

Valorization and inertization of galvanic sludge waste in clay bricks

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Abstract

Galvanic sludge wastes (GSW) are produced by the physico-chemical treatments of wastewater generated by electroplating plants. These materials have a significant potential for the production of clay ceramic bricks. This paper focuses on the viability of the inertization of heavy metals from GSW mixed with clays. The original materials

1 were obtained by mixing three types of raw clay (red, yellow and black) in equal parts
2 with GSW. These mixtures were characterized by XRD, XRF, and chemical elemental
3 analysis CHNS. The dosage of GSW in the Clay-GSW bricks was up to 5 wt%. The
4 bricks were then manufactured using conventional processes. The influence of the
5 amount of GSW was evaluated after firing the clay-GSW composites at 950°C for 1
6 hour. The engineering properties of the fired samples, such as density, water absorption,
7 open porosity, water suction and compressive strength, with and without the GSW, were
8 determined. The incorporation of GSW into the clay mix clearly decreased the linear
9 shrinkage and bulk density of the bricks in comparison with the fired clay used as a
10 control. These GSW-clay composites also showed lower open porosity. According to
11 the results obtained for the bulk density of the bricks, samples with GSW addition
12 showed slightly lower values of open porosity than clay bodies, indicating that the
13 GSW-clay samples had slightly higher closed porosity values. This was also shown by
14 SEM. The open porosity, SEM and pore size distribution tests indicated that the
15 porosity generated by the addition of GSW was mainly closed and, therefore, GSW
16 bricks had excellent mechanical properties. The environmental risks of the
17 incorporation of GSW, rich in heavy metals (Cr, Zn, Ni and others), to a clay matrix
18 was evaluated by leaching tests of the fired products. The results indicated a successful
19 inertization of the pollutants.
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48 *Keywords:* galvanic sludge waste, clay ceramics, bricks, inertization, valorization
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52 **1. Introduction**

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Galvanization and surface treatments prevent corrosion in metals and alloys. These processes consume a large amount of water in the processes of production, as well as in washing steps (Ribeiro et al., 2004). This results in large amounts of waste water, which need a series of treatments to reach the environmental requirements before being discharged out of the plant. In addition, large amount of sludges are produced by the physico-chemical treatment of wastewater generated in electroplating plants. These sludges contain a noticeable amount of heavy metals, colloidal aluminium hydroxide, aluminium sulphate (used as a flocculating agent), sodium and calcium ions (generated in neutralizing solutions) and water, and are considered as potential eco-toxic residues (Dufour, 1999). To solve the environmental problems posed by the sludge, it is subjected to exhausted baths. The presence of Cr (III) in this waste can promote the formation of free Cr (VI), which is soluble in water and carcinogenic in nature (Silva et al., 2008). In the European Union 100.000-150.000 ton/year of this type of sludge are produced (Magalhaes, 2002, 2005a; Ribeiro et al, 2002, 2004), which is a serious waste management issue.

The production of galvanic sludge wastes (GSW) in the developed and underdeveloped countries is higher than 1.000.000 ton/year (Silva et al., 2008). The most common way to dispose of these wastes is landfill deposition. However, the deposition of galvanized sludge in landfill is a not a very environmentally friendly alternative. To solve this problem, hydrometallurgical technologies can be applied to reuse the valuable metals in the effluents (Rossini and Moura-Bernades, 2006). There are important research works on the extraction and reuse of heavy metals (Ni, Zn, Cu and others) extracted from the dry residue and effluents (Silva et al., 2005).

The chemical characteristics of the GSW are important parameters in recycling processes. Ceramic products, such as bricks, stoneware or tiles, have a very

1 heterogeneous composition since they are formed by clay materials which have a wide
2 range of compositions (Couto et al., 2003). According to Reinoso et al. (2010), the
3 building industry is the most suitable technological activity sector to consume solid
4 wastes. The reason for this is the large quantity of raw materials used by the sector as
5 well as the large volume of final products required. Clays usually exhibit high cation
6 exchange capability, due to their surface charge properties (Benjelloun et al., 2001;
7 Bergaya et al., 2006). Clay can also be used to immobilize harmful heavy metals ions
8 (Addy et al., 2012; Churchman et al., 2006). Furthermore, clay minerals are silicate
9 phases that can incorporate considerable amounts of metals in their structures.
10 Therefore, the ceramic industry is one of the best candidates to consume large amounts
11 of industrial wastes, such as combustion ashes, granite cutting sludge and wastewater
12 sludges (Martínez-García et al., 2012; Reijnders, 2007; Torres et al., 2004). The
13 incorporation of residues such as GSW containing heavy metal ions into a ceramic
14 matrix can be a promising solution to reduce the environmental risks.

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34 There are some studies on the characterization of GSW (Magalhaes et al.,
35 2005.), for manufacturing vitrified ceramics (Ferreira et al., 1999; García-Vallés et al.,
36 2007; Mello-Castanho et al., 2006; Silva and Mello-Castanho, 2004) and to obtain
37 vitrified tiles (Reinoso et al., 2010). There are also studies on the encapsulation of GSW
38 in a mixture of calcium sulfoaluminate cement and coal bottom ash (Luz et al., 2006).
39 Recent research works showed the results of in depth studies on the immobilization,
40 inertization and release kinetics of GSW in ceramic matrix (Magalhaes et al., 2004a,
41 2004b, 2005a). However, there are few available studies on the use of GSW as raw
42 material for the production of clay bricks (Ferreira et al., 1999. Mymrine et al., 2013).
43 According to the existing literature, the use for GSW as a raw material in the cement
44 industry has been reported (Cioffi et al., 2002; Espinosa and Tenorio, 2001; Luz et al.,
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2009; Riganti et al., 1986). Espinosa and Tenorio (2001) studied the influence of the addition of different amount of waste in the clinkerization process analyzing the inertization of sludge in the cement matrix. They concluded that up to 2 wt% of galvanic sludge did not affect that process. Luz et al. (2009) used the galvanic sludge to design calcium sulfoaluminate cement with 25 wt% of residue and studied the phases generated during the cement hydration including the hydrated encapsulation of Cr. According to these authors, the formation of ettringite (hydrated calcium sulfoaluminate phase formed during the early stages of hydration of Portland cement) is crucial to understand the processes of solidification/stabilization of many heavy metals, since this compound is able to incorporate them into its structure to form sulphoaluminate cements. Magalhaes (2002) and Magalhaes et al. (2004a) studied the role of the mixing time, the composition of GSW and clay and the calcination step on the fixing level of several metal-containing species for inertization after sequential leaching in different media. They concluded that the composition, the physical properties of the sludge and the stirring during the preparation of the sludge-clay mixtures seem to have a vital role in the inertization of metallic species. Subsequently, the same authors (Magalhaes et al., 2004b) studied the inertization of GSW in ceramic matrixes analyzing the amount of sludge and the physical aspect of the sample (powdered or pressed pellets) by leaching in different media. They found that the relative amount of sludge in the mixture, the calcination temperature and agglomeration state of the sample were the most influential factors in the inertization process. Finally, Magalhaes et al. (2005b) studied the kinetics of the immobilization of galvanic sludge in clay-based matrixes in different media and found that clay-based ceramics are an effective matrix for inerting galvanic sludges by means of creating a physical barrier that confines sludge-containing species in the matrix and the formation of less soluble metallic components (oxides) via chemical

1 reactions induced by increasing the temperature. Ferreira et al. (1999) added GSW to
2 plastic red clay and studied the physical properties of mixed bricks. They concluded that
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4 the incorporation of low amount of residues (5 wt%) did not affect the technological
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6 properties of the ceramic products.
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9 Further applications for GSW encountered in the existing literature include the
10 recovery of heavy metals (Buzaeva et al., 2011; Rossini and Moura-Bernades, 2006;
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12 Sun et al., 2001; Silva et al., 2005), the stabilization and/or solidification using asphalt
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14 emulsions (Bednarik et al., 2005), and the development of a pigment-based material by
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16 using chromium waste as precursor (Andreola et al., 2008; Berry et al., 2002).
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21 The objective of the present work was to investigate the feasibility and the effect
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23 of the incorporation of different amounts of the residue GSW to industrial clay. Physical
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25 and mechanical properties were determined in fired bricks, along with microstructural
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27 characterization. The environmental risks of the incorporation of GSW have also been
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29 evaluated by leaching tests of the fired products.
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36 **2. Experimental**

37 38 39 40 41 *2.1 Materials*

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43 The clay was supplied by a clay pit located in Bailén, Jaén (Spain). It was
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45 obtained by mixing three types of raw clays in equal parts: red, white and black. The
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47 galvanic sludge waste (GSW) was generated during the surface treatment of galvanized
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49 metals by the company Algama Industries Ltd. at Linares, Jaén (Spain). The as-received
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51 GSW was dried at 105°C for 24 hours.
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58 *2.2 Processing method*

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To obtain a uniform particle size, the clay and the GSW were crushed and ground to a powder with a particle size suitable to pass through a 150 μm sieve. The mixture was homogenized in a blender and moulded under 54.5 MPa using a uniaxial laboratory-type pressing equipment Mega KCK-30 A. The necessary amount of deionized water (8 mass %) was added to the mixture to obtain adequate plasticity and absence of flaws, mainly cracks, in the compression stage. To enable comparative and statistical results, ten samples per series were prepared for the tests. Waste-free samples of clay were also prepared as a control. Solid bricks with 30 x 10 mm cross sections and a length of 60 mm were obtained. The shaped samples were dried for 24 h at 110°C. The dried samples were then fired in a laboratory-type electrically heated furnace at a rate of 5°C/min up to 950°C for 1 h. Samples were cooled to room temperature, by natural convection, inside the furnace. The fired samples were designated as C for the brick without GSW and C-xGS for the mixtures, where x denotes the content (%) of GSW in the matrix clay (C).

