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Onsite Testing of Ammonium Oxalate Treatment Applied to Historical Salt-Infested Limestone

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Abstract: Ammonium oxalate treatment, previously extensively studied on limestone in the laboratory, was applied to powdering historical stonework (limestone) situated on the shoreline in the Mediterranean Island of Malta. This paper presents the results obtained from onsite testing that aimed at evaluating the treatment in terms of its aesthetic performance, the depth of treatment, the mechanical properties of the consolidated stone and the influence on water transport. To this end, the testing program included colorimetry, DRMS (drilling resistance measurement system) and water absorption through the contact sponge method. This study is Part One of the final phase of a wider research program which included two previous phases progressing from treating this same very porous stone type in a laboratory-based controlled environment to uncontrolled site conditions, seeking to quantify this treatment's effectiveness in the field. Results showed that onsite consolidation was achieved and that although some changes in colour and water absorption were brought about by the treatment, these were within acceptable tolerance limits. Besides carrying out these treatments and evaluations directly on the coast, this study anticipates further studies which will look at rural and urban sites where the types and concentrations of salts are expected to be different.

Key words: Historical stonework, limestone consolidation, ammonium oxalate treatment, onsite treatment, onsite testing.

1. Introduction

The Maltese Islands in the central Mediterranean, measuring 316 km^2 and located 93 km south of Sicily and 288 km north of Africa are home to an immense wealth of architectural heritage which dates back to prehistoric times. These buildings and monuments were built using Maltese Globigerina Limestone—a highly porous calcareous stone (up to 41% porosity). This stone occurs as a range of types where the two extreme ends include the more durable *franka* which usually weathers well and the less durable *soll* which deteriorates badly even in the same environment. Previous research [1] found the porosity accessible to water to be greater in *franka* (21.36%) than in *soll* (19.48%). The percentage of mesopores (6 nm < Ø < 50 nm) was 12.60% in *franka* and 24.35% in *soll* while the percentage of macropores (Ø > 50 nm) was found to be 87.25% in *franka* and 75.65% in *soll* [1]. The marginally higher incidence of clay minerals in *soll* could contribute to faster deterioration in this stone type, when compared with *franka*, by occluding pore space [2]. Both types visibly deteriorate in an environment that is exposed to both water and soluble salts as well as fluctuating environmental conditions, thus regularly requiring conservation action.

When the stone is not sufficiently deteriorated to warrant replacement, consolidation may be considered. This is often the case when the damaged stone is not posing a structural problem or is decorative. Unfortunately, a well-established intervention procedure does not yet exist for cases where very high salt loading is present. Globigerina Limestone which has lost cohesion, usually manifested as powdering/granular disintegration, often eventually leading to back-weathering, requires a treatment which will bridge the loose powder/grains together and bind them to the sound stone beneath while retaining the water transport properties of the stone. Ammonium oxalate

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treatment on calcareous stone has to date given promising results, suggesting its potential use in this respect.

Ammonium oxalate treatment is based on a chemical reaction between ammonium oxalate and calcium carbonate of the stone being treated, to form calcium oxalate. Naturally occurring calcium oxalate layers on stone surfaces and the protection that they provide started to be explored in Italy at the Opificio delle Pietre Dure in Florence in 1985 [3]. These naturally occurring calcium oxalate films were found to be more resistant than calcium carbonate to acid attack, and this led to studies involving the artificial formation of oxalates through ammonium oxalate treatment [4].

Studies have been carried out in recent years on the surface conversion of Maltese Globigerina Limestone to calcium oxalate [5, 6]. These were followed by a research project where the treatment was investigated with single salts present in the stone, under laboratory, controlled conditions [7-9]. The study was later extended from the laboratory to the field, where salt-laden laboratory samples were treated and exposed on site prior to testing [1, 10]. In general, it was concluded that, as part of the overall conservation process, ammonium oxalate treatment on weathered Globigerina Limestone containing soluble salts (chlorides, sulfates or nitrates) is very valid, but it was also decided that further *in situ* investigations on stone with salt mixtures and uncontrolled environmental conditions were needed.

These positive results thus initiated a large-scale research project to validate this treatment's use in actual environments and real site conditions on historical architecture built in Globigerina Limestone, where both soluble salts and water are naturally present in a fluctuating environment.

