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Orimulsion fly ash in clay bricks—part 3: chemical stability of ash-bearing products

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Abstract

The chemical stability of clay bricks containing Orimulsion ash (up to 6 wt.%) was assessed with a laboratory simulation of the brickmaking process. The development of efflorescence, the amount of water soluble salts and their elution, the fraction of S, V, Ni, Mg, Ca, Na and K immobilized in the ceramic matrix, and the amount of volatile elements potentially released during firing were determined by ICP–OES, XRPD, TGA, SEM and EMP analyses. The stabilizing mechanism acts through the capture of metals into the crystalline structure of silicates formed at high temperature. However, the firing conditions adopted in the brick industry (about 900 °C) do not permit the complete reaction of sulphates; there is considerable efflorescence and soluble salts are formed, even with 1.5% of ash added, producing a risk of sulphate attack to the mortars. On the other hand, the decompostion of sulphates during firing could bring about remarkable SO_x emissions, particularly in carbonate-free bodies. In conclusion, the disposal of Orimulsion ash in clay bricks must be practiced with caution and an amount of ash below 1 wt.% weight is strongly recommended.
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Keywords: Bricks; Chemical properties; Clays; Fly ash; Waste materials

1. Introduction

This work is focused on the appraisal of the chemical stability of clay bricks containing various amounts of Orimulsion fly ash. The approach involved the determination of:

(a) efflorescence;
(b) amount and speciation of soluble salts present in the fired products;
(c) efficacy of the inertization process of ash into the ceramic matrix;
(d) mechanisms of immobilization of magnesium, sulphur, vanadium and nickel;
(e) elution, particularly the concentration of V and Ni mobilized in a weakly acid environment;
(f) amount of volatile components (SO_x, V) that can be potentially released from the clay brick during firing.

The chemical and phase composition, physical properties and thermal behaviour of the ash have been presented and discussed in the first part of this study, while the laboratory simulations of the brickmaking processing have been the subject of the second part.

2. Materials and methods

The ashes resulted from the combustion of the bitumen-in-water emulsion carried out in two Italian thermal power plants, located in Brindisi, Apulia (ash B) and in Fiume Santo, Sardinia (ash F) respectively. These wastes were mixed together with two clay bodies, currently used in two brickworks located near the above-mentioned plants: body L (Lucera, Apulia) and body S (Porto Torres, Sardinia). Body formulation, chemical composition and processing conditions of these clay/ash mixes have been described in the second part of this work.

These ash-bearing bodies were characterized measuring:

- efflorescence on both fired and unfired specimens (standard UNI 8942-3);

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- phase composition of efflorescent deposits by X-ray powder diffraction (Rigaku, Miniflex) with Ni-filtered CuK_α radiation;
- water-soluble components (Na^+, K^+, Ca^{2+}, Mg^{2+}, Ni^{2+}, $SO_4{}^{2-}$, $Cro_4{}^{3-}$, $Vo_4{}^{3-}$) of fired bricks, following the prEN 772-5 standard procedure of soluble salt extraction and successive analysis by means of inductively-coupled plasma spectrophotometry (ICP–OES, Varian, Liberty 200) with an analytical error within 5% relative;[1]
- efficiency of inertization of the elements constituting the fly ash calculated as:

  $$I_e = \frac{C_{i,e}}{C_{t,e}} \cdot 100$$

  where I_e is the efficiency index for the element e in percentage, $C_{i,e}$ and $C_{t,e}$ are the water insoluble and the total concentration of the element e respectively, determined by ICP–OES;
- chemical composition of the crystalline phases of the bricks, performed by energy-dispersive X-ray fluorescence spectrometry (EDS–XRF) with electronic microprobe (Link Analytical, eLXI) on graphite-sputtered fracture surfaces;[2]
- elution according to the prescriptions of the Italian law (D.M. 5/2/1998), i.e. the amount of Ni and V released from bricks during contact with an aqueous solution of acetic acid 0.5 M (pH about 5) for 24 h, determined by means of ICP–OES.

The potential release of polluting elements during firing was estimated on the basis of the sulphur and vanadium concentrations in unfired (C_u) and in fired samples (C_f) determined by ICP–OES with microwave-assisted acid dissolution. To compare correctly these values, it is necessary to take into account the weight loss during the thermal treatment (Δ_f) determined by thermogravimetric analysis (Netzsch, STA 1402, thermal gradient 10 °C min^{-1}). In order to express the release in terms of mg of element per kg of fired product, the initial concentration was corrected as follows:

$$C'_u = 100 \cdot C_u / (100 - \Delta_f).$$

The average potential release (Ψ) was, therefore, calculated as:

$$\Psi = C'_u - C_f \left(\text{mg kg}^{-1} \text{ of fired brick}\right).$$

3. Results and discussion

3.1. Efflorescence

A certain efflorescence occurred already in unfired bricks, in the form of thin whitish films in bodies L and chestnut to greenish yellow deposits in mixtures S. In particular, efflorescent salts are absent in mixes containing 1.5% ash, just visible in those containing 3% ash and very diffuse in bodies L6 and S6, where they cover almost the entire specimen. Efflorescence on dry bricks is essentially formed by:

- magnesium sulphate monohydrate and vanadyl hydrogen sulphate, with minor quantities of vanadyl sulphate monohydrate (bodies L);
- magnesium sulphate, both in monohydrate and hexahydrate forms, and vanadyl hydrogen sulphate (bodies S).

