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Izbira najprimernejšega utrjevalca pri obnovi Langusovih stenskih poslikav v cerkvi Marijinega oznanjenja v Ljubljani

Izvirni znanstveni članek

UDK

75.052Langus

75.025(497.451.1)

75:693.611

693.611:620.3

Ključne besede: utrjevanje stenskih poslikav, nanodelci kalcijevega hidroksida, nanokalk, nanotehnologija, analiza ometov.

Povzetek

Celovit konservatorsko-restavratorski poseg vključuje med drugim tudi temeljit pregled predhodnih restavratorskih posegov, umetnostnozgodovinskih dejstev; historiat, predhodne naravoslovne preiskave ter interpretacijo rezultatov preiskav, ki se logično nadaljujejo z določitvijo tehnologij materialov in njihove izvedbe. Pod izvedbo razumemo izdelavo in testiranje postopkov utrjevanja poslikav, testiranje postopkov odstranjevanja neustreznih plasti nad originalno poslikavo itd. V prvem delu prispevka je predstavljena klasifikacija obsega poškodb na Langusovih poslikavah v vseh kapelah, ki so posledica neustreznih klimatskih pogojev. Glede na vrsto poškodb je bil izbran anorganski pristop utrjevanja, kjer so uporabljeni izključno kompatibilni materiali, kot so kalcijev hidroksid, barijev hidroksid, amonijev oksalat; tj. materiali, ki imajo podobno kemično naravo kot ostali arhitekturni artefakti, ometi na apneni osnovi. V nadaljevanju je delno predstavljen konservatorsko-restavratorski poseg na Langusovih poslikavah s poudarkom na izdelavi in testiranju postopkov utrjevanja ometa in poslikav v prvi kapeli ter testiranju učinkovitosti izbranega načina utrjevanja z nanodelci kalcijevega hidroksida v vseh naslednjih kapelah sočasno *in situ* in v laboratoriju.

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Uvod

Leta 2006 se je začel pilotski projekt na Langusovih poslikavah v prvi¹ od šestih kapel v cerkvi Marijinega oznanjenja v Ljubljani, ki ga že četrto leto izvaja Zavod za varstvo kulturne dediščine, Restavratorski center, pod vodstvom Martine Lesar Kikelj. V letu 2010 bo zaključena obnova v kapeli sv. Srca Jezusovega, nadaljevanje del poteka v kapeli Sv. treh kraljev. Pomemben del izvajanja projekta predstavljajo tudi analize ometov, ki so natančneje predstavljene v prispevku. Prvi rezultati analiz ometov obravnavanih poslikav so bili predstavljeni in objavljeni na konferenci *RIPAM 3 (3th International Meeting on Architectural Heritage of the Mediterranean)* na Portugalskem oktobra 2009.

Odnos do estetske in umetniške vrednosti nekega dela se stalno spreminja. Cikličnost, ki je glede kritičnega odnosa do umetniških del od nekdanj prisotna v različnih stopnjah upoštevanja avtentičnosti originala, nam je včasih bližje, drugič spet ne. Pomembna je današnja drža z upoštevanjem etike konservatorsko-restavratorske stroke, ki postavlja integriteto predmeta pred vse druge vidike. Dejstvo je, da širša javnost zaznava le likovnoestetško stran, navadno pa je za restavratorja bistvenega pomena segment utrditve nosilca in barvne plasti, ki postavlja estetski videz na drugo mesto. Kajti šele, ko je temelj oziroma nosilec barvne plasti ustrezno utrjen, se lahko ukvarjamo tudi z vprašanjem barvne reintegracije.

Določitev tehnike Langusovih poslikav

Nosilec stenskih slik je praviloma zidana struktura, ki je nato ometana z eno ali več plastmi ometa. Prerez stene (stratigrafija) idealne freske poteka v naslednjem vrstnem redu: zid iz kamna z vezivno malto, sledijo ometi; vezalec, ravnalec, hrapavec (*arriccio*), glajenec (*intonaco*), nato gladilec in nazadnje barvna plast. O visoki tehnološki ravni v srednjeveškem freskoslikarstvu priča sorazmerno dobra ohranjenost fresk iz tega obdobja. Najstarejši sledovi segajo v dvanajsto stoletje, čeprav so v tem času povečini slikali le na večkrat prebeljene stene. Tehnika je popolnoma dozorela v 15. stoletju, kasneje pa je tehnološka disciplina močno popustila.

Sestavine ometa, ki ga uporabljamo kot slikarsko podlogo, so apno, pesek in voda. V zlati dobi freskotehnike so bili do potankosti znani kakovost omenjenih sestavin, njihovo razmerje in način mešanja ter debelina posameznih plasti (Hudoklin, 1955). Glede na to, da je tehnika prave freske sčasoma začela zgubljati kvaliteto, je hitrejšje propadanje mlajših fresk popolnoma pričakovano. Že po sestavi in kvaliteti slikovnega ometa, na katerem je poslikava, lahko presodimo, ali gre za pravo fresko ali ne. Praviloma so bili materiali za slikovni omet skrbno izbrani; omet je navadno vseboval veliko količino več let staranega apna. Pesek za izdelavo ometa je bil brez naključnih primesi.² To govori o določenih pravilih in znanju, pridobljenem iz izkušenj, ki so se prenašale v slikarskih delavnicah

