Orimulsion fly ash in clay bricks—part 2: technological behaviour of clay/ash mixtures

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Abstract

In order to appraise the technological feasibility of the Orimulsion ash recycling in clay bricks, a laboratory simulation of the brickmaking process was carried out with various clay/ash mixtures up to 6% waste. Two different clays were selected and mixes were characterized by XRF, XRPD, TGA–DTA, TDA and PSD analyses. Plasticity, extrusion and drying behaviour, and mechanical strength, were determined on unfired mixtures, while shrinkage, water absorption, bulk density, modulus of rupture, pore size distribution, microstructure and phase composition were measured on fired bricks. Orimulsion ash caused some detrimental changes of technological properties of both unfired and fired products, concerning particularly plasticity, drying rate and drying sensitivity, porosity and colour. These effects were slightly different on the two raw materials, the carbonate-rich clay being less sensitive to the presence of ash with respect to the carbonate-free clay. In all events, drawbacks appeared to be tolerable, in technological terms, for low waste additions, approximately 1–2% ash. © 2002 Elsevier Science Ltd. All rights reserved.

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1. Introduction

This study is aimed at assessing the feasibility, in technological terms, of Orimulsion fly ash disposal and inertization in clay bodies used in brickmaking. The approach was basically a laboratory simulation of the industrial processing, which allowed the comparison of the technological behaviour and technical performance of ash-free bodies with respect to clay/ash mixtures. The first part of this work deals with the chemical and phase composition, physical properties and thermal behaviour of ash. Further considerations, concerning chemical stability of ash-bearing bricks, will be developed in the third part of this paper.

This investigation is the first attempt to recycle in brickmaking a peculiar, sulphate- and vanadium-rich waste. As a matter of fact, previous experiences of fly and bottom ash recycling in clay bricks were carried out exclusively on wastes from thermal power plants fed with coal, which produce basically silicatic ash.[1] These materials exhibit low amounts of the elements characterizing the Orimulsion ash: at maximum 4% MgO, 2% SO$_3$, 0.2% V$_2$O$_5$ and contents always below 0.1% for NiO.[1] Therefore, the chemical differences between the ashes from coal and from bitumen-in-water emulsion are so many to make their comparison insignificant, as well as poorly indicative are the results achieved adding coal fly ash to clay bricks.[1] The unique experiences carried out on sulphate-rich (up to 16.8% SO$_3$) and/or nickel-rich (up to 7.6% NiO) wastes concern slurries coming from water purification of:

   (i) galvanizing and metal working plants,[2]
  (ii) a plant performing anodic oxidation of aluminium,[3]
 (iii) a lamp factory.[3]

The laboratory tests performed introducing these slurries in clay bricks, in percentages between 2 and 30 wt.%, evidenced some strong limitations, mainly represented by the development of efflorescence and by intolerable changes of porosity, mechanical properties and firing shrinkage of bricks. The presence of slurry from metal galvanizing appeared to be acceptable up to 5 wt.%,[2] while in the case of slurries from anodic oxidation of

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aluminium and from the lamp factory the amounts tolerable are not over some percent.[3]

2. Materials and methods

The ashes taken into account 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. Two clay bodies, currently used in two brickworks located near the above-mentioned thermal power plants, were considered: body L (Lucera, Apulia) and body S (Porto Torres, Sardinia). These bodies were characterized determining: chemical composition by XRF–WDS (Philips, PW 1480) on pressed powder pellets; mineralogical composition by XRPD (Rigaku, Miniflex) with CuK_α radiation; particle size distribution by X-ray monitoring of gravity sedimentation (Micromeritics, SediGraph 5100).

For each brickwork, four different clay/ash mixtures (clay L + ash B; clay S + ash F) were experimented on: clay without waste (L0 and S0) and with the following additions of ash: 1.5% (L1 and S1), 3% (L3 and S3) and 6% (L6 and S6) in weight respectively.

The technological behaviour of mixtures was assessed during the body preparation and the shaping, drying and firing phases through a simulation, on a laboratory pilot line, of the industrial processing of clay bricks. In particular, the following working phases were carried out:

(i) clay grinding with a jaw crusher (< 20 mm) and a hammer mill (< 0.75 mm);
(ii) hand mixing of clay, ash and water, and successive storage for 7 days;
(iii) plastic extrusion of $100 \times 20 \times 10$ mm³ bars, with a pneumatic apparatus without vacuum;
(iv) drying at ambient temperature in non-controlled atmosphere for 48 h and successively with an electric oven at 100 °C for 24 h;
(v) firing in an electric chamber kiln, in static air, with three different thermal cycles for each series of mixtures: one analogous to the industrial firing and two designed in order to increase the time and/or the maximum temperature (Fig. 1).

Unfired and fired products were characterized determining:

- working moisture (ASTM C 324);
- plasticity by means of Atterberg's consistency limits (CNR UNI 10014): plastic limit (W_P), liquid limit (W_L) and plastic index ($I_P = W_L - W_P$);
- drying and firing shrinkage (ASTM C 326);
- Bigot's curve[4] with Adamel apparatus on $80 \times 20 \times 10$ mm³ moulded bars, with calculation of a drying sensitivity index;[5]

- drying behaviour of extruded cylinders (200 mm long×30 mm diameter) enveloped with an aluminium film taking care to leave uncovered the basal faces, in an oven at 80 °C (30–40% R.H.) for 6 h; the difference of moisture between the central and the outermost parts of cylinders allowed the calculation of an index of susceptibility to ruptures[6] as the weight change served to estimate an average drying rate expressed in mg cm⁻² h⁻¹;
- modulus of rupture of dry and fired samples (ISO 10545-4);
- water absorption, open porosity, bulk density and apparent specific weight (ISO 10545-3);
- pore size distribution between 0.001 and 100 μm, by means of mercury intrusion porosimetry (Carlo Erba, Porosimeter 2000);
- microstructure of fired bricks through scanning electron microscopy observations (Cambridge, Stereoscan 360) on graphite sputtered polished sections;
- colour, using a spectrophotometer with a d/8° geometry (Hunterlab, MSX P-4000);
- quantitative phase composition by XRPD (Rigaku, Miniflex, CuK_α radiation) with the RIR method;[7]
- thermodilatometric analysis of unfired bodies (Netzsch, 402 E) on cylindric specimens (40 mm long and 3 mm in diameter) obtained from the extruded bars, with thermal gradient of 2 °C/min up to about 900 °C.