2.3 *Techniques of characterization*

The mineralogical composition was studied by X-ray diffraction (XRD). The original samples were gently ground in an agate mortar and random and oriented preparations were used for XRD. Oriented preparations were also saturated using ethyleneglycol vapours to investigate the presence of smectites. The X-ray diffractometer X'PERT PRO from PANalytical was used at 36 kV and 26 mA with Ni-filtered CuK (α) radiation and graphite monochromator. The 2θ range was from 3 to 70°, step size 0.03° (2 θ), scan speed 0.05/240 (2 θ /s.) and counting time 240 s. The divergence slit was $\frac{1}{2}$ (° θ) and anti-scatter slit $\frac{1}{4}$ (° 2θ) with detector X'Celerator. The chemical composition was determined by X-Ray Fluorescence (XRF)

1 analysis using the Philips Magix Pro XRF model PW-2440, measurement uncertainty
2 was approximately ± 2 units of the last significant figure reported and verifiable
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4 detection limit was ~ 0.01 wt%. The total content of carbon, hydrogen, nitrogen and
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6 sulphur in the GSW and in the clay was determined by combustion in oxygen
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8 atmosphere using the CHNS-O Thermo Finnigan Elementary Analyzer Flash EA 1112.
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11 12 13 14 *2.4 Properties of fired samples*

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16 To verify whether the resulting fired brick samples fulfilled the building
17 standards, tests for linear shrinkage, mass loss on ignition, bulk density, water
18 absorption capacity, water suction, open porosity and compressive strength were
19 performed.
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26 The linear shrinkage (%) was determined from the length of the samples before
27 and after firing using a calliper with a precision of ± 0.01 mm. The mass loss on ignition
28 was determined as the mass loss between drying at 110°C and firing at 950°C . It is
29 expressed as a percentage. The bulk density (g/cm^3) of the fired bricks was determined
30 as the quotient of the dry mass of the fired sample and its volume, being determined
31 according to a standard method (EN 772-13:2001).
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41 Water absorption capacity (weight %) was determined according to the standard
42 procedure UNE 67-027 using dried samples (110°C for 24 h) and weighed repeatedly
43 until the mass difference was < 1 %. Open porosity (in vol %) was calculated from the
44 values determined of bulk density and water absorption capacity.
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51 Water suction of a brick is the volume of water absorbed during a short partial
52 immersion. In this study, the water suction was determined through capillary action
53 according to the standard procedure UNE 67-031. The water suction was calculated and
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The compressive strength was measured for fired samples according to the standard procedure EN 772-1 in a Suzpecar CME 200 SDC laboratory testing equipment. All shaped samples were tested by applying the load centred on the upper face of the brick with a speed <20 MPa/s until fracture. The area of both bearing surfaces was measured and the average taken. The compressive strength of each sample was obtained by dividing the maximum load by the average surface of both bearing surfaces with 0.1 MPa accuracy. For this trial, six fired samples were tested.

The development of porosity and microstructure in the samples was also evaluated by means of Scanning Electron Microscopy (SEM) using the high-resolution SEM equipment JEOL SM 840 and the Energy Dispersive X-Ray Spectroscopy (EDS) for chemical analysis (20 KV). The samples were placed on an aluminium holder and coated with carbon using an ion sputtering device JEOL JFC 1100. Adsorption-desorption isotherms of N_2 at 77 K after outgassing for 2 h. at 150°C, the specific surface area (BET), micropore area, BJH cumulative volume of pores, BJH average pore diameter and pore size distribution were obtained in a Micromeritics equipment, (TriStar II 3020 model), following the BJH method (Barrett et al., 1951).

Finally, an environmental assessment study was carried out to evaluate the leaching of heavy metals present in GSW for a better characterization of the fired product and to determine if they were ceramized and immobilized into the clay matrix. The bricks were subjected to a leaching test according to the Toxicity Characteristic Leaching Procedure (TCLP), Method 1311-1 (TCLP, 1992). Chemical analysis of heavy metals in the leachates was carried out using Inductively Coupled Plasma Mass Spectrometry (ICP-MS) on a 7500 Agilent Instrument with Ar plasma ionization and quadrupole detector.

3. Results and discussions

3.1 Characterization of raw materials

GSW was obtained from the electroplating process and heavy metals, such as Cr or Zn, are the main pollutants present in this sludge. The GSW contained large amounts of ZnO (23.79 wt%), Cr₂O₃ (12.73 wt%) and CaO (7.77 wt%), and lower amounts of Fe₂O₃ (3.35 wt%) and MgO (3.77 wt%) with 36.62 wt% loss on ignition (Table 1). The high content of fluxing oxides in the waste precludes a low temperature sintering during firing. Therefore, this material would have a higher industrial interest if it is mixed with clays. The composition of the clay used in the study was similar to that of typical clays used in industrial brick manufacturing with Si, Al, Ca, Fe and K as the main components. There were also minor amounts of Ti and Na and the loss of ignition was 10.55 wt%.

The XRD pattern of the clay sample in oriented preparation (Figure 1 a) exhibited the presence of clay minerals such as kaolinite and illite, with montmorillonite (d_{001} -value at 1.497 nm). Quartz, calcite and feldspars (microcline and albite) were also identified as well as iron oxide. The random XRD pattern demonstrated that quartz is the main component and illite and kaolinite are the predominant clay minerals, with minor calcite and feldspars. The XRD pattern of this sample in oriented preparation after saturation with ethyleneglycol vapours evidenced that the montmorillonite d_{001} -value changed from 1.497 nm to 1.715 nm. The XRD pattern of dried GSW (Figure 1b, compare the intensity scales with Figure 1a) only revealed the presence of calcite and quartz as the crystalline phases. A large amount of amorphous material can be observed according to the background of the XRD pattern and some broad bands.

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In comparison with the mineral composition of the clay, the elemental analysis of GSW (Table 2) indicated relative large amounts of carbon and hydrogen, with lower amounts of nitrogen and sulphur. The presence of these elements is associated with carbonates and mainly organic matter present in both samples. The high weight loss of the GSW (36.62 wt%) could be due to the decomposition of organic matter, heavy metal hydroxides and calcite.

3.2 Properties of GSW-clay mixtures

Experimental tests were carried out with mixtures of different proportions of GSW (0-5 wt%) and clay in order to study their engineering properties. First of all, no flaws such as cracks and bloating were observed after firing the GSW-clay mixtures at 950°C. No significant colour differences were observed between the fired clay used as a control and the bricks containing GSW (1-5 wt%).

The quality of the brick can be further assessed from the degree of linear shrinkage. The samples showed little in linear shrinkage after firing, with variations of ca. -0.3% for clay bricks and lower than ca. -0.5% for GSW-clay mixtures (Table 3). Therefore, clay samples as well as samples containing GSW contracted slightly when fired at 950°C resulting in a typical behaviour of porous bodies. The sintering mechanisms encouraged greater proximity between the particles and thus caused shrinkage. The low shrinkage can be associated with the relative high content of quartz in the clay sample. Quartz is considered an inert phase at least up to 950°C in this context. The quartz grains reduce the possible contraction of the ceramic body. On the other hand, the clay bricks had a loss on ignition of 13.84 wt% due to elimination of physical water, organic matter by combustion, dehydroxylation reactions of clay minerals and decomposition of calcite. Thus, the brick weight loss on firing depends of

1 the organic and inorganic materials in both clays and GSW. Weight loss on ignition in
2 GSW-clay mixtures increased from 10.32 to 13.87 wt% when the amount of GSW was
3 higher. The last sample with 5 wt% of GSW showed a weight loss similar to that of the
4 original clay.
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9 The bulk density of the fired clay was 1.760 g/cm³ (Table 3). The addition of
10 GSW (1-5 wt%) produced a decrease of ca. 18% in bulk density (1.450 g/cm³) and the
11 increase in the percentage of addition of GSW to the clay promoted no significant
12 change (Figure 2). Hence, the lighter bricks/material generated by the addition of GSW
13 to the clay had a lower thermal conductivity, thereby providing better insulation
14 properties in building construction (Eliche-Quesada et al., 2011).
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24 The results of water absorption capacity, open porosity and water suction tests
25 are shown in Table 4. Water absorption is an effective index for the evaluation of the
26 quality and densification of building bricks and it is based on the amount of open pores
27 in fired specimens. The total porosity of the fired samples is the addition of open and
28 closed pores. Low water absorption values result in bricks with more durability and
29 higher strength in the natural environment (Eliche-Quesada et al., 2011; Muñoz-Velasco
30 et al., 2014; Raimondo et al., 2009). The water absorption capacity (w.a.c.) of the
31 samples after addition of GSW, as compared with the original clay (sample C), showed
32 little variation (Table 4), between 16.400 (+/- 1.001) and 15.467 (+/- 1.354). It was
33 assumed that the addition of GSW at 1 wt% would produce a sintering effect (pores will
34 be more closed) on the fired clay particles, but the w.a.c. value does not reflected a great
35 change. When the addition of GSW to the clay was 4-5 wt%, a slight decrease of
36 experimental w.a.c. values was observed. It could be explained by the greater effect of
37 sintering, although the change in w.a.c. was not as expected. However, the values of
38 open porosity (o.p.), determined using the apparent density values and w.a.c. values for
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each composition, showed variation. The open porosity decreased from 28.86% after addition of 1 wt% of GSW, to 23.42% (*ca.* 6% of difference). This experimental observation was associated with the effect of sintering on the fired clay particles produced by the metal composition of GSW. The values of open porosity changed little after addition of higher amounts of GSW (2-3 wt%). When the addition was 4 wt% or higher (5 wt%), the o.p. values decreased a little more because the sintering produced by the effect of GSW addition was more effective.

The values of open porosity (vol %) in Table 4 showed the porosity as a property that is closely related to other physical properties such as absorption and water suction (decreasing open porosity will also reduce both absorption and water suction). The fired clay without GSW, with higher bulk density (Table 3), showed the highest open porosity (28.86 vol %). The addition of 1 wt% of GSW decreased the open porosity to 23.42 vol %, being minimum (21.98 vol %) when the addition of GSW was 4 wt%. The value of open porosity slightly increased (22.43 vol %) by addition of 5 wt% of GSW but was still lower than the sample with 1 wt%. Since the results on water absorption and open porosity indicate that samples with 4 wt% of GSW had the lowest values of both parameters, porosity must be further closed. The incorporation of GSW could generate a greater quantity of vitreous phase (possibly very viscous at 950°C), which would fill in the pores and promoting a decrease in the open porosity. This assumption is in accordance with the high chemical content of heavy metals present in GSW (Table 1).