1 Kapela sv. Lucije, Apolonije in Agate.

2 Gre za odsejano rečno mivko granulacije od pol do enega milimetra, zdrobljen marmor ali čisti apnenec.

iz roda v rod. V kasnejših obdobjih sta se enotnost in skrbnost pri pripravi slikovnih ometov izgubili, pesek za omete poslikav je mnogokrat vseboval primesi glin, ki obarvajo apno, poleg tega se na ta račun zmanjša tudi njegova vsebnost. Takšni ometi so slabši in poslikave na njih manj trajne (Butina, 2005). Langusove poslikave so naslikane na ometu slabše kvalitete, poleg tega pa so bile večino časa v izredno neugodnih klimatskih razmerah. Glede na močno pulverizacijo pigmentov je bilo sprva težko trditi, da je Langus uporabil tehniko prave freske, čeprav viri iz različne literature to potrjujejo: »*Langusova glavna dela so: v fresko tehniki: kupola v stolnici (1834) ter oboki in kapele v franč. cerkvi (1845-55),...*« (Stele, 1935) Z različnimi vrstami analiz sta bila določena stanje poslikav in slikarska tehnika. Ugotovljeno je bilo, da so analizirani pigmenti mešani s karbonatiziranim apnom. Analitična ugotovitev je, da je bil pretežni del slikarskega ciklusa izveden v freskotehniki, nekateri predeli pa v freskotehniki, ki prehaja v sekotehniko. O mešani fresko- in sekotehniki govorimo takrat, ko je barva nanescena na podlago v več plasteh. Prvi nanos je še pravi fresko, naslednji nanosi pa se ne vežejo več dovolj močno, ker kalcijev hidroksid ne more enako temeljito prepojit več barvnih plasti in povsod enakomerno karbonatizirati. Zato se na takšnih mestih barvna plast (posebno pri nekaterih barvah) rada briše. V času romanike in gotike je bil omet intonacco zglažen z železno lopatico in valovit, medtem ko so ga v času baroka zravnali in zgladili z leseno plaznico. Površina tega ometa je zrnata, hrapava. Osnovna risba kompozicije je vtisnjena v svež omet. Barve so nanescene lazurno in pastozno v mešani fresko- in sekotehniki. V tej tehniki so pri nas slikali Quaglio, Jelovšek, Lerchinger, Langus idr. Ti ometi so solidni in dobro držijo (Pirnat, 1972). Tako opisana tehnika je lahko ustrezna le, če so bili pri nastajanju freske uporabljeni dovolj kvalitetni materiali. V primeru Langusovih poslikav v kapelah ni bilo tako, saj je bila kvaliteta ometa zelo slaba, groba in fina malta domnevno nista bili dovolj skrbno pripravljene. Viktor Steska omenja, »*da omet za freske v kapeli ni posebno dober, ker je v njem preveč peska; omet je zato razpadljiv in freske se ne morejo dolgo ohraniti*«.

Obseg in vrsta poškodb obravnavanih poslikav

Največji dejavnik propadanja zidu, malte³ in ometa ter s tem tudi stenskih poslikav je vlaga. Ta je neposreden vzrok razkroja apnenega veziva v malti in ometu ter pogoj za sleherni pojav različnih topnih soli (soliter, epsomit, sadra), plesni, alg in rje. Največkrat vlaga prihaja v malto in omet iz temeljnih tal pod objektom s kapilarnim dvigom,⁴ lahko pa je vanj vnesena z gradbenimi materiali ali higroskopno iz zraka.⁵ K razkroju Langusovih poslikav v kapelah je pripomogla tudi meteorna vlaga, ki je dolga leta pronicala skozi dotrajano kritino na stikih kapel. Na mestih, kjer je voda pronicala skozi zidavo oboka, je apneno vezivo razpadlo.

Predhodni konservatorsko-restavratorski posegi

Poleg preslikav in retuš, ki so medtem potemnele oziroma so se spremenile, lahko opazimo

3 Izraz malta označuje gradbeni vezivni material iz peska, vode in apna, omet pa na zid enakomerno nanesceno malto (1995): Slovar slovenskega knjižnega jezika, Ljubljana.

4 Kapilarna vlaga.

5 Kondenzna vlaga.

tudi poškodbe slikarske plasti, ki so nastale zaradi neprimerne mehanškega čiščenja; ponekod je morala biti poslikava agresivno čiščena z neprimernimi sredstvi oziroma orodji, kar ji daje videz zmečkanine (sl. 1).

Vsi kapele in oboki so bili po potresu leta 1887 restavrirani. Po do zdaj ugotovljenih arhivskih podatkih naj bi bili na poslikavah v kapelah narejeni štirje večji restavratorski posegi. Leta 1882, komaj štiri desetletja po nastanku, je Janez Wolf na novo poslikal kapelo sv. Frančiška Asiškega, eno izmed prvih dveh, ki jih je poslikal Langus. Toda tudi Wolfova tehnika se zaradi prevelike vsebnosti proteinov v vezivu (tehnika jajčne tempere) ni izkazala za preveč obstojno.

Drugi restavratorski poseg sta izvedla dunajska slikarja Kastner in Kleinert tik po potresu (Stele, 1935). Restavratorja se nista omejila le na dopolnitev poškodb, dovolila sta si preslikati dovršen del originala v prezbiteriju in ladji. Nekoliko bolj obzirna sta bila pri obnovi poslikav v kapelah. Uporabila sta neprimerne oljne barve. Danes je to opaziti tudi kot neenakomerno reakcijo slikovne površine na uporabljena čistilna in utrjevalna sredstva. Prisotnost olja na poslikavah je dokazana tudi z analizo barvnih plasti.