This current research includes three distinct sites—coastal, rural and urban—representing three typical site scenarios with respect to the soluble salts expected to be present. This paper discusses the results from onsite testing from the first site, St. Sebastian Bastion, Marsamxett Harbour, Valletta (Figs. 1 and 2). This is coastal bastion wall with high levels of sodium chloride.

2. Methodology

The study on site commenced with characterizing the stone blocks through colorimetry using a Konica Minolta spectrophotometer CM-700d, with the standard illuminant D65, observer 10°, target Ø = 8 mm (EN 15886.2010) [11], and for hardness by DRMS (drilling resistance measurement system) 5 mm diamond-end drill bit at a penetration rate of 20 mm/min and 300 revs/s.

Fig. 1 Ortho map showing area studied and its proximity to the sea

Source: Malta Environment and Planning Authority, Orthos 2016, http://geoserver.pa.org.mt/publicgeoserver.

Fig. 2 St. Sebastian Bastion, Marsamxett Harbour (arrow indicates the area studied).

Two poultice types were then applied to the selected stones, one as a blank (water only) poultice and the other with ammonium oxalate. The blank poultice was used to be able to identify any effects of poulticing on the stone with water only, independently of the ammonium oxalate.

Both poultices included a cellulose pulp (300 μm). The blank poultice consisted of deionised water and the treatment poultice included a 5% ammonium oxalate monohydrate solution. Both poultices were applied *in situ* at approximately 7 m above street level (Fig. 2). The area included in the testing is illustrated in Fig. 3. The mean ambient temperature during application was 26 °C and the mean relative humidity was 72%. The two poultices were applied for 24 hours and left uncovered. Following application, the still-damp poultices were manually removed and the excess pulp was brushed off with a dry, soft nylon brush. In both cases, the stone was left to air dry for 3 days at ambient conditions (22-40 °C temperature and 34-89% relative humidity).

Onsite testing was then carried out, and included colorimetry, DRMS—both methods as described above for characterization—and water absorption through the contact sponge (NORMA UNI 11432:2011) [12]. All testing included 3 runs.

3. Results and Discussions

3.1 Characterization

Visual inspections were carried out at close range on the scaffolding on site. Natural differences in the stones in terms of colour, texture and deterioration pathology were observed. These differences under close-range inspection are to be expected on a historical wall that has been exposed for centuries. Within this context, those stones which were visually perceived to be most similar and having the same deterioration pathology—in this case powdering—were identified and tested for colour differences using colorimetry and

Fig. 3 Area tested; arrow in Fig. 1.

Table 1 Pre-poultice colour characterization.

CHARACTERIZATION COLORIMETRY	
	ΔE
COLOUR DIFFERENCE BETWEEN 2 STONES TO BE TESTED	1.54 ± 1.10

for drilling resistance using DRMS.

The ΔE value before poultice application (blank and ammonium oxalate treatment) between the two stones considered in this study was 1.54 ± 1.10 (Table 1). A colour difference between the stones was expected and the value obtained is considered to be low (less than 5) and acceptable [13, 14] for direct comparison purposes with post-poultice application.

The DRMS graphs obtained for the two selected stones, which were both untreated, are illustrated in Fig. 4. The shape and ranges of these graphs were seen to be similar with an average drilling resistance of 4.43 N (before blank poultice) and 4.97 N (before treatment poultice). These are directly comparable with previously obtained results [1] where quarry Globigerina Limestone had an average drilling resistance of 4.94 N in the case of *franka* type and 7.71 N in the case of *soll*. This may suggest that the Globigerina Limestone present on site and considered in this study is of the *franka* type.

In both cases (Fig. 4), the drilling resistance was less in the outermost 1.0-2.0 mm, beyond which this datum was seen to stabilize. This implies that the weathering/powdering of the stone is located within the outer 1.0-2.0 mm of the stone.

3.2 Poultice Application

After poultice application, the colour changes recorded were 2.77 ± 1.54 for the blank poultice and 3.14 ± 0.58 for the treatment poultice (Table 2). These ΔE values are greater than the colour differences between the untreated stones in the characterization phase (Table 1).

This increase is attributed, at least in part, to salt mobilization induced by the poultice action that was also observed by SEM (scanning electron microscopy) [15] and also observed by others [16].