3. Results and discussion

3.1. Body composition and preparation

The clay bodies exhibit very different compositions (Table 1) which well represent two widespread typologies in the Italian industry.[8] In particular, body L contains similar amounts of the clay, quartz-feldspathic and carbonatic components. Clay minerals are represented by illite, kaolinite and chlorite, with minor quantities of randomly interstratified illite/smectite. Both plagioclase and K-feldspar are present in the feldspathic fraction, while among carbonates, calcite is neatly prevailing over dolomite. The particle size distribution is rather selected (50% of particles are between 1 and 20 μm) and characterized by a clay fraction prevailing over silty particles with just a small percentage of sand. On the other hand, body S is prevalently made up by clay minerals, essentially represented by kaolinite and illite in the same proportions plus a fair amount of muscovite and iron oxide-hydroxides, and eventually a small contribution of chlorite. Quartz is abundant and is associated to modest percentages of both plagioclase and K-feldspar. Carbonates are completely absent. The particle size
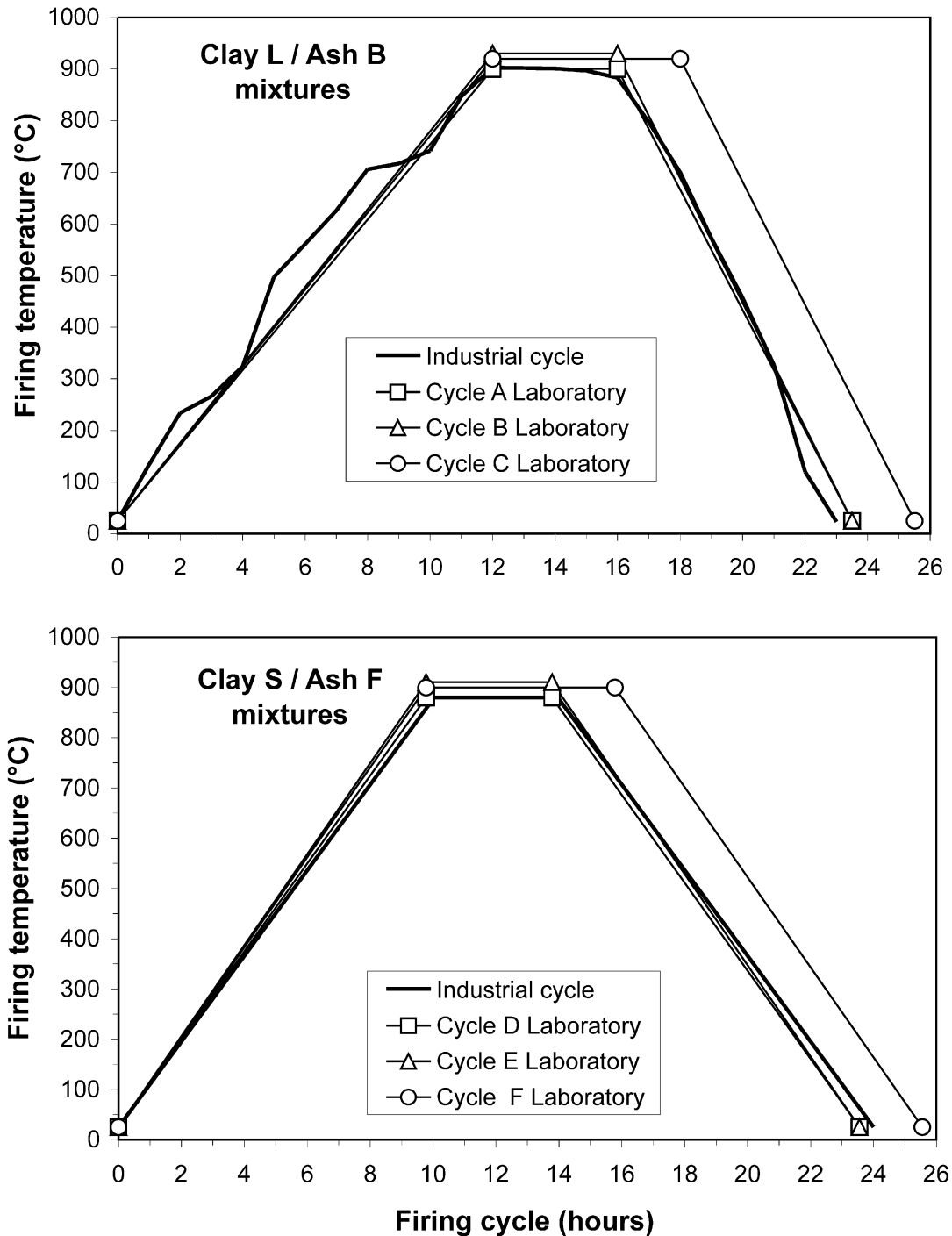
Fig. 1. Time versus temperature cycles adopted in the laboratory firings of clay L + ash B mixtures (cycles A, B and C) and clay S + ash F mixtures (cycles D, E and F).

distribution is characterized by both an abundant sandy fraction and a noteworthy amount of submicronic particles (49% < 1 µm); this circumstance indicates a very scarce size selection of particles.

The formulation and the calculated chemical composition of clay/ash mixtures are summarized in Table 2. Additions of 6% ash brought about particularly an increase of SO_3 (3.3% in L6 and 2.8% in S6), VO_2 (1.1% in L6 and 1.4% in S6) and, to a lesser extent, NiO (maximum 0.2%).

During body preparation, distributing uniformly the ash into the clay body was rather difficult, even operating in the laboratory with materials dried at 100 °C. In fact, the ash is very hygroscopic and it tends easily to form

agglomerates of some millimetres in diameter. Once the addition of water to the clay/ash mixture is completed, and especially after adequate storage, no particular dishomogeneities can be seen in the body, except for the occurrence of blackish concentrations, obviously more frequent in the mixes containing more ash.

