PHYSICO-CHEMICAL EXAMINATION OF AGED BRICKS AND "COTTO" TO STUDY THE MECHANISM OF ALTERATION

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Abstract

Bricks and terracotta cornices from Church of S. Cristoforo in the Certosa of Ferrara, Italy, were studied.

Samples at different degree of alteration were observed carrying out the fol‐lowing analyses:

- morphological observation by S.E.M.
- elemental analysis by energy dispersive X-ray fluorescence,
- mineralogical composition by X-ray diffraction and thin-section observa‐tion,
- pore-size distribution by mercury porosimetry,
- soluble salts quantitative analysis.

Aim of the study is to individuate the difference between bricks and terra‐cottas and among differently altered samples in order to hypotize the mechani‐sms of alteration.

1. Introduction

In order to investigate the mechanisms of alteration of the ceramics em‐ployed as building and decorative materials some samples from Church of S. Cristo‐foro in the Certosa of Ferrara were studied.

The foundation stone was laid in 1452 (Gruyer, 1897); the church has a huge front, lined with symmetrical constructions ending in two cloisters; very elegant terracottas decorate the whole of the buildings. These terracottas are very often in a bad state of conservation (photo n.1) as well as the most of other "cotto" decorations and bricks, so extensively used in the town of Ferrara.

Four samples from the church of S. Cristoforo, have been studied. Each sample represented a different condition:

sample n.1 is a very decayed terracotta specimen from the cornice, that had been exposed to atmospheric agents,

sample n.2 is a terracotta specimen that had been exposed to atmospheric agents, but which is not visibly decayed,

sample n.3 is a terracotta specimen that had never been exposed to atmospheric agents, found in the loft, during the restoration works.

sample n.4 is a brick from the foundation.

"Cotto" samples are from the cornice on the North side of the church.

2. Experimental Part

2.1 X - Ray diffraction analyses

The analyses were carried out using a Siemens apparatus cristalloflex IV equipped with an X-Ray tube with a copper anticathode, a goniometer and a paper recorder.

The obtained results are given in table n.I, in which a semi-quantitative evaluation of the different phases is also given.

Samples n.1,2 and 3 have the same qualitativ composition: quartz, calcite, anorthite, hematite (traces), micas-illites.

Sample n.1 shows also probable traces of paligorskite. External and internal parts of samples n.1 and 2, were analysed separately; the only important differences are: gypsum is more concentrated on the surfaces of the pieces (in sample n.1 it is practically absent in the internal part). Micas-illites are not detectable in the external part of sample n.2, probably due to a higher temperature reached on the surface during the firing. This surface has also a deeper red collor in comparison with the core.

Sample n.4 has a higher content of calcite and doesn't show the presence of clays.

XRD analyses were repeated on samples submitted to increasing firing temperatures from 500°C to 850°C with steps of 50°C.

In samples n.1,2,3 the reflexes of micas-illites disappear between 750°C and 800°C. That indicates a firing temperature lower than 800°C.

In the case of samples n.4, supposing the use of the same raw clay material, the presence of calcite indicates a firing temperature lower than 900°C and higher than 750°C.

2.2. Energy Dispersive X-Ray Analysis

The elemental composition of the four samples was obtained by means of an Energy dispersive X-Ray Spectrometer (EDS). For this purpose the samples were ground to pass a 40 mesh sieve (420 μm), mixed 10% w/w of H_3BO_3 (Kim, 1981) and pelleted in an evacuable die under vacuum at a pressure of 15,000 psi for about 2 minutes. Each finished pellet, of 13 mm diameter, weighed about 600 mg. Duplicate pellets were prepared for each sample.

The pellets were mounted on SEM stubs and carbon coated for electrical conductivity. The analysis was carried out on 10 or more 1 mm^2 areas on each pellet at 20 KV for 200 seconds.

A standardless routine for the calculation of the concentration of the elements was used as we were mainly concerned with a comparative study of the four samples.

The values obtained, reported in table II, were averaged and the standard deviations obtained ranged from 0.1 for Al to 0.4 for Si, the major constituents (12.0% and 48.0% respectively), and from 0.1 for K to 0.3 for S, the minor constituents (4.5% and 0.6-3.3% respectively). These values agree with the reported literature (Kim, 1981) values for this type of analysis.