V letih 1925–1933 je poslikave v kapelah restavriral Matej Sternen, ki je veljal za restavratorja z visoko sposobnostjo prilagajanja značilnostim izvornika in obdobja. Dobro pa je obvladoval tudi tehniko prave freske. Sternenove rekonstrukcije, ki jih je v kapeli kar veliko, so tehnološko kvalitetnejše od originala. Sternen je predvidoma nadomestil originalno poslikavo z rekonstrukcijo na mestih, kjer sta *intonacco* in *arriccio* odstopila od podlage. Omet je na nekaterih mestih popolnoma odpadel ali pa se je v obliki mehurja obdržal na nosilcu. Od Sternenovega restavratorskega posega dalje se je odstopanje preostalega ometa od podlage nadaljevalo. Proces propadanja torej ni bil ustavljen, kar se danes kaže kot ponovno podmehurjanje in odstopanje ometa v večjih kosih. Sternenove večje in manjše plombe z rekonstrukcijami so dobro ohranjene in ne odstopajo od podlage. Še danes je omet tam zelo trden in obstojen.

Zadnji restavratorski poseg na poslikavah v kapeli sv. Frančiška Asiškega je bil narejen leta 1972 pod vodstvom restavratorja Franca Kokalja s sodelavci (ZSV).

Razpadanje in odpadanje ometa

Preveč vlage v zidu povzroča počasno mehčanje in razkrajanje apnenega veziva v malti in veziva na notranji strani ometa (na ploskvi ob zidu). Malta zaradi razkroja veziva (apna) izgublja kohezijo, zato zid postopoma propada. Omet, ki mu je vlaga razkrojila vezivo, s katerim je bil vezan tudi na zid, po malem odstopa, se drobi in odpada. Zelo tanka plast finega apnenega ometa **intonacco**, na katero je slikar nanašal barvo, skupaj z barvno plastjo odpada. Poškodbe so še globlje, odpada tudi **arriccio**, debelejša plast bolj grobega ometa.

Kristalizacija topnih soli

Topne soli v tleh ob temeljih ali v materialih v zidu z vodno raztopino potujejo skozi steno v omet in skozi omet na površino slike (sl. 2). Pojav sulfatizacije oziroma kristalizacije sulfatnih soli na stenskih poslikavah v kapelah je bil zelo razširjen in prisoten pri vseh vzorcih,

vzetih na različnih predelih poslikave. Sulfatna korozija, identificirana pri vseh vzetih vzorcih, je s površine polagoma prodrla proti notranjosti slikarskega materiala. Zelo verjeten vzrok za reakcijo je močno atmosfersko onesnaženje v osemdesetih in devetdesetih letih. Notranjost frančiškanske cerkve do sredine 19. stoletja ni bila poslikana. Med letoma 1845 in 1855 je Matevž Langus poslikal stranske kapele, prezbiterij in ladjo. Potek svojega dela je Langus zapisal na zahodni steni na koru v dveh vzporednih napisih v nemškem in slovenskem jeziku (Stele, 1935). Ker notranjščina ni bila poslikana, je bil omet neposredno izpostavljen sajam zaradi gorenja sveč, izpušnim plinom iz zunanjega prostora, prahu, drugim vrstam umazanije, mrčesu in mikroorganizmom. Stari zidovi so zato prepojeni z organskimi izparinami, žveplovim dioksidom in drugim. Nosilec stenskih poslikav v frančiškanski cerkvi je bil že pred poslikavo poškodovan. Čeprav so bili stari ometi odstranjeni in je bil nosilec temeljito izpran, so v fugah ostajale snovi, ki so pripomogle k hitrejšemu propadanju fresk. Langus je namreč poslikal notranjščino, kot rečeno, šele sredi 19. stoletja. Pri iskanju krivcev za propadanje fresk se ne smemo omejiti le na notranjščino, temveč ima velik pomen tudi nepravilno izdelana in slabo vzdrževana fasada. Ta je bila dolga leta izpostavljena delovanju kislega dežja, dima, kurišč in avtomobilskih izpušnih plinov, ki so s svojimi agresivnimi sestavinami korodirali vsa gradiva na fasadi. Posebej nezaželeno je bilo njihovo delovanje na stenske poslikave. Čeprav so te v notranjosti, je zunanji vpliv ogrožajočih dejavnikov prek nosilca prenesen tudi v notranjost, le da so posledice delovanja nekoliko drugačne. Fasada je bila sicer obnovljena leta 1992, s čimer se je delovanje ogrožajočih dejavnikov za nekaj časa upočasnilo.

Glede na rezultate odvzetih vzorcev pred posegom (Ropret, 2008), ki so pokazali, da vsebuje barvna plast visok odstotek žvepla, je bila uporabljena metoda čiščenja in utrjevanja z amonijevim karbonatom. Primerjava masnega deleža žvepla, ki ga je pokazala večina vzorcev, vzetih na različnih področjih pred čiščenjem, z masnim deležem žvepla v vzorcih, vzetih po aplikaciji amonijevega karbonata, je pokazala, da se je masni delež žvepla pri večini vzorcev zmanjšal za več kot 50 odstotkov (Ropret, 2008).

