STONE CONSERVATION IN THE MARINE ENVIRONMENT. THE CASE OF THE IGNIMBRITES USED IN CAMPANIA (ITALY).

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ABSTRACT

Sea level rise will increase the areas exposed to saline atmospheres and the risk for deterioration of monuments close to the shore line, especially in Naples and other Italian coastal cities. The aim of this paper is to report test results that will assist in determining how environmental change and protective activities might influence the preservation of the cultural heritage of the Campania Region, and in particular of Naples, where the use of pyroclastic rocks was so common.

Among local building stones used in the region, the Campanian Ignimbrite (CI) plays a significant role. This pyroclastic represents the most important, widespread volcanic product of Campania. It has a lower, gray, mostly feldespathic unit, which is often overlaid with an upper, yellow, lithified and zeolitic one. Because of the abundance of these materials in Campania and their easy workability, they were used extensively in Campanian architecture. This paper deals with the behaviour of these lithotypes under a simulated marine environment after appropriate protection.

Samples were collected in two important outcrops located between the provinces of Naples and Salerno. They were chemically and mineralogically characterized, and the following physical properties were determined: specific gravity, bulk density, open porosity, water absorption, ultrasonic transmission velocity, and Hg-porosimetry. Accelerated ageing tests: wetting-drying, and salt crystallization resistance cycles indicate both rock types are moderately resistant to weathering. The use of consolidants is unadvisable, mainly for the yellow facies, whereas the decay phenomena can be positively reduced by creating on the stone surface a barrier with a hydro-repellent.

INTRODUCTION

In *Campania*, since Greek–Roman times the most common building stones were the Neapolitan Yellow Tuff (NYT) and the Campanian Ignimbrite (CI). The latter volcaniclastic rock due to its wide areal distribution is the most used building material within the region. It has been often used *facciavista* in some relevant monuments such as the Mastio del Castello of Casertavecchia (CE), Castle of Manocalzati (AV), Cathedral of Sessa Aurunca, Basilica of S. Angelo in Formis and the Cathedral of Casertavecchia.

In spite of a thorough knowledge from volcanological and petrographical standpoints, little attention was devoted to the study of the mineralogical and petro-physical features of this stone and the interpretation of its behavior when used as building or ornamental stone. The present research aims at filling this gap by means of a detailed mineralogical and petro-physical characterization of this volcanic rock.

EXPERIMENTAL

MATERIALS

CI is the product of a fissure eruption that occurred in the eastern sector of the Phlegraean Fields, about 39 ka ago [1,2]; and covers an area of about 30 000 km² [3-7]. Its most peculiar *facies* shows a chaotic texture (Campanian Grey Tuff *auct.*) represented by a grey ashy groundmass (more than 50%), dark grey pumiceous scoriae and subordinate lava and crystal fragments [3]. The CI also shows a typical yellow or reddish-yellow chaotic texture, deeply affected by secondary mineralization processes related to a possible interaction between infiltrating waters and the glassy matrix in a still hot system. This led to the crystallization of chabazite, phillipsite and rare analcime [4,5].

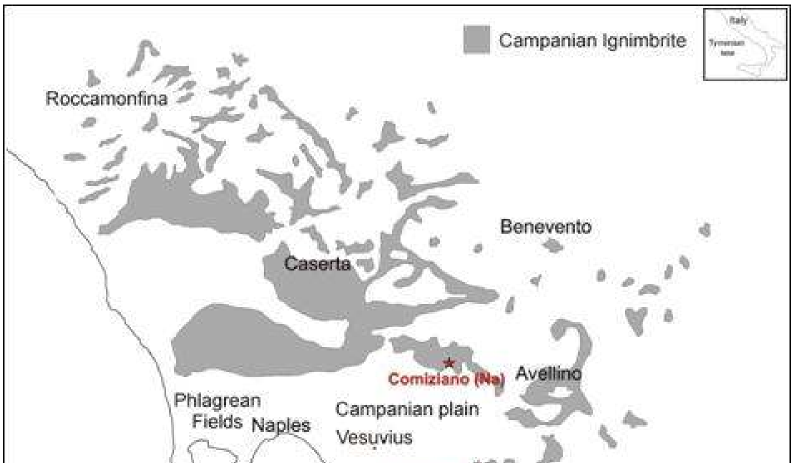

Figure 1. Sketch map showing the approximate distribution of the Campanian Ignimbrite (shaded area). Stars indicate the sampling locations.

The most highly exploited areas were located in the *Caserta* and in the *Sarnese-Nocerino* areas even though several quarries were identified over the whole region [6].