In the fired bricks, efflorescence is heavily affected by the presence of ash in the body, though in a different way for the two series of clay/ash mixes and the various firing cycles (Table 1). In the clay L + ash B mixtures, the ash-free material showed practically no efflorescence or, at most, exhibited after cycle B a very weak white film, basically consisting of calcium carbonate and calcium sulphate approximately in the same proportions, with traces of sodium sulphate. In contrast, after cycle A, bodies L1 and L6 effloresce to a medium degree, which became strong for L3; after the cycles B and C, the efflorescence is strong for L1, medium-strong for L3 and almost absent for L6. In all ash-bearing bricks, the salt deposits present a yellowish–white colour and consist of about two thirds of calcium sulphate and one third of sodium sulphate, with a small contribution of calcium vanadate.

In the clay S + ash F mixtures, efflorescence varied more or less in the same way for the various firing cycles. The saline deposits of the ash-free bricks are so scarce that it was impossible to collect enough material for their analysis. On the other hand, the efflorescent thin films on

Table 1
Efflorescence of bricks obtained from clay/ash mixtures[a]

Clay/ash mix	Cycle A	Cycle B	Cycle C
L0	None/weak	Weak	None/weak
L1	Medium	Strong	Strong
L3	Strong	Medium/strong	Medium/strong
L6	Medium	None/weak	None/weak
	Cycle D	Cycle E	Cycle F
S0	Weak	Weak	Weak/medium
S1	Medium/strong	Medium	Medium/strong
S3	Strong	Strong	Medium/strong
S6	Weak	None/weak	None/weak

[a] Expression of results (UNI 8942-3): none = no appreciable deposit of salts on the surface; weak = formation of a thin white film non uniformly distributed on the surface; medium = formation of a thin uniform film; strong = formation of a thick layer of salt, with uniform thickness and distribution, and with easily removable superficial crystallizations.

samples S1 and S3 were formed from calcium sulphate, but appeared bright yellow instead of the usual white. This colouring is probably connected to the presence of a small quantity (below 10%) of potassium vanadate (KV_5O_{13}); it appeared even in body S0, though with a lower intensity. This latter circumstance posed the problem of a possible volatilization of vanadium during firing. The efflorescence of sample S6, in contrast, was a uniform layer, of appreciable thickness and "earthy" consistency, chestnut–buff in colour, consisting approximately of equal parts of calcium sulphate and potassium vanadate (KVO_3). Since it was already present in the fired brick before immersion in water, the efflorescence test did not produce changes of aspect and thus the result was "efflorescence none or weak". This result is to be considered as "tendency to develop efflorescence during firing"; as a matter of fact, the efflorescent salts cover entirely the S6 bricks already after drying.

3.2. Soluble salts

In the ash-free brick L0, the most abundant soluble ions are Ca^{2+} and SO_4^{2-} in all the firing cycles, while the other elements are always in concentrations $\leqslant 0.01\%$. The introduction of ash produced a considerable and progressive increase in the amount of soluble salts, with Ca^{2+} and SO_4^{2-} still predominant, but accompanied by significant quantities of K^+ (up to 0.21%), Na^+ (up to 0.07%) and VO_4^{3-} (up to 0.11%). The soluble magnesium is negligible, while chromium and nickel are systematically below the detection limit ($<0.0005\%$).

The various firing cycles influenced especially the concentration of SO_4^{2-} and, to a lesser extent, those of VO_4^{3-}, Na^+ and K^+ (Fig. 1). In particular, the cycle A (maximum temperature 900 °C) made it possible to obtain appreciably lower contents of soluble sulphate and vanadate in the bodies L0 and L1. As regards alkalis, a complex picture was found: the firing conditions did not affect the ash-free body, while they had, vice versa, a noteworthy effect on the ash-bearing ones. After cycle A, the maximum sodium and potassium mobilization was found for body L3; after cycles B and C, the alkali solubilization is extended also to body L1. The mixture L6 presented always the lowest Na^+ and K^+ values, particularly after firing at the highest temperatures.

The soluble salts are very scarce in the S0 brick: the most abundant soluble ions are Na^+, K^+ and SO_4^{2-} in all the firing cycles, while the other elements are always