Through analysis of variance (Woolf, 1968) F values were calculated for pairs of samples to test for significant differences between the concentrations of some of the elements in the sample, i.e., S and Si. It was found that at a 95% confidence level there was a significant difference in the concentration of S in all the samples. The spread of the data obtained for S can be explained by the fact that: (a) atmospheric SO_2 contributes a significant amount of the total S found, (b) alkaline sulfates and also gypsum are soluble and therefore capable of migrating in the "cotto" whenever water is present. On the other hand, o significant differences were found for the concentration of Si at this confidence level.

2.3. Pore-size distribution measurements

A mercury porosimeter, Carlo Erba series 1500, was employed. The field of application of the instrument ranges from pore diameters of approximately 0,01 microns to 100 microns.

The technique used and the way of expressing result have been standardized by the Italian NORMAL Committee (NORMAL, 1980) the result are given by:

$P\% = V_c^{max} \rho a \ 100$ where:

ρa = bulk density of the sample (g/cm^3)

V_c^{max} = maximum value of mercury penetrated, per unit mass into the sample (cm^3/g)

The pore-size distribution is expressed as V% correspondig to pores with diameter within fixed intervals. The results are given in table III.

The results reported in tables n.I and 2, indicate that, excluding sample n.4 (brick from the foundation), all the samples have the same raw composition, and were fired at the same temperature.

On the base of these results we can consider the samples n.1 and n.2 (exposed to the atmosphere) as alterated in respect of sample n.3 (not exposed).

The alteration seems to produce an increase of the integral open porosity (P%), a considerable decrease of the finer pores and, correspondently, an increase of the coarser ones.

Pore size distribution of sample n.3 is a bimodal one (peacks at $0.1-0.2\,\mu$m and at $1-2\,\mu$m), while in samples n.1 and 2 the distribution becomes flatter.

Samples n.4 has a higher P % and a different distribution with only one peack at $1-2\,\mu$m. The observed structural differencies (in respect to sample n.3) can be due to the slightly different composition, to an initial alteration and to the higher firing temperature.

This last hypothesis seems to be confirmed by the results obtained on fragments of sample n.3 submitted to a new firing process at 850°C and at 950°C.

In fact P % changes from 43% to, respectively, 51% and 65%. The firing process increases the percentage of coarses pores and flattens the distribution.

These results confirm also the hypothesis on firing temperature based on the XRD results and are in agreement with some bibliographic references (Mamillan, 1979), (Peruzzi, 1980).

Sintering processes, which produce a lowering in porosity with the increase of firing temperature (Dunn, 1976), don't take place in this range of firing temperature.

2.4. Observation of thin sections

These observations, carried out using a Leitz mineralogical microscope Dialux Pol, confirm the similarity of samples n.1, 2 and 3.

The minerals of the filler are similar in composition and in grain size (the most of them seem to be in the range 0,25 - 0,12 mm and are rather well sorted).

The % in volume of the filler is rather high, between 30 and 60 %. The porosity is very high; it seems to be due mainly to the contact surfaces between clay and filler and secondly to the clay matrix itself.

The sample n.4 has a higher content of calcite which, differently from the

other samples, has crystals rather large in size; these crystals very often fill the fractures of the clay body or surround some nodules of "chamotte". In comparison with samples n.1 and 3 the samples n.4 has a lower micas content and a lower homogeneity.

2.5. Scanning Electron Microscopy Observations

The samples were examined in fracture surface and from this study evidence can be found for the type of decay that has occurred in the deteriorated specimen. Figures 1A and B exemplify the difference between an undeteriorated specimen (n.2) and a deteriorated one (n.4). What can be observed from these micrographs is that there is a breaking up of the matrix of the "cotto" with consequent flaking and breaking loose of the smaller mineral grains held together by the matrix. How this occurred can be seen from the next series of micrographs.