The results of water suction tests (Table 4) showed the same trend compared to water absorption data. Water suction of the clay was 2.91 g/cm².min and decreased with the addition of GSW. Water suction decreased from 2.24 g/cm².min when 1 wt% of GSW was incorporated and it reached a minimum of 1.76 g/cm².min in samples with 4

1 wt% of GSW. An increment of 1 wt% of GSW to 5 wt% produced an increase of water
2 suction up to $2.07 \text{ g/cm}^2 \cdot \text{min}$. Therefore, the incorporation of GSW to the clay produced
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4 a decrease in the interconnected surface porosity that could be related to the water
5 suction in the fired bricks. Sample C-4GS, with 4 wt% of GSW, showed the lowest
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7 water absorption and open porosity results. Thus, the increase of closed porosity in this
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9 sample could be associated to the formation of internal pores. In this sense, it is also
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11 suggested that the heavy metal ions, as hydrated cations forming hydroxides, present in
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13 the GSW have slightly lower susceptibility of hydration than that the cations present in
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15 the clay, combined mainly as silicates (Figure 1). Therefore, the incorporation of GSW
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17 could increase the durability of the fired bricks.
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27 *3.4 Microstructure of the fired samples*

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29 The microstructure of the samples containing clay and GSW fired at 950°C for 1
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31 h have been studied by SEM combined with chemical analysis by EDS. The selected
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33 surfaces of fired clay bricks at 950°C for clay, clay with 1% of GSW, 2%, 3% and 4%
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35 are shown in Figures 3, 4, 5, 6 and 7, respectively. Clay porosity, either small sized and
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37 closed (mesoporous), resulted from intergrain porosity (Figure 3). The composition
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39 analyzed by EDS was typical of clays, with a predominance of Si and O in a grain area
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41 (identified as quartz) and several areas that constituted parts of the original silicates (Si,
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43 Al, Mg, Ca, K and Fe among others), and of Ca as part of the original calcite (Figure 1).
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45 Open pores (macropores) and pores at the surface can also be observed and they
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47 changed slightly by the addition of GSW. A homogeneous distribution after addition of
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49 GSW at 1-4 wt% to the clay ceramic matrix can be deduced from the SEM observations
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51 (Figures 3-7). The apparent predominance of vitreous phase can be associated with the
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53 silicate matrix with the clay as the main component. The addition of increasing amounts
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of GSW (1-4 wt%) caused a decrease in water absorption capacity and open porosity (minimum 21.98 vol % by addition of 4 wt% GSW). A large amount of vitreous phase was generated as the GSW content was increased. This vitreous phase could fill in the pores promoting a decrease in the porosity. The SEM-EDS observations, in fractured surfaces, was in accordance with a greater sintering effect of the samples after addition of 1-5 wt% of GSW as compared to the clay without GSW. At the same time, the addition of GSW produced an increase in the closed porosity. Water absorption and suction data showed the increase in micropores.

The C-3G mixture had a very low adsorbed N_2 , indicating that the brick had a low porosity in the range that can be measured by the N_2 . However, the rapid increase in the amount adsorbed at high relative pressures indicates that the largest number of pores were present in the mesoporous region.

The logarithmic pore diameter versus pore volume plot shows that the pattern of clay C exhibits a maximum pore distribution of 25.5 nm, while the mixture C-3G shows a distribution with a maximum at 39.1 nm. The addition of increasing amount of GSW did not significantly change the mesoporous structure (pore diameter between 2 and 50 nm) of the obtained materials (39.1 nm for addition of 3% and 44.3 nm for 5%).

3.5 Compressive strength results

Compressive strength of ceramic materials is the most relevant engineering property for structural applications of building materials. According to the standard test (EN 772-1: 2011), compressive strength of fired bricks must be at least 10 MPa.

The compressive strength of the fired samples is presented in Figure 10. The compressive strength values increased with the addition of GSW. The values increased almost linearly with the addition of GSW up to 2-3 wt% where a maximum value of ca.

1 86 MPa was reached. This maximum increase was of 31% in comparison with the clay.
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3 Nevertheless, in all cases, compressive strength rates were always higher than the
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5 minimum value required by the UNE-EN 772-1:2011 standard period. It is suggested
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7 that this increment in compressive strength can be due to the decrease in open porosity
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9 (from 28.86 vol % to 22.43 vol %, see Table 4). Subsequently, for percentages above
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11 3% of galvanizing sludge a decrease in the compressive strength took place (Table 10),
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13 probably due to their irregular shape and microscopic imperfections, which allows open
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15 pores to concentrate pressures (Carty and Senapati, 1998; Eliche-Quesada et al., 2014).
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17 However, only a slight decrease was observed by addition of 4 and 5 wt% of GSW,
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19 although the values still were higher than that of the fired clay without addition of
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21 GSW. A plausible explanation for this behaviour could not be found.
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29 *3.6 Leaching test*

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31 The environmental study carried out on the fired samples was performed to
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33 evaluate the degree of metal immobilization that can be achieved by the brick
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35 manufacturing process. Leaching tests (TCLP method, 1992) were applied to ground
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37 fired bricks. The leachate concentrations have been compared with US Environmental
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39 Protection Agency (USEPA) limits (Table 6).
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43 In general, in light of the presented results, the fired clay bricks with GSW (1-5
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45 wt%) met the USEPA regulated TCLP limits. According to these results, these fired
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47 clay bricks can be classified as acceptable at landfills for inert and non-hazardous waste.
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49 Therefore, the leaching test indicated a degree of immobilization of the heavy metals
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51 suggesting that the incorporation of GSW into ceramic products is an efficient
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53 inertization method. Hence, no environmental problems due to heavy metals disposal
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55 can be expected by the use of the GSW-clay fired bricks. Possibly these results can be
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1 further improved if higher temperatures than 950°C are used, being a matter for future
2 research concerning vitrified ceramics.
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7 **4. Conclusions**

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11 This work showed that GSW from electroplating industry can be used in the
12 manufacturing process of clay bricks. These clay bricks were manufactured after firing
13 a mixture of clays typically used in the ceramic industry and GSW with a dosage
14 ranging from 1 to 5 wt%. The incorporation of low dosages of GSW in the composition
15 of clay ceramic bricks could be an opportunity to improve the engineering properties of
16 the traditional bricks. In particular, the decrease in the suction and water absorption and
17 the increase in the compressive strength can promote the formation of higher quality
18 products.
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31 The mineralogical analysis and the chemical composition of the GSW revealed
32 that this waste sample contained quartz, calcite, organic matter and heavy metals which
33 make it potentially suitable for structural ceramics. Therefore, the use of GSW in
34 different dosages could replace the use of non-renewable natural resources, leading to a
35 more sustainable industrial process.
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44 The addition of GSW (1-5 wt%) to the clay promoted a significant modification
45 in the properties of the final fired bricks. In general, the fired bricks prepared using
46 GSW, in comparison with the original fired bricks prepared without GSW, showed
47 similar linear shrinkage, but lower bulk density, lower water absorption capacity and
48 water suction. The open porosity was also lowered from ca. 29 vol % to ca. 22 vol % by
49 addition of GSW (1-5 wt%) but, in contrast, the GSW-clay composites were
50 mechanically more resistant than those prepared from fired clay.
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1 The microstructural study revealed a homogeneous distribution of GSW (1-4
2 wt%) in the fired clay ceramic matrix including the formation of a vitreous phase. This
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4 phase filled in the pores of the fired clay, and as phase GSW content increased, a
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6 decrease in porosity took place (minimum open porosity is 21.98 vol % by addition of 4
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8 wt% of GSW).
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11 Regarding the environmental study, no serious problems are expected for the use
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13 of the GSW according to USEPA regulated TCLP limits, since a good inertization of
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15 GSW was reached in this study. These results also point to an attractive way of
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17 valorizing GSW avoiding the negative impact associated with its disposal in landfills.
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26 **List of captions**

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31 Figure 1. XRD patterns of (a) clay and (b) galvanic sludge waste used as raw materials
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33 in the preparation of bricks.
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36 Figure 2. Bulk density of the fired bricks a function of GSW addition (1-5 wt%) to the
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38 clay.
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41 Figure 3. Porosity (arrow) and SEM micrograph with EDS analysis at different points of
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43 fired clay brick (950°C for 1 h) without GSW: 1) quartz grain, 2 and 3) correspond to
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45 different zones of the matrix with the presence of Si, Ca, Al and Fe, the presence of K in
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47 point 3 from clay, a larger amount of Ca and the presence of S from GSW is appreciated
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49 in point 2.
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52 Figure 4. SEM micrograph with EDS analysis at different points of fired clay brick
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54 (950°C for 1 h) with 1 wt% of GSW: 1) quartz grain, 2) the EDS analysis represent the
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56 clayey matrix.
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Figure 5. SEM micrograph with EDS analysis at different points of fired clay brick (950°C for 1 h) with 2 wt% of GSW: 1 and 2) Both represent two points with similar chemical composition.

Figure 6. SEM micrograph with EDS analysis at different points of fired clay brick (950°C for 1 h) with 3 wt% of GSW: the EDS acquisition in zones labelled 1 and zones labelled 2 indicate chemical homogeneity.

Figure 7. SEM micrograph with EDS analysis at different points of fired clay brick (950°C for 1 h) with 4 wt% of GSW: 1) quartz grain, 2) represent the clayey matrix.

Figure 8. Adsorption-desorption isotherms of N₂ at 77 K of fired clay bricks (C and C-3GS).

Figure 9. Pore size distribution determined from adsorption data using the BJH method for samples C and C-3G.

Figure 10. Effect of GSW addition (1-5 wt%) to the clay on compressive strength of fired clay bricks (950°C for 1 h).

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- GSW from electroplating industry can be used in the manufacture of clay bricks.
- Addition of GSW (1-5 wt %) to the clay changed some properties of final fired bricks.
- Composites with GSW were mechanically more resistant as compared with the fired clay.
- The results establish a way to valorize GSW avoiding the impact of landfills.

Table 1. Chemical composition of GSW and industrial clay obtained by XRF.