Table 1
Chemical and mineralogical composition, and particle size distribution of the two bodies used in clay/ash mixtures

Wt.%	Clay body L	Clay body S
SiO_2	47.53	60.23
TiO_2	0.61	0.96
Al_2O_3	11.99	20.26
Fe_2O_3	4.38	7.10
MnO	0.10	0.16
MgO	2.56	0.72
CaO	13.59	0.27
Na_2O	1.05	0.56
K_2O	2.19	3.50
P_2O_5	0.16	0.07
L.o.I. (1000 °C)	15.84	6.17
Organic matter	0.75	0.02
Illite	15	21
Muscovite	Traces	7
Kaolinite	12	20
Chlorite	10	3
Quartz	21	29
K-feldspar	6	5
Plagioclase	9	6
Calcite	22	Absent
Dolomite	5	Absent
Iron oxi-hydroxides	Traces	7
Accessories	1	2
Median particle size	1.9 μm	1.1 μm
Fraction > 63 μm	6	24
Fraction 4–63 μm	31	14
Fraction < 4 μm	63	62
Fraction > 20 μm	14	28
Fraction 2–20 μm	35	16
Fraction < 2 μm	51	56

3.2. Shaping behaviour

The introduction of ash B made the bodies L more plastic, with a slight increment of the working moisture and a certain improvement of the "fluidity" during extrusion. In contrast, ash F had the effect of reducing the plasticity of bodies S, with less working moisture for
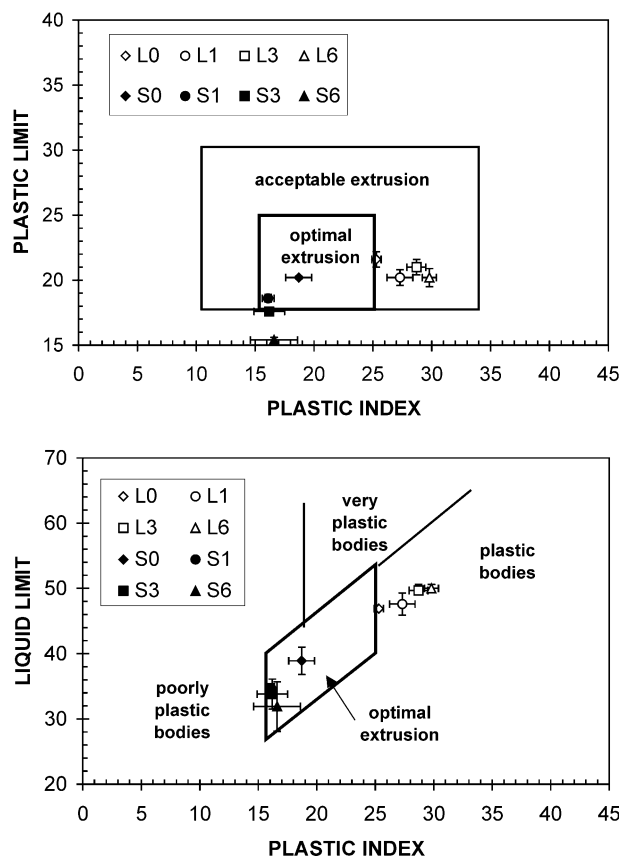

Fig. 2. Prediction of the extrusion behaviour of clay/ash mixtures on the basis of their Atterberg's plasticity limits.[9]

Table 2
Calculated chemical composition of the clay/ash mixtures (wt.%)

	Clay L+ash B				Clay S+ash F			
	L0	L1	L3	L6	S0	S1	S3	S6
Ash %	0	1.5	3	6	0	1.5	3	6
SiO_2	56.48	55.70	54.92	53.35	64.19	63.24	62.28	60.37
TiO_2	0.72	0.72	0.71	0.70	1.02	1.01	1.00	0.98
Al_2O_3	14.25	14.08	13.90	13.56	21.59	21.27	20.95	20.32
Fe_2O_3	5.20	5.16	5.12	5.04	7.57	7.48	7.38	7.20
MnO	0.12	0.11	0.11	0.11	0.17	0.17	0.17	0.16
MgO	3.05	3.31	3.58	4.12	0.76	1.09	1.41	2.07
CaO	16.15	15.94	15.73	15.32	0.28	0.31	0.34	0.40
Na_2O	1.25	1.24	1.23	1.21	0.60	0.60	0.60	0.60
K_2O	2.60	2.56	2.53	2.45	3.73	3.67	3.61	3.50
P_2O_5	0.19	0.18	0.18	0.18	0.08	0.08	0.07	0.07
SO_3	0.55	1.23	1.91	3.28	0.04	0.73	1.42	2.79
VO_2	0.03	0.29	0.54	1.06	<0.01	0.34	0.68	1.35
NiO	<0.01	0.04	0.08	0.16	<0.01	0.05	0.11	0.22

the mix S6, and a certain worsening of the rheological properties. In both series, however, the bodies appeared to be progressively softer and stickier as the ash percentage increased.

These qualitative observations are confirmed by the Atterberg's limits (Fig. 2). As far as L mixtures are concerned, the presence of ash did not influence significantly the plastic limit, but produced, on the other hand, an increase of both the liquid limit and the plastic index. These variations correspond, in terms of shaping behaviour, to a progressive shift from the optimal field, at which border is situated the ash-free body, towards values typical of very plastic mixes (Fig. 2).[9] In the

bodies S, on the contrary, the occurrence of ash decreased appreciably the plastic limit and, to a lesser extent, the liquid limit; the effect on the plastic index was a plain diminution passing from S0 to S1, without further substantial changes in S3 and S6. This trend corresponds to a progressive shift towards values typical of poorly plastic mixes, though the bodies S1 and S3 are plotted within the optimal field; only the body S6 seems to have an insufficient plasticity, at least in terms of plastic limit (Fig. 2).[9]
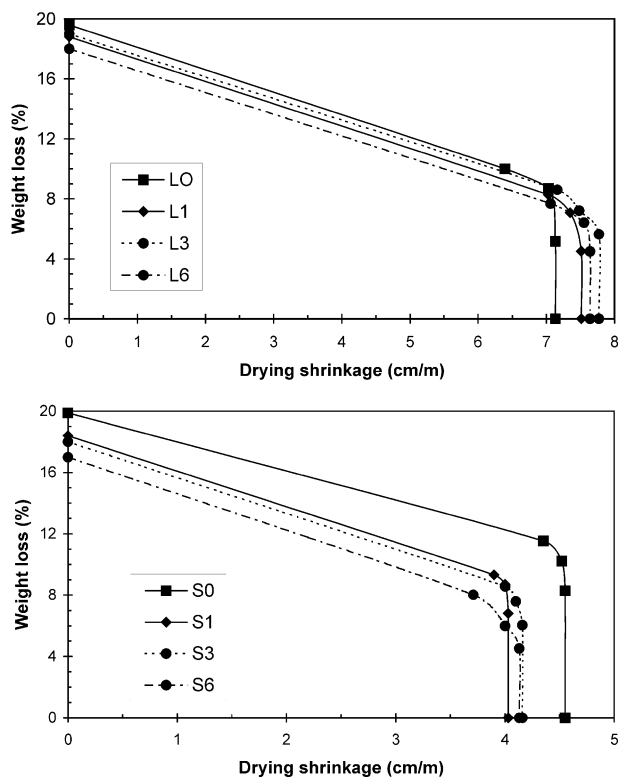