In Figures 2A and B, we have a comparison of the unexposed "cotto" sample (n.3) to the exposed but not as yet visibly decayed specimen (n.2). The region compared in this last specimen is a fracture surface close to the exterior, exposed side of the specimen and therefore more open to the action of atmospheric agents. Even a cursory examination of the figures shows the effect of acid pollutants by the etching of the gypsum grains in the exposed sample. Furthermore, the presence of other air pollutants is evidenced by the large amount of fly ash present in this sample.

When the "cotto" has been exposed for longer periods of time to the action of acidic air pollutants, the attack will also make itself felt on the glassy matrix, the binding material that holds together the mineral components of the "cotto". Figures 3A and B show a comparison between a sample exposed but not decayed (n.2) and the deteriorated specimen (n.1). In this last specimen it is of interest to note the cracks and general decay of the glassy matrix that surrounds the clay particles. There is a pronounced flaking and loosening up of the embedded quartz and feldspar grains.

Finally, Figures 4A and B compare an unexposed specimen (n.3) to an exposed and deteriorated one from the cornice (n.1). The unexposed specimen show a fairly uniform glassy matrix binding together the fused clay particles and other mineral grains. The decayed specimen shows the deterioration and weathering away of the glassy matrix with the consequent exposure of poorly fused together clay particles.

2.6. Water soluble salts analyses

The analyses were carried aut on powders obtained from the external surfaces of the samples. The extraction of water soluble salts was perfomed following the temptative recommendation RILEM (doc. 82/39, 1982). The analyses of $SO_4^=$, Cl^-, NO_3^-, NH_4^+, and Ca^{++} were carried out using an Autoanalizer Technicon II following colorimetric and turbidimetric metodologies; the analyses of NA^+ and K^+ were carried out using an Elvi Flame Photometry, equipped with interferential filters. The result of these analyses are reported in table n. IV.

The sample n. 3, not exposed and not deteriorated "cotto", has the lowest content of soluble salts. The amount of these salts increases passing from the sample n.4 (brick from the foundation) to n.1 and 2, respectively very altered and not visibly altered samples.

Concerning the type of salts, nitrates are in a very low concentration in all the samples (nitrite are are non-detectable) as well as chlorides even if the last ones are in a slight higher amount in the exposed sample (n.1 and n.2). amount of cations seems to be mostly related to the amount of sulphate ion even if they are in a slight excess. The unknown anions that could balance the remainder are probably the carbonate and bicarbonate which, however were not mesured. The higher sulphate contents of sample n.2 in respect to that of sample n.1, visibly more altered, seems to indicate that the alteration produces the subsequent elimination of the parts reacher in sulphates.

3. Conclusions

The results obtained from the different analyses indicate a good similarity among all the studies samples concerning their raw materials. In fact, the chemical and mineralogical composition of the "cotto" samples (n.1, 2 and 3) and of the brick (n.4) are very similar, nevertheless, the manifacture was slightly different. The decorative "cotto" was fired at a temperature lower than that used for the brick; this one has a higher calcite content, with a larger crystal size, and, moreover, a certain amount of "chamotte" was mixed to the clay minerals.

These differences in the manufacturing process influence the structural caracteristics as shown by the porosimetric analyses.

Concerning the alteration process, the brick from the foundation seems to be in a first step of deterioration not yet visibly valuable but probably related to the presence of water soluble salts, even if in a low amount.

The main cause of deterioration in the particular case of the "cotto" from the Church of S. Cristoforo della Certosa seems to be an attack by the acid components of air pollutants such as SO_2. The first step in the attack is against the $CaCO_3$ present in the "cotto" if it is not covered, and thus protected, by the glassy matrix (see Fig. 2B).

After these reactions, and at a much lower rate, follows the attack on the glassy matrix (Lewin, 1979) and any feldspar components (Berner, 1982) (Lewin, 1981) present in the "cotto". The fact that there is no significant change in the concentration of Si from an unexposed specimen to a decayed one is evidence for the slowness of this attack. The partial dissolution of the glassy phase weakens the mechanical strength of the bond between the fused booklets of clay particles and other mineral grains. Thus, when the "cotto" is exposed to any stress such as water freezing in the pores, crystallization of salts (see Fig. 3A for the presence of NaCl crystals even in the not visibly decayed sample), or thermic variation with the consequent differences in expansion and contraction of the components of the "cotto", the glassy matrix will crack (see Figs. 3B, 4B) thus exposing more material to attack. The increased porosity will favor a faster decay throught all of the above mentioned factors.