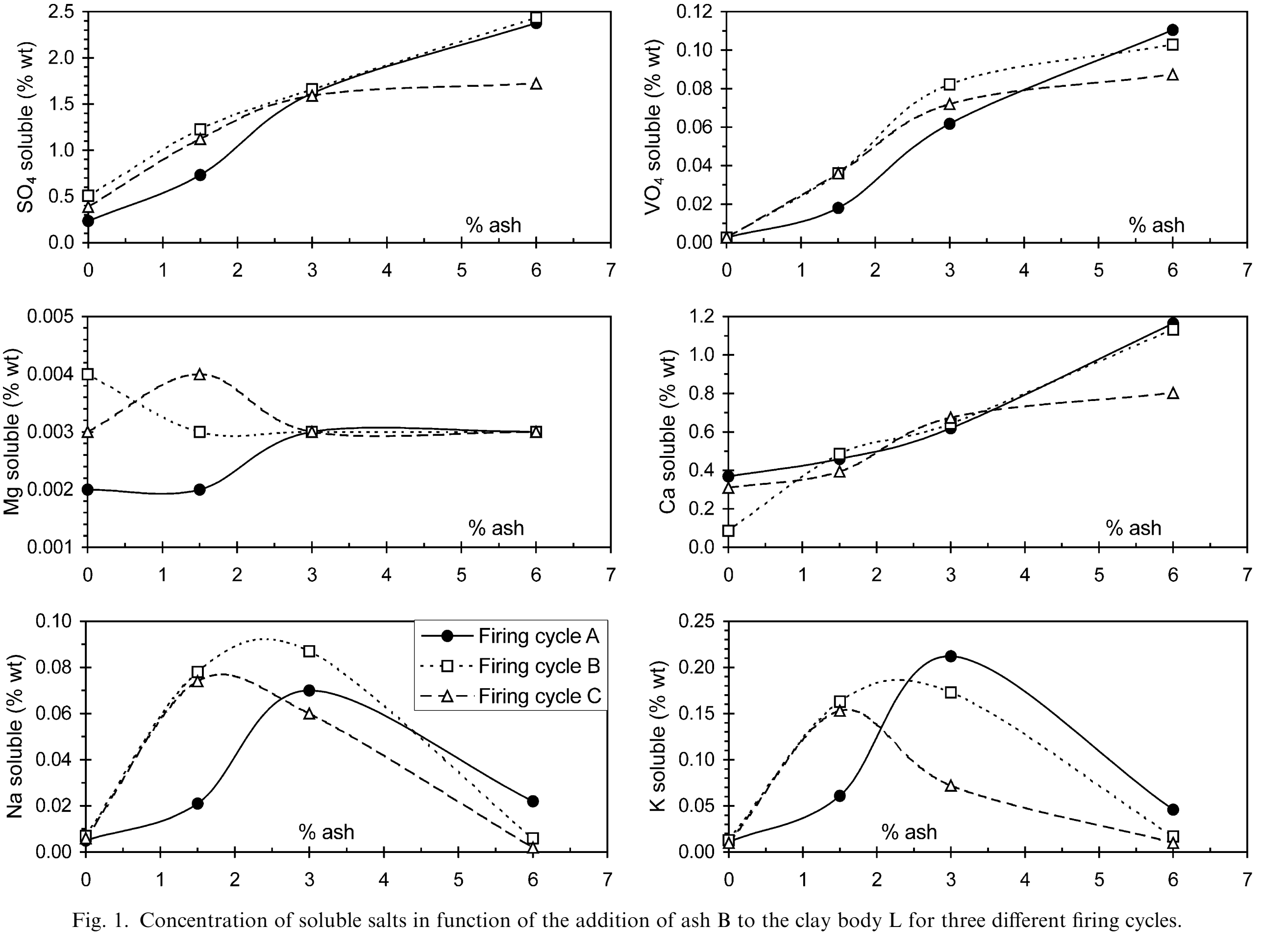

Fig. 1. Concentration of soluble salts in function of the addition of ash B to the clay body L for three different firing cycles.

in concentrations $\leqslant 0.01\%$, especially chromium and nickel, which are systematically below the detection limit ($<0.0005\%$). The introduction of ash produced different effects depending on the firing cycle (Fig. 2). In conditions analogous to those of the industrial kiln (cycle D) a considerable and progressive increase in the amount of soluble salts occurred, especially SO_4^{2-}, Ca^{2+} and VO_4^{3-}, and to a lesser extent Mg^{2+}; the concentration of soluble alkalis, in constrast, had little variation. The cycles E and F brought about substantially similar results, which suggested that an increment of the firing temperature restrained the formation of most soluble ions, with the exception of vanadium.

The European standard prEN 771 states that brickmakers must classify their own products on the basis of the content of active soluble salts (Na^+, K^+ and Mg^{2+}), which would be those promoting sulphate attack on the mortars.[3] For this purpose, the values of active soluble salts in the experimented bodies are compared to the limits of the above-mentioned standard; this latter indicates three categories of products, with a growing quality going from No. 0 to No. 2 (Table 2). The utilization of Orimulsion waste caused a qualitative worsening of the mixtures with ash B, which from the best category (No. 2 of body L0) passed to No. 1 and eventually No. 0 in the bodies L1 and L3 respectively. The firing cycle A is quite favourable, since it would permit the classification of body L1 in category No. 1. At all events, the risk of sulphate attack to the mortars is real, if account is taken of the SO_4^{2-} values, which are already rather high in the ash-free body (0.2–0.5%) and increase rapidly to 0.7–1.2% even with the addition of 1.5% ash.

In contrast, the occurrence of ash in body S did not imply any qualitative worsening of the materials, which always fulfills the requirements of the best category (No. 2). In any event, the firing cycle D is less favourable than the other two cycles tested, since it would allow the formation of a fair quantity of soluble alkalis (0.03%) not too far from the standard limit (0.06%). However, the risk of sulphate attack to the mortars cannot be absolutely excluded, since the content of SO_4^{2-} in the ash-bearing bodies is remarkable (0.15–0.30%).

3.3. Inertization process

The use of ash implies a change of chemistry in the clay body, which of course is proportional to the percentage of waste introduced. The addition of elements such as sulphur, magnesium, vanadium and nickel, in