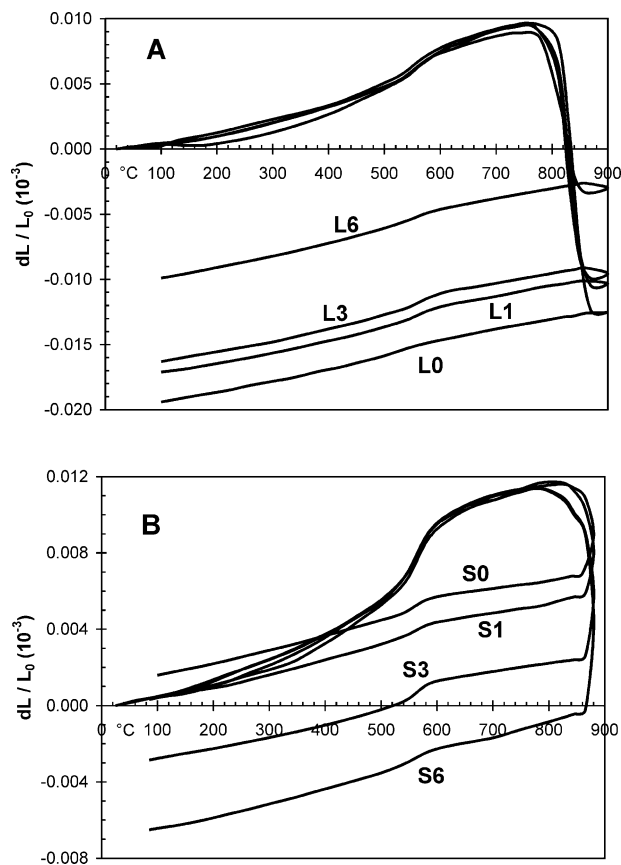Fig. 3. Bigot's curves (drying shrinkage versus weight loss) of clay/ash mixtures.

Fig. 4. Thermodilatometric curves of clay L + ash B mixtures (A) and clay S + ash F mixtures (B).

Table 3
Drying behaviour of the clay/ash mixtures

Mix	Working moisture (wt.%)	Dry modulus of rupture (MPa)		Susceptibility to ruptures (adim.)		Drying rate (mg cm^{-2} h^{-1})		Drying shrinkage (cm/m)		Weight loss with shrinkage (%)		Drying sensitivity (adim.)	
		Average	S.D.	Average	S.D.	Average	S.D.	Average	S.D.	Average	S.D.	Average	S.D.
L0	26.3	12.8	1.3	17.5	0.1	167	12	7.1	0.2	10.8	0.2	0.77	0.02
L1	23.7	14.4	1.5	8.8	1.6	97	6	7.5	0.2	11.2	0.2	0.84	0.02
L3	23.8	15.6	1.2	7.0	0.3	94	1	7.8	0.2	11.5	0.2	0.89	0.02
L6	24.3	16.2	2.6	3.4	1.0	88	4	7.6	0.2	11.3	0.2	0.86	0.02
S0	21.3	4.6	0.3	10.5	2.1	147	10	4.5	0.2	8.8	0.2	0.40	0.02
S1	22.2	5.1	0.2	8.5	0.9	156	16	4.0	0.2	9.5	0.2	0.38	0.02
S3	21.0	8.2	0.2	2.6	0.7	72	9	4.2	0.2	9.1	0.2	0.38	0.02
S6	20.0	12.0	1.0	0.3	0.1	48	2	4.1	0.2	6.9	0.2	0.29	0.02

3.3. Drying behaviour

The ash affected conspicuously the behaviour during the drying phase, though with different effects on the two series of bodies. The Bigot's curves exhibit the two characteristic phases of the drying process: (i) initial weight loss with shrinkage and (ii) successive weight loss with no more shrinkage. The wider the phase 2 in respect of phase 1, the easier is the drying and vice versa (Fig. 3). In mixes L, progressive increments of shrinkage and weight loss with shrinkage can be remarked passing from body L0 to L3; in contrast, the body L6 denoted a slight diminution of the above-mentioned parameters, which, however, are neatly higher than those of the ash-free body. In the case of bodies S, the effect of the ash is represented by a small decrease of shrinkage, in respect of body S0, as well as by a slight increase of the weight loss with shrinkage in the bodies S1 and S3.

Furthermore, increasing the ash percentage the following occurred (Table 3):