A colour change induced through sodium chloride contamination only on *franka* stone in the laboratory was recorded at 2.09 ± 0.27 in previous research [1].

Furthermore, although the poultice was manually removed and dusted off after application, smaller particles of paper pulp inevitably get lodged within the

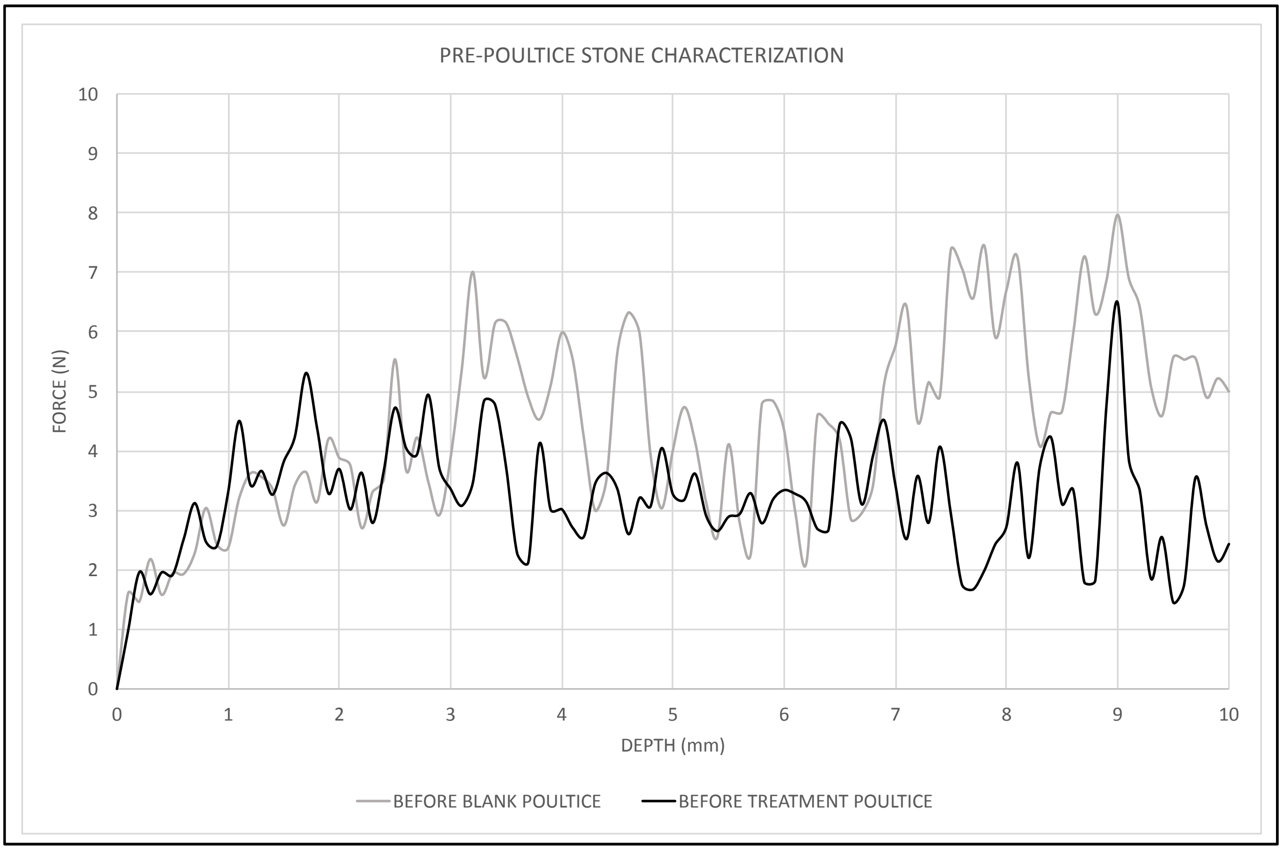

Fig. 4 DRMS stone characterization prior to poultice applications.

Table 2 Post-poultice colour change.

POULTICE COLORIMETRY	
	ΔE
BLANK POULTICE	2.77 ± 1.54
TREATMENT POULTICE	3.14 ± 0.58

surface of the weathered stone, which is not flat and smooth but rough and granular. This contributes to an additional whitening of the stone that is reflected in the ΔE values.