To sum up, the most important factors in the structural deterioration of "cotto" appear to be the joint effect of acid leaching and mechanical stress.

Acknowledgments

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TABLE I - X-Ray Diffraction Analyses

SAMPLE		QUARTZ	CALCITE	ANORTHITE	HEMATITE	MICAS-ILLITES	PALYGORSKITE	GYPSUM
1	Ext.	+++	+	+	±	±	±	±
1	Int.	+++	+	+	±	±		
2	Ext.	+++	+	+	±			+
2	Int.	+++	+	+	±	±		
3		+++	+	+	±	±		
4		+++	++	+	±			

+++ : very large amounts

++ : large amounts

+ : presence

± : traces

TABLE II - Energy Dispersive X-Ray Analyses *

SAMPLE	WEIGHT %			
	Si	Al	K	S
1				2,0±0,2
2	48,0±0,4	12,0±0,1	4,5±0,1	3,3±0,3
3				1,0±0,1
4				0,6±0,1

* these results, obtained with a standardless routine analysis, cannot the compared with those reported in table IV.

TABLE III - Pore-Size Distribution

SAMPLE	1	2	3	3 fired at 850°C	3 fired at 950°C	4
ρ_a (g/cm³)	1,63±0,02	1,58±0,02	1,62±0,02	1,46±0,01	1,47±0,01	1,55±0,02
P%	44±3	47±1	43±1	51±2	65±3	52±3
V% d<0,05 μm	14	11	16	8	19	15
V% 0,05<d<0,01 μm	5	3	16	2	1	3
V% 0,1<d<0,2 μm	8	4	30*	2	2	4
V% 0,2<d<0,4 μm	10	4	11	5	2	7
V% 0,4<d<0,6 μm	6	5	2	7	2	6
V% 0,6<d<0,8 μm	5	5	1	3	4	7
V% 0,8<d<1 μm	4	5	1	4	4	6
V% 1<d<2 μm	24*	21	13*	17	11	36*
V% 2<d<4 μm	15	29*	4	31*	28*	8
V% 4<d<10 μm	3	7	1	16	17	2
V% d>10 μm	6	6	5	5	10	6

* Peack in the pore size distribution

220

TABLE IV - Quantitative determination of water soluble salts (weight %)

SAMPLE n.	$SO_4^=$	Cl^-	NO_3^-	NH_4^+	Ca^{++}	Na^+	K^+
1	1,0	0,2	<0,1	<0,1	1,3	1,3	0,2
2	10,1	0,2	"	"	6,9	0,9	0,1
3	<0,1	<0,1	"	"	n.d.	1,0	0,2
4	0,2	<0,1	"	"	0,5	0,5	0,1