Samples of the CI grey facies were collected from an old quarry located in Nocera Inferiore (Sa) (Fig. 2 - left) whereas those of the yellow facies were collected in an active quarry in Comiziano (Na) (Fig. 2 – right) (Figure 1).

Figure 2. Sampling location of CI grey (left) and yellow (right) facies

All samples were cut to the shapes and sizes established in the reference test procedures (*NorMaL, UNI EN* recommendations). This operation was preceded by a careful removal of any surface weathering trace. Specimens were conditioned by drying them in a stoven at 60±5 ºC until constant weight.

METHODS

Petrographic observations on thin sections were carried with a Nikon Optiphot Pol optical microscope. Chemical analysis was performed with a Philips PW1400 X-ray fluorescence spectrosmeter. Mineral characterization was carried out by XRD with a Panalytical X' Pert PRO PW 3040/60 diffractometer equipped with a RTMS X' detector and a MPD PW 3710 unit. Micromorphological observations were performed with a Jeol JSM-5310by Scanning Electron Microscope with an Oxford Inca X-sight X-Ray energy dispersive system.

The following physical properties were also determined: specific gravity, bulk density, open porosity, water absorption, ultrasonic transmission velocity, and Hg-porosimetry, according to the specific national and EEC standard procedures (NorMaL, UNI EN).

Bulk unit weight, expressed as kg/m^3, was measured with a He-pycnometer (Micromeritics Multivolume Pycnometer 1305) on cylindrical specimens (2.5 cm diameter; height 3 cm) and a ±0.1 to 0.2% accuracy. The measured apparent and real volumes allowed the open porosity to be calculated. Pore size distribution was evaluated by mercury porosimetry using a Thermo Finnigan (Pascal 140 and 440). The ultrasonic transmission velocity (direct measure) was determined by a PROETISA ETI-HO395 tester at 55KHz (UNI EN 14579).

Laboratory ageing tests (wet-dry and salt crystallization cycles) were carried out on cubic (5x5x5 cm) or (prismatic 2X5X5 and 10X5X5cm) samples. Each trial was carried out on 10 samples of both lithotypes and duplicated on the same number of specimens treated with a TEGOVAKON V100 (T-CON, ethyl silicate, density 0.95 g/cm^2) consolidant, a hydro-repellent solution TEGOSIVIN D100 (T-VIN, silicone) and a mixture of both, in order to evaluate their efficiency. Consolidant was applied by total immersion of the specimen for 30 minutes whereas the hydro-repellent was distributed on the whole surface of the prismatic sample by gently brushing it twice. In order to enable a complete polymerization of the consolidant specimens were conditioned at room temperature for one week.

Wetting-drying tests (WDT) involved at least 15 imbibition cycles in deionized water for two hours followed by heating stages in oven at 60°C up to 15 hours.

Salts crystallization tests have been carried out by saturating specimens for 8 hours at room temperature and atmospheric pressure followed by a drying cycle in oven at 105±5 ° C for Test a and 60±5 ° C for Test b. The following solutions have been used:

Test a) sodium chloride 10%P/V (SWT1) solution.
Test b) starting from the composition of Naples sea water (Table 1) a four time more concentrated solution (SWT2) was prepared (Table 2) and used for the salt crystallization tests in order to accelerate the weathering process.

Table 1: Chemical composition of sea water in Naples (mg/l)

HCO3	Cl^-	$SO_4^{=}$	Na^+	K^+	Mg^{2+}	Ca^{2+}
160,9	22390,0	2096,0	12250,0	446,0	1397,0	447,0

Table 2: Chemical composition of mixture A for sea-water simulations (SWT2) (g/l).

NaCl	$MgCl_2$	$CaCl_2$	KCl	Na_2SO_4	$NaHCO_3$
118,80	46,75	4,80	3,45	12,40	0,89

Table 3 summarizes the short-term environmental test performed and samples.

Table 3: Accelerated weathering test conditions

TEST	**Weathering Agent**	**Drying T°C**	**Cycles n°**	**Samples**
WDT	Deionized water	-	15	Grey and yellow IC With T-CON or T-VIN
SWT1	NaCl solution 10% P/V	105	15	Grey and yellow IC
SWT2	Mixture solutions	60	15	Grey and yellow IC With T-CON and/or T-VIN

The weathering evolution was analyzed visually and by measuring weight changes. Open porosity by water absorption and ultrasonic velocity variations were also evaluated.