In all cases, the ΔE values obtained after poultice treatment—both blank and treatment—were within tolerance limits (ΔE < 5) [13, 14].

After the blank poultice application, DRMS results showed an increase of 1.10 N within the external 1.1 mm of the stone's surface (Fig. 5).

This, once again, may be attributed to the mobilization of salts to the surface of the stone due to the action of the poultice, as observed in previous results [15] and by others [16] and described above.

The influence of soluble salts on the drilling resistance was also studied in previous research work [1, 17] where an increase was recorded from 4.94 N to 5.53 N in *franka* stone after contamination with sodium chloride.

This corroborates the theory that the blank poultice increased the drilling resistance of the stone post poultice application because of the salts that were brought to the surface with the poultice.

Additionally, the dissolution of calcite from within the stone and its deposition at the surface [2] is another contributing factor to this increased hardness.

After ammonium oxalate treatment, the drilling resistance registered a peak drilling resistance of 7.75 N within a depth of 0.6 mm and a general increase within the surface 1.1 mm when compared to the untreated stone (Fig. 6).

This increase is greater than the increase produced

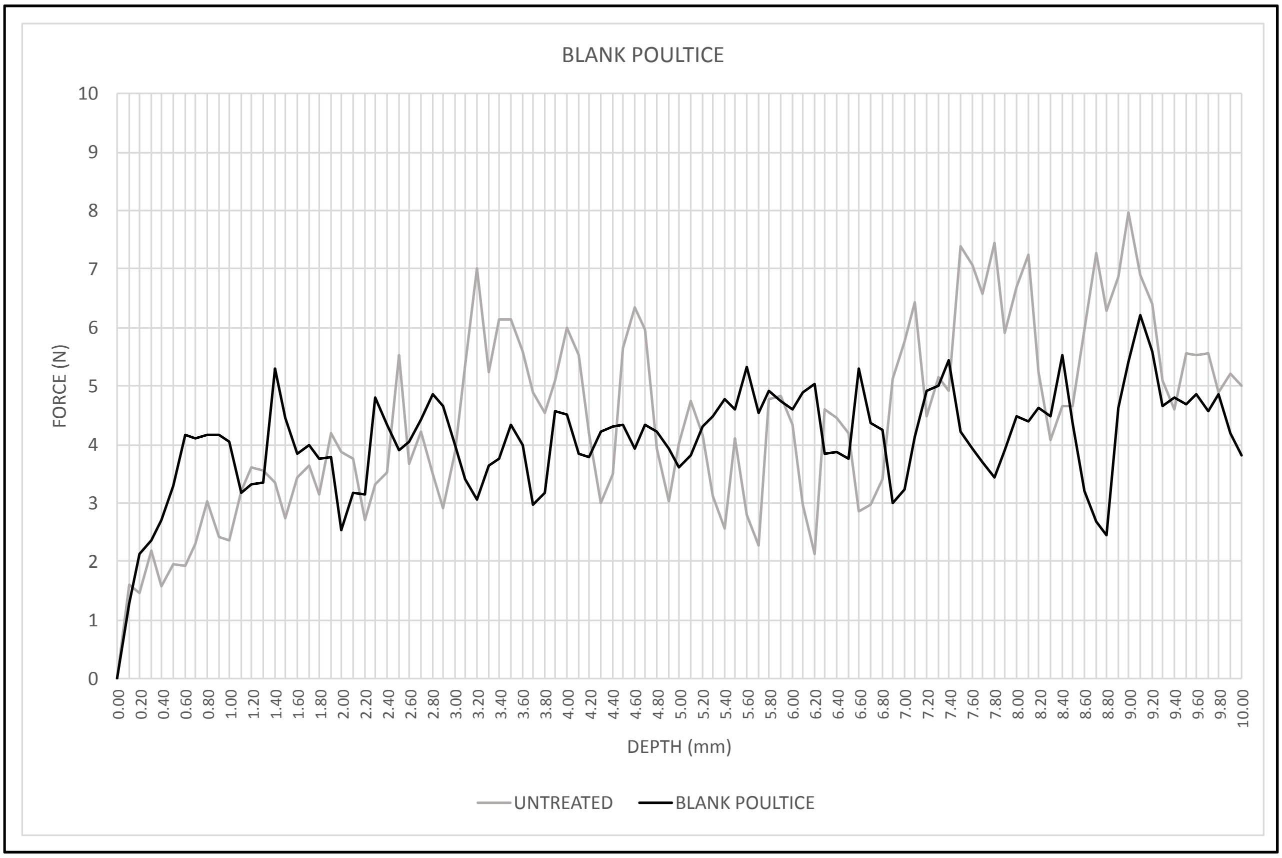

Fig. 5 DRMS before and after blank poultice application.