Pulverizacija, zmanjšanje lastnosti veziva slikarske plasti

Kalcitne površine umetniških predmetov, kot na primer stenske poslikave in kamniti kipi, so večinoma zelo izpostavljene propadanju. Med najbolj škodljive naravne dejavnike, ki vplivajo na propadanje barvnih slojev stenskih poslikav v notranjosti cerkva, spadajo nihanja temperature in relativne vlage, ki imajo za posledico kondenzacijo vlage na površini predmetov. Zaradi žveplovega dioksida v zraku, ki je vodopen, je kondenzacijska vlaga na površini rahlo kislila in topi površinski sloj. Ob izsuševanju pride v prvi fazi do izločanja kalcijevega sulfita, ki z oksidacijo preide v kalcijev dihidrogen sulfat (sadro). Omenjena mineraloška pretvorba kalcita v sadro se manifestira v zmanjšanju vezivnosti in upraševanju površine (Ropret, 2008) (sl. 3).

Razširjena prhkost slikarske površine nastaja tudi zaradi migracije vlage. Vlaga v steni navadno potuje proti poslikani površini in povzroča upraševanje barvne plasti; pred čiščenjem smo odstopajočo in pulverizirano barvno plast utrdili. Pri tem niso smeli biti bistveno spremenjeni fizikalni parametri, kot na primer barvni karakter, poroznost in napatost originalnih barvnih substanc.

Razpoke

Večina razpok je nastala v času potresa leta 1887. Debel sloj umazanije saj in črnega dima se je počasi, a intenzivno spojil z barvno plastjo in skozi razpoke prodril tudi v omet. Nekatero razpoke so zelo globoke; zaradi sile, ki je nastala pri potresu, se ni prelomila le barvna plast, temveč tudi vsi ometi do nosilca – zidu. Ponekod smo s posegom mikroinjektiranja ugotovili, da injektirna apnena masa nekontrolirano odteka med zidovje, kar ni imelo nobenega učinka pri zagotavljanju ponovne vzpostavitve trdnosti površine barvne plasti.

Temnenje barvne površine

V preteklosti so notranjost cerkve vsakodnevno ogrevali z neprimernimi grelnimi telesi. Snov, ki nastaja pri izgorevanju grelnih teles, se je več let nalagala na površino barvne plasti. Na barvno plast in med razpokami so se usedale tudi saje od gorenja sveč. Plast nečistoče oziroma sajasto prašne umazanije je dala poslikavi spremenjen, temačen in nejasen videz, ki je ponekod spominjal na negativ (sl. 4). Določeni deli poslikave so zaradi potemnelosti izgubili prvotno globino in so delovali zelo ploskovito. Vse kasnejše preslikave so bile za odtenek ali nekaj odtenkov temnejše. Potemnele so lahko zaradi sprememb pigmentov, bolj verjetno pa je, da se je na nerestavriranih predelih nadaljeval proces propadanja in odpadanja mikrodolcev barvne plasti, kar je posledično povzročilo svetlejši videz poslikave, saj je na površje prosevala svetla barva intonacca. Ker je kondenzacijska vlaga na površini topila površinski sloj, so se v strukturo samega barvnega sloja na površini ujeli tudi prašni delci iz zraka, kar je povzročilo temnenje celotne površine.

Predhodni poskusi utrjevanja in čiščenja poslikav v prvi kapeli

V prvi kapeli sv. Lucije Apolonije in Agate je bila na zelo različno poškodovanih predelih poslikave narejena cela vrsta poskusov za določitev pravilne metodologije čiščenja in utrjevanja poslikav.⁶ Po prvih raziskavah je bilo ugotovljeno, da je celotna slikarska plast popolnoma potemnela, kar pa se ni zgodilo pri drugih slikarskih ciklusih slikarja. Poslikava v podružnični cerkvi Matere božje na Šmarni gori je popolnoma nespremenjena; ohranjena je prvotna Langusova kromatična lestvica (sl. 5). Optične mikroskopske analize so pokazale, da se material uprašuje, kar je najverjetneje posledica močne sulfatizacije. Izvedena je bila termografska raziskava, s katero so bili določeni predeli odstopanja ometa od podlage. V nadaljevanju so bile s pomočjo UV-luči določene kromatske neenotnosti, ki so bile dokaz za prisotnost tujega materiala na površini freske. S takimi spoznanji so bile izvedene raziskave z izbiro vzorcev za ugotovitev slikarske tehnike in vrsto snovi, ki so povzročile spremembo na poslikavi. V nadaljevanju je bila določena metodologija utrjevanja poslikav in ometa.

Prvi izsledki čiščenja in utrjevanja

Pri iskanju metodologije utrjevanja in čiščenja so bistvenega pomena strukturne poškodbe znotraj slikarske plasti, ki so nastale zaradi naravnega staranja (razgradnje mineralnih in

⁶ V prvi kapeli sv. Lucije, Apolonije in Agate je s predhodnimi poskusi čiščenja in utrjevanja sodelovala Marta Bensa.

organskih barvnih veziv), zaradi sprememb temperature in vlažnosti v prostoru (različne napetosti znotraj slikarskih plasti) ter tudi zaradi poškodb, ki so nastale kot posledica predhodnih restavratorskih posegov (kar ima za posledico slabšo adhezivnost in kohezivnost). V primeru Langusovih poslikav je bil v veliki meri ta proces podprt s tehničnimi slabostmi takratnega freskoslikarstva.