RESULTS & DISCUSSION

The investigated samples are characterized by pyrogenic and authigenic phases. Polarized light micrograph of the C1 gray and yellow facies are shown in Figure 3. The grey facies (Fig. 3 left) contains large crystals of pyrogenic feldspar set in an apparent glassy matrix shomewhat affected by devitrification processes. The yellow facies (Fig. 3 right) is characterized by contrast, by abundant pumices set in an ashy matrix. The intense transformation of the glass to zeolitic phases is evident, mainly on the rims of the frequent voids as well as in the pumice

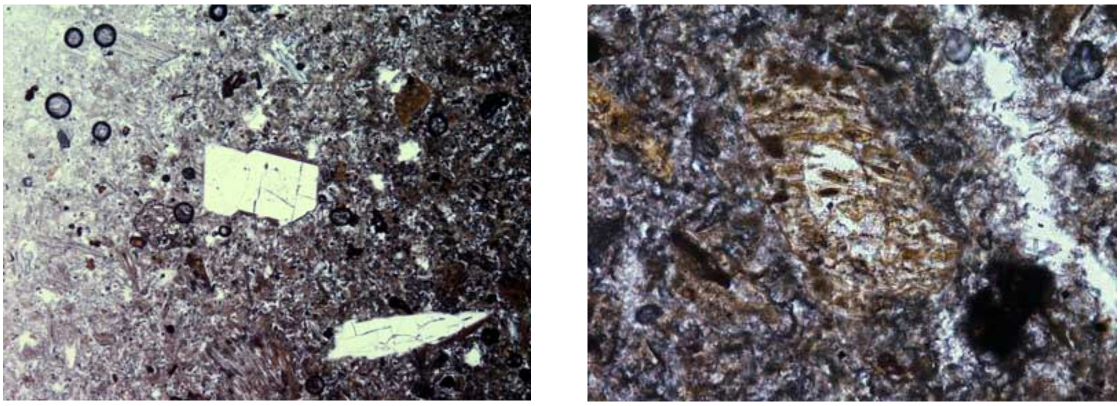

Figure 3: Polarized light micrographs of CI grey facies (left) and yellow facies (right)

Based on XRD analyses (Table 4), the CI grey facies is characterized by a K-feldspar content of about 90 wt.%, traces of pyroxene and biotite with minor amounts of an amorphous residue. The adundance of feldspar confirms the supposed devitrification process related to vapour phase crystallization processes. The prevailing authigenic phases of the CI yellow facies are phillipsite (~30 wt.%) and chabazite (~25 wt. %). Pyrogenic phases, K-feldspar (about 20 wt.%) and minor amounts of pyroxenes and biotite, were also detected. Subordinate smectite also occurs.

Table 4: Mineralogical composition of CI grey and yellow facies (wt.%)

Sample	Smectite	Biotite	Feldspar	Phillipsite	Chabazite	Pyroxene	Amorphous
Grey	0	tr	90	0	0	5	5
Yellow	8	1	17	30	25	5	14

Chemical analyses reported in table 5 represent the typical trachytic composition of Phlegraean volcanoclastic products, characterized by a high K_2O content. This composition, analogous to that of the precursor glass, favours the crystallization of K-feldspar in the grey facies and of intermediate type zeolites [7] such as phillipsite and chabazite [8,1] in the yellow one.

Table 5: Chemical composition of CI in grey and yellow facies (%)

Sample	SiO_2	TiO_2	Al_2O_3	Fe_2O_3	MnO	MgO	CaO	Na_2O	K_2O	P_2O_5	SUM	LOI	TOT
Grey	60,43	0,42	15,98	3,53	0,20	0,67	2,19	4,43	7,04	0,06	94,96	5	99,95
Yellow	54,85	0,47	15,10	4,24	0,15	1,03	5,13	1,09	6,46	0,11	88,64	12	100,64

Scanning electron micrographs observations illustrate the thick aggregate of tabular K-feldspar crystals typical of the CI grey facies (Fig. 4 – left) and abundant small acicular shaped phillipsite (PHI) clusters along with larger twinned rhombohedral chabazite (CHA) crystals in the yellow facies (Fig. 4 – right).