by the blank poultice, suggesting that besides the contribution of the mobilized salts/calcite to the drilling resistance, the ammonium oxalate also reacted with the calcium carbonate of the stone to form calcium oxalate, which is harder than calcium carbonate, therefore contributing to the increased drilling resistance.

This is in keeping with previous results obtained in the laboratory, where ammonium oxalate treatment applied to sodium chloride contaminated *franka* increased the drilling resistance to a maximum of 14.79 N which occurred up to a depth of 0.3 mm [1, 17].

In the quarry samples, during previous research [1, 17], the stone was intact (un-weathered) and the salt contamination was carried out using a saturated single salt solution. In this current research, the stones considered were weathered and the salt contamination was naturally occurring and contained salt mixtures.

The greater maximum drilling resistance of 14.79 N obtained for quarry stone when compared to the 7.75 N in the weathered stone may be due to actual stone pathology as well as to the amount of salts present in the stone.

Although further research is required, the reason for this difference may be due to the powdering pathology in the weathered stone, where the network of pores was disrupted through weathering, thus allowing deeper absorption of the ammonium oxalate solution and promoting the reaction further into the stone (in this case 0.6 mm). In the quarry samples, the intact nature of the pore network in the stone provided more material at the surface available to react with the ammonium oxalate, which was used up before being able to penetrate further (at 0.3 mm) [1, 17].

Therefore, although the overall amount of calcium oxalate formed is thought to be the same in both cases, since the same amount of product was applied per unit