Čiščenje s smolami na osnovi ionskih izmenjav ni dalo zadovoljivih rezultatov, ker ni popolnoma desulfatiziralo barvne plasti. Želeni rezultat je bil dosežen s kombinacijo ionskih smol in amonijevega bikarbonata, ki poleg tega, da skoraj popolnoma desulfatizira površino (z najmanj polurnim nanosom), zmehča umazanijo. Ta se nato odstranjuje z vlažno naravno spužvo čez japonski papir, ne da bi poškodovali barvno plast. Barijev hidroksid je bil uporabljen samo v nujnih primerih. Pri čiščenju z amonijevim karbonatom se je na nekaterih predelih pojavila belkasta površina. V takšnih primerih je bil predhodno na barvno površino nanesen TBT (tributilfosfat).

V nadaljevanju je bilo na podlagi že zbranih podatkov sklenjeno, da se poslikava na površini enega kvadratnega metra poskusi čistiti in utrjevati z oblogami 10-odstotnega amonijevega bikarbonata v celulozni kaši Arbocell 1000 in 200. Poudariti je treba, da je bila poslikava na tem mestu v dobrem stanju. Rezultati so bili zadovoljivi, barve so pridobile sijaj, kakršnega lahko vidimo na drugih, dobro ohranjenih Langusovih freskah. Na najslabše ohranjenih predelih fresk, kjer so odstopali deli slikarske plasti, je bilo predhodno utrjevanje nujno. Za ta poseg je bil izbran tip utrjevalca, katerega funkcija ni bila samo globinsko utrjevanje, ampak tudi lepljivost oziroma vezivnost, ki deluje na površini poslikave. Uporabljena je bila tyloza, raztopljena v vodi (pribl. 1-odstotna raztopina). Naknadno je bila uporabljena mešanica etilnega silikata v White spiritu, ki je bil nanesen s čopičem v odmerjeni količini, da ne bi prišlo do zasičenosti poroznega ometa in s tem do spremembe kromatske lestvice. Količina nanesenega utrjevalca je bila omejena na približno 500 gr/m² (Bensa, 2008).

Večmesečno raziskovanje ter določanje metodologije utrjevanja in čiščenja barvne plasti je bilo uspešno. Za utrditev slikarske površine so bili v večini uporabljeni samo anorganski materiali. Izkazalo se je, da z dosedanjimi metodami utrjevanja pri problemu globinskega razpadanja ometa Langusovih poslikav sicer dobimo zadovoljive rezultate, vendar ne optimalnih. Zato smo v Slovenijo povabili italijanske strokovnjake, ki so v tem času raziskali področje utrjevanja stenskih poslikav na apneni osnovi z anorganskimi utrjevalci, nanodelci kalcijevega hidroksida,⁷ ter preizkusili njihovo učinkovitost tudi na originalnih poslikavah.

Mednarodni strokovni seminar; tehnika utrjevanja stenskih poslikav z nanodelci kalcijevega hidroksida

Leta 2007 sta na Oddelku za stensko slikarstvo v Restavratorskem centru ZVKDS potekala dva mednarodna seminarja: na temo *Metodologija uporabe amonijevega karbonata in barijevega hidroksida* pod mentorstvom italijanskega restavratorja Sabina Giovannonija ter

⁷ Nanodelci kalcijevega hidroksida, v nadaljevanju nanokalk. Nanokalk je koloidna suspenzija kalcijevega hidroksida. Koloid je snov, dispergirana v drugi snovi (disperznem sredstvu), tako, da so delci prve snovi veliki od 1 nanometra do 1 mikrometra.

na temo *Tehnika utrjevanja stenskih poslikav z nanodelci kalcijevega hidroksida* pod mentorstvom prof. kemije in fizike Luigija Deia.⁸

Na delavnici je dr. Luigi Dei nazorno predstavil celotno študijo ter rezultate utrjevanja z nanodelci kalcijevega hidroksida.⁹ Restavradorjem sta bila natančno predstavljena tudi pravilno razmerje disperzije ter način priprave nanokalka. Nanokalk¹⁰ zdaj že več let pripravljamo v laboratoriju na naravoslovnem oddelku Restavratorskega centra, čeprav je na tržišču že komercialna oblika nanokalka – Nanorestore. Ker vsaka stenska poslikava potrebuje svojevrsten pristop, smo kljub dobrim referencam anorganskega utrjevalca tudi sami naredili analize ometa pred utrjevanjem poslikav z nanodelci kalcijevega hidroksida in po njem.

Utrjevanje Langusovih poslikav z nanodelci kalcijevega hidroksida

Sestava ometov v kapelah frančiščanske cerkve

Ometi stenskih poslikav v večini primerov predstavljajo »žrtveni« material, ki je pogosto odstranjen ali pa nadomeščen. Utrjevanje stenskih poslikav je zelo pomembna naloga, pri čemer ponovno obnovimo oziroma ustvarimo kohezijo materiala in s tem povečamo njegovo mehansko trdnost (Paradise et al., 2008). Čeprav je utrjevanje dokaj razširjena praksa, je izbira pravega utrjevalca še vedno precej zahtevna naloga.

Na podlagi preiskave ometov v dveh kapelah frančiškanske cerkve z optično (sl. 6) in elektronsko mikroskopijo lahko zaključimo, da je originalen omet apnen. Agregat sestavljajo zaobljena karbonatna zrna (kalcit in dolomit) ter litična zrna magmatskih kamnin. Zaobljeni delci nakazujejo na rečni izvor agregata – mivke. Opazne so bile tudi kasnejše

8 Organizacija mednarodnega seminarja: Marta Bensa, Martina Lesar Kikelj.

9 Prispevek je omejen predvsem na izbiro primernega utrjevalca – nanokalka, zato je predstavljen le del seminarja, ki se nanaša na tehniko utrjevanja z nanodelci kalcijevega hidroksida.