- moderate changes of shrinkage, with opposite trends in the two series: increasing contraction in bodies L and vice versa in bodies S;
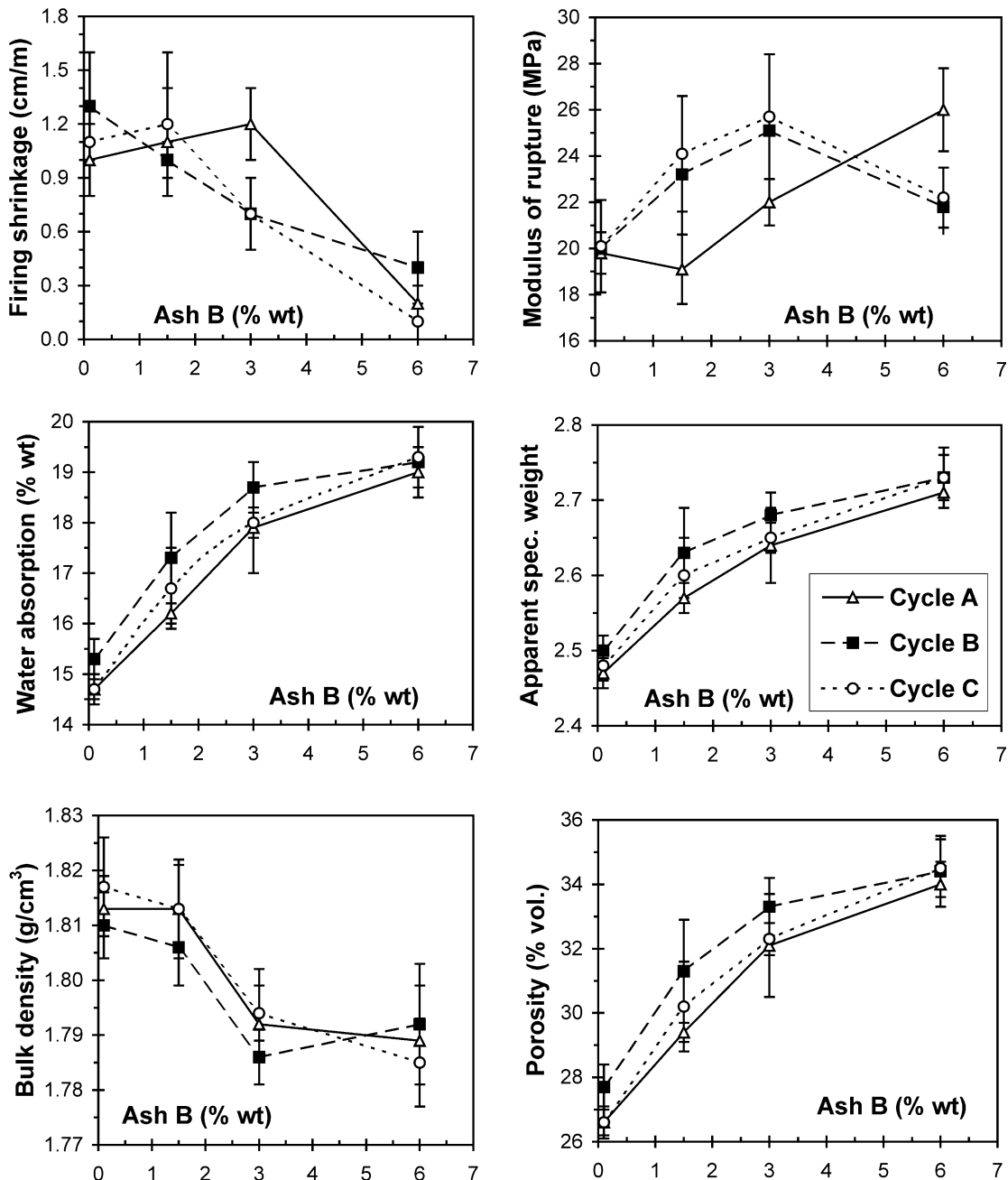

Fig. 5. Firing behaviour of clay L in function of ash B additions.

- a remarkable augment of the modulus of rupture, which passed from about 13 MPa to over 16 MPa in bodies L and from about 5 to 12 MPa in bodies S;
- a noteworthy decrease of the susceptibility to ruptures, which went from about 17 down to 3 (bodies L) as well as from approximately 10 to zero (bodies S). This index exprimes in practice the distribution of the moisture in the specimen during drying: the lower is the index, the more uniform is the water content in the brick, with minor differential shrinkages and, therefore, less possibilities of ruptures during the drying process;[6,11]
- an appreciable diminution of drying rate, which decreased from about 170 to 90 mg/h cm^{-2} (series L) and from approximately 150 to 50 mg/h cm^{-2} (bodies S), though the trends of drying rate are somehow different in the two series;
- an increment of drying sensitivity in bodies L (from 0.77 to 0.89) but a certain reduction in bodies S (from 0.40 to 0.29).

In conclusion, these results demonstrate a general worsening of the properties of bodies L during the drying process; in contrast, a certain improvement of drying behavi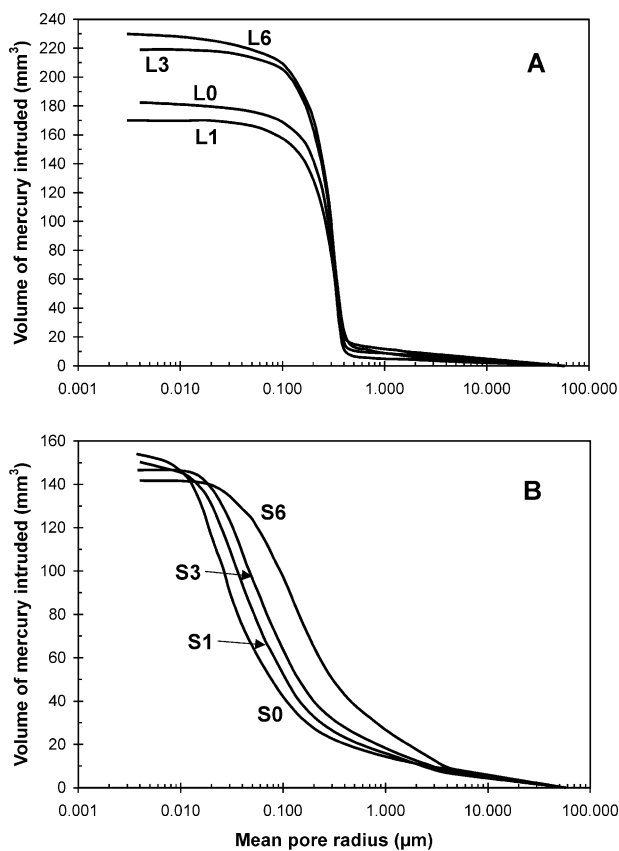our of bodies S appeared, though it is modest for ash additions as high as 1.5 and 3%, becoming appreciable in the mix containing 6%.[5,10,11]

3.4. Firing behaviour

The introduction of ash into the clay body caused various changes in both firing behaviour and properties of bricks, as it can be appreciated by the thermodilatometric analyses performed using thermal cycles analogous to the industrial ones (Fig. 4).