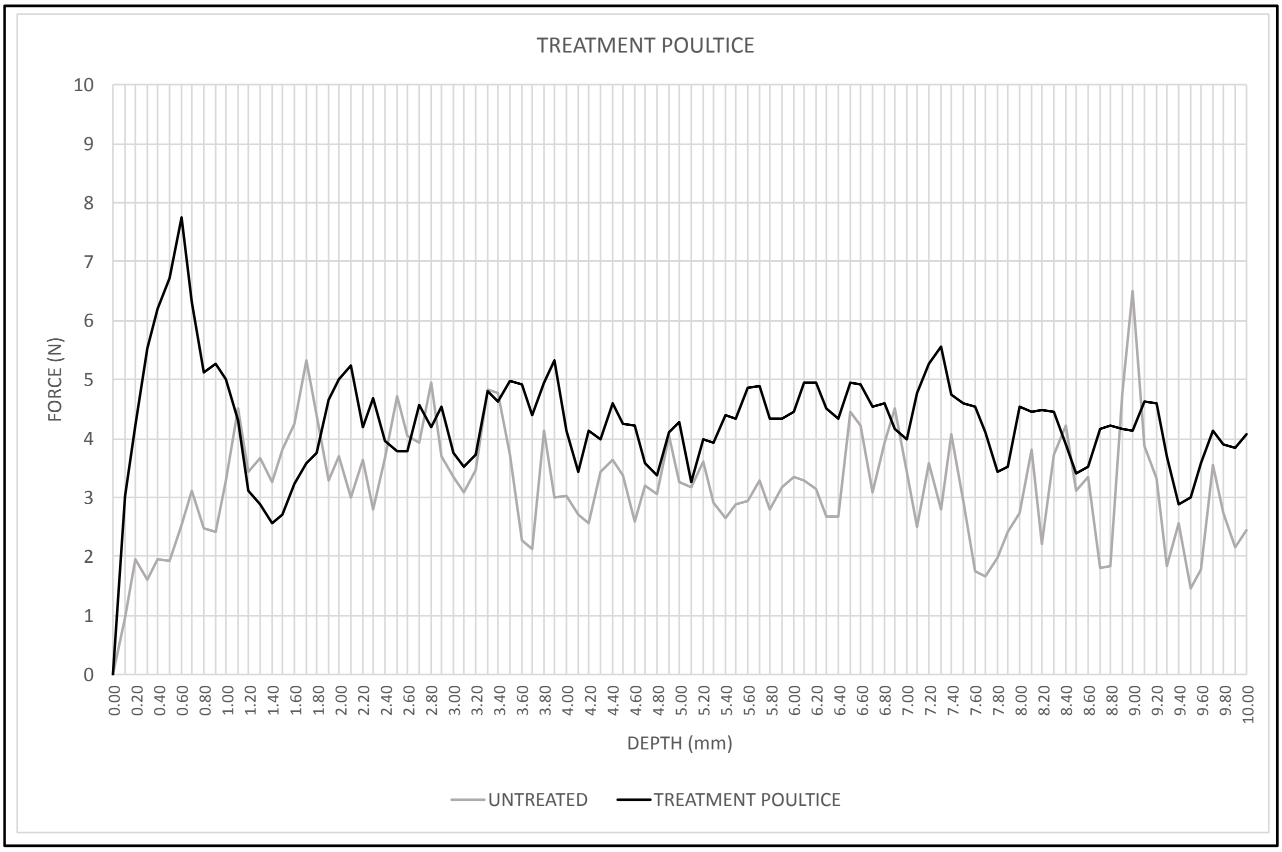

Fig. 6 DRMS before and after treatment poultice application.

Table 3 Water absorption before and after treatment.

WATER ABSORPTION THROUGH CONTACT SPONGE	
	Wa (g/cm^2.min)
BEFORE TREATMENT POULTICE	0.029 ± 0.011
AFTER TREATMENT POULTICE	0.027 ±0.005

area, results indicate that calcium oxalate distribution is different and is directly related to the stone's pathology. Further research is required.

Furthermore, the incidence of soluble salts on the stone's surface, which was greater in the quarry samples [1, 17], when compared to the site samples, may also contribute to the shallower depths recorded in the former case, through the blocking of pores.

Water absorption through the contact sponge test showed a slight reduction from 0.029 ± 0.011 g/cm^2·min to 0.027 ± 0.005 g/cm^2·min following ammonium oxalate treatment (Table 3).

This reduction is considered to be low and acceptable, and indicates that water transport in the liquid phase by capillarity, after ammonium oxalate treatment, is still possible in the stone.

5. Conclusions

Some important conclusions may be drawn from this study, which are specific to onsite testing. From a diagnostic point of view, the tests used to characterize the stone—colorimetry and DRMS—show that relevant information can be obtained by non-destructive and micro-destructive tests, which may serve to characterize the stone as well as to establish baseline data prior to intervention.

This study also highlights that some of the changes to treated stone, may be due, at least in part, to the application method as well as to the treatment itself, as was proved by the blank poultice where changes in colour and drilling resistance were recorded even though no ammonium oxalate was used. Although colour changes were also recorded with ammonium oxalate treatment, these were all within acceptable tolerance limits.

The stone's pathology—intact versus weathered—as well as the concentration of soluble salts present in the stone before treatment, were both seen to influence the distribution of the calcium oxalate within the treated stone, although the overall amount of ammonium oxalate applied was the same.

The retained water transport properties in the liquid phase after treatment show that ammonium oxalate treatment on Globigerina Limestone *in situ* in the presence of naturally occurring sodium chloride (and possibly other salts) does not hinder the continued permeability of the stone.

Finally, the range of tests considered which covers the overarching properties of aesthetics, depth of treatment, physical characteristics and water transport, may be considered to be pertinent to the general case where a historical building is to undergo restoration/conservation interventions, for both general characterization as well as post-intervention evaluation.

6. Further Research

Ongoing research includes further testing of the same site samples discussed in this paper. These include XRD (X-ray diffraction) and ion chromatography to evaluate the mineralogical and chemical composition of untreated and treated stone. Additionally, helium pycnometry and mercury intrusion porosimetry are also envisaged and aimed at determining the porosity and pores size distributions of the untreated and treated stones.

Preparations for two other sites representative of a rural and urban environment are underway. Research is ongoing.

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