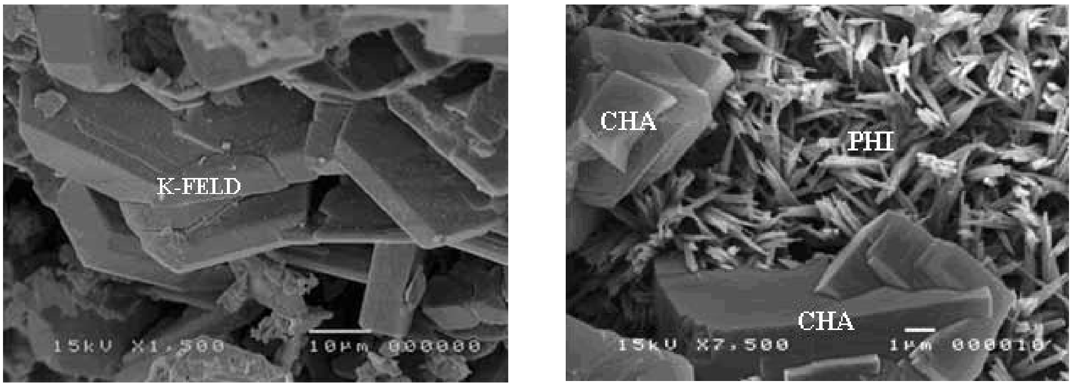

Figure 4. SEM micrographs of CI samples (Left - grey facies; right – yellow facies)

Table 6 reports the most relevant petrophysical parameters for the two facies. These materials are characterized by high porosity values (≥ 50%), due to their particular texture consisting of abundant and different grain-size pumices and subordinate lithic fragments set in an ashy matrix. These features also account for the low ultrasonic transmission velocities. The data define these materials as weak, porous and low strength rocks [9].

Table 6: Petrophysical parameters

		Bulk density (kg/m^3)	Specific gravity (kg/m^3)	Open porosity (%)	US (m/s)
Grey CI	mean min-max (st. dev)	1160 1110-1220 (31)	2600 2580-2620 (11)	55,5 53,5-57,7 (1,3)	1968 1894-2085 (56)
Yellow CI	mean min-max (st. dev)	1110 1060-1140 (35)	2320 2310-2360 (34)	50,8 48,2-54,9 (2,1)	1751 1681-1838 (50)

Wetting-drying tests (WDT) defined the overall mass loss either in consolidated samples or those treated with hydro-repellent (Table 7). The highest mass loss in the grey facies was recorded in samples treated with consolidant (8,92 % P/P). Limited mass loss is evidenced in both untreated and hydro-repellent treated samples. Intermediate values (4,1 % P/P) were recorded in samples treated with a mixture of consolidant and hydro-repellent. The high weight loss in samples treated with the pure consolidant can be related to a partial solubility of this product, considering that the specimen remained substantially undamaged. By contrast, weight loss recorded on untreated or hydro-repellent treated specimens may be ascribed to small loss of material.

Porosity values are substantially unchanged in untreated specimens and those with hydro-repellent whereas a more or less significant decrease was recorded for samples treated with consolidant and consolidant + hydro-repellent. Thus, the WD does not define significant material loss whereas the porosity decrease in consolidated specimens was related to the specific treatment technique (total immersion of the sample).

Analogous considerations can also be revelead for the yellow facies either in terms of mass loss or porosity changes. The only difference is evidenced by a higher mass loss of the untreated and hydro-repellent treated specimens thus confirming the lower resistance to humidity variation of this facies. Furthermore, weathering processes defined by this treatment (WDT) are much more evident on the yellow facies as testified by the occurrence of a crack net (Figure 5) through the specimens.

Figure 5: Crack net occurring after WDT on a CI yellow facies sample treated with T-CON

Table 7: Mass variation and porosity values after WDT test

Sample		Δm (%)	Open porosity (%)
Grey CI	Without Treatment	-0,17	54,8
	T-CON Treatment	-8,92	42,8
	T-VIN Treatment	-0,42	51,5
	T-CON & T-VIN Treatment	-4,10	44,1
Yellow CI	Without Treatment	-2,47	50,1
	T-CON Treatment	-5,97	44,8
	T-VIN Treatment	-1,89	49,9
	T-CON & T-VIN Treatment	-4,43	45,0

The grey facies showed a fairly good resistance to Salt Weathering Test with sodium chloride (SWT1). These specimens do not undergo any apparent damage even though they are affected by efflorescences developing a continuous whitish patina at the end of the test (Figure 6 and Table 8).

Figure 6: Specimens of CI grey facies after 2 cyles (left) and at the end of SWT1 (right)

Table 8: Weathering forms occurring after the SWT1 test

Cycles	5	10	15
Grey CI	Ef	Ef	Ef
Yellow CI	Ef, Fi,	RS, Ef, Fi, GD, S-Ef	RS, Ef, Fi, GD, S-Ef

RS: Rounding of shapes, Ef: Efflorescences, Fi: Fissures, GD: Granular Disintegration, S-Ef: Subefflorescences

This behavior is confirmed by the slight mass increase and the essentially unchanged values of the open porosity and ultrasonic velocity tests (Table 9). On the contrary, this test revealed a severe weathering in CI yellow facies samples that was visible in terms of a prompt rounding of the specimen edges, up to the complete breakdown of the sample prior the completion of the test (Figure 7). As a matter of fact, all specimens showed efflorescence along with an incipient crack net immediately after the first cycle (Figure 7 and Table 8).

