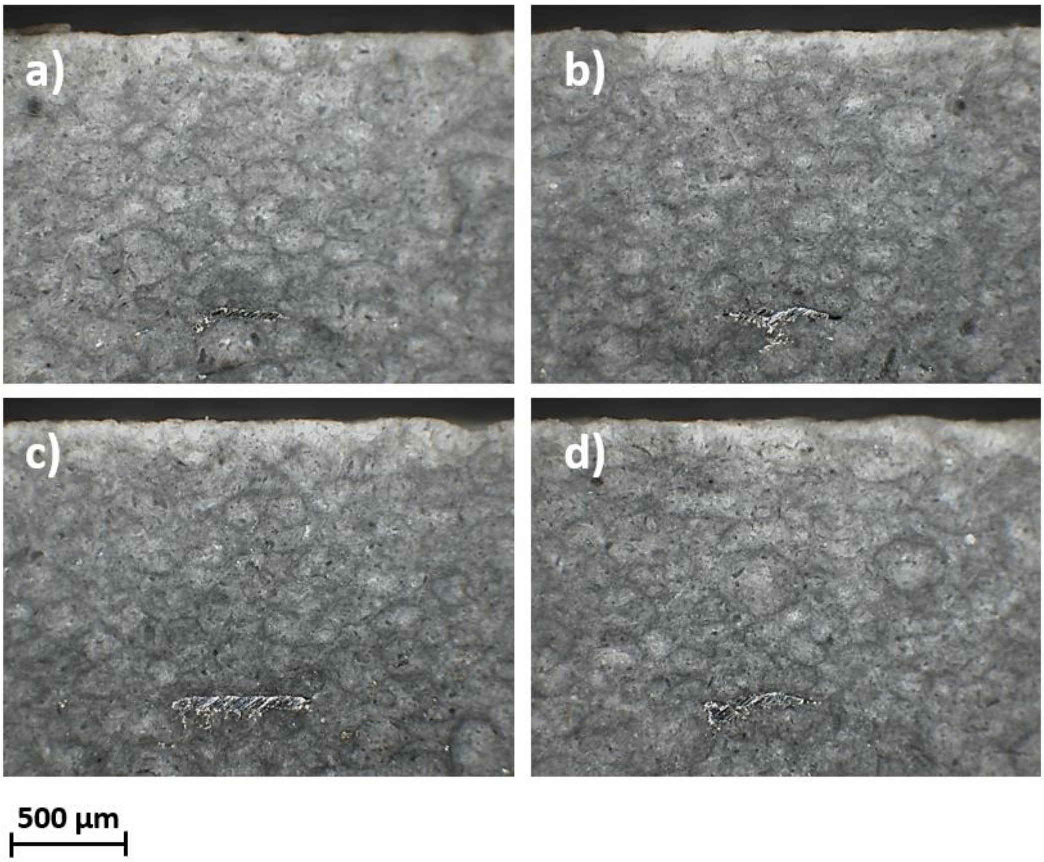


Figure 54: Microscope images of the cross section of embedded silver printed lines of 30, 40, 50 and 60 layers (from (a) to (d) respectively) in the porcelain stoneware substrate.

Next, in order to analyse what effect might have the encapsulation and embedding of the printed lines between two layers of porcelain stoneware ceramic powder over the adhesion and integrity of such silver lines, as explained in **section 5.2.2.1. "Printing of solvent-based inks"** and described in **section 5.2.1.1. "Printing of water-glycerol dye ink"**, a layer of the ceramic powder was pressed over substrates on which lines of 30, 40, 50 and 60 layers of ink had been printed. Initially, this process was going to be performed over the three substrates A, B and C. However, after some first trials we realised how it was quite difficult to accomplish a good adherence between both layers of porcelain stoneware powder during pressing. Difficulties were present mostly when performing such process with substrate A; after extracting the final substrate with both layers of ceramic, delamination was observed between the layers, reflecting bad adherence.