Element Oxides	Content (mass %)	
	Galvanic sludge	Clay
SiO ₂	3.01	55.82
Al ₂ O ₃	0.11	12.13
Fe ₂ O ₃	3.35	4.83
MnO	0.09	0.03
MgO	3.77	1.49
CaO	7.77	9.21
Na ₂ O	2.20	0.49
K ₂ O	0.04	2.78
TiO ₂	-	0.83
P ₂ O ₅	0.43	0.12
Cl	0.89	-
Co ₃ O ₄	0.14	-
Cr ₂ O ₃	12.73	-
CuO	1.52	-
NiO	1.58	-
SO ₃	1.78	-
SrO	0.16	-
ZnO	23.79	-
Loss on ignition at 950 °C	36.62	10.55
Total	99.98	98.28

Foot note: The slight difference with the loss of ignition results for clay reported in Table 3 can be associated to processing conditions of the green solid bricks.

Table 2. Elemental chemical analysis (CHNS) of raw materials.

Element	Content (mass %)	
	Galvanic sludge	Clay
C	8.758	2.406
H	2.253	0.442
N	0.111	0.051
S	0.133	0.057

Table 3[Click here to download Table: Table 3.docx](#)**Table 3.** Technological properties of fired bricks made from clay and GSW mixtures.

Sample	Waste content (mass %)	Linear Shrinkage (%)	Mass loss on ignition (%)	Bulk density (g·cm⁻³)
C	0	-0.265 ± 0.102	13.84 ± 0.21	1.760 ± 0.051
C-1GS	1	-0.455 ± 0.154	10.32 ± 0.38	1.455 ± 0.040
C-2GS	2	-0.413 ± 0.101	11.18 ± 0.46	1.456 ± 0.039
C-3GS	3	-0.444 ± 0.087	11.38 ± 0.27	1.456 ± 0.037
C-4GS	4	-0.455 ± 0.098	11.65 ± 0.30	1.454 ± 0.046
C-5GS	5	-0.458 ± 0.055	13.87 ± 0.33	1.450 ± 0.048

Table 4. Water absorption, open porosity and water suction of bricks made from clay and GSW.

Sample	Waste content (mass %)	Water absorption (%)	Open Porosity (vol %)	Suction water (kg/m²·min)
C	0	16.400 ± 1.001	28.86 ± 1.06	2.91 ± 0.23
C-1GS	1	16.097 ± 0.807	23.42 ± 0.84	2.24 ± 0.29
C-2GS	2	16.867 ± 1.295	24.56 ± 1.29	2.03 ± 0.28
C-3GS	3	16.679 ± 1.020	24.28 ± 1.01	1.82 ± 0.29
C-4GS	4	15.119 ± 1.003	21.98 ± 1.00	1.76 ± 0.27
C-5GS	5	15.467 ± 1.354	22.43 ± 1.37	2.07 ± 0.38

Table 5[Click here to download Table: Table 5.docx](#)**Table 5.** BET Surface, micropore area, BJH cumulative volume of pores and BJH average pore diameter for C, C-3GS and C-5GS samples.

Sample	Waste content (mass %)	BET Surface Area (m ² /g)	t-Plot micropore area (cm ³ /g)	BJH cumulative volume of pores (between 1,7 and 300 nm) (cm ³ /g)	BJH average pore diameter (nm)
C	0	0.7236	0.3347	0.001369	14.0195
C-3GS	3	0.4173	0.8413	0.001146	39.1898
C-5GS	5	0.3833	0.8617	0.001079	44.3341

Table 6[Click here to download Table: Table 6.docx](#)

Table 6. TCLP leaching test results (ppb) in the fired samples with different GSW content and the maximum concentration (EPA regulated TCLP limits) of contaminants for toxicity characteristics.

Component	Concentration (ppb)					
	Galvanic Sludge content					USEPA regulated TCLP limits (ppb)
	1 wt %	2 wt %	3 wt %	4 wt %	5 wt %	-
Al	11.1	10.7	7.32	63.6	58.2	N/A
Ca	255024	204174	213723	403823	432145	N/A
Fe	207.5	83.62	175.8	548.5	457.8	N/A
Co	32.5	34.7	67.4	162.2	165.4	N/A
Ni	47.0	74.0	117.0	1726.3	1845.1	250000
Cu	9.4	10.5	16.0	90.7	95.4	N/A
Zn	478	1151	2239	115100	120567	250000
Cr	5450	9333	8906	8552	8756	5000

N/A Not applicable

Figure 1

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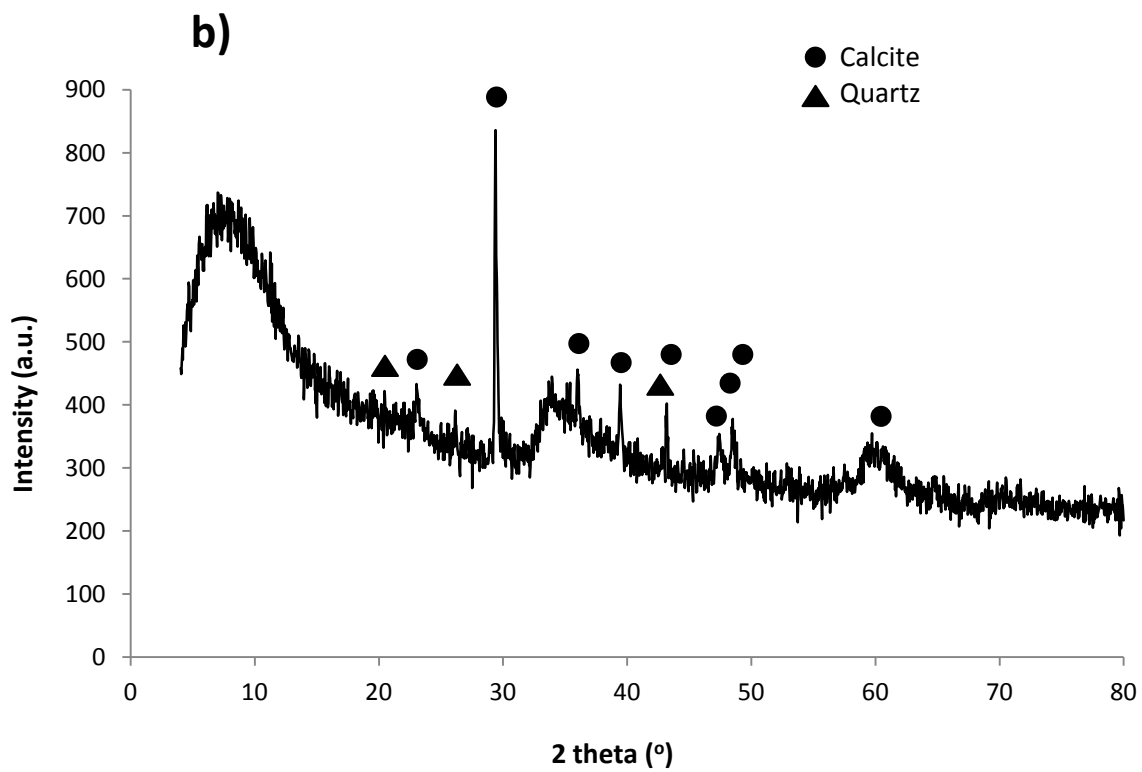
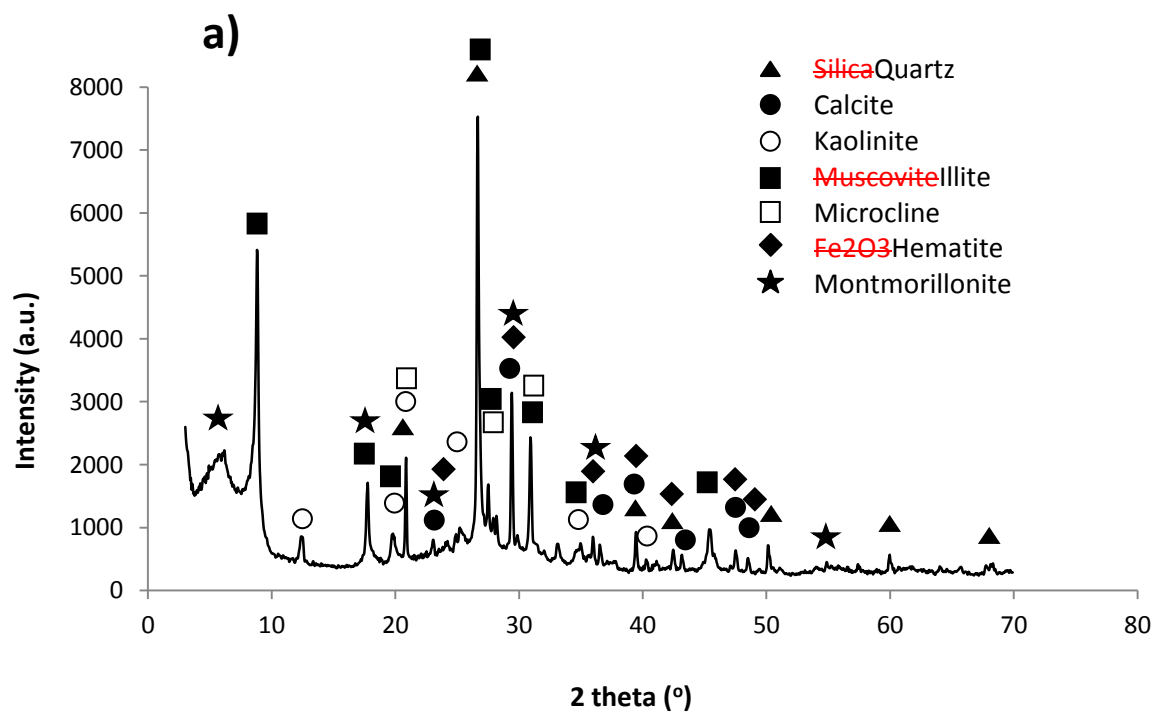