Figure 7: Specimens of CI yellow facies after 1 cycle (left) and at the end of SWT1 (right)

Table 9 reports weight loss, open porosity and ultrasonic velocities. Both facies record a slight decrease of porosity related to a partial closure of pores as a consequence of salt crystallization. There was a slight weight increase of the grey facies samples whereas the yellow facies produced a high weight decrease due to significant mass loss. Ultrasonic velocity is substantially unchanged for the grey sample whereas the total breakdown of the yellow specimen did not allow the measurement of this parameter.

Table 9: Mass variation, porosity and US velocities after SWT1 test

	Δm (%P/P)	Open porosity (%)	US (m/s)
Grey CI	0,49	53,3	1930
Yellow CI	-20,7	50,2	broken

Table 10 summarizes the weathering forms recorded during the Salt Weathering Test (SWT2). Samples of both facies are characterized by the occurrence of efflorescence. The only exception is given by the yellow facies treated with consolidant that showed other weathering forms indicative of a deep decay of the stone. Table 11 reports physical parameters measured on specimens treated with consolidant and hydro-repellent. No meaningful variations are recorded on samples of the grey facies, except for the expected weight increase due to salt crystallization and the permeability decrease due to the use of the hydro-repellent. More critical is the behavior of the yellow facies, especially when the treatment with consolidant is concerned, which defines an evident disaggregation along with edge rounding (Figure 8). Despite this clear macroscopic decay a slight mass increase is recorded at the end of the test.

Table 10: Weathering forms description for SWT2 test

Cycles		15
Grey CI	Without Treatment	Ef
	T-CON Treatment	Ef
	T-VIN Treatment	Ef
	T-CON & T-VIN Treatment	Ef
Yellow CI	Without Treatment	Ef
	T-CON Treatment	Ef, Fi, GD, RS, S-Ef
	T-VIN Treatment	Ef
	T-CON & T-VIN Treatment	Ef

Ef: Efflorescences, Fi: Fissures, GD: Granular Disintegration, RS: Rounding of shapes, S-Ef: Subefflorescences

Table 11: SWT2 Results

		Δm (%P/P)	Water absorption (%)	US (m/s)
Grey CI	Without Treatment	9,80	35,20	1966
	T-CON Treatment	7,27	24,28	1911
	T-VIN Treatment	-0,04	5,13	1981
	T-CON & T-VIN Treatment	-2,21	18,94	2070
Yellow CI	Without Treatment	13,06	27,48	1758
	T-CON Treatment	4,83	29,02	broken
	T-VIN Treatment	3,57	13,42	1804
	T-CON & T-VIN Treatment	-1,92	28,77	1579

Figure 8: Specimens of CI grey (left) and yellow (right) facies treated with consolidant at the end of SWT2 test

It is hard to explain the mass loss recorded at the end of the SWT2 test in samples treated with consolidant and hydro-repellent for both grey and yellow facies.

CONCLUSIONS

Campanian Ignimbrite has been used since historical times in the entire Campanian architecture. Among the two facies characterizing this material, the grey one, due to its wider availability, was the most used in the architectural heritage, mainly in Caserta province and in Naples province, subordinately, even though some relevant monuments built with the yellow facies are also common (e.g. Aversa Cathedral and Belltower - 11th 15th century). The good petro-physical features of the grey facies account for a better response to weathering agents in a Mediterranean climate if compared to the yellow one. The rich field observations along with laboratory tests carried out on these materials used as building stones *facciavista* [10,11] have been supported by data on ageing tests performed in the present research.

Treatments carried out with consolidant evidenced, mainly in the yellow facies, a dramatic worsening of the resistance to the decay agents and in particular, to the crystallization of soluble salts, even after few treatment cycles. This phenomenon had already evidenced in sandstones treated with the same consolidant but with a different application procedure [12]. This behavior was attributed to the occurrences of fissures existing within the consolidation film. The specimens used for the present investigation were totally immersed in the consolidant solution but it should be hypothesized that it did not reach all the voids of the stone. These “untreated” areas became a preferential repository of the salt rich solutions that, by crystallization, defined a severe crack net, even higher than that observed in untreated samples. On the other hand, the use of a hydro-repellent provided an efficient barrier, thus preserving both stones from salt intrusion.

On the basis of the results of the present investigations it should be remarked that the use consolidants is definitely unadvisable, mainly for the yellow facies of CI, whereas the decay phenomena can be positively reduced by creating on the stone surface a barrier to the water infiltration.

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