Namen študije (L. Dei, B. Salvadori, 2006), ki je bila izvedena junija leta 2006, je bil oceniti učinkovitost postopkov z anorganskimi kompatibilnimi materiali, ki temeljijo na delcih kalcijevega hidroksida (gašenega apna) v nanovelikosti, razpršenih v alkoholnem mediju kot konsolidantu za apnenec/kamen in poslikane površine, ki so zaradi različnih vzrokov propadli. Sintetične polimerne materiale so v zadnjem času prepričljivo zamenjali anorganski materiali. Do nedavnega je bil namreč kalcijev hidroksid neprimeren za konsolidacijo/utrjevanje poslikanih površin, saj je vodna raztopina/apnena voda prešibak konsolidant zaradi slabe topnosti apna (pribl. 1,6–1,7 g/l), poleg tega je vodna disperzija komercialnega gašenega apna (apneno mleko) preveč nestabilna – sedimentacija delcev namreč povzroča pobelitev obdelovane površine in ne uspe fiksirati propadlih plasti stenskih poslikav. V študiji je predstavljena inovativna priprava delcev gašenega apna z obsegom okoli 100 nm in manj. Ta velikost je desetkrat manjša kot pri najboljšem komercialnem apnu. Narejenih je bilo veliko poskusov na poškodovanih/uprašenih apnenih površinah. Za najboljše topilo se je izkazal izopropilni alkohol, mešan z deionizirano vodo v volumskem razmerju 98 : 2. Takšna mešanica je omogočila idealno hitrost izhlapevanja. Pripravljene so bile tudi številne koncentracije nanokalka. Tako je bila določena najboljša formulacija za aplikacijo utrjevalca na originalnih zidnih poslikavah. Vizualni učinek je bil po nanosu nanoapnene disperzije zelo dober, kar so dokazale tudi znanstvene meritve, ki so potrdile dobre lastnosti novega materiala in tehnike. Uporaba anorganskega materiala omogoča konserviranemu predmetu ohranitev visoke trajnosti in kemične stabilnosti, značilne za anorganske snovi.

10 Slovenskega poimenovanja za angl. (nanolime), nem. (nanokalk), it. (nanocelce) še ni; za zdaj je uporabljena prevzeta beseda nanokalk, v prihodnosti se morda uveljavi slovenska beseda nanoapno.

plombe, izvedene v tehniki prave freske, ki se razlikujejo od originalnega ometa predvsem po uporabljenem agregatu, ki ga v tem primeru predstavljajo ostroroba zrna kalcita. Na površni ometov je opazna kristalizacija soli – prisotna je sadra, ki je posledica procesov propadanja. Z uporabo FTIR-spektroskopije smo v ometu določili prisotnost epoksidne smole in proteinov (Kramar in Kavkler, 2009). Čeprav so znani razni organski dodatki za izboljševanje lastnosti ometov (Kučková et al., 2009), namenski dodatek proteinov v našem primeru ni potrjen. Prisotnost proteinov je po vsej verjetnosti posledica predhodnega utrjevanja stenskih poslikav z uporabo amonijevega kazeinata, ki so ga pogosto uporabljali in ga še vedno pri konservatorsko-restavratorskih posegih. Temu v prid govori tudi dejstvo, da so bili proteini prisotni tako v primarnih kot v sekundarnih plasteh.

Utrjevanje z nanokalkom *in situ*; preverjanje učinkovitosti utrjevalca

Stenske poslikave v kapeli frančiškanske cerkve so bile utrjene z uporabo nanodelcev kalcijevega hidroksida (tako imenovani nanokalk). Nanokalk velja za zelo primerne za utrjevanje apnenih ometov zaradi dobre fizikalno-mehanske ustreznosti (kompatibilnosti) in tudi primernosti v smislu tehnologije, ki je uporabljena za izdelavo stenskih poslikav, ter ne nazadnje tudi zaradi dobrega prodiranja v globino, ki ga omogočajo majhni delci (Baglioni in Giorgi, 2006; Dei et al., 2006).

Suspenzija produkta v nevodnem mediju (2-propanol) je bila nanesena od 10- do 20-krat s čopičem čez japonski papir, ki je bil položen na barvno površino.

Učinkovitost utrjevanja na stenskih poslikavah je bila ocenjena na podlagi meritev prehoda ultrazvočnih valov (v nadaljevanju USV), ki so bile izvedene pred posegom in po njem (po petih mesecih) v kapeli sv. Pashala Bajlonskega. Metodo meritve hitrosti zvoka skozi stensko poslikavo (USV) smo izbrali ob predpostavki, da večja trdnost substrata po nanesenem utrjevalcu vodi k večji hitrosti zvoka. V ta namen smo izbrali štiri merilne poligone (sl. 7). Hitrost zvoka smo ugotavljali z meritvami časa potovanja zvoka od oddajnika do sprejemnika in razdaljo med njima. Uporabili smo oddajnik s frekvenco 60 kHz. Vsega skupaj je bilo 246 meritev.

Pri meritvah pred utrjevanjem smo z metodo lahko ugotovili mesta, kjer je mehanska trdnost substrata zmanjšana. Na poligonu 1 je bilo tako videti mesto odstopanja poslikave med točkama 12 in 14, kjer je bila hitrost zvoka izrazito nizka (sl. 8).