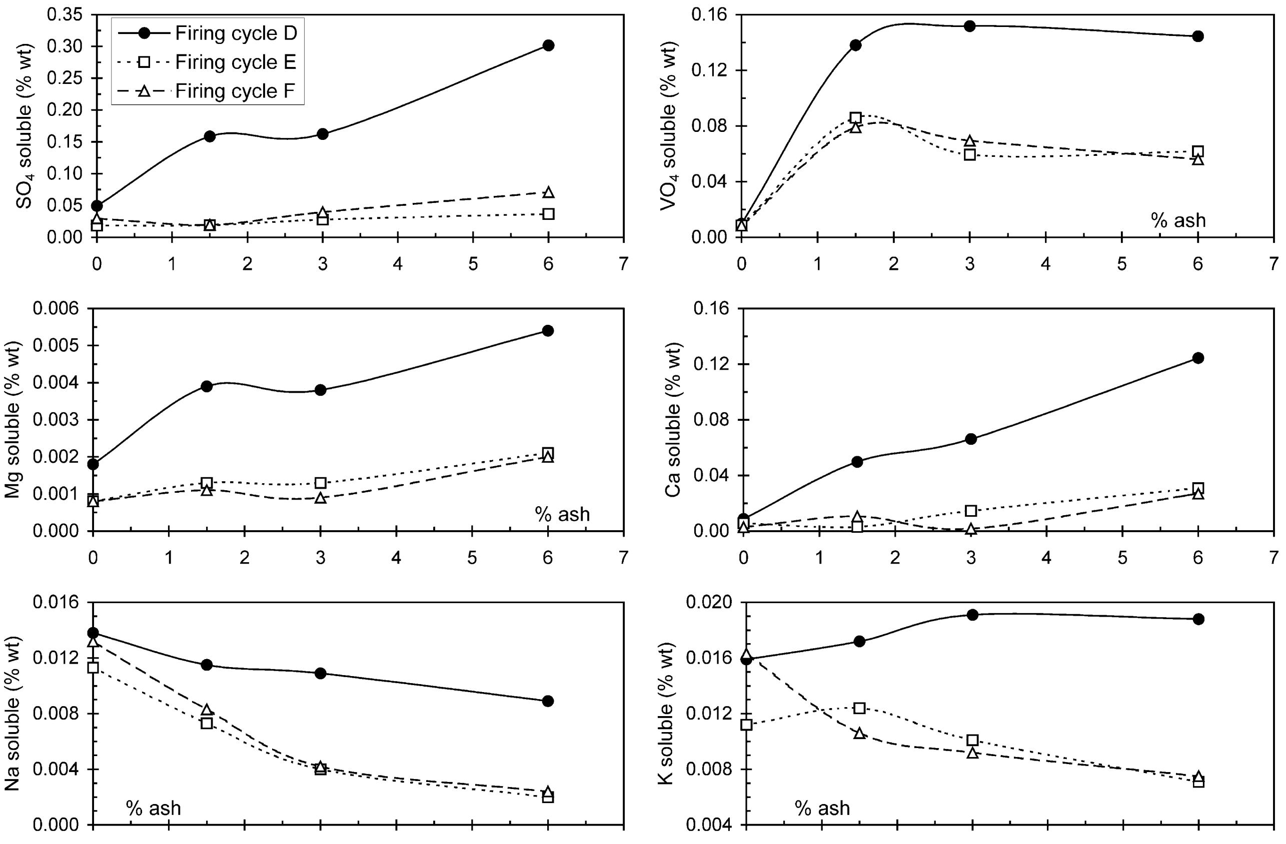

Fig. 2. Concentration of soluble salts in function of the addition of ash F to the clay body S for three different firing cycles.

Table 2
Active soluble salts in clay/ash mixtures and classification according to standard prEN 771[a]

Wt.%	$(Na^+ + K^+)$			Mg^{++}			Classification		
Firing	Cycle A	Cycle B	Cycle C	Cycle A	Cycle B	Cycle C	Cycle A	Cycle B	Cycle C
Mix L0	0.02	0.02	0.02	<0.01	<0.01	<0.01	No. 2	No. 2	No. 2
Mix L1	0.08	0.24	0.23	<0.01	<0.01	<0.01	No. 1	No. 0	No. 0
Mix L3	0.28	0.26	0.13	<0.01	<0.01	<0.01	No. 0	No. 0	No. 1
Mix L6	0.07	0.02	0.01	<0.01	<0.01	<0.01	No. 1	No. 2	No. 2
Firing	Cycle D	Cycle E	Cycle F	Cycle D	Cycle E	Cycle F	Cycle D	Cycle E	Cycle F
Mix S0	0.03	0.02	0.03	<0.01	<0.01	<0.01	No. 2	No. 2	No. 2
Mix S1	0.03	0.02	0.02	<0.01	<0.01	<0.01	No. 2	No. 2	No. 2
Mix S3	0.03	0.01	0.01	<0.01	<0.01	<0.01	No. 2	No. 2	No. 2
Mix S6	0.03	0.01	0.01	<0.01	<0.01	<0.01	No. 2	No. 2	No. 2

[a] Requirements of category No. 2: $(Na^+ + K^+) \leqslant 0.06\%$, $Mg^{++} \leqslant 0.03\%$; requirements of category No. 1: $(Na^+ + K^+)$ 0.06–0.17%, Mg^{++} 0.03–0.08%. Requirements of category No. 0: none.

particular, poses the problem of their stabilization into the ceramic body. The appraisal of the effectiveness of such an "inertization" process was possible by estimating, for each element, the fraction made insoluble in water at the end of firing.