The trend of thermodilatometric curves is the same for every sample of each series; the influence of ash was recorded appreciably in the heating phase, between approximately 750 and 850 °C (bodies L) or between 780 and 890 °C (bodies S). In mixtures L, the presence of ash contrasted the clear tendency to shrink exhibited by the body L0: already the addition of 1.5% ash determined a slight diminution of shrinkage, which became especially noticeable in the mix L6. Moreover, the larger the waste addition, the earlier the beginning

Fig. 6. Porosimetric curves of clay L + ash B mixtures (A) and clay S + ash F mixtures (B).
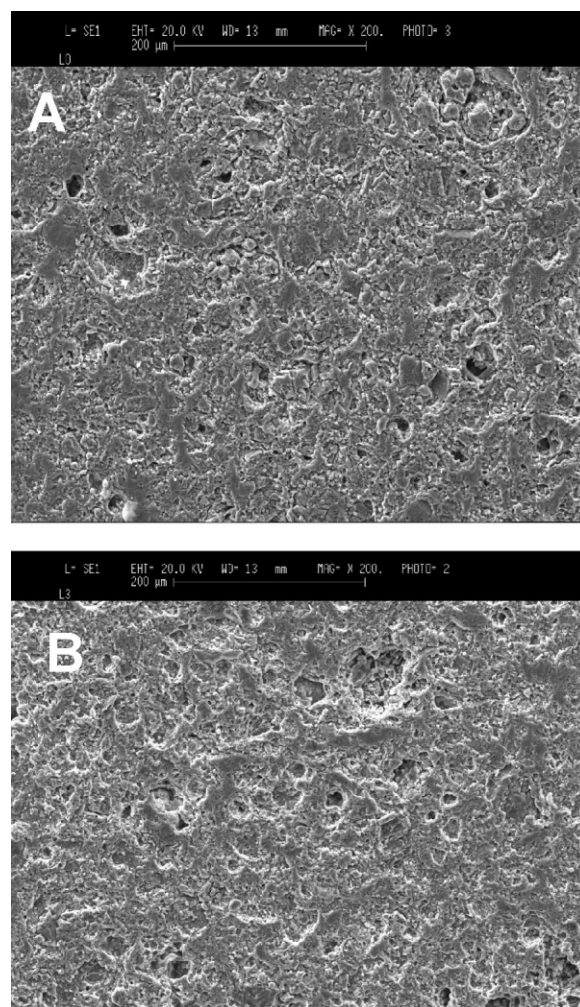

Fig. 7. SEM photomicrographs on section of (A) brick L0 and (B) brick L3 (bar = 200 μm).

of the shrinkage phase, that shifted from about 800 (L0) to about 770 °C (L6). In the bodies S, the higher the ash content, the larger the shrinkage. In these cases too, the ash anticipated the beginning of the above-mentioned shrinkage phase, that shifted from about 840 (S0) to about 760 °C (S3 and S6).

3.4.1. Firing behaviour of clay L + ash B mixtures

In the laboratory trials, firing shrinkage did not change significantly with the addition of 1.5% ash, in all three thermal cycles. The body L3 denoted conversely a slight decrease of shrinkage in cycles B and C, while the mixture L6 shrank much less than the others in every firing condition (Fig. 5).

Concerning the modulus of rupture, cycle A produced a different effect with respect to firings B and C; these latter exhibit similar results (Fig. 5). In fact, in the cycle A bodies L0 and L1 present analogous values and a progressive increment of the mechanical strength occurred only passing to bodies L3 and L6; in the other two thermal cycles, a clear increase of the modulus of rupture arose moving from L0 to L3, followed by a deterioration of the mechanical properties in the body L6.

Orimulsion ash promoted a progressive and regular increment of open porosity and water absorption, this latter growing from around 15% (L0) to 19% (L6). This trend is found in every firing cycle, though it is more conspicuous in cycle B, carried out at a higher temperature. On the other hand, bulk density did not change substantially with the addition of 1.5% ash, but percentages of 3 and 6% lowered it distinctly from approximately 1.81 to 1.79 g cm^{-3}. Apparent specific weight remarkably increased from 2.45–2.50 (L0) up to 2.70–2.75 (L6), suggesting that ash fostered the formation of denser phases (Fig. 5).

Porosimetric analyses pointed out that the main difference among the four mixtures is constituted by the amount of porosity, since no significant distinction can be made concerning the pore size distribution (Fig. 6). In effect, the mean pore diameter is around 0.6 μm in all samples. It is a small value that, however, is consistent with the typical pore size of the Italian bricks with the same composition as body L.[8] As a matter of fact, microstructural observations confirmed the increase of porosity due to the presence of ash in the body (Fig. 7).

The phase composition of fired bricks was appreciably modified already introducing 1.5% ash; further variations at higher ash percentages appear to be moderate (Table 4). In particular, the addition of ash promoted the development of calcium, magnesium and aluminium silicates (plagioclase, pyroxene, wollastonite, melilite) during firing, which grew from 58% (L0) to 66–68% (L1–L6); among these silicates, a clear increment of pyroxene and plagioclase is observed, in spite of wollastonite and melilite. On the other hand, the introduction of ash slightly diminished the quartz content, but it did not affect the other crystalline and amorphous phases.

Fired bricks present the same colouring after all the thermal cycles (Fig. 8). The effect of ash is a gradual shift from a "deep rose" (L0) to a "pale rose" (L1) to a "light yellow" (L3) until the variegated colour of L6, which displays yellowish zones alternated with reddish ones.
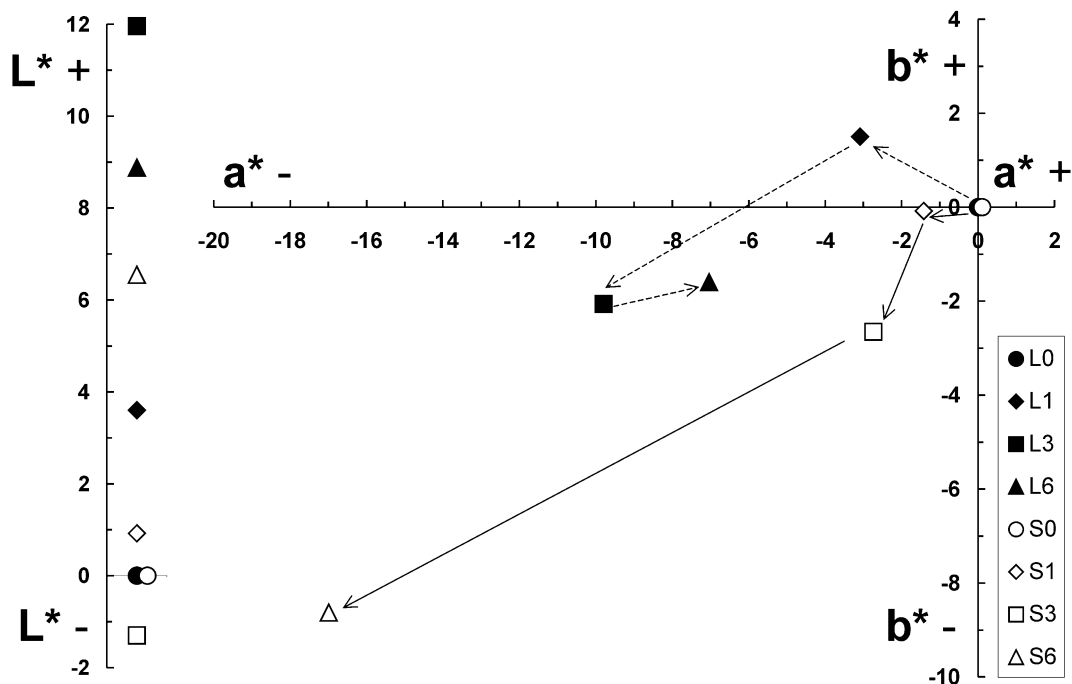

Fig. 8. Colour change of fired clay/ash mixtures, expressed in variations of CIE LAB parameters (ΔL^*, Δa^*, Δb^*).