Čeprav je metoda v veliki meri odvisna od pogojev meritve (na primer od vlažnosti substrata in posledično od temperature), rezultati kažejo, da se je hitrost zvoka po nanosu utrjevalca na splošno povečala (sl. 9). Za vrednotenjem rezultatov smo izvedli še meritve v laboratorijskih pogojih.

Vrednotenje utrjevanja z nanokalkom na laboratorijskih preizkušancih

Učinkovitost utrjevanja z nanokalkom smo preverjali tudi na laboratorijskih preizkušancih. Uporabljene so bile različne koncentracije mešanice ter različni nanosi. Trenutno se izvajajo raziskave ugotavljanja globine penetracije nanokalka in spremembe v fizikalno-mehanskih lastnostih kompozita po utrjevanju, pri čemer se uporabljajo različne analitske

tehnike. Projekt nastaja v sodelovanju z Zavodom za gradbeništvo Slovenije, Univerzo v Granadi ter Consiglio Nazionale delle Ricerche, Istituto de Scienza e Tecnologia dei Materiali Ceramici iz Faenze. V nadaljevanju so predstavljeni rezultati analiz, tj. meritev USV ter kapilarnega dviga.

Za izpeljavo analize smo najprej naredili laboratorijske preizkušance apnenih malt. Po karbonatizaciji so bile na preizkušance nanosene mešanice nanokalka v različnih koncentracijah (1 : 9, 3 : 7, 4 : 6, 10 : 0) ter z različnim številom nanosov (1-krat, 10-krat, 15-krat).

Pred nanosom nanokalka in nato po določenem času, ko je potekla karbonatizacija (po petih mesecih), smo preizkušance izmerili z USV. Kot je razvidno s fotografije 10, je opazno povečanje hitrosti po utrjevanju skoraj pri vseh vzorcih. Hitrost narašča s koncentracijo mešanic, medtem ko število nanosov ne vpliva na hitrost po nekem pravilu.

Prav tako je tudi iz rezultatov kapilarnega dviga razvidno, da število nanosov ne vpliva bistveno na kapilarno vpijanje v primeru mešanic 1, 2 in 3. Značilna razlika v številu nanosov pa je opazna v primeru mešanice 4, ki predstavlja maksimalno koncentracijo. V tem primeru je opazna razlika med 1-, 10- in 15-kratnim nanosom. Pričakovali bi, da bosta večja koncentracija in večje število nanosov povzročila manjše kapilarno vpijanje, vendar se je izkazalo, da je ta korelacija obratno sorazmerna (sl. 10).

Zaključek

Predstavljene raziskave in rezultati, ki so bili podani med delom na Langusovih poslikavah, so del širšega raziskovanja na področju stenskega slikarstva in so zelo pomembni s stališča pridobivanja najprimernejših utrjevalcev za poslikane površine na apneni osnovi. Pomembno je zavedanje, da z rezultati, dobljenimi na nekem objektu, še zdaleč nismo dosegli optimalne točke in da je treba vedno znova iskati še boljše rešitve. Konservatorsko-restavratorski poseg mora biti zastavljen na odprt in dovteten način, ki sprejema vedno nove možnosti izboljšav. Interdisciplinarno sodelovanje se je ponovno izkazalo kot nujno s stališča pridobivanja kompleksnih rešitev za določen konservatorsko-restavratorski problem. Ko enkrat razumemo, zakaj so stenske poslikave tako zelo poškodovane, znamo tudi postaviti vprašanja, na katera lahko odgovorimo le s pravilno izbranimi in zastavljenimi raziskavami. Zavedanje, da umetnina pod vplivom naravnih dejavnikov ali restavratorskih posegov z leti neprestano spreminja svojo sestavo, je ključno za neprestano iskanje novega in boljšega načina minimalnega poseganja vanjo. Nanokalk je vsekakor sredstvo, ki ga lahko uvrstimo med tiste utrjevalce, ki imajo možnost nadgradnje in ki gre lahko v korak s časom; sedanost lahko poveže s preteklostjo.

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1. M. Langus, cerkev Marijinega oznanjenja, stenska poslikava, last: RKC; detajl na južni steni kapele sv. Lucije, Apolonije in Agate; neprimerno čiščenje; videz zmečkanine na barvni površini (foto: arhiv ZVKDS RC)

M. Langus, Church of the Annunciation, wall painting, property: RC Church; detail on the south wall of the chapel of St Lucy, St Apollonia and St Agatha; unsuitable cleaning; appearance of bruising on the painted surface (photograph: ZVKDS RC)



2. M. Langus, cerkev Marijinega oznanjenja v Ljubljani, kapela sv. Lucije, Apolonije in Agate; detajl; pojav kristalizacije topnih soli na barvni površini (foto: arhiv ZVKDS RC)

M. Langus, Church of the Annunciation in Ljubljana, chapel of St Lucy, St Apollonia in St Agatha; detail; crystallisation of soluble salts on the painted surface (photograph: Archives of the ZVKDS RC)