Photo n.1 - Ferrara - Church of S. Cristoforo in the Certosa.
Detail of deteriorated "cotto" cornice.
(Photo by Arch. Cesari, Comune di Ferrara)
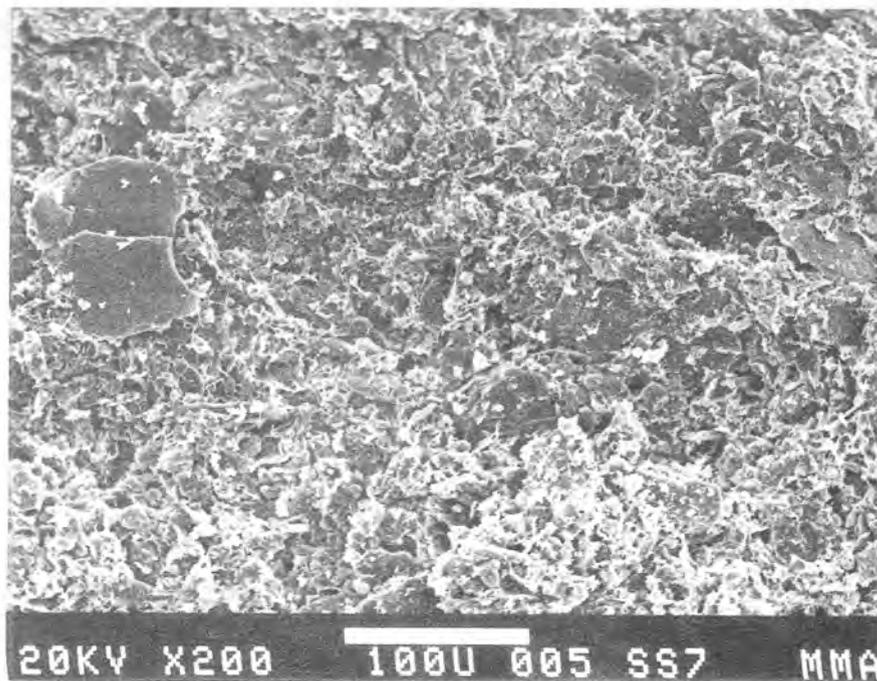
Figure 1A. Sample n.2 – Fracture surface of undecayed specimen of cotto from the cornice.
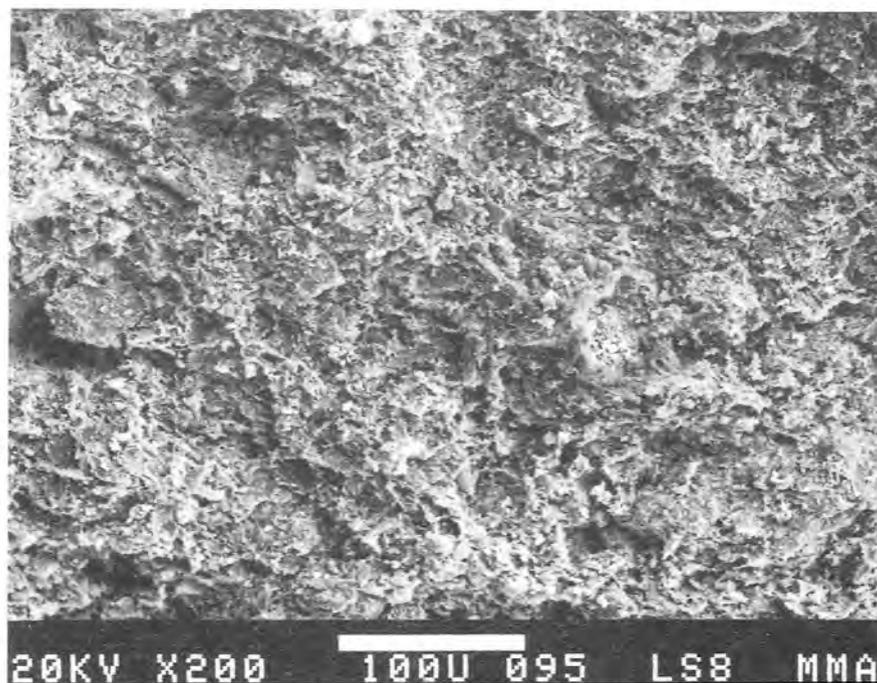