Figure 2
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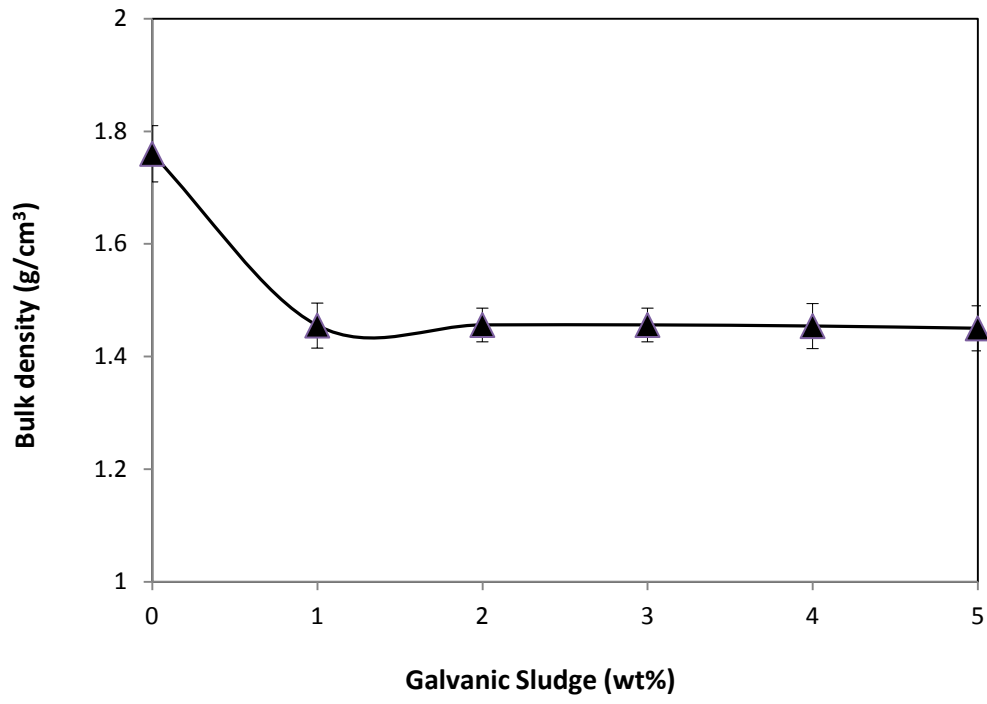


Figure 3
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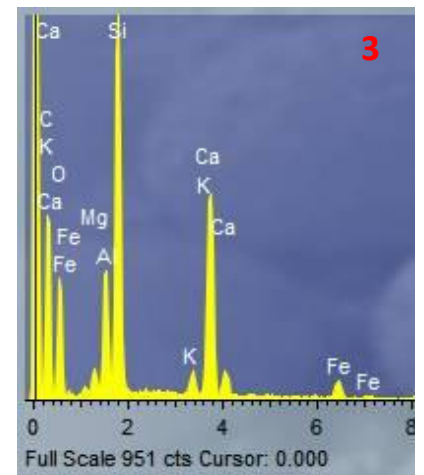
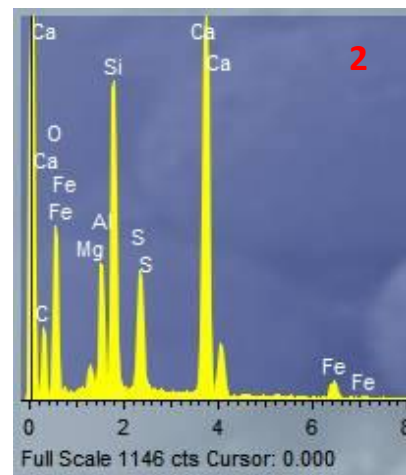
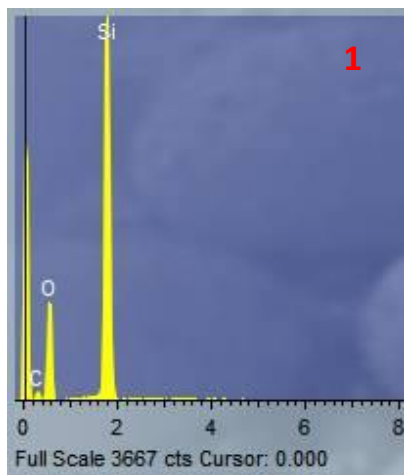
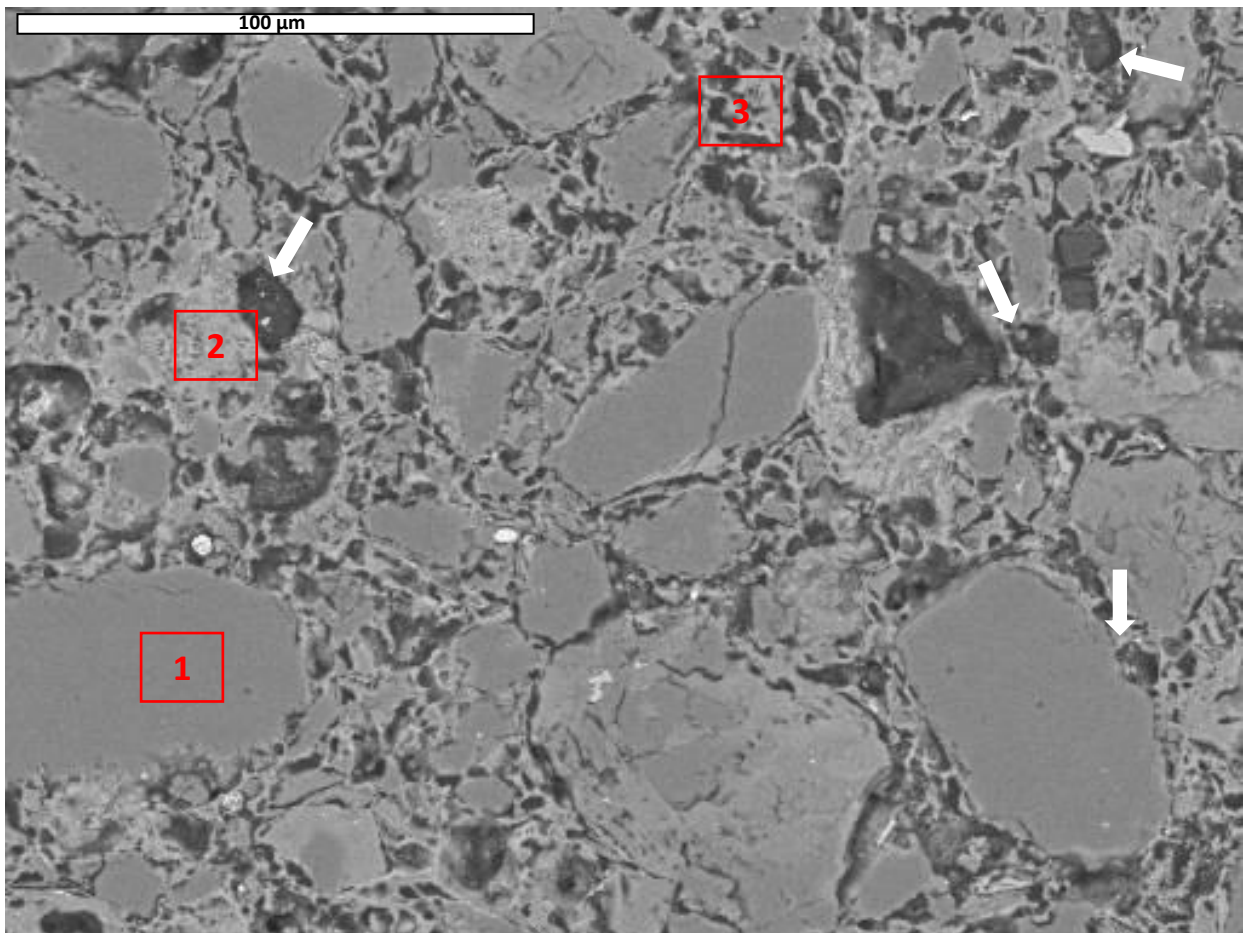


Figure 4
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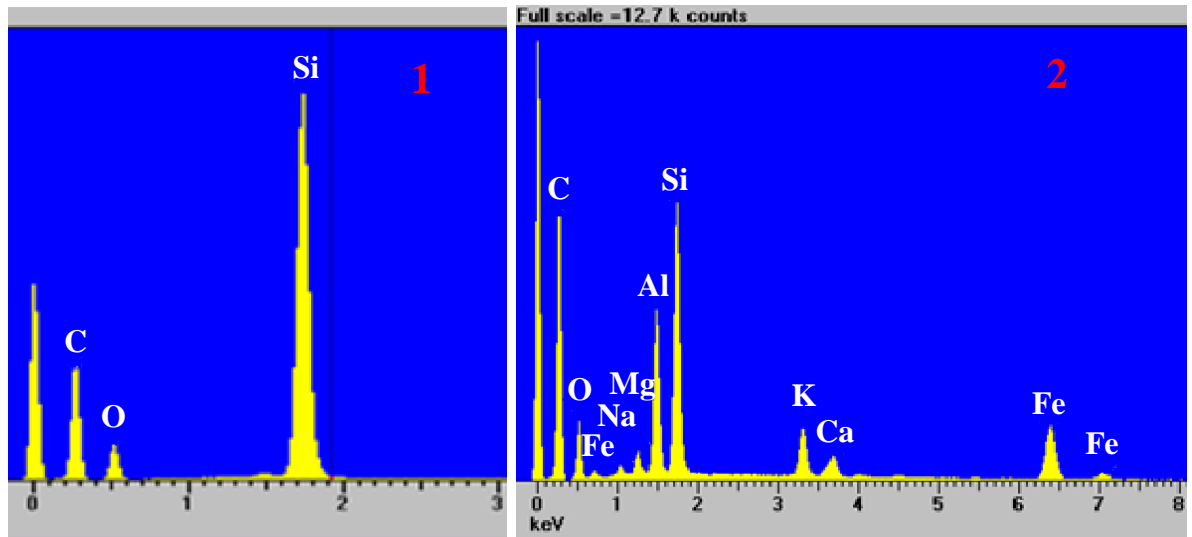
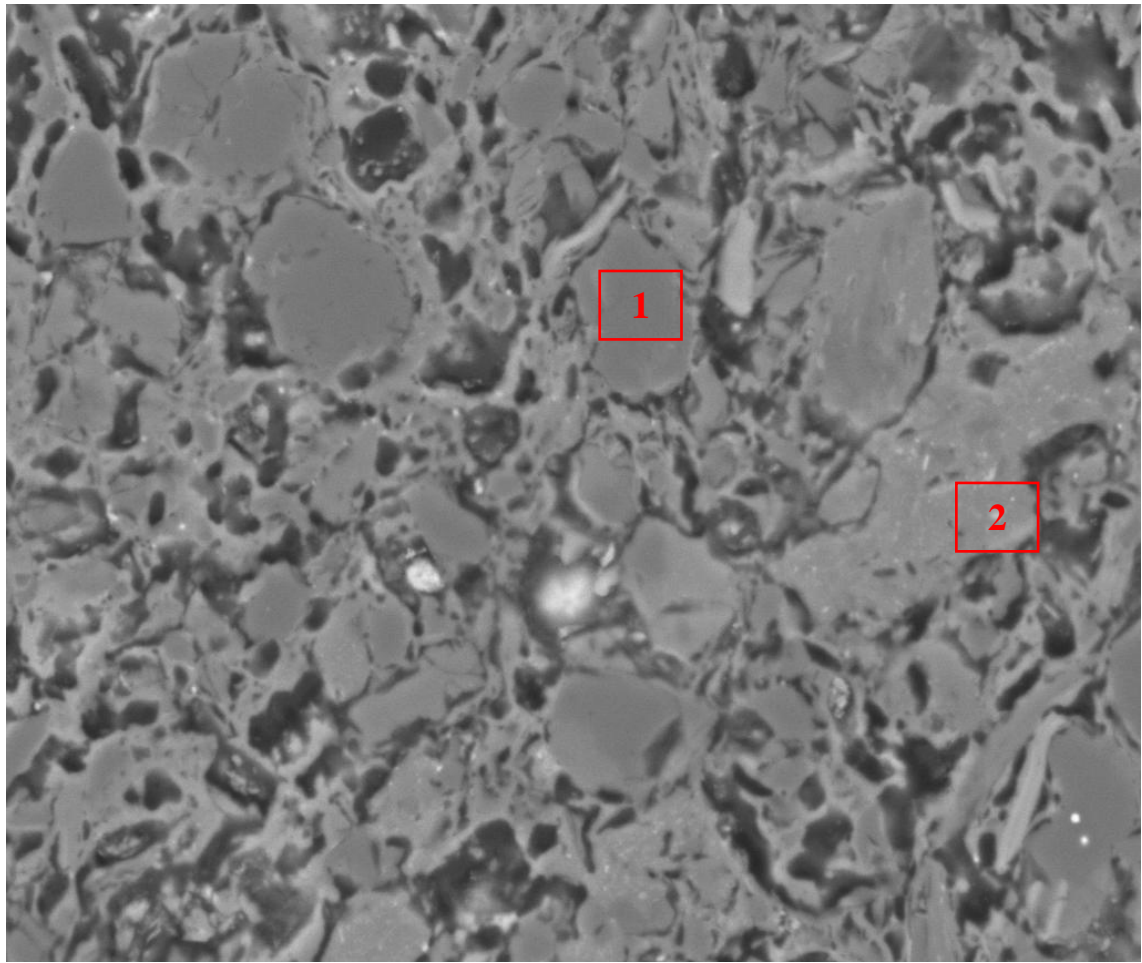