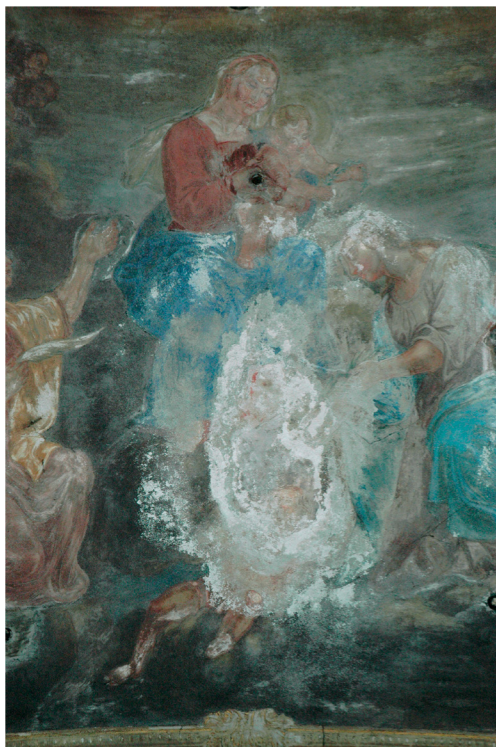
3. M. Langus, cerkev Marijinega oznanjenja v Ljubljani, kapela sv. Lucije, Apolonije in Agate; detajl Marije; pojav upraševanja/pulverizacije pigmentov na barvni površini (foto: arhiv ZVKDS RC)

M. Langus, Church of the Annunciation in Ljubljana, chapel of St Lucy, St Apollonia in St Agatha; detail of the Virgin Mary; pulverisation of pigments on the painted surface (photograph: Archives of the ZVKDS RC)



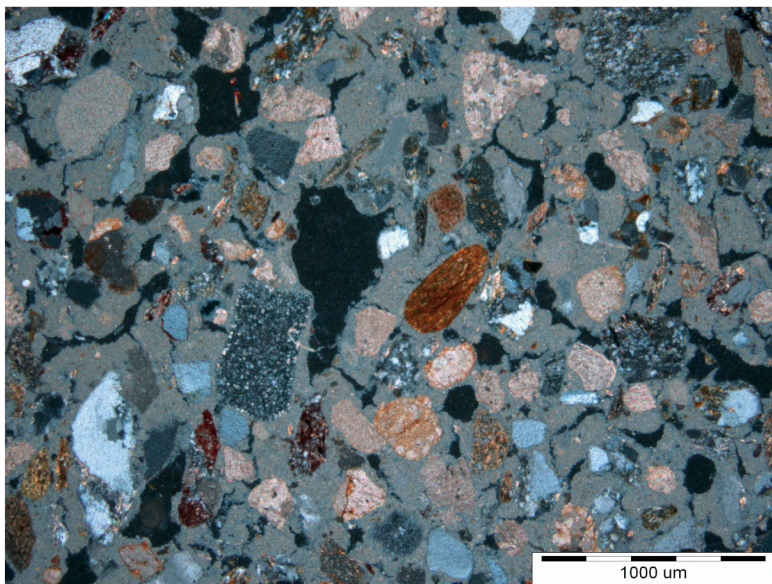
4. M. Langus, cerkev Marijinega oznanjenja v Ljubljani, kapela sv. Lucije, Apolonije in Agate; detajl na severni steni; pojav negativnega videza in temnenja barvne površine (foto: arhiv ZVKDS RC)

M. Langus, Church of the Annunciation in Ljubljana, chapel of St Lucy, St Apollonia in St Agatha; detail on the north wall; »negative« effect and darkening of the painted surface (photograph: Archives of the ZVKDS RC)



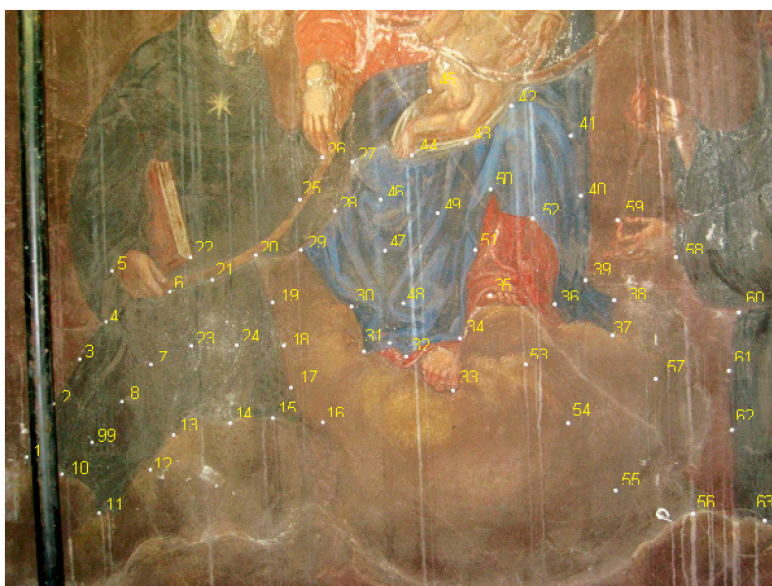
5. Primerjava dveh različnih Langusovih stenskih poslikav, ki sta nastali istega leta, danes pa je stanje obeh popolnoma različno (levo cerkev Marijinega oznanjenja v Ljubljani, desno podružnična cerkev Matere Božje na Šmarni gori) (foto: arhiv ZVKDS RC)

Comparison of two different wall paintings painted by Langus in the same year. The condition of the two paintings today is very different (on the left, the Church of the Annunciation in Ljubljana; on the right, the chapel of ease dedicated to the Virgin Mary on Šmarna Gora) (photograph: Archives of the ZVKDS RC)



6. Posnetek arriccia z optičnim mikroskopom: karbonatna in silikatna zrna agregata ter karbonatizirano apneno vezivo. Presevna