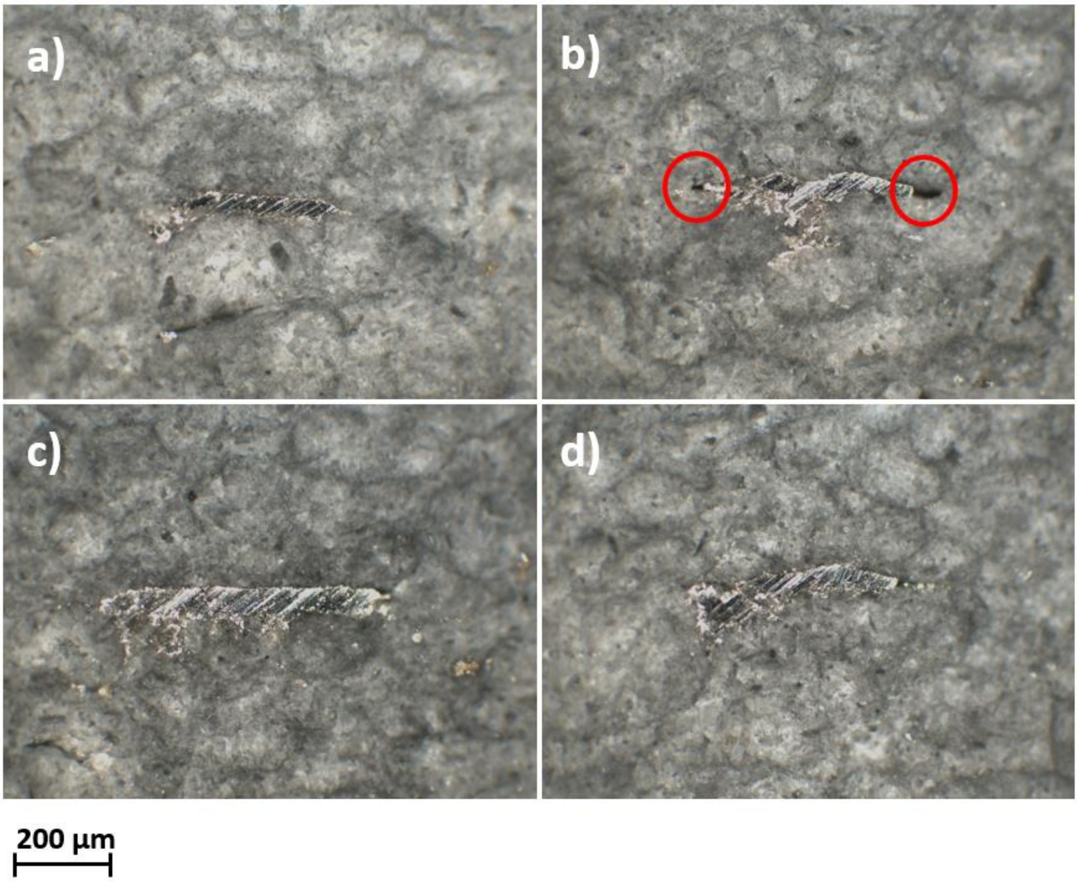


Figure 55: Microscope images of the cross section of embedded silver printed lines of 30, 40, 50 and 60 layers (from (a) to (d) respectively) in the porcelain stoneware substrate. Defects in the ceramic substrate are indicated with circles at the sides of the printed line in image b).

However, as the pressing load of the base substrate upon which the second layer was deposited was lowered, adherence with the top layer improved substantially, since the powder particles of this base substrate hadn’t been fully compressed and meshed better with the powder deposited on top. From the three substrates, the best result was obtained when substrate C was used as the base substrate, on which first silver lines were printed and subsequently, powder was deposited on top and pressed with the hydraulic press. After the double-layer sample or “sandwich” sample as prepared, it was sintered in the tube furnace under helium gas flow under the same conditions as the previous samples. In ***figure 54***, the section of a “sandwich” sample is shown, where substrate C was used as a base substrate. As it is possible to see, silver lines have not reacted as in the previous cases and remains embedded in the ceramic matrix with good structural integrity. In addition, the ceramic matrix also shows a good structural integrity with no presence of cracks or defects. In ***figure 55,*** a close-up view of the same sample is shown for each line, in which the section of the silver lines is easier to appreciate, such sections appear smooth and homogeneous. However, in image b) from ***figure 55,*** voids can be appreciated, meaning that in those zones, ink has not fully adhered to the ceramic body.

This phenomenon was not appreciated in any of the other analysed sections, which leads us to think that the quality and homogeneity of the printed line is a critical factor for the adherence between both porcelain stoneware layers and between these and the printed silver. It is important to note that, dark coloration of the ceramic substrate occurred once again, but at the same time this phenomenon did not affect the quality and integrity of the silver lines as in the previous cases. This might have been due to the fact that in this case only one substrate at a time was fired, eliminating the possible interaction of the H_2O and Ag_2O produced by one substrate (as described in the previous hypothesis) with another substrate present in the tube furnace during firing.