3.4.2. Firing behaviour of clay S + ash F mixtures

In the laboratory simulations, firing shrinkage did not vary appreciably with 1.5% ash, in all three thermal cycles. On the contrary, an increase of shrinkage occurred in the bodies S3 and S6, moderate after cycle D and relevant after cycle E and F (Fig. 9).

The mechanical strength did not change remarkably with the addition of ash, ranging from about 11 up to 14 MPa (Fig. 9). Different trends can be noticed for the three thermal cycles with increasing ash contents: modest increments of modulus of rupture in cycles D and F,

but a gradual diminution of bending strength at a higher temperature (cycle E).

For water absorption and open porosity, the presence of ash had a scarce effect in cycle D, since going from S0 to S6 only limited changes were registered. Firings E and F provided similar results: i.e. ash promoted a progressive decrease of porosity, small up to 1.5%, then more conspicuous. The addition of 1.5% ash did not modify substantially the bulk density, while conversely the addition of 3 and 6% brought about a plain increase of density. On the other hand, the ash had a decisively
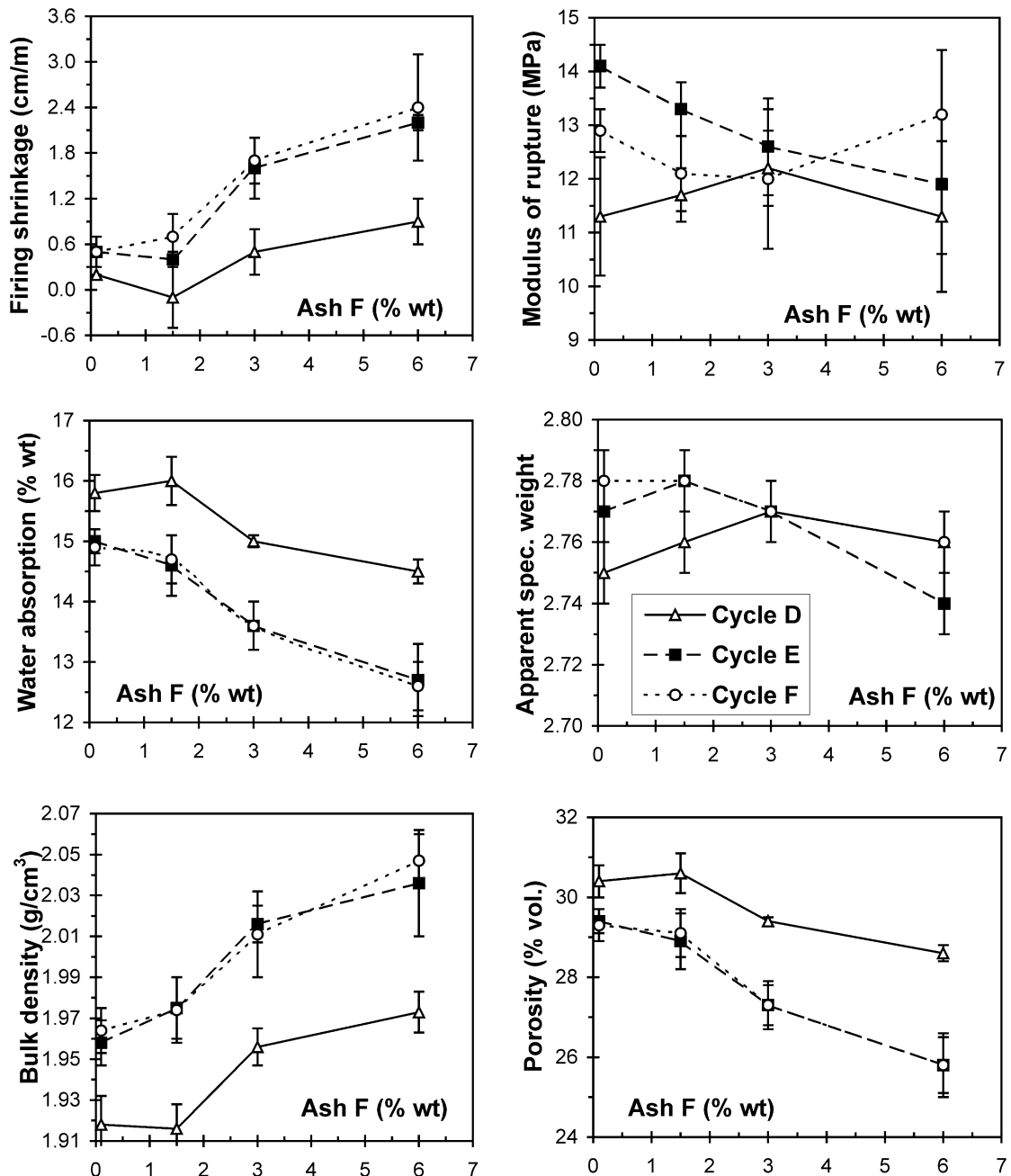

Fig. 9. Firing behaviour of clay S in function of ash F additions.