Figure 5
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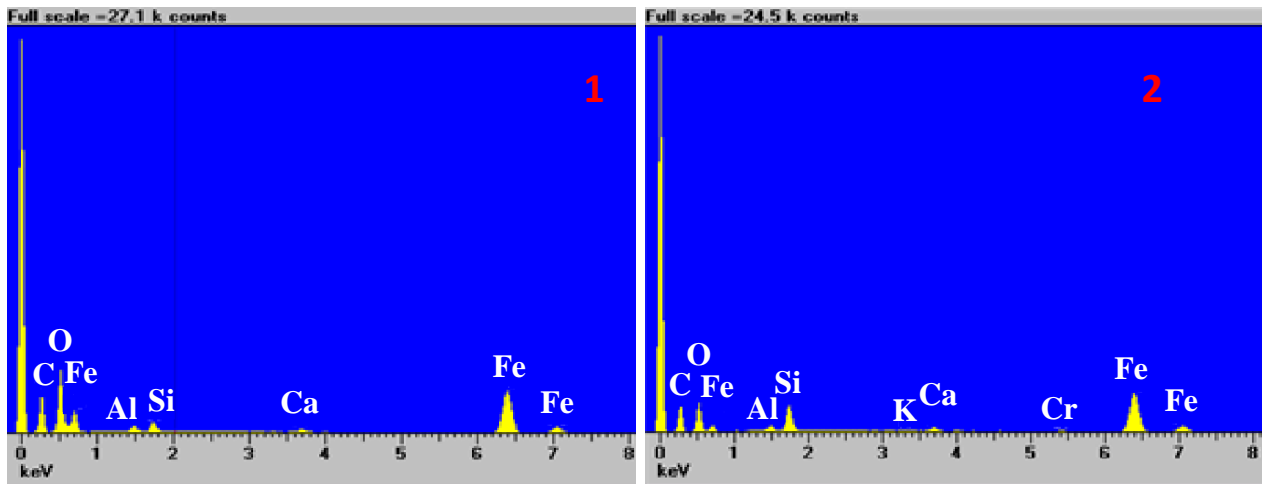
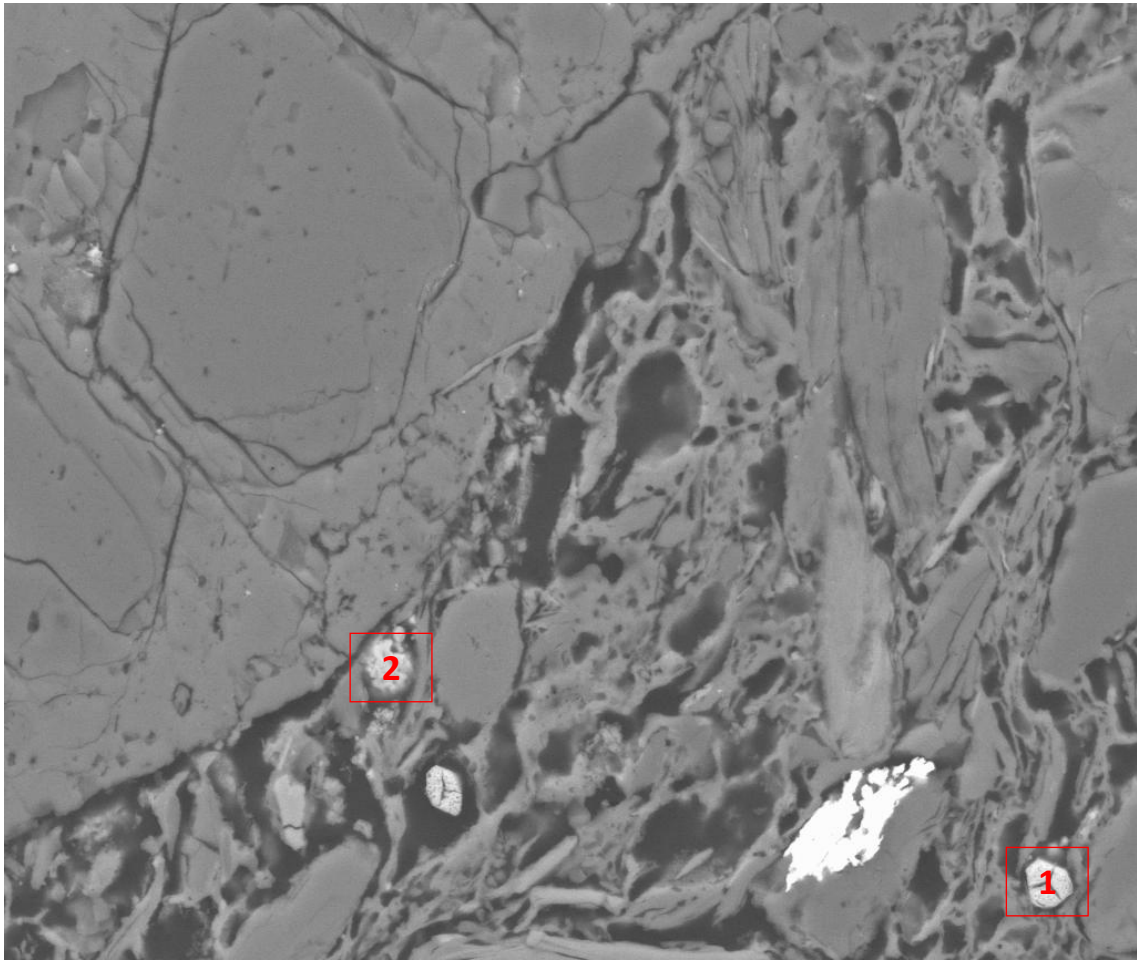