Then, once the sections of the samples had been optically analysed, they were taken for conductivity measurements. Since the section of the revealed silver lines were quite small, silver paint was applied over each of the revealed section of the silver lines in order to allow a better contact between the ends of the silver lines and the probes of the measuring equipment.

However, we were not able to measure any conductivity in any of the lines. This leads us to think that possibly, after depositing and pressing the layer of porcelain stoneware powder on top of the base substrate with the printed layers and further sintering of the sample, the lines might have divided loosing electrical conductivity due to the pressure exerted by the ceramic mass.

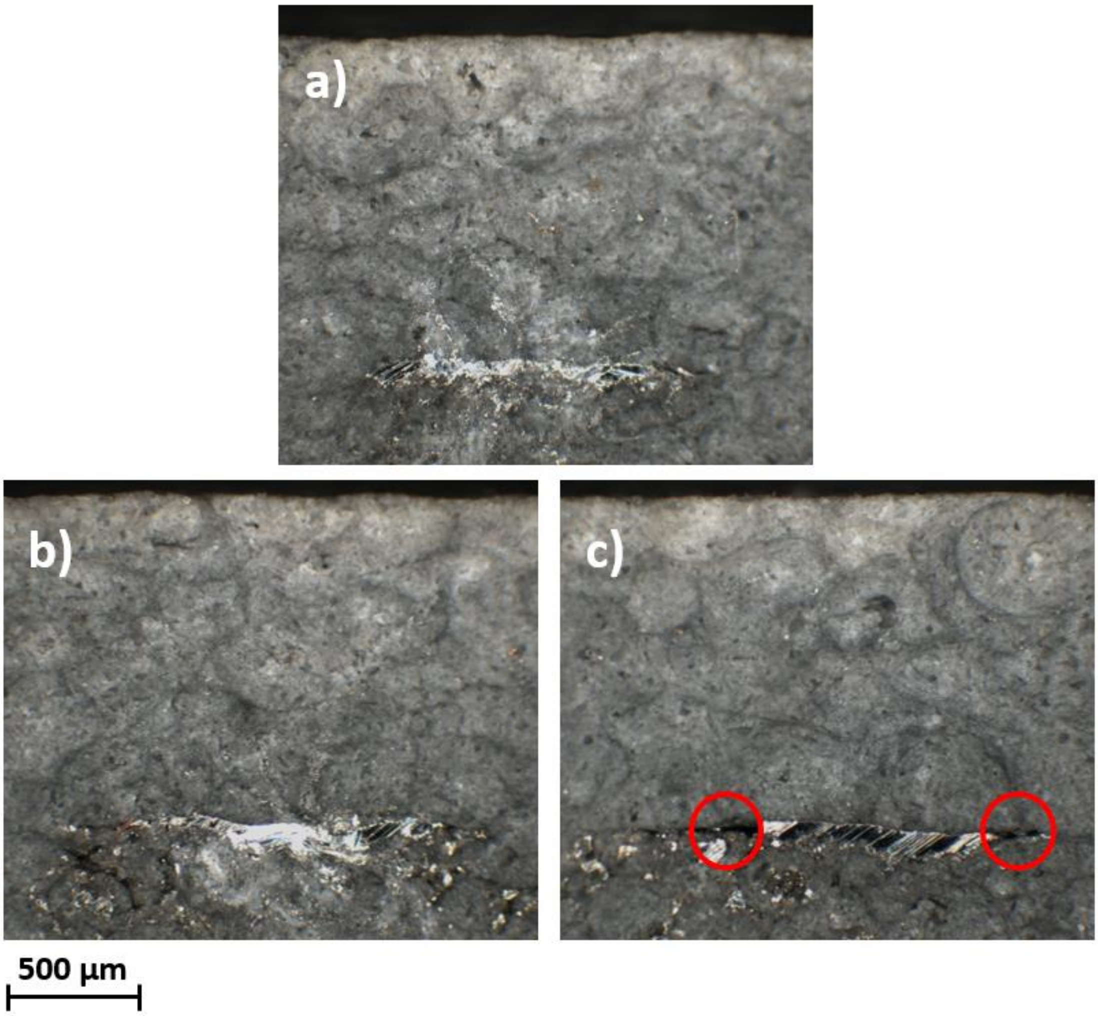


Figure 56: Microscope images of the cross section of embedded silver printed lines with 100 layers in the porcelain stoneware substrate. Defects in the ceramic substrate are indicated with circles at the sides of the printed line in image c).