Figure 1B. Sample n.4 – Fracture surface of decayed cotto from the foundation.
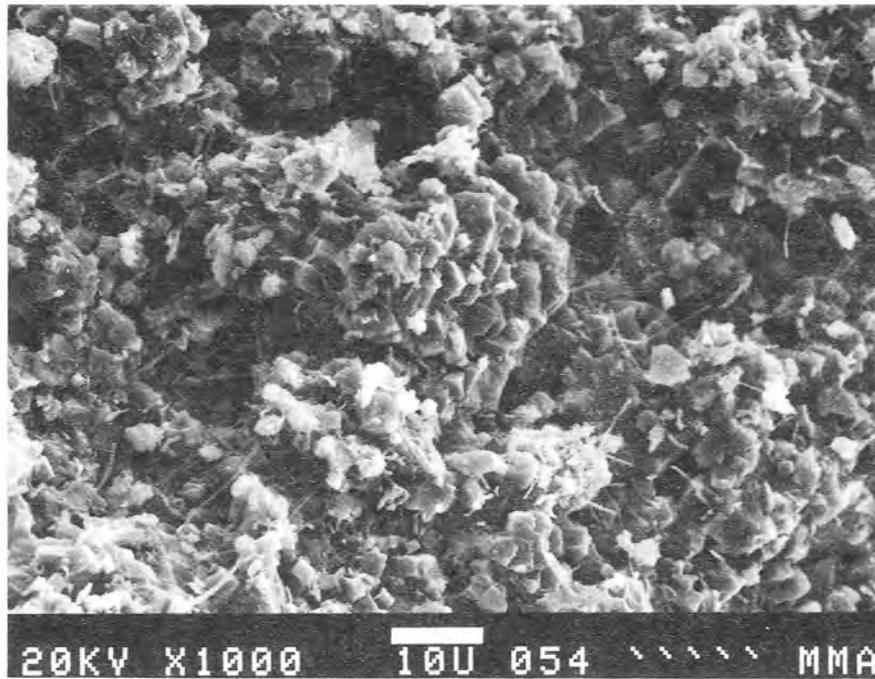
Figure 2A. Sample n.3 - Cotto sample unexposed to atmospheric pollu_
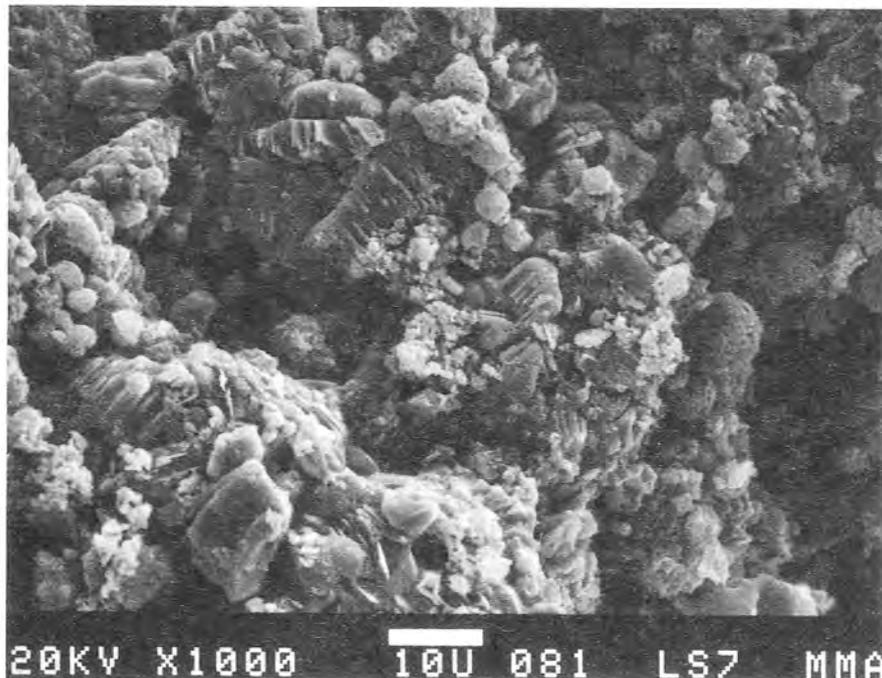tants showing a mass of calcite and gypsum crystals embed-
ded in the cotto matrix.