Table 4
Quantitative phase composition of bricks L (cycle A) and bricks S (cycle D)

| Wt.%	Clay L + ash B mixtures								Clay S + ash F mixtures							
	L0		L1		L3		L6		S1		S1		S3		S6	
	Average	S.D.	Average	S.D.	Average	S.D.	Average	S.D.	Average	S.D.	Average	S.D.	Average	S.D.	Average	S.D.
Quartz	15	2	12	1	13	1	10	1	42	4	35	4	29	3	44	4
K-feldspar	5	1	4	1	4	1	6	1	10	1	8	1	3	1	8	1
Plagioclase	19	2	22	2	26	3	27	3	Traces		Traces		Traces		Traces	
Pyroxene	15	2	26	3	27	3	29	3	13	1	3	1	5	1	5	1
Wollastonite	11	1	9	1	8	1	5	1	Absent		Absent		Absent		Absent	
Melilite	13	1	10	1	5	1	4	1	Absent		Absent		Absent		Absent	
Hematite	2	1	2	1	2	1	1	1	3	1	6	1	6	1	8	1
Spinel	Absent		Absent		Absent		Absent		Absent		Absent		Absent		4	1
Illite–mica	Traces		Traces		Traces		Traces		5	1	3	1	2	1	3	1
Amorphous	20	2	15	2	15	2	18	2	27	3	45	5	55	6	28	3
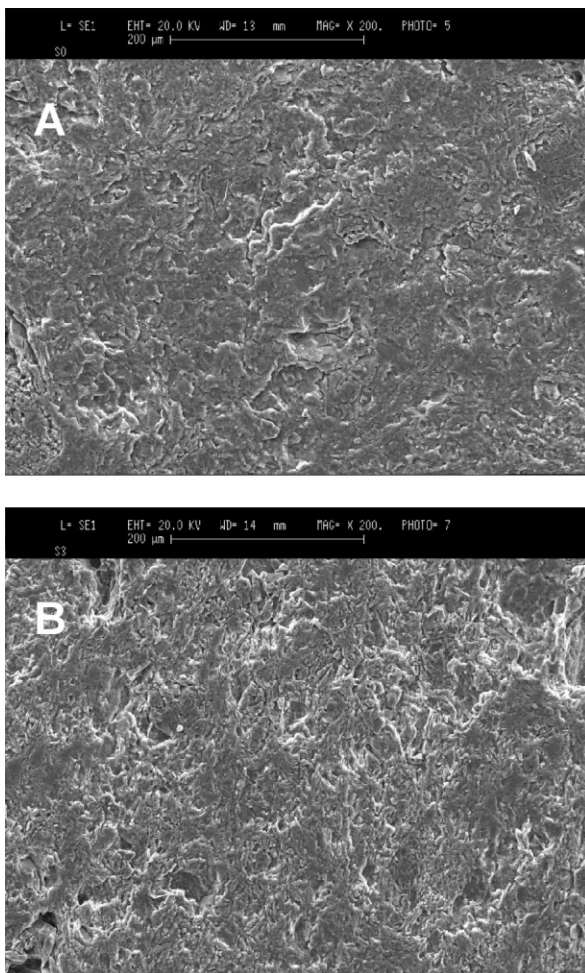
Fig. 10. SEM photomicrographs on section of (A) brick S0 and (B) brick S3 (bar = 200 μm).

poor effect on apparent specific weight, which is around 2.75–2.78 in all bodies for every firing condition, with at the most a slight decrease in body S6 (Fig. 9).

The porosimetric curves demonstrate that the waste played an important role both on the amount of poros-ity and the pore size distribution (Fig. 6) and this effect is proportional to the amount of ash added to the clay body. As this quantity grew, the open porosity decreased slightly, while the pore size distribution became gradually coarser. In fact, the mean pore diameter shifted from 0.08 (S0) up to 0.35 μm (S6). In particular, the microstructure of the ash-free brick seems to be more "compact", while the ash-bearing brick appears to be more porous, mainly due to the larger size of pores, that makes them more easily visible with the magnification used in the photomicrographs (Fig. 10).

Orimulsion ash caused a gradual modification of the phase composition up to 3%; at higher percentages an inversion of this trend occurred (Table 4). In particular, the ash seems to act as a "flux" in bodies S0, S1 and S3, promoting on one side the decompostion of quartz and potassic feldspar and on the other side fostering the formation of amorphous phases; conversely, body S6 exhibits a mineralogy similar to S0. Furthermore, the ash tended to inhibit the formation of pyroxene (hyperstene) during firing, in favour of spinel and hematite; the development of this latter phase explains the colour changes of bricks. In effect, the "orange red" colour of the body S0 became gradually browner going to bodies S1 and S3, after all the thermal cycles (Fig. 8). The bricks S6 are absolutely different: they exhibit a variegated aspect, with a reddish–brown tint mottled with yellowish–buff zones.

4. Conclusions

The utilization of Orimulsion fly ash in brickmaking caused a series of effects both on unfired and fired products, somehow depending on the characteristics of the clay bodies. As a matter of fact, a certain difficulty in mixing homogeneous clay with ash cropped up, since the waste is highly hygroscopic and mostly water-soluble.

In fine-grained and very plastic clays, such as body L, the ash increased further the plasticity, making advisable the introduction of a "tempering" material (for example sand) to achieve a suitable extrusion and balance the effect of the waste. In contrast, the ash worsened the plastic behaviour of bodies with a medium plasticity, such as sample S, suggesting a reduction of the amount of "tempering" materials currently added to the clay. For ash contents below 5% approximately, the worsening of the shaping behaviour appears to be acceptable in the industrial practice.[9,10]

In the drying phase, the ash coupled some positive effects (i.e. improvement of mechanical properties and reduction of the susceptibility to drying ruptures) with some drawbacks, mostly represented by a reduced drying rate. Other negative effects, such as a prolonged 'weight loss with shrinkage' phase and an increased drying sensitivity, concerned exclusively the clay L, being negligible in the body S. As a consequence, Orimulsion ash has tolerable influence on the drying behaviour of relatively coarse-grained bodies, but some relevant negative repercussions in the case of fine-grained clays, even for small ash additions.[5–11]

The effect on fired bricks depends to a large extent on the amount of ash introduced into the body. In particular, the addition of 1.5% ash seems not to deteriorate the material performances, while percentages as high as 3 or 6% induced several changes of the technological properties (firing shrinkage, mechanical resistance, porosity, and bulk density) slightly differing in the two clay types. An important limitation concerns a conspicuous change of aspect of bricks, which exhibited, for growing amounts of ash, a colouring progressively yellower and less homogeneous. An augment of the maximum temperature and/or firing time did not produce any significant improvement of the technological and aesthetic properties in the carbonatic mixes (bodies L), but it is detrimental in the carbonate-free ones (bodies S), with a too high shrinkage and a too low porosity.[10,12]

In conclusion, the recycling of Orimulsion fly ash in clay bricks is possible, with tolerable drawbacks, for additions of approximately 1–2wt.%. This statement is based exclusively on the technological behaviour, since any consideration regarding the chemical stability is concerned in the following part of this work.

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