Lastly, double layer/sandwich samples were once again prepared, but this time three lines with 100 layers of silver ink were printed over substrate C as the base substrate. The section of the three lines is shown in ***figure 56*****.** The result was quite similar as with the samples prepared in the previous case. Section of the printed lines increased in relation to the printed lines with 30, 40, 50 and 60 layers and the silver particles which can be seen around the silver line sections of were originated during the cutting of the samples with the circular saw, displacing some of the material of the lines over the ceramic surface. As seen in image c) of ***figure 56*****,** voids are once again present as in the previous case. Dark coloration of the ceramic substrates was still present.

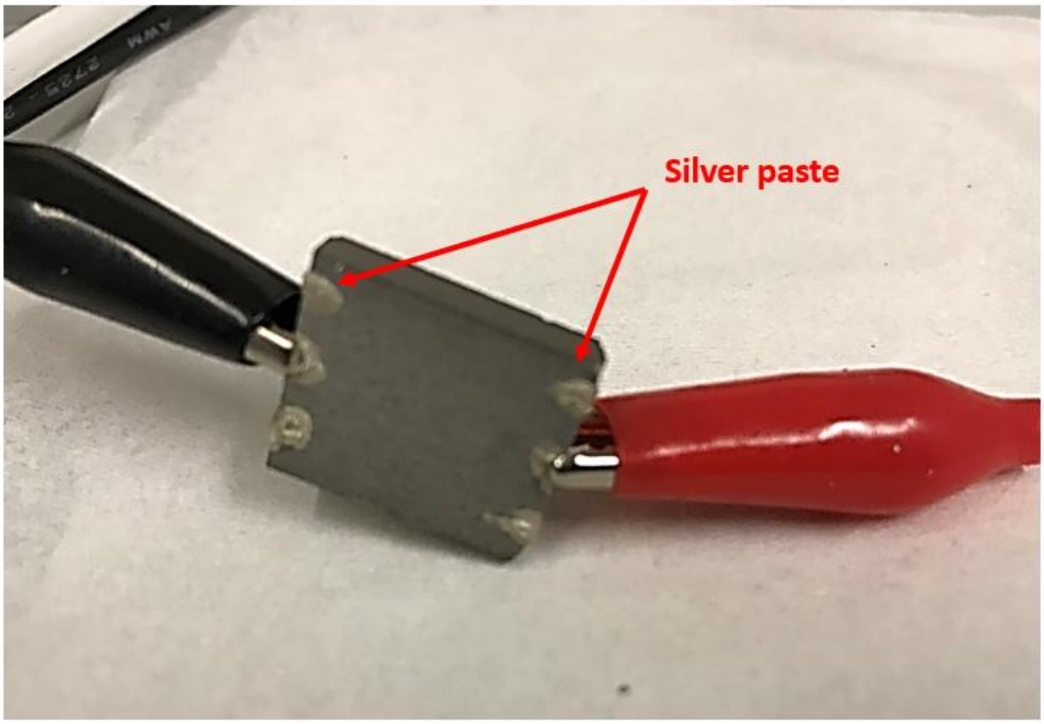


Figure 57: Setting for the conductivity measurement of the silver lines embedded in the "sandwich" porcelain stoneware sample. Silver paste which was applied in order to generate a good electrical contact is indicated with arrows.

With this samples, electrical contact was already able to be established by using a two-probe traditional measuring equipment, as seen in ***figure 57***, but it was difficult to maintain the contact and measure resistance values since slight movements of the probe lead to the loss of contact with the printed lines. In order to improve this contact, silver paint/paste was applied over the sections of the silver lines and drawing a contact towards the surface of the ceramic substrate.

After measuring with the two-probe multimeter, different values of resistance were measured, being the best measured value of 0,9 Ω and the worst of 3,9 Ω. These values were obtained when the contact between the probes and the silver paint was stable.

Thus, by estimating the section of the silver lines and by measuring the length of these, it is possible to calculate the resistivity of the embedded silver printed lines by applying the following equation:

$$\rho_{silver\ line} = R_{measured} \cdot \frac{S_{silver\ line}}{L}$$

The length of the silver lines is of approximately 20 mm, without taking into account the length of the small portions of silver paint applied over the surface of the ceramic substrate, which would slightly increase this value.