Figure 2B. Sample n.2 - Cotto from exposed cornice sample that was
not visibly deteriorated. Note the etching of the gypsum
grains.
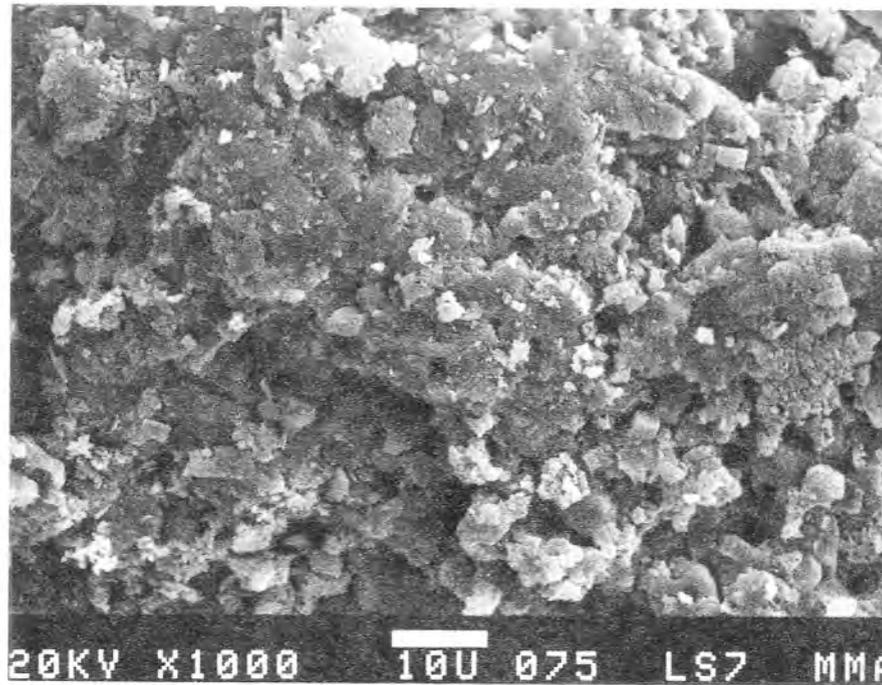
Figure 3A. Sample n.2 – Undecayed cotto showing the caracteristic glassy matrix embedding the residual stacked clay particles.
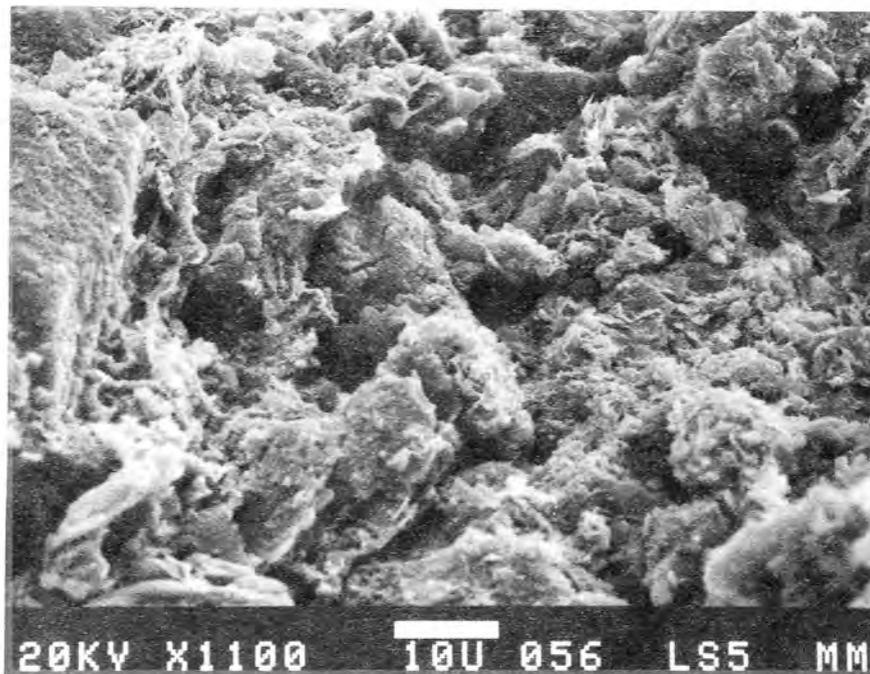