This effectiveness varied, in the different bodies L, depending on the elements and the thermal treatment (Fig. 3). In the ash-free body L0, the mobilization phenomena concerned only sulphur and calcium: the firing cycle A made it possible to achieve the maximum inertization of sulphate, while the cycle C minimized the percentage of soluble calcium. The higher the firing temperature, the more efficaceous are the reactions leading to the formation of calcium silicates, insoluble in

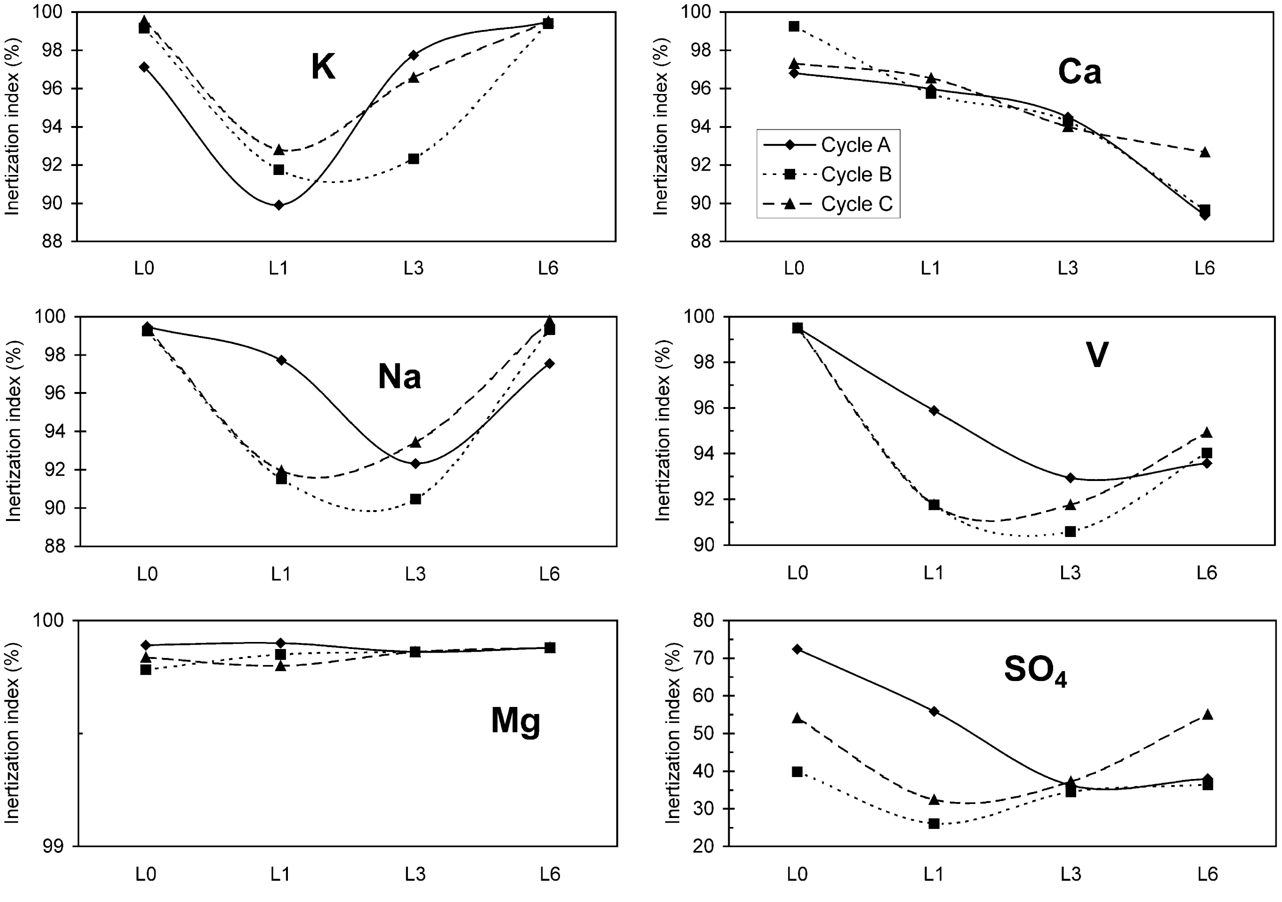

Fig. 3. Efficiency of the inertization in function of the addition of ash B into the clay body L for three different firing cycles.