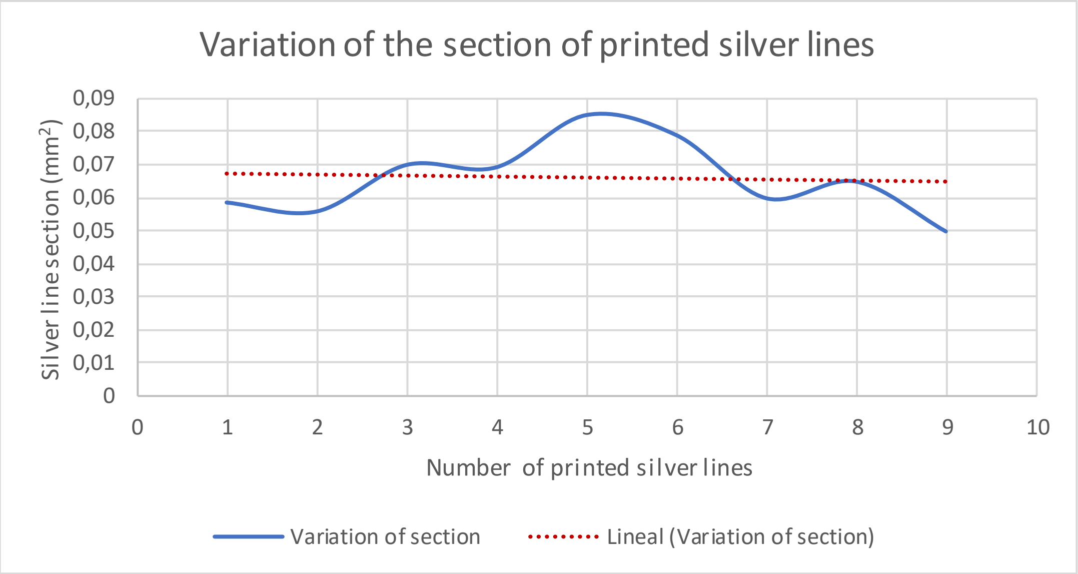


Figure 58: Variations of the printed silver line section in the different substrates that were produced.

Since the section of the all of the silver lines was irregular, it was measured for all of the different lines by image analysis with FIJI Studio Max Software, which allows to measure areas for example by indicating which colour of the image to measure. These results were then plotted in the plot which appears in the ***figure 58*** above. Then, with the average value of 0,067 mm^2 calculated from all the values of section measured for the different lines, resistivity was calculated by applying the defined formula, using the best and worst values of measured silver line resistance:

$$\rho_{silver\ line\_0,9\Omega} = 0,9 \cdot \frac{0,067}{20} = 0,003015\ \Omega \cdot mm = 301,5\ \mu\Omega \cdot cm$$

$$\rho_{silver\ line\_3,9\Omega} = 3,9 \cdot \frac{0,067}{20} = 0,013065\ \Omega \cdot mm = 1306,5\ \mu\Omega \cdot cm$$

In order to be able to evaluate the calculated resistivities, we must take into account the theoretical resistivities defined in the materials datasheet. For the silver ink in question, resistivities are defined as ≤10 μΩ·cm when printed over ITO and sintered at 150 °C during 30 min, ≤10 μΩ·cm when printed over Kapton and sintered at 150 °C during 30 min and ≤12 μΩ·cm when printed over PET and sintered at 130 °C during 30 min. Subsequently, it is possible to see how the resistivity values calculated for the silver lines printed and embedded in our ceramic substrates are higher than the theoretical values. However, it is also important to take into account two factors: on one hand, our substrate is very different from what is normally used for the printing of the solvent-based silver ink utilised, since it has been tailored for its printing over polymer substrates such as ITO, PET and Kapton.

Furthermore, the values of resistance which were measured with the two probe multimeter are resistances composed both by the printed silver line resistance and a series resistance introduced in the system by the silver paste which has been applied in order to generate a good electrical contact between the silver lines and the measuring probes. So, the actual resistance value of the silver lines should be even lower than what was measured. Thus, the values of measured and calculated resistivity for the silver printed lines which are embedded in the ceramic substrates, are between 30 and 130 times higher than the theoretical resistivity values provided in the specifications of the silver ink.

7. Conclusions

As it is possible to see, embedding of conductive tracks and complex ink patterns in ceramic substrates has been accomplished.

- By using a water-glycerol dye ink as a representative of water-based inks, complex patterns were printed on ceramic substrates following a “layer by layer” process, being able to generate channels of ink from the surface of the substrate towards its core, thus demonstrating the possibility of printing 3D patterns in a ceramic body. Solvent-based inks on the other hand, have proven less suitable for the printing of such structures.