Figure 3B. Sample n.1 – Decayed cotto from cornice. The glassy matrix has been etched away in some parts with the con sequent formation of cracks and loosening up of the constituent material.
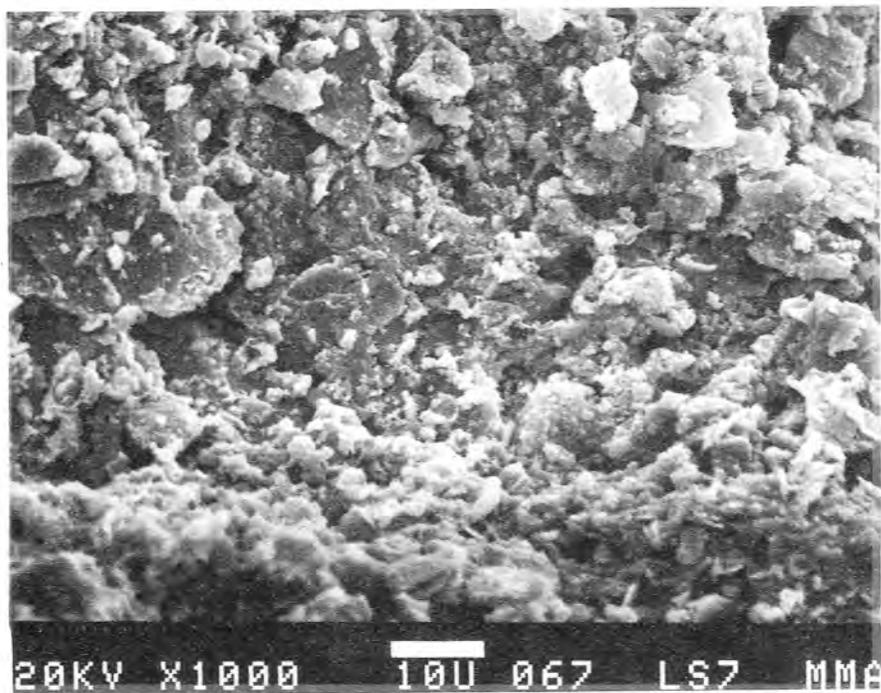
Figure 4A. Sample n.3 - Cotto unexposed to atmospheric agents.
The glassy matrix holds together the bonded platy mi-
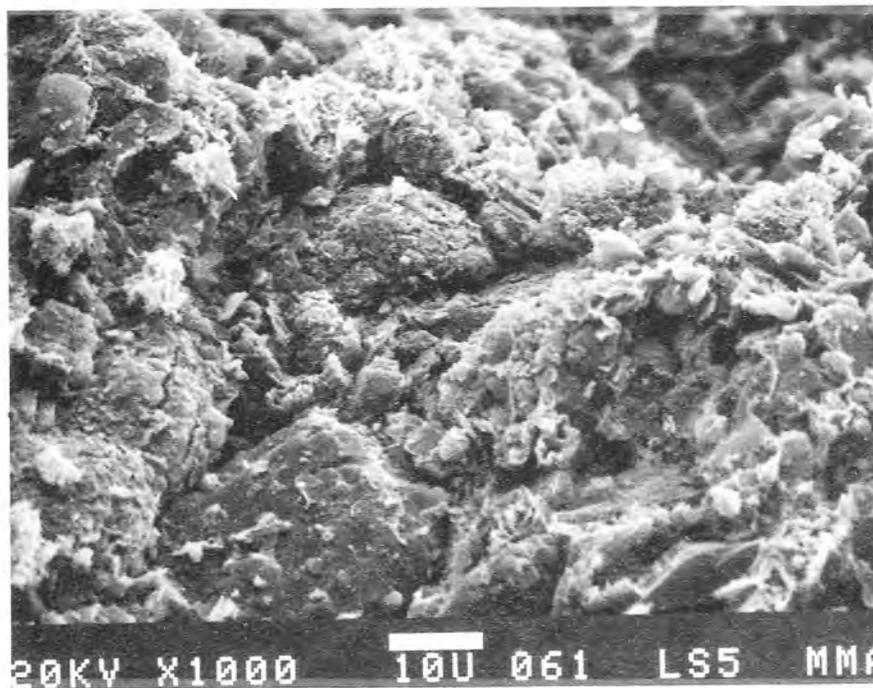nerals to the other mineral grains.

Figure 4B. Sample n.1 - Deteriorated cotto from the cornice. The
glassy matrix has broken up in cracks and has uncovered
agglomerations of poorly fused platy clay minerals.

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CONTRIBUTI PRESENTATI AL CONCORSO
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