Figure 6
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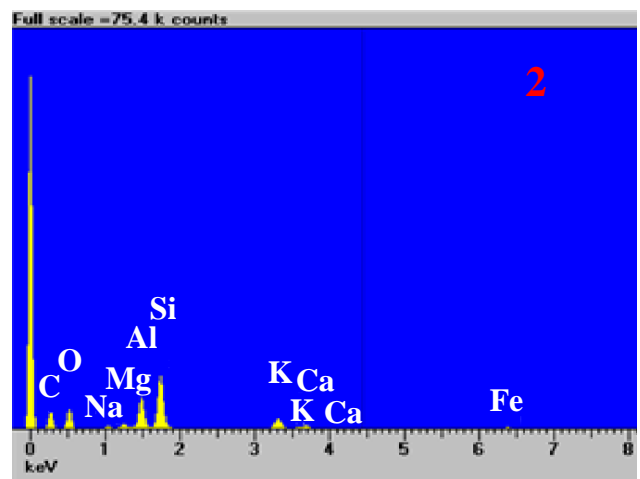
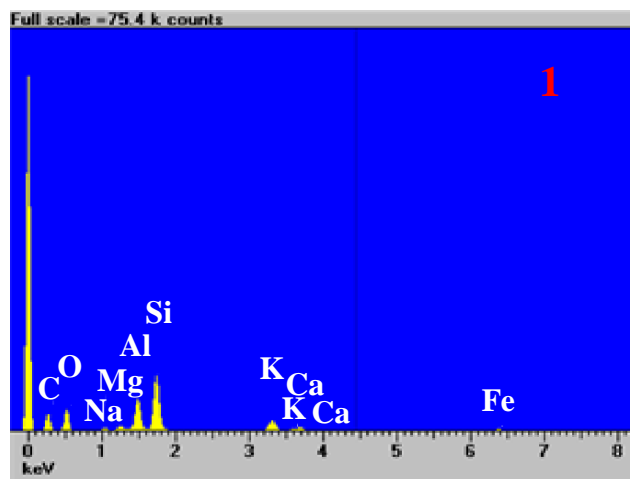
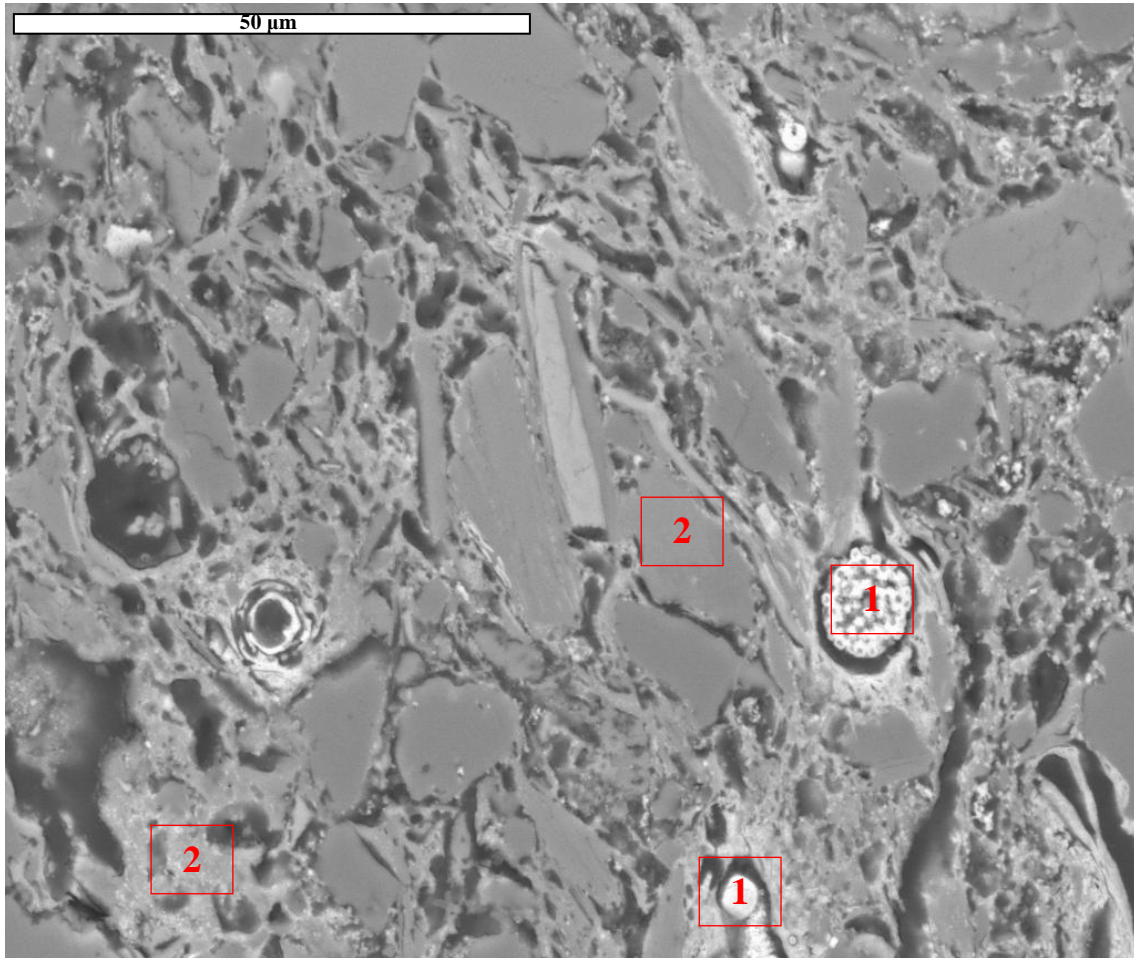


Figure 7
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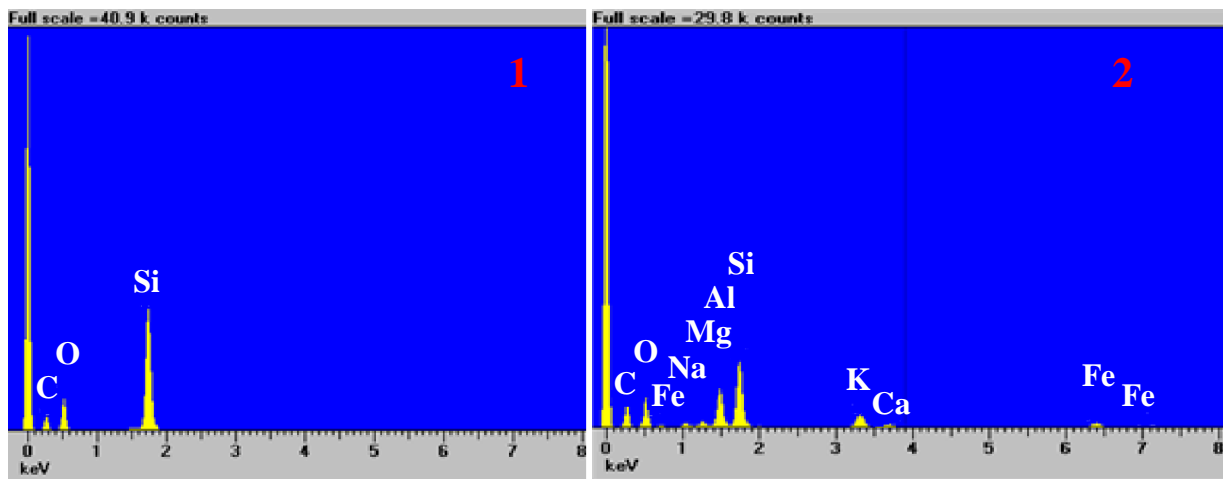
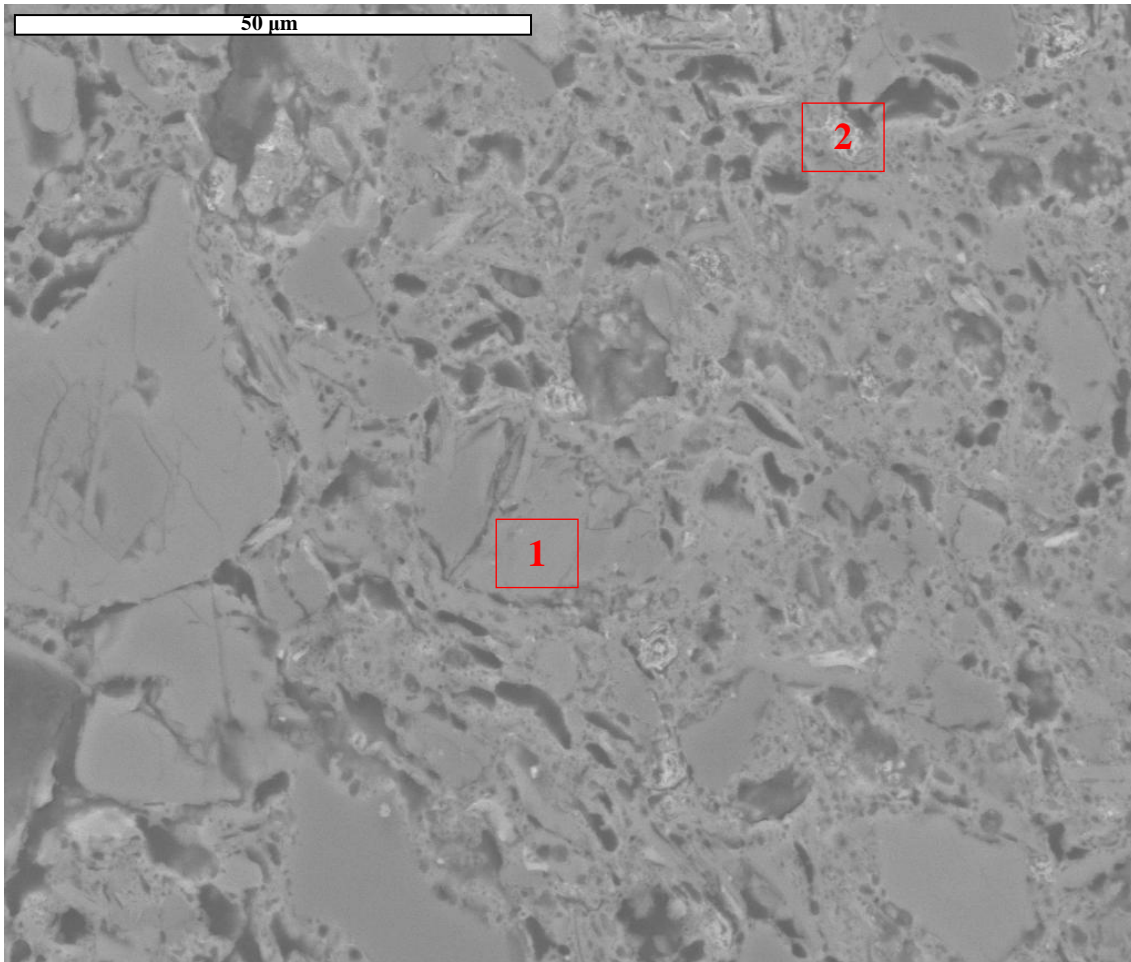


Figure 8

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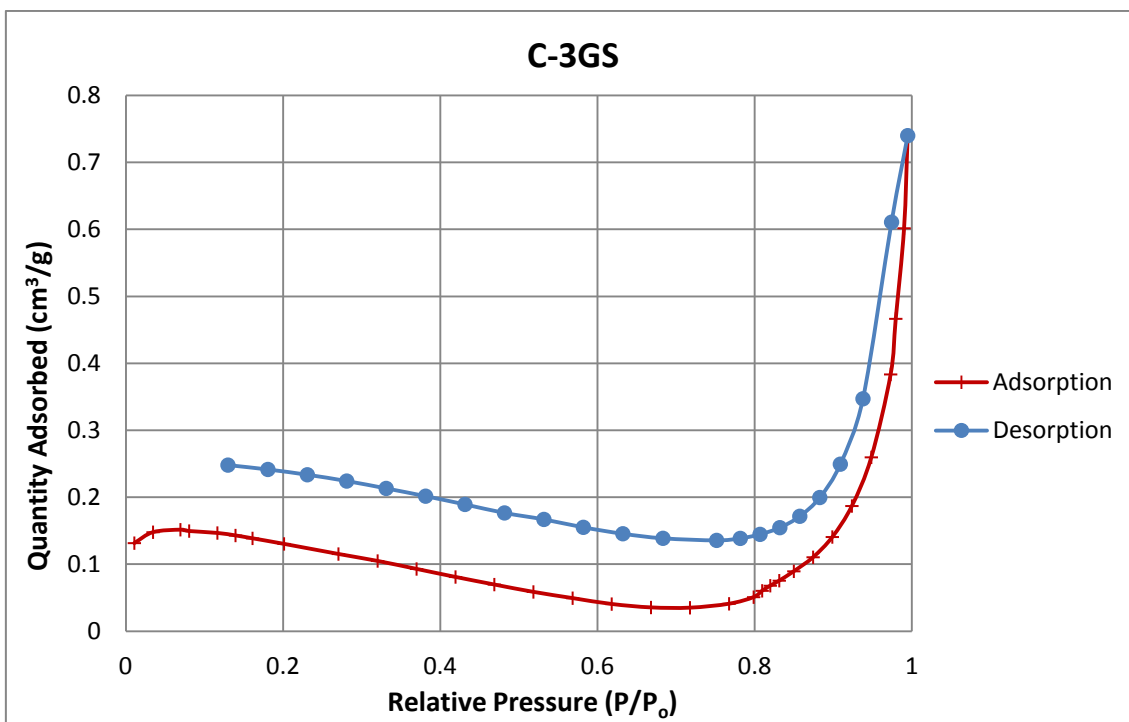
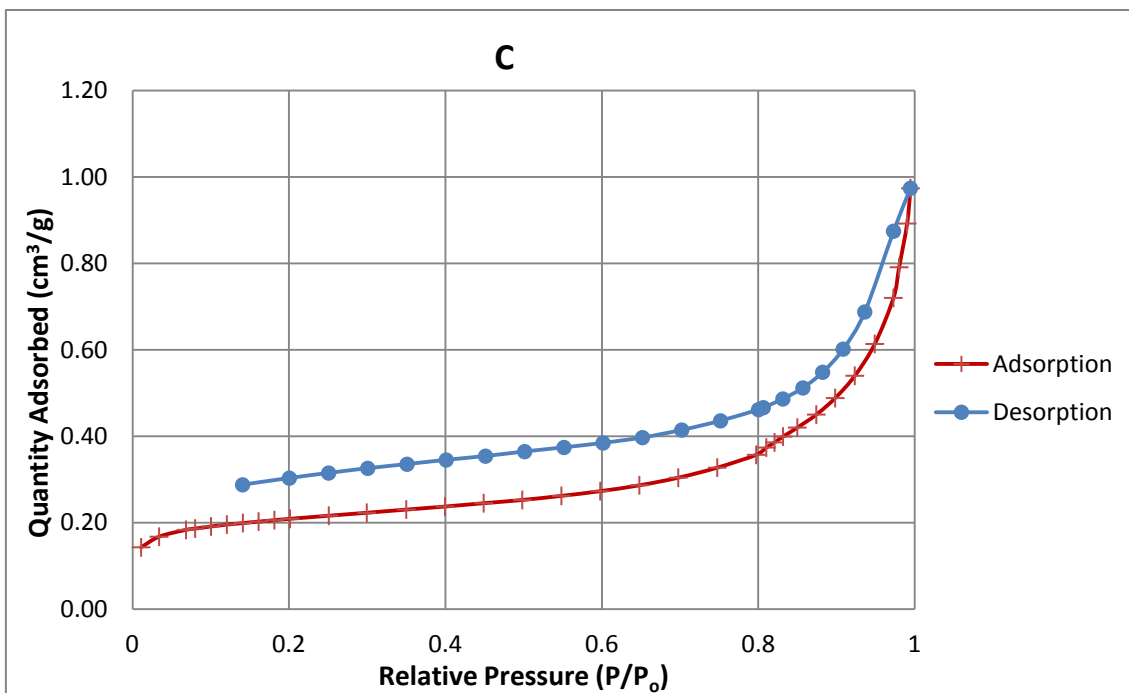


Figure 9
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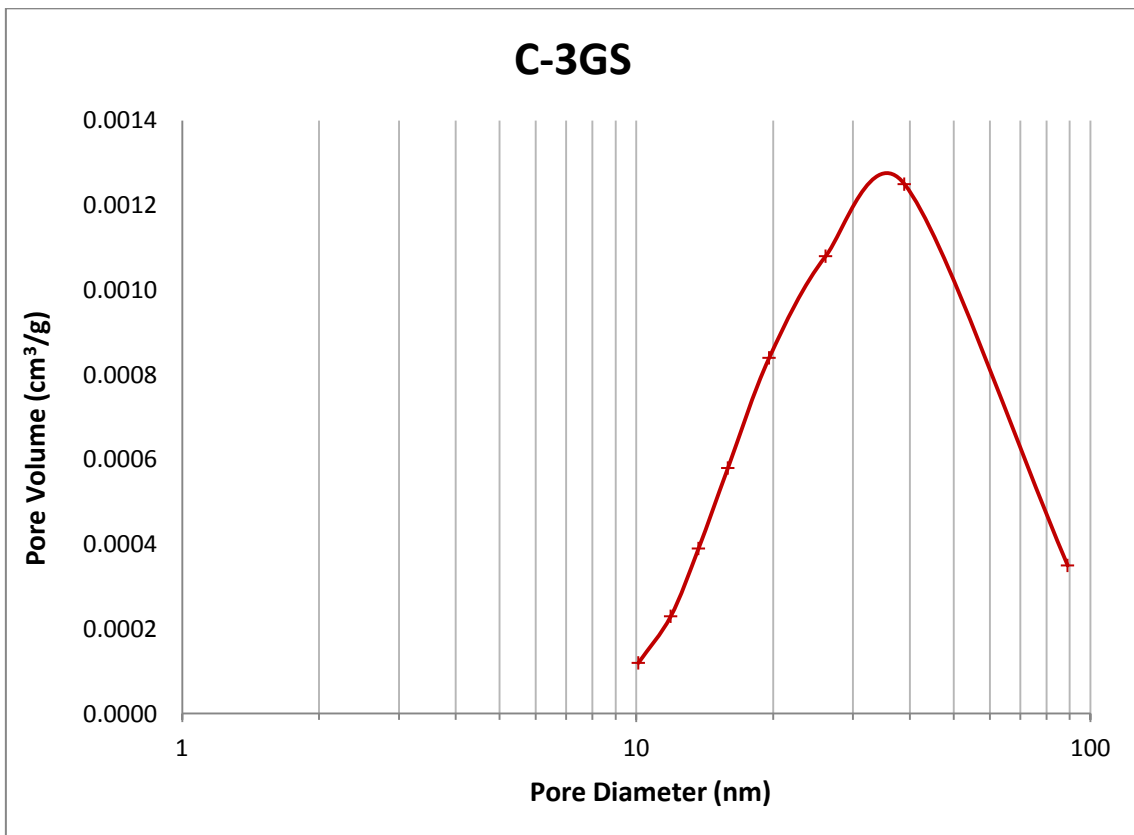
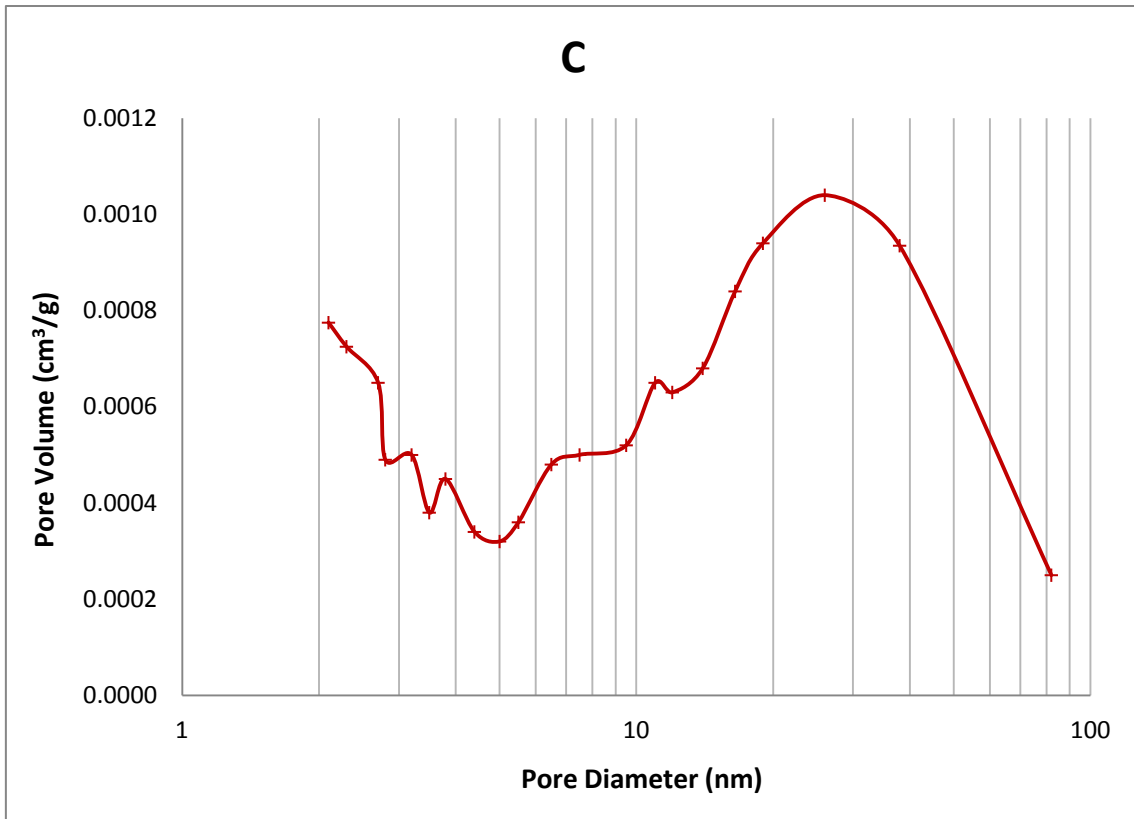


Figure 10
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