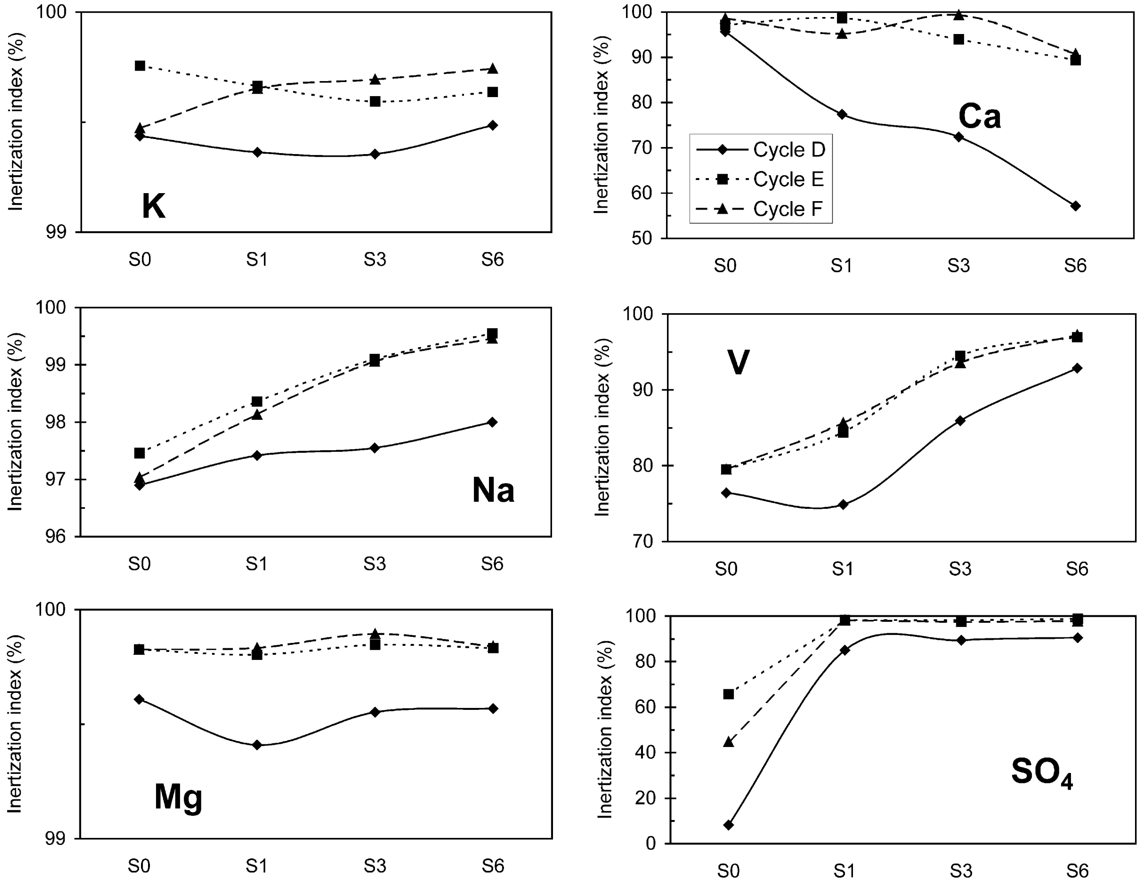

Fig. 4. Efficiency of the inertization in function of the addition of ash F into the clay body S for three different firing cycles.

water. On the other hand, the lower firing temperatures ensure a minor decomposition of calcium sulphate, that is scarcely soluble and appears to be to a large extent "immobile". The introduction of ash in the clay body modifies this picture, promoting a stronger mobilization, not only of sulphur and calcium, but also of sodium, potassium and vanadium. In contrast, magnesium and nickel are perfectly immobilized after all the firing cycles. As far as alkalis and vanadium are concerned, an evident worsening occurred passing from body L0 to those containing 1.5–3% ash, though the mix L6 exhibited values comparable to those of L0. In the case of calcium, a progressive decrease of the inertization index is connected with an increase of the ash percentages, while for sulphate this trend is stopped at body L3. The firing cycle with the lowest temperature (A = 900 °C) made it possible to achieve the better stabilization of sodium, vanadium and sulphate, excluding body L6, but at the same time worsened the results regarding potassium. The best inertization of the latter element is obtained with cycle B (930 °C). The mobilization of calcium is not affected conspicuously by the thermal cycle.

On the other hand, the reactions occurring during firing between ash F and clay S allowed an almost complete inertization of magnesium, nickel and potassium. Moreover, a stabilization of over 95% of sodium and calcium is achieved, if the cycle D is excluded, since it appears to be less effective than the others, particularly when the ash amount grows (Fig. 4). Also, in the case of vanadium, the firing cycles at higher temperature are more efficaceous; they were, however, not able to immobilize entirely the element, which was converted to soluble ion in percentages as high as 15–25% (S1) and 5–15% (S3) of total vanadium. As for as concerns the sulphate ion, a peculiar behaviour arose: the presence of ash seems to promote a stabilization of sulphur, especially after treatments at a temperature over 900 °C. In reality, it is probable that this "insoluble" sulphur would be released in the flue gas of the kiln rather than immobilized in phases insoluble in water.

The mechanism of stabilization of S, Mg, V and Ni seems to be connected to the dissolution of metals in the silicate phases formed during firing. For example, in Table 3 the chemical compositions of melilite and pyroxene found in bricks L0 and L3 are compared. In effect, the silicates of the ash-bearing body are frequently richer in magnesium, vanadium and nickel with respect to the corresponding phases formed in the ash-free body. In these structures, vanadium is expected to be in trivalent form, substituting for Al^{3+} and Fe^{3+} in octahedral sites; similarly Ni^{2+} is substituted in Mg^{2+} octahedra. Sulphur is basically immobilized as calcium sulphate (Fig. 5).

Table 3
Comparison of the crystallochemical composition of Ca–Mg–Al silicates formed during the firing of clay L without ash (L0) and with 3% ash (L3)

Wt.%	Melilite				Pyroxene	
	L0	L3	L3	L3	L0	L3
SiO_2	29.59	36.76	32.97	30.12	49.64	47.19
TiO_2	0.42	0.23	0.59	0.95	0.42	0.56
Al_2O_3	15.48	13.57	13.24	11.93	15.73	17.23
Fe_2O_3	5.38	4.58	11.18	14.72	7.12	5.13
V_2O_3	0.00	0.54	1.52	2.30	0.00	0.80
NiO	0.00	0.01	0.15	0.30	0.00	0.00
MgO	2.95	4.93	2.17	1.56	2.56	3.56
CaO	43.90	35.77	34.08	35.60	21.61	22.34
Na_2O	1.82	2.34	2.76	1.41	1.78	2.36
K_2O	0.45	1.28	1.35	1.12	1.15	0.82
O	14	14	14	14	6	6
Si	2.826	3.373	3.105	2.891	1.804	1.718
$Al^{[IV]}$	1.740	1.466	1.468	1.348	0.196	0.282
$Al^{[VI]}$	–	–	–	–	0.477	0.457
Ti	0.030	0.016	0.042	0.069	0.011	0.015
Fe	0.387	0.317	0.793	1.063	0.195	0.141
V	0.000	0.082	0.236	0.364	0.000	0.048
Ni	0.000	0.001	0.011	0.023	0.000	0.000
Mg	0.419	0.674	0.305	0.223	0.139	0.193
Ca	4.482	3.509	3.431	3.653	0.840	0.870
Na	0.339	0.417	0.506	0.264	0.126	0.167
K	0.054	0.149	0.161	0.136	0.053	0.038
T[a]	5.402	5.928	5.959	5.981	2.000	2.000
M1[a]	4.875	4.075	4.098	4.053	0.822	0.854
M2[a]	–	–	–	–	1.019	1.075
Total	10.277	10.003	10.057	10.034	3.840	3.930

[a] T = total occupancy of tetrahedral sites; M = total occupancy of octahedral sites.

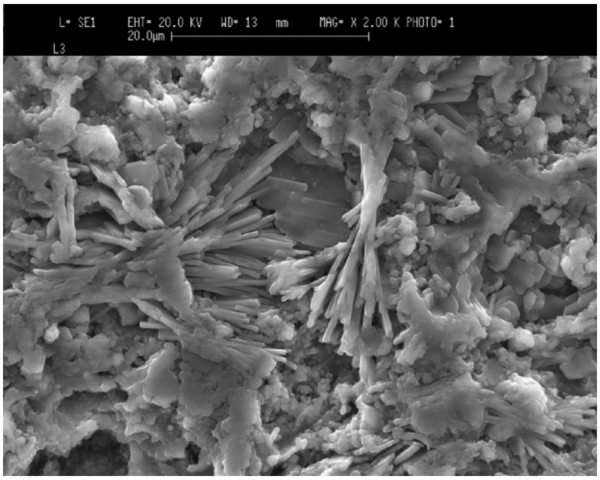

Fig. 5. Calcium sulphate crystals formed during the firing of body L3. SEM photomicrograph (bar = 20 µm).

3.4. Elution

The possible mobilization of heavy metals, particularly nickel and vanadium, was assessed in a weakly acid aqueous solution (pH 5) as in the case of acid rains. This elution test indicated (Table 4):

Table 4
Concentration of elution from clay/ash mixtures, expressed in percentage of fired weight

Body	Nickel		Vanadium	
	Average	S.D.	Average	S.D.
L0	< 0.0001	< 0.0001	0.001	0.000
L1	< 0.0001	< 0.0001	0.020	0.001
L3	< 0.0001	< 0.0001	0.040	0.002
L6	0.0001	< 0.0001	0.047	0.002
S0	0.0001	< 0.0001	0.002	0.000
S1	0.0001	< 0.0001	0.043	0.001
S3	0.0001	< 0.0001	0.047	0.002
S6	0.0001	< 0.0001	0.050	0.003

(i) a complete stabilization of nickel, probably hosted in acid-resistant silicate structures;
(ii) a modest mobilization of vanadium (at the most 0.05% of fired brick) presumably due to a small amount of soluble vanadate.

The amount of vanadium mobilized in an acid environment is lower than in neutral pH (Fig. 6) as already found in previous studies.[4]

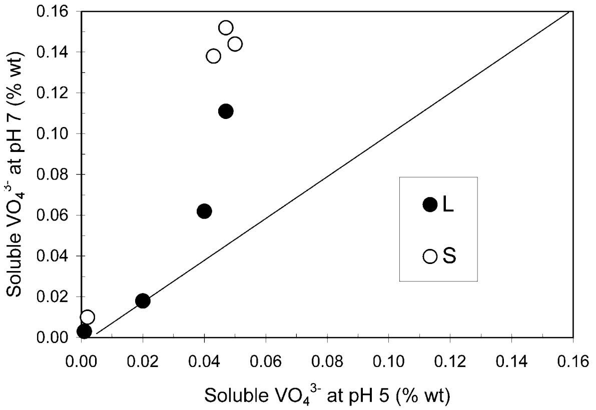

Fig. 6. Soluble vanadium in ash-bearing clay bricks: comparison of the concentrations determined in weakly acid and in neutral environments.

3.5. Estimate of gaseous release

There are two completely different situations regarding the carbonate-rich bodies (series L) and the carbonate-free ones (series S). In fact, the sulphur amounts in the fired bricks L are practically the same as the initial contents, thus the SO_3 release, in the laboratory firing conditions, was very low for bodies L0, L1 and L3, but up to 800–900 mg kg^{-1} for L6 (Table 5). The experimental uncertainty of data, however, is frequently high, so that a certain risk cannot be excluded for bodies L1 and L3, which could release significant amounts of SO_3 in all the thermal cycles tested.

In contrast, the sulphur amounts in bodies S are clearly lower than the initial contents. Therefore, the SO_3 release in the laboratory firing conditions appeared to be proportional to the ash added (Table 5). There are no significant variations in the potential releases recorded after the three thermal cycles tried. In fact, the average SO_3 release could range from 1700 to 3100 mg kg^{-1} of fired product in the ash-free body, to 4000–5500 mg kg^{-1} in S1, to 9000–10,500 mg kg^{-1} in S3 and eventually to values over 20,000 mg kg^{-1} in S6. There are, in all cases in which ash is present, very high releases, systematically over the legal limit (2000 mg kg^{-1}).

As far as vanadium is concerned, there are no hints of volatilization in the bodies containing up to 1.5% ash, while conversely in the mixtures with higher waste contents a vanadium release can occur, with values up to 100–400 mg kg^{-1} (Table 6). This phenomenon could explain the occurrence of very weak vanadium efflorescence even in S0 bricks, which might be derived from the flue gas of the kiln.

Table 5
Potential release of SO_3 during the firing of clay/ash mixtures

SO_3	L.o.I. 900 °C (wt.%)	Initial content corrected C' (wt.%)		Final content in fired bricks C_f (wt.%)		Potential release Ψ (mg kg^{-1} of fired brick)
		Average	S.D.	Average	S.D.	Average
L0A	16.0	0.66	0.04	0.54	0.18	< 100
L1A	16.9	1.17	0.18	1.25	0.23	< 100
L3A	16.0	1.93	0.37	2.00	0.21	< 100
L6A	16.7	3.23	0.20	3.14	0.25	890
L0B	16.0	0.66	0.04	0.83	0.23	< 100
L1B	16.9	1.17	0.18	1.58	0.27	< 100
L3B	16.0	1.93	0.37	2.08	0.33	< 100
L6B	16.7	3.23	0.20	3.15	0.35	800
L0C	16.0	0.66	0.04	0.73	0.13	< 100
L1C	16.9	1.17	0.18	1.32	0.15	< 100
L3C	16.0	1.93	0.37	2.25	0.30	< 100
L6C	16.7	3.23	0.20	3.29	0.52	< 100
S0D	5.3	0.49	0.01	0.30	0.10	1900
S1D	5.6	0.88	0.29	0.32	0.10	5500
S3D	6.6	1.53	0.45	0.60	0.31	9400
S6D	7.8	2.83	0.25	0.60	0.35	22,300
S0E	5.3	0.49	0.01	0.32	0.12	1700
S1E	5.6	0.88	0.29	0.49	0.14	3900
S3E	6.6	1.53	0.45	0.64	0.18	8900
S6E	7.8	2.83	0.25	0.29	0.10	25,400
S0F	5.3	0.49	0.01	0.18	0.10	3100
S1F	5.6	0.88	0.29	0.38	0.18	5000
S3F	6.6	1.53	0.45	0.47	0.11	10,600
S6F	7.8	2.83	0.25	0.66	0.20	21,700

Table 6
Potential release of vanadium during the firing of clay/ash mixtures

V	L.o.I. 900 °C (wt.%)	Initial content corrected C'_u (wt.%)		Final content in fired bricks C_f (wt.%)		Potential release Ψ (mg kg^{-1} of fired brick)
		Average	S.D.	Average	Wt.%	Average
L0A	16.0	0.01	0.00	0.02	0.01	< 50
L1A	16.9	0.17	0.01	0.17	0.01	< 50
L3A	16.0	0.34	0.01	0.33	0.01	100
L6A	16.7	0.67	0.02	0.66	0.01	100
L0B	16.0	0.01	0.00	0.01	0.01	< 50
L1B	16.9	0.17	0.01	0.18	0.01	< 50
L3B	16.0	0.34	0.01	0.33	0.01	100
L6B	16.7	0.67	0.02	0.64	0.01	300
L0C	16.0	0.01	0.00	0.02	0.01	< 50
L1C	16.9	0.17	0.01	0.17	0.01	< 50
L3C	16.0	0.34	0.01	0.34	0.01	< 50
L6C	16.7	0.67	0.02	0.65	0.01	200
S0D	5.3	0.02	0.01	0.02	0.01	< 50
S1D	5.6	0.21	0.01	0.22	0.01	< 50
S3D	6.6	0.42	0.02	0.42	0.01	< 50
S6D	7.8	0.79	0.02	0.81	0.01	< 50
S0E	5.3	0.02	0.01	0.01	0.01	100
S1E	5.6	0.21	0.01	0.21	0.01	< 50
S3E	6.6	0.42	0.02	0.38	0.01	400
S6E	7.8	0.79	0.02	0.78	0.01	100
S0F	5.3	0.02	0.01	0.02	0.01	< 50
S1F	5.6	0.21	0.01	0.20	0.01	150
S3F	6.6	0.42	0.02	0.40	0.01	200
S6F	7.8	0.79	0.02	0.79	0.01	< 50

4. Conclusions

The chemical stability of clay/ash mixtures is crucial for Orimulsion ash disposal in clay bricks. However, the brickmaking process, and especially the current industrial firings carried out at moderate temperatures, do not allow the complete inertization of ash. In effect, all magnesium and nickel, together with most vanadium, are immobilized in the crystal structures of silicates constituting the ceramic matrix; on the other hand, a large part of sulphur as well as a small but significant amount of vanadium remain in water soluble form. Furthermore, the firing reactions between clay and ash promote a mobilization of calcium and alkalis; consequently efflorescence is strongly increased. These phenomena appear to be unacceptable even for ash additions as high as 1.5%; there is, moreover, a tangible risk of sulphate attack to the mortars in brick masonry.

The thermal decomposition of sulphates constituting the Orimulsion ash may bring about considerable SO_x emissions during the firing of carbonate-free bodies and, in the case of carbonate-rich clays, may lead to the formation of remarkable amounts of calcium sulphate. This process is associated with a small vanadium release in both bodies. This critical situation cannot be overcome by managing the firing conditions, because a temperature increase augments soluble salts in the carbonate-rich body as well as leading to an increase in the gaseous release from the carbonate-free clay.

In conclusion, the Orimulsion ash recycling in brickmaking is feasible, but must be practiced with caution, as an addition as low as 1.5% is already able to worsen appreciably both the aesthetic appearance of products and the environmental impact of production. Therefore, maximum amounts of ash below 1% weight are strongly recommended.

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