- Furthermore, also by a “layer by layer” process, conductive silver tracks have been embedded in the interior of ceramic substrates by printing of a silver solvent-based ink, being able to control possible oxidation and adhesion issues, with decent conductivity values measured after the sintering process. Even though vertical contacts between the substrate’s surface and the embedded tracks hasn’t been possible to perform, such contacts could easily be generated by traditional processes such as punching of holes in the ceramic substrate and filling with a conductive paste.

- We have also learned that spreading and penetration of inks are complex phenomena. For instance, particle size and shape are highly influent on the spreading and of the printed material on the substrate, as well as on the penetration of the ink and should be studied in greater detail, since they define material distribution and homogeneity, which are critical when talking about printed conductive patterns.

- Moreover, changes in the reology ink, such as surface tension and viscosity, have also a great impact over ink/substrate interaction. Whilst water-based inks will generally present higher penetration values, solvent-based inks have proven

- Adhesion of the ink to the substrate is also critical and must be controlled and improved, since issues such as de-wetting of ink and crack formation also strongly define the integrity of the printed material and consequently also define the technical performance of the printed functional material, such as conductivity in printed conductive inks for example.

- Even though sintering atmosphere was controlled in order to prevent oxidation, oxidation of the printed conductive material was still present due to the presence of water and oxygen in the ceramic mass. Such process should also be studied with more detail, in order to gain insight and find ways to avoid oxidation of the printed materials during the sintering process.

- Consequently, depending on the application and desired printing pattern or structure, water-based inks and solvent-based inks can be more suitable in some cases than in others.

- On the other hand, for the future development of this work, different improvements can be added in the defined process for the integration and embedding of conductive structures in ceramic substrates. Additives can be added to the ceramic powder in order to facilitate and increase the adhesion between the different ceramic layers. Also, alternative inkjet printing processes can be adapted for the integration of conductive structures in ceramic substrates. For instance, RIP (Reactive Inkjet Printing) could be a way of also embedding conductive tracks within ceramic substrates and also creating the mentioned contacts between the embedded tracks in the interior of the ceramic body and its surface, since it is a technique based on printing of different aqueous solutions, which react once printed to form crystalline conductive metals. We also consider it would be important to evaluate, during further stages of the development, the effect that the ink-jet printed materials might have over the recycling processes existing in the ceramic industry, since recycling, energy efficiency and environmental impact are some of the most determining factors in the success of the introduction of new technologies and developments into the global market. In relation to this, also consider the use of other types of ceramic substrates, such as ceramics produced from the wastes of other ceramic products and industries, lessening the environmental impact of the ceramic tiles.

Thus, it is possible to see how the carrying out of this project has signified and important, first step towards the development of ceramic tiles suitable for photovoltaic, electronic and energy efficient applications, combining different technologies whilst taking into account various and critical factors.

8. References

[1] *El sector del azulejo en España a través de 21 grandes empresas. KPMG, 2018, pp 2-47. [Online] Available: https://kpmg.es.*

[2] D.A. Manzanedo. *Análisis sector cerámico en España,* final degree distertation, Univ. Miguel Hernández, 2015, pp 2-15

[3] Gabaldón-Estevan, Daniel; Criado, Emilio; Monfort, Eliseo. *The green factor in European manufacturing: a case study of the Spanish ceramic tile industry*. Journal of Cleaner Production, 2014, 70, pp 242-250

[4] Sanz Solana, Dr. Vicente. *Inkjet printing for ceramic tile decoration, Qualicer, 14, 2014, p 2*

[5] Hutchings, Ian. *Inkjet printing for the decoration of ceramic tiles: technology and opportunities,* Univ. of Cambridge, Qualicer, 10, 2010, p 4

[6] J.Llop , T. Stoyanova Lyubenova , E. Barrachina, M.D. Notari, I. Nebot, J.B. Carda. *The ceramic sector in Spain: Challenges and opportunities,* Escuela Superior de Cerámica d'Alcora, Univ. Jaume I, Qualicer, 14, 2014, pp 1-9

[7] Víctor Echarri-Iribarren et. al. *Iridescent Techniques in Ceramics: Physico-Chemical Analysis and Colorimetric Characterization of the Headquarters of the Botín Foundation in Santander*, Appl. Sci. 2019, 9, 1521, pp 1-20

[8] B. Mazzant, S. Fazio, A. Salomoni, S. Dei Svaldi, C. Zevi, G. Rotunno. *Fachadas exteriores de los edificios con baldosas cerámicas fotovoltaicas,* Centro Cerámico de Bolonia, DICASM, ICIE, Qualicer, 8, 2008, pp 95-106

[9] *Demonstration of an innovative Building Integrated PhotoVoltaic system toward net-zero-energy buildings.* [Online] Available: http://www.agc-bipvlife.com/

[10] Joachim Benemann, Oussama Chehab, Eric Schaar-Gabriel. *Building-integrated PV modules,* Solar Energy Materials & Solar Cells, 67, 2001, pp 345-354

[11] Saleem Khan, Leandro Lorenzelli, Ravinder Dahiya. *Technologies for Printing Sensors and Electronics over Large Flexible Substrates: A Review,* IEEE Sensors Journal, 2014, pp 1-22

[12] P. T. Bishop, L. J. Ashfield, A. Berzins, A. Boardman, V. Buche, J. Cookson, R. J. Gordon, C. Salcianu and P. A. Sutton. *Printed gold for electronic applications,* Gold Bulletin, Volume 43, No. 3, 2010, pp 181-188

[13] Emrah Biyik et. al. *A key review of building integrated photovoltaic (BIPV) systems,* Engineering Science and technology an Internationla Journal, 20, 2010, pp 833-858

[14] Jackson P., Hariskos D., Lotter E., Paetel S., Wuerz R., Menner R., Wischmann W., Powalla M. *Progress in Photovoltaics: Research and Applications*, 19(7), 2011, pp 894-897

[15] Danielle Iencinella et. al. *Thin film solar cells on commercial ceramic tiles,* Solar Energy Materials & Solar Cells, 93, 2009, pp 206–210

[16] Alfonso Uranda-Usón et. al. *Phase change material applications in buildings: An environmental assessment for some Spanish climate severities,* Science of the Total Environment, 444, 2013, pp 16-25

[17] S.r.James. *Principles of Ceramic Processing,* Wiley-Interscience, 2nd edition, 1995

[18] M.Dondi, G. Ercolani, C. Melandri, C. Mingazzini, M. Marsigli. *Chemical composition of Porcelain Stoneware tiles and its influence on microstructural and mechanical properties,* InterCeram: International Ceramic Review, Vol. 48, No. 2, 1999, pp 75-83

[19] *Tecnología Cerámica Aplicada,* SACMI: Asociación Española de Técnicos cerámicos, Faenza Editrice Ibérica, vol. 1, 2004

[20] C. Zanelli*, M. Dondi, M. Raimondo, CNR-ISTEC, Inst. Science and Technology for Ceramics, Faenza (Italy); L. Beccaluva, C. Vaccaro, Dept. Earth Sciences, University of Ferrara (Italy). *Phase transformations during liquid phase sintering of porcelain stoneware tiles: A petrological approach,* An International Conference on the Science, Technology & Applications of Sintering, 2003, pp 1-6

[21] Jorge Martín-Márqueza, Angeles G. De la Torre b, Miguel A. G. Aranda b, Jesús M. Rincóna, Maximina Romero. *Evolution with temperatura of crystalline and amorphous phases in porcelain stoneware,* Journal of the American Ceramic Society, 92, 2009, pp 229-234

[22] Jorge Martín-Márquez, Jesús Ma. Rincón, Maximina Romero. *Mullite development on firing in porcelain stoneware bodies,* Group of Glass and Ceramic Materials. Department of Building Construction Systems, Eduardo Torroja Institute for Construction Sciences-CSIC, 28033 Madrid, Spain.

[23] Jorge Martín-Márquez, Angeles G. De la Torre, Miguel A. G. Aranda, Jesús Ma Rincón, and Maximina Romero. *Evolution with temperature of crystalline and amorphous phases in porcelain stoneware*, J. Am. Ceram. Soc., 92, pp 229-232

[24] M.Romero, J.M. Pérez. *Relation between the microstructure and technological properties of porcelain stoneware: A review*, Materiales de Construcción, Vol. 65, Issue 320, 2015

[25] R.J. Galán-Arboledas et.al. *Ternary diagrams as a tool for developing ceramic materials from waste. Relationship between technological properties and microstructure,* 2019, p 7

[26] *Tecnología Cerámica Aplicada,* SACMI: Asociación Española de Técnicos cerámicos, Faenza Editrice Ibérica, vol. 2, 2004

[27] Magdassi. S. *Chemistry of inkjet inks,* World Scientific, 2010

[28] Mr Raghu Das, dr Khasha Ghaffarzadeg, Dr Xiaoxi He. *Flexible, Printed and Organic Electronics 2019-2029: Forecasts, Players &* Opportunities. [Online] Available: https://www.idtechex.com

[29] Shlomo Magdassi , Michael Grouchko and Alexander Kamyshny. *Copper nanoparticles for printed electronics: Routes towards achieving oxidation stability,* Materials, 3, 2010, pp 4626-4638

[30] Y. Kobayashi, T. Sakuraba. *Silica-coating of metallic copper nanoparticles in aqueous solution,* Colloids and Surfaces A: Physicochem. Eng. Aspects, 317, 2008, pp 756-759

[31] Yoshio Kobayashi, Mitsuru Horie, Mikio Konno, Benito Rodríguez-González and Luis M. Liz-Marzán. *Preparation and properties of silica-coated cobalt nanoparticles*, J. Phys. Chem., 107, 2003, pp 7420-7425

[32] Jan Maslik, Ivo Kuritka, Pavel Urbanek, Petr Krcmar, Pavol Suly, Milan Masar and Michal Machovsky. *Water-based Indium Tin Oxide Nanoparticle Ink for Printed Toluene Vapours Sensor Operating at Room Temperature,* Sensors 2018, 18, 3246

[33] Sureeporn Uttiyaa, Cristina Berninia, Maurizio Vignoloa, Ilaria Pallecchia, Daniele Marréa, Antonio Sergio Siria and Luca Pellegrinoa. *Inkjet printing of conducting silver patterns on alumina and insulating ceramic-glass by saline precursors,* Thin Solid Films 642, 2017, pp 370-376.

[34] Nikola Perinkaa, Chang Hyun Kim, Marie Kaplanovaa, Yvan Bonnassieux. *Preparation and chracterization of thin conductive polymer films on the base of PEDOT:PSS by ink-jet printing,* Physics Procedia, 44, 2013, pp 120-129

[35] SoomanLim, MargaretJoyce, PaulD.FlemingN, and AhmedTausifAijazi. *Inkjet printing and sintering of nano-copper ink,* Journal of Imaging Science and Technology, 57(5), 2013, pp 1-7

[36] S. Arcidiacono, N.R. Bieri, D. Poulikakos, C.P. Grigoropoulos. *On the coalescence of gold nanoparticles,* International Journal of Multiphase Flow, 30, 2004, pp 979-994

[37] S. Uttiya, I. Pallecchi, C. Bernini, M. Vignolo, D. Marré, A.S. Siri, and L. Pellegrino. *Grain coalescence of inkjet-printed Ag patterns studied by means of magnetotransport measurements,* Flex.Print.Electron, 2, 2017, pp 1-7

[38] Amorós, J. L.; Cantavella, V.; Llorens, D.; Feliu. *Método y aparato no destructivo para la medida de la densidad en baldosas cerámicas,* C. Patente PCT/ES2005/000397

[39] M.Dondi, M.Raimondo, C.Zanelli. *Stain resistance of ceramic tiles,* Ceramic World Review, no. 73, 2007

[40] Jorge Martín-Márquez, Jesús Ma. Rincón, Maximina Romero. *Mullite development on firing in porcelain stoneware bodies,* Journal of the European Ceramic Society, Vol. 30, Issue 7, 2010, pp 1599-1607

[41] R. Hevia, A. Inocencio, E. Barrachina, J. Gómez, C.Gil, J.B. Carda. *Manufacture of porcelain tile with selected raw materials from the argentine republic*, Qualicer, 2006, pp 125-134

[42] Richard, K.Holman, Michael, J.Cima, Scott, A.Uhland, and Emanuel Sachs. *Spreading and Infiltration of Inkjet-Printed Polymer Solution Droplets on a Porous Substrate,* Journal of Colloid and Interface Science, 249, 2002, pp 432-440

[43] Seung Hun Huh. *Thermal Reduction of Graphene Oxide*, Physics and Applications of Graphene Experiments, Dr. Sergey Mikhailov (Ed.), InTech, 2010, pp 75-90. [Online] Available: http://www.intechopen.com/books/physics-and-applications-of-graphene-experiments/thermal-reduction-ofgraphene-oxide

[44] Shuntao Xu, Zhengfu Zhang, Jinkun Liu, Yashan Wang, and Junlong Hu. *Facile preparation of reduced graphene by optimizing oxidation condition and further reducing the exfoliated products*, J. Mater. Res., Vol. 32, No. 2, 2017, pp 383-391

[45] B. Derby. *Inkjet printing ceramics: From drops to solid,* Journal of the European Ceramic Society, 31, 2011, pp 2543-2550