

Physico-chemical characterisation of bricks all through the manufacture process in relation to efflorescence salts

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Abstract

Due to the high competitiveness of the ceramic product market, quality and technical requirement are increasing. The efflorescence problem is a phenomenon that affects the aesthetic quality of brick facades and which is not easily dealt with. The aims of this work are to study the key physical and chemical parameters for this phenomenon in all activities of the brick manufacturing process and to evaluate the influence of the additives employed on the appearance of the efflorescence phenomenon. Porosity and specific surface, mineralogical analysis, total chemical content and soluble salts were determined on green, dried and fired brick, both when no additives were added to the manufacturing process and also when ammonium lignosulphonate and barium carbonate were used as additives. The main mineralogical phases and water soluble salts in the efflorescence phenomenon have been obtained. In some cases, relationships between soluble salts in the end product and soluble salts in the efflorescence have been established. From the obtained results, the use of a mixture of ammonium lignosulphonate and barium carbonate together with the control of the firing process variable is recommended in order to prevent this phenomenon.

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1. Introduction

Coarse ceramic industry products, brick and roof tiles, are produced in large quantities and are used as materials in numerous branches of building and contracting. For the most part, brick and tiles are not designated according to the shaping technique used, but according to the intended application: building bricks (e.g. clay blocks, facing bricks, clinker bricks and lightweight bricks); roof tiles (e.g. extruded tiles, pressed tiles); paving bricks and chimney bricks. In 2003, the European clay brick and roof tile industry had total sales of around EUR 6800 million and a work force of around 50,000.¹

Characteristic properties of ceramic products include high strength, wear resistance, long service life, chemical inertness and non-toxicity, resistance to heat and fire, (usually) electrical resistance and sometimes also a specific porosity. However one of the most frequent anomalies to be detected in the façade of bricks is the appearance of the efflorescence phenomenon,

which consists in crystallised salts accumulating on the surface of the brick. Efflorescence is not only an aesthetic problem but can also cause serious microstructural damage²; it is a pathology that affects the quality of the product. Although damage from salts has been intensively investigated for several decades,^{3–5} the mechanisms and factors that control the formation of salt crystals in porous building materials and the development of damage by crystal growth are poorly understood. Efflorescence appearance is also influenced by external agents such as climatic and land conditions.⁶ Although numerous studies have been carried out to elucidate the causes of efflorescence, it is such a complex phenomenon that is still a permanent problem. Specifically, there have been many attempts to make the salts inside the brick non soluble, so that no migration to the surface can occur. Traditionally, barium compounds, like barium carbonate^{7,8} are used for this purpose, but the dosage of this additive must be optimum otherwise its use can have a self-defeating effect. Other kinds of additives have been investigated, such as alkaline and alkaline-earth chlorides, ammonium chloride and tricalcium aluminate,⁹ the most interesting ones, from an economical point of view, being the low cost additives, as long as they do not cause corrosion and environmental problems. On the other hand, the use of

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lignosulphonate^{10–14} as an additive due to its dispersant properties in building materials has also been studied and can be considered as usual additive in brick manufacturing.

In order to successfully prevent efflorescence, the chemical clay composition, the use of additives and the manufacturing process must all start to be controlled and the transport and storage operations must also be taken into account. Furthermore, the soluble salts content in bricks has been recently regulated by the European EN 771-1.¹⁵ Some authors have evaluated the chemical composition of the clay and the soluble salts content,^{9,16,17} the firing conditions such as temperature and kiln atmosphere¹⁸ and, more recently, a greater effort to establish a relation between the efflorescence and the microstructure of the material and pore morphology has been made.^{19–21} However, these parameters all through the manufacturing process have not been studied yet. In this study a physico-chemical characterisation of the raw material, the intermediate products, the end products and the efflorescence salts when two different kind of additives, barium carbonate and ammonium lignosulphonate and a mixture of both have been used, is presented. The aim of this research is to study the influence of the physical and chemical parameters, porosity, specific surface and mineralogical analysis, chemical content and soluble salts, in relation to the efflorescence phenomenon throughout the manufacturing process.

2. Materials and methods

2.1. Materials

Bricks analysed in this work have been manufactured on industrial scale at a plant located in Cantabria (Northern Spain). Fig. 1 shows a flowchart of the brick manufacturing process where material sampling strategy is detailed. The raw material, clay (R), the intermediate manufacturing products such as green product (GP) and dried product (DP) and the end-product (EP) have been analysed. Samples of efflorescence salts (EF)

have been collected from the brick surface after efflorescence phenomenon appearance. The bricks have been manufactured with and without the use of two traditional additives, barium carbonate and ammonium lignosulphonate as additives.

2.2. Methods

Mineralogical analysis was evaluated by X-ray diffraction (DRX) using a Siemens D-500 diffractometer of Bragg–Brentano geometry. Specific surface and pore volume were analysed as physical parameters through BET surface using Micromeritics ASAP 2000 and Micromeritics Poresizer 9310 equipment respectively. Total chemical content was determined using Atomic Emission Spectrometer with Mass Spectrometry by an external laboratory (Activation Laboratories in Canada). Soluble salts were analysed after extraction following the standard method UNE-EN 772-5²²; in the extracts, chlorides, sulphates and carbonates were measured by DX-120 Ion Chromatograph and Warder volumetric method. Calcium, magnesium and vanadium were analysed by Atomic Emission Spectrometer with Inductively Coupled Plasma Perkin Elmer 400 and sodium and potassium by Atomic Absorption Spectrometer Perkin Elmer 1100B. All the determinations were carried out in triplicate.

3. Results and discussion

3.1. Mineralogical analysis

High reproducibility in the mineralogical analyses is obtained from the analysed samples, which have been performed in triplicate. The main mineralogy species identified in the samples of raw material, green, dried and end-product, together with the efflorescences in all studied samples are collected in Table 1 and Fig. 2. The minerals, Illite and Kaolinite are the main components in clay used in manufacturing of bricks, and, as non-clayey

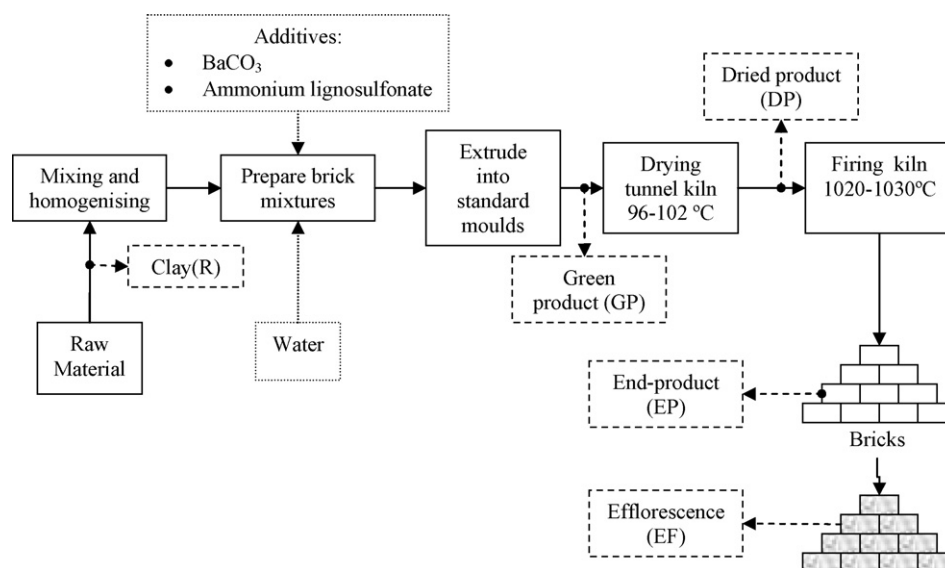


Fig. 1. Flowchart of the brick manufacturing process.

Table 1
Results of mineralogical analysis.

	Raw Materials		Products			Efflorescence
	Clay R	GP	DP	EP	EF	
Quartz SiO_2						
Illite $(\text{K},\text{H}_3\text{O})\text{Al}_2\text{Si}_3\text{AlO}_{10}$						
Kaolinite $\text{Al}_2\text{Si}_2\text{O}_5(\text{OH})_4$						
Albite $\text{NaAlSi}_3\text{O}_8$						
Microcline AlSi_3O_8						
Mullite $\text{Al}_6\text{Si}_2\text{O}_{13}$						
Spinel $\text{Mg}_2\text{Al}_2\text{O}_4$						
Bassanite $\text{CaSO}_4 \cdot 0.5\text{H}_2\text{O}$						
Calcite CaCO_3						
Hematite Fe_2O_3						

mineral is Quartz and, as feldspars, Albite and Microcline, and finally Hematites. According to the mineralogical composition, these samples correspond to Kaolinite clays, which are typical of a wet climate. The mineralogical composition of clay, green and dried product is the same, meaning that the mixing, extrusion and drying treatments in the manufacturing process do not alter the mineralogical composition.

However, as it can be seen in Fig. 2(b), during the firing stage of clay, physical and chemical transformations of their constituents are produced, giving as a result new mineralogy phases identified as Mullite and Spinel which replace Illite and Kaolinite. Besides the crystalline phases, the amorphous phase usually represents approximately 50% in the fired matrix for this type of Kaolinite clays.²³ The diffractogram of the efflorescence has been shown in Fig. 2(c). On the one hand, the presence of Quartz, Microcline, Mullite, Spinel and Hematite in the efflorescence is justified with the non-selective sampling of the efflorescence. On the other hand, efflorescence samples exhibit the presence of Bassanite and Calcite, which are not present in any other sample, so the efflorescence phenomenon could be attributed to the presence of $\text{CaSO}_4 \cdot 0.5\text{H}_2\text{O}$ and CaCO_3 .

3.2. Physical characterisation of the product all through the manufacturing process

Physical characterisation of the product all through the manufacturing process is determined by measuring pore volume and specific surface parameters. Macropores (>50 nm) and mesopores (2–50 nm) are represented in Fig. 3 and specific surface is shown in Fig. 4 for each studied additive. In Fig. 3 it can be observed that macropore volume increases slightly through the manufacturing process, from 0.077 ± 0.013 to $0.098 \pm 0.005 \text{ cm}^3/\text{g}$ and no additive influence on this physical parameter is detected.

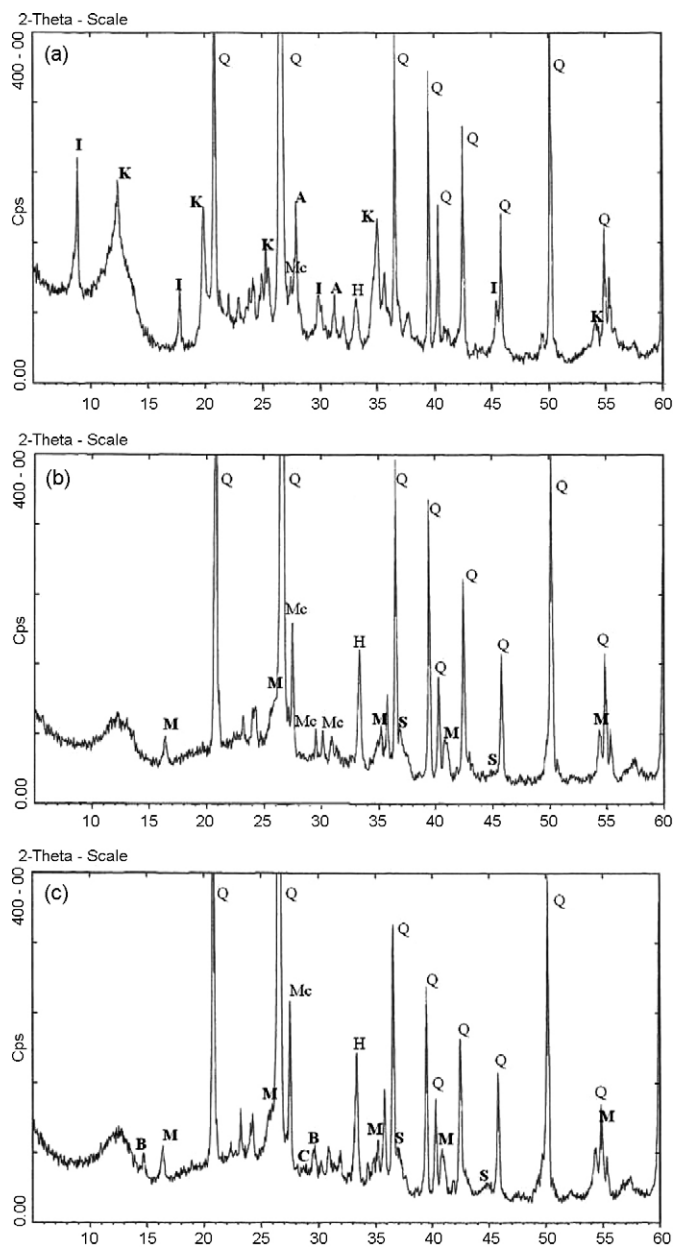


Fig. 2. Diffractograms: (a) clay sample, R; (b) end-product, EP; (c) efflorescence sample, EF. Q: Quartz, I: Illite, K: Kaolinite, A: Albite, Mc: Microcline, M: Mullite, S: Spinel, B: Bassanite, C: Calcite, H: Hematite.

The mesopore porosity can also be observed in Fig. 3. The volume of mesopore decreases through the manufacturing process from 1.3 to $2.8 \text{ cm}^3/\text{g}$ in the green product to a constant value $0.4 \text{ cm}^3/\text{g}$, in the end-product. It can also be pointed out that in this case, although mesopore volume varies in the green and dried products according to the additives used, the end-product presents very similar values of these parameters in all the cases. This behaviour is the same as that observed in the influence of additives on macropore volume.

Regarding the specific surface (Fig. 4), this parameter has a similar behaviour to the mesopore porosity, it decreases during the firing process from a range of values of 16 – $18 \text{ m}^2/\text{g}$ in green product to surface values ranging from 0.3 to $0.5 \text{ m}^2/\text{g}$ in the end-

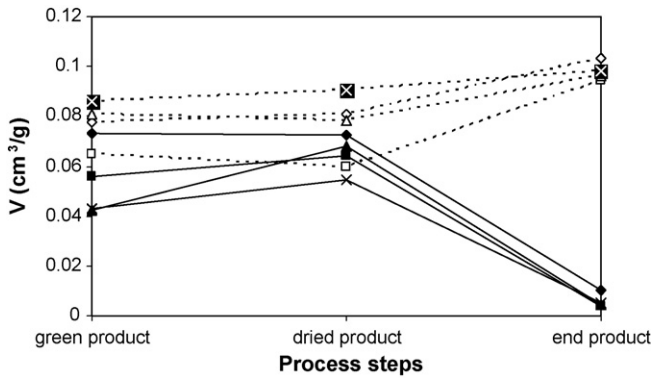


Fig. 3. Macropore and mesopore porosity: dot lines and empty symbols represent macropore volume data; solid lines and filled symbols represent mesopore volume data; (◆) no additives, (■) barium carbonate + ammonium lignosulphonate, (▲) ammonium lignosulphonate, (×) barium carbonate.

products. The firing process causes shrinkage of the material in the end product that explains the reduction of the specific surface. The degree of shrinkage in the bricks can be assessed for quality control.

The influence of temperature over porous size distribution has been studied by several authors.^{20,24,25} They have proposed that the total porosity increases between 400 and 800 °C. Between 400 and 600 °C, the weak increase is due to the loss of structural water of the clay minerals and is accompanied by a volumetric shrinkage of the body and a size-reducing process of its finest pores. However, starting from 600 °C, the increase in porosity is more significant and attains its maximum when the decarbonation of CaCO_3 is completed at approximately 800 °C. This is accompanied by a significant dilation of the pores. At higher temperature, above 800 °C, the variations in the average pore size diameter is mainly due to two factors that are produced simultaneously but with opposite effects. As a consequence of the micro-structural heterogeneity of raw brick bodies, with the increase in the firing temperature, a progressive elimination of the smaller pores has been found, which bring about differential contractions among the different micro-regions of brick body and as a consequence the average pore size diameter increases.

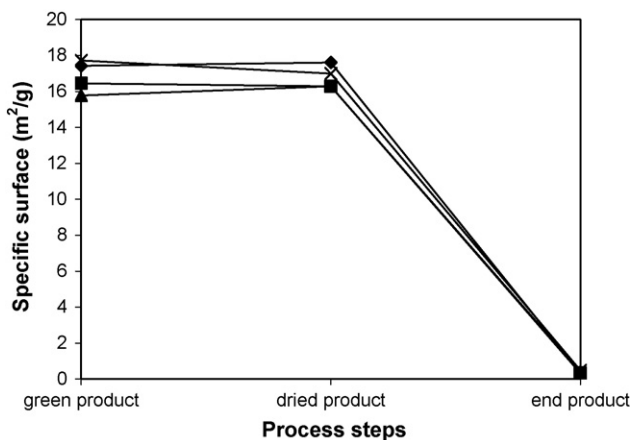


Fig. 4. Specific surface: (◆) no additives, (■) barium carbonate + ammonium lignosulphonate, (▲) ammonium lignosulphonate, (×) barium carbonate.

Table 2
Chemical composition of clay.

Compound	wt. %	Element	wt. %
SiO_2	63.58	Si	30.76
Al_2O_3	17.13	Al	9.02
Fe_2O_3	6.06	Fe	3.58
MnO	0.072	K	2.68
MgO	0.97	Na	0.925
CaO	0.57	Mg	0.538
Na_2O	0.63	Ca	0.206
K_2O	3.08	Ti	0.410
TiO_2	0.85	S	0.010
P_2O_5	0.12		
LOI	6.03		
Total	99.11		

On the other hand, as the liquid phase content increases and its viscosity decreases, besides producing the reduction in the porosity of the bodies, the pre-existent capillary system is partially blocked, which reduces the interconnected porosity even more. As a result of these two conflicting effects the sintering noticeably reduces the total porosity while the end-product exhibits a higher macropore volume and smaller mesopore volume.^{20,24} This similar behaviour can also be observed in the data collected in Figs. 3 and 4 in this study.

3.3. Chemical characterisation of the product all through the manufacturing process

Chemical characterisation has been carried out all through the manufacturing process. The total metal content has been analysed. Table 2 collects the concentration of major oxides and elements of clay raw material, and Tables 3 and 4 collect

Table 3
Elements concentrations (% dw) higher than 1% dw in the studied samples.

	No additive	Both additives	Ammonium lignosulphonate	Barium carbonate
Si				
GP	30.85	30.70	30.88	30.66
DP	31.10	30.91	30.97	30.99
EP	33.72	33.22	33.25	33.20
EF	31.90	32.01	32.14	31.82
Al				
GP	9.17	9.03	9.02	9.03
DP	8.90	8.85	8.93	9.04
EP	8.34	8.28	8.53	8.60
EF	8.79	8.68	8.80	8.83
Fe				
GP	3.64	3.55	3.56	3.53
DP	3.42	3.40	3.43	3.47
EP	3.60	3.51	3.63	3.57
EF	3.72	3.67	3.84	3.82
K				
GP	2.73	2.67	2.66	2.64
DP	2.57	2.58	2.66	2.66
EP	2.48	2.46	2.51	2.51
EF	2.61	2.57	2.69	2.63

Table 4
Elements concentrations (% dw) smaller than 1% dw in the studied samples.

		No additive	Both additives	Ammonium lignosulphonate	Barium carbonate
Na	GP	0.729	0.828	0.845	0.841
	DP	0.819	0.765	0.703	0.798
	EP	0.717	0.756	0.698	0.810
	EF	0.868	0.878	0.775	0.853
Mg	GP	0.504	0.508	0.528	0.511
	DP	0.476	0.486	0.482	0.481
	EP	0.444	0.503	0.517	0.476
	EF	0.536	0.524	0.568	0.545
Ca	GP	0.212	0.204	0.204	0.212
	DP	0.211	0.217	0.216	0.201
	EP	0.289	0.280	0.286	0.275
	EF	0.844	0.619	0.759	0.775
Ti	GP	0.309	0.518	0.554	0.309
	DP	0.600	0.588	0.619	0.54
	EP	0.402	0.594	0.418	0.600
	EF	0.631	0.878	0.403	0.415

the total metal content for the majority and minority metals respectively in the different products considered. The chemical composition of clay used in this work is within the range of compositions applied in the facing brick industry in different European countries.¹

Data with a concentration higher than 1% in dried weight corresponds to silicon, aluminium, iron and potassium are shown in Table 3. Together they represent 45% of the total metal content, the silicon being the main metal presenting at approximately 30%. The percentage of these metals is kept constant throughout the process, even in the efflorescence, and no influence of the additive is observed.

The minority elements are sodium, magnesium, calcium and titanium, representing 5% of the total. In Table 4 it can be observed that all metal percentages continue to show similar values in all studied materials, except for the calcium. In the salts efflorescence, the increase in the amount of calcium is three to fourfold, ranging from $0.208 \pm 0.005\%$ to $0.75 \pm 0.09\%$ depending on the studied material. This result is expected as Basanite and Calcite are the species responsible for efflorescence, detected in the mineralogical analysis. The use of both additives leads to the lower increase in calcium contents. Although no mineralogical sodium species is detected in the end-product and efflorescence salt, the sodium percentage remains constant from the raw material up to the efflorescence, and it is sim-

ilar to that for calcium. No additive influence on the sodium content is detected at any moment of the manufacturing process.

An analysis of sulphur has been carried out. Since the sulphur mostly occurs as sulphides (pyrite) in the raw materials, it does bear influence on the efflorescence phenomenon. During firing, at about 550°C , a clay contents pyrite gives off SO_2 and SO_3 . A certain proportion of these gases is retained in the clay, chemisorbed or adsorbed in the walls of capillary system, and that proportion depends on the nature of clay and of the specific conditions of firing. Sulphur retained by clay in these conditions is the one that produces efflorescence.⁹ The elemental sulphur content in clay raw material in this work has been 0.010% and in fired product, 0.008%, there being a 20% decrease. This suggests that the contribution of sulphur in the end-product is primarily from the clay. These clays belong to cold colour surface clays with organic matter and small quantities of pyrite of the order of 1%.

3.4. Soluble salts

Cations, sodium, calcium, magnesium, vanadium, and the anions, chloride, sulphate and carbonate have been shown in a previous work²⁶ to be the main components in efflorescence of bricks manufactured with the clay used in this work. Table 5

Table 5
Soluble ions concentration in the clay (R).

Element	Concentration (mg/l)
Na ⁺	2.83
Ca ²⁺	4.79
Mg ²⁺	1.74
V ³⁺	0.017
Cl ⁻	0.47
SO ₄ ²⁻	12.4
CO ₃ ²⁻	6.01

shows the soluble ion concentrations obtained from the used clay.

3.4.1. Cations

The evolution of cation concentration throughout the manufacturing process, with different additives is represented in Fig. 5. Fig. 5(a) shows the evolution of sodium concentration, where it can be observed that the concentration does not vary significantly throughout the process, and no additive influence is observed. The lowest concentration in the end product is obtained with all the additive combinations, except with ammonium lignosulphonate. The soluble calcium concentration is shown in Fig. 5(b). It can be observed that during the manufacturing process the soluble concentration of this cation increases. The soluble calcium concentration in the end-product is not affected by the additives employed, although barium carbonate seems to reduce the soluble concentration of this metal in the green and dried product. The soluble magnesium concentration is shown in Fig. 5(c), and in all the cases the magnesium concentration tends to decrease, the lowest value being reached in the end-product. In these cases barium carbonate presents the lowest soluble concentration of these cations, sodium, calcium and magnesium in green and dried product, but does not reduce the final concentration in the end product.

The vanadium soluble concentration is shown in Fig. 5(d), and it behaves like the calcium concentration, but in this case it is ammonium lignosulphonate the additive that permits the lowest vanadium concentration in the green and dried product to be obtained, although this concentration is the highest in the end-product. The lowest vanadium concentration in the end product is obtained when both additives are employed together.

Based on these results, it can be said that additive influence on soluble cation concentrations in the dosage employed in this study is not clear, although the use of both additives slightly decreases the soluble concentration of these cations for the end product; the critical stage of the process, which reduces the solubilisation of magnesium and favours the solubilisation of calcium and vanadium, is the firing stage.

3.4.2. Anions

In Fig. 6 the evolution of soluble anions, chlorides, sulphates and carbonates during the manufacturing process with different additives, is shown. Fig. 6(a) shows the evolution of soluble chloride concentration. Most clay contain trace levels of chloride, often deriving from an original marine formation, but also from the additives or the water containing chloride, which could be possible sources of chloride mobility. It can be observed that the chloride concentration increases significantly in the green and dried product in relation to raw material (Table 5), when a mixture of ammonium lignosulphonate and barium carbonate is used, and when only ammonium lignosulphonate is employed. This can be explained by the fact that ammonium lignosulphonate contributes to the chloride anions due to its own composition.^{13,14} In the end-product the chloride concentration decreases; this can be attributed to inorganic gaseous chlorine compounds stated as HCl during the firing process, due to the decomposition of organic compounds and mineral salts containing chloride at 450–550 °C and 850 °C respectively.²⁷

The evolution of soluble sulphate concentration during the process is shown in Fig. 6(b), where can be observed that the

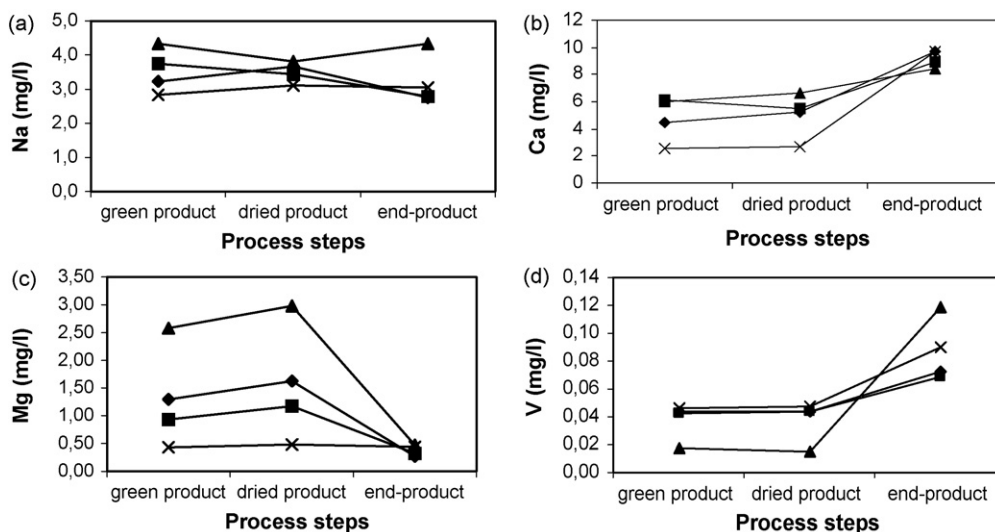


Fig. 5. Soluble cations along the manufacture process with: (◆) no additives, (■) barium carbonate + ammonium lignosulphonate, (▲) ammonium lignosulphonate, (×) barium carbonate.

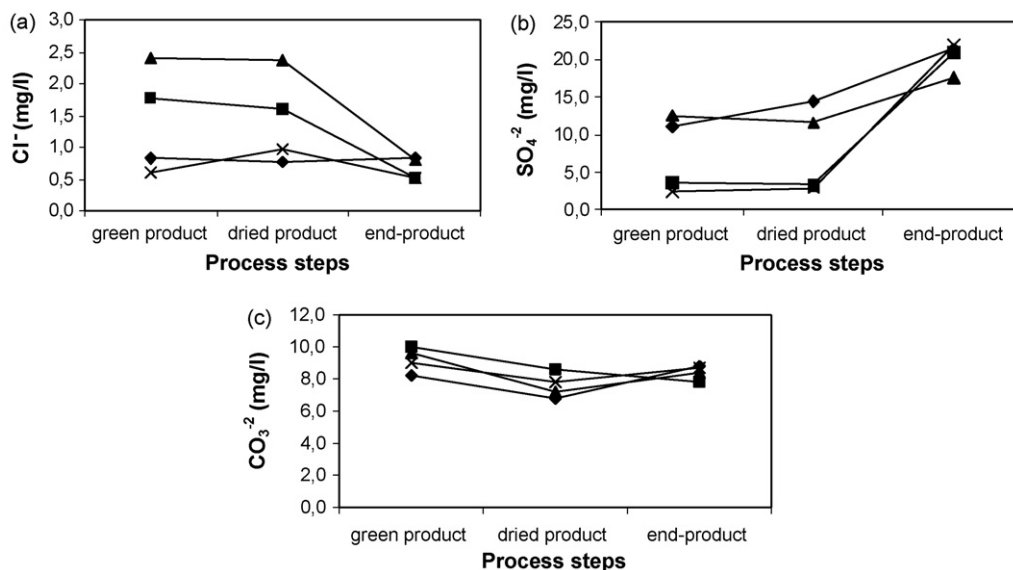


Fig. 6. Soluble anions along the manufacture process with: (◆) no additives, (■) barium carbonate + ammonium lignosulphonate, (▲) ammonium lignosulphonate, (×) barium carbonate.

sulphate concentration increases in all the cases, reaching values in the end-product from 15 to 20 mg/l, which are higher than the sulphate concentration of 12 mg/l detected in the raw material (Table 5). Taking into account that sulphur is necessary for forming sulphates, efflorescence can be present in the raw clay as: soluble sulphate; insoluble sulphates and; insoluble sulphides. Several studies have clearly shown that insoluble sulphates and sulphides play a far more important role, specially the latter, than soluble sulphates in the formation of efflorescence.^{9,28} Brownell argued that sulphate salts can also be formed in the end product during firing by exposure to sulphurous gases coming from oxidation of sulphides in the product, and reaction of a sulphate with silicates. The behaviour of sulphate salts formed in this way is the same as if the salts were originally present in the raw material. This explains the retention of sulphates in clay bodies when no soluble sulphates are present in the raw material.²⁸ Nevertheless, the use of both additives and barium carbonate decreases the sulphate concentration in the green and dried product in relation to the use of no additives or the use of ammonium lignosulphonate, although during the firing process the expected effectiveness of these additives is not verified.

Fig. 6(c) shows the evolution of the soluble carbonate concentration. No additive influence is observed, nor is a significant influence of the process detected in the evolution of the soluble carbonate concentration. Therefore, from these results, the thermal dissociation of alkali and earth alkali carbonates during firing, forming calcium oxide and releasing carbon dioxide, which might happen in this type of ceramic process, is not appreciated. This could be attributed to the addition of the additives to ceramic bodies, like barium carbonate or high oxygen conditions in the kiln.

3.4.3. Soluble salts and efflorescence phenomenon

Once soluble salts have been analysed in the raw material, and throughout the manufacturing process with different additive compositions, data for soluble salts in the efflorescence have

been collected in order to establish a relation between soluble salts in the material and the efflorescence phenomenon.

Soluble salts results obtained from the efflorescence are shown in Fig. 7. The concentration of soluble ions is higher in the efflorescence samples, due to the concentration of soluble or relatively soluble salts on the surface. As can be observed, the biggest values of the concentration of the soluble salt in the efflorescence (hatch columns) in relation to the end-product (solid columns) are the sulphate and calcium. This is in accordance with the mineralogical analysis and, therefore, the main phase identified in the efflorescence is the bassanite, $\text{CaSO}_4 \cdot 0.5\text{H}_2\text{O}$.

The lower soluble salts concentrations in efflorescence samples are obtained when both additives are employed and the higher concentrations are obtained without additives (Fig. 7). Table 6 shows the ratio between the concentration in the efflorescence salt and the concentration in the end-product of each analysed ion from the results obtained without additives and with both additives. In the case of sodium, calcium and sulphate

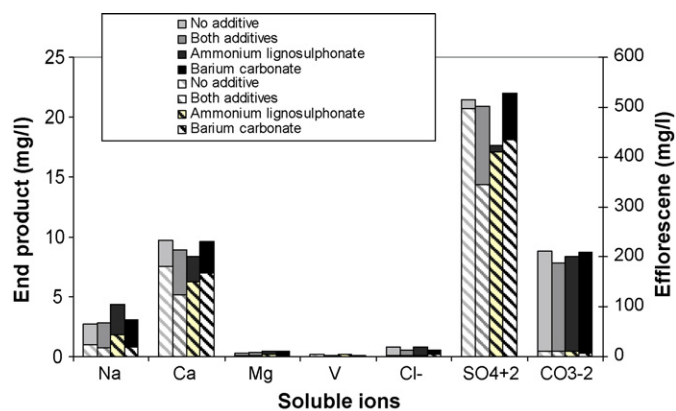


Fig. 7. Soluble ions results: solid column (left axis) for the end-product and hatch columns (right axis) for the efflorescence.

Table 6

Results of soluble salts in efflorescence in relation to the results in the end-product.

	Na	Ca	Mg	V	Chlorides	Sulphates	Carbonates
Without additives	4.8–11	15–25	7.4–16	44–82	0.21–3.8	18–28	0.9–1.8
With both additives	5.6–6	14.9–15	5.1–8.2	24–52	0.23–4.6	17–19	1.1–2.2

Bold data have a narrow interval when both additives are used.

ions the ratio falls in a narrow interval when both additives are used.

Based on these results, it can be noted that the use of ammonium lignosulphonate and barium carbonate permits a constant relation between end-product and efflorescence, to be obtained for the sodium, calcium and sulphate soluble concentration. Although some authors^{29,30} postulate that the sulphates extracted from inside brick often have a composition different from that of efflorescence, it is due to the different solubility of the salts. In contrast, the soluble salts content in the brick has been regulated³¹ and recently by European standard²² in order to prevent efflorescence in brick construction, emphasizing the importance of soluble salts content in the end-product regards potential efflorescence. This approach corroborates the results obtained in this work.

So if the presence of a high concentration of calcium, sodium and sulphate is controlled in the end-product, the efflorescence caused by the solubilisation of these species can be also controlled. Since the increment of soluble calcium and sulphate concentration is produced in the firing of brick manufacturing, the operation variables in the kiln such as the rate of heating as well as the level of the firing temperature can affect to the efflorescence phenomenon.⁸

Table 7 shows the ratio of the end-product cations to raw material with and without additives under the studied manufacturing process conditions (Fig. 1). It has not been possible to establish a relationship because the ratio falls at wide intervals. The ratio of cations is not influenced by the use of additives significantly, excepting in the case of magnesium, in which the use of both additives makes this ratio higher.

In Fig. 8, the relationship between the concentrations of soluble anions and those of soluble cations, expressed as meq/l, analysed in the efflorescence is reported. A linear relation is obtained with a regression coefficient of $r^2 = 0.996$ and a slope of almost 1. This behaviour indicates that the anions and cations have the same equivalents, suggesting that no other ionic components in the samples contribute in a significant way to the composition of water-soluble salts.

Table 7

Ratio of soluble salts in end-product/raw material.

	No additive	Both additives
Na	0.98 ± 0.42	0.98 ± 0.64
Ca	2.03 ± 0.67	1.85 ± 0.19
Mg	0.15 ± 0.007	1.86 ± 0.02
V	4.28 ± 2.02	4.04 ± 2.34
Cl ⁻	1.79 ± 0.43	1.08 ± 0.21
SO ₄ ²⁻	1.74 ± 0.49	1.69 ± 0.31
CO ₃ ²⁻	1.47 ± 0.53	1.30 ± 0.30

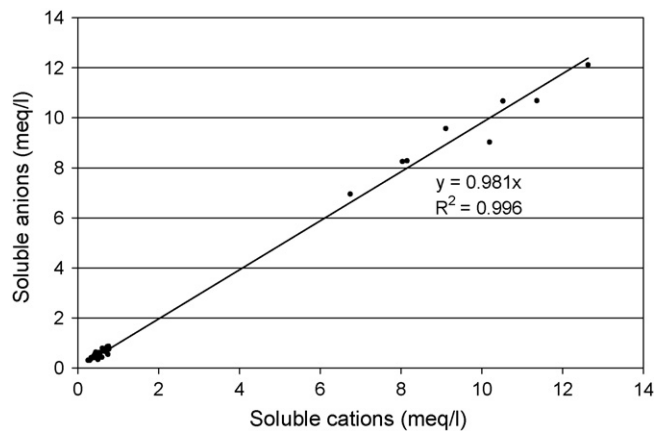


Fig. 8. Results of soluble ions in efflorescence.

4. Conclusions

Based on the results of the physical and chemical characterisation of bricks during the manufacturing process presented in this work, the efflorescence phenomenon detected can be attributed to the presence of Bassanite and Calcite, as the results of the mineralogical analysis demonstrate. Data for total metal content and soluble salts of sulphate and calcium also corroborate the presence of these salts, in particular Bassanite, which is why it is so relevant to analyse the soluble salts in the final product as a variable of the process.

Regarding the results for porosity and specific surface, only additive influence on the mesopore volume and specific surface is observed in the green and dried products, however, no additive influence on the end-product is detected. On the one hand, in firing stage the range of the finest pores (mesopore volume) of final products seems to change noticeably while the largest pores (macropore volume) are not very affected, which could be favoured by different causes, such as entrapped air in the ceramic slurry; formation of voids during the different drying steps; gases released in the thermal decomposition of carbonates and sulphates or even by the liberation of gases dissolved in quartz particles. On the other hand, the firing process causes a linear shrinkage of the material that explains the reduction of the specific surface.

The metals percentage remains constant throughout the process, even in the efflorescence, except for the calcium. In efflorescence salts, the amount of calcium increases three to four-fold, depending on the studied material. This is to be expected, taking into account that Bassanite and Calcite are the species responsible for efflorescence, detected in the mineralogical analysis.

Water soluble salts analysis is recommended as a key parameter in relation to the efflorescence phenomenon. In this case, sodium, calcium, magnesium and vanadium as cations and chloride, sulphate and carbonate as anions are the main soluble salts. The sulphate concentration increases throughout the process, reaching values in the end product higher than those detected in the raw material. This shows that during the firing process the insoluble sulphates and sulphides could play a more important role than soluble sulphates in the formation of efflorescence.

A constant relationship between the sodium, calcium and sulphate concentration found in efflorescence salts and the end-product has been detected when the use of a mixture of ammonium lignosulphonate and barium carbonate is used. Therefore, as the main target is to reduce the efflorescence salts in the final product, the use of both additives together and the control of the firing process variable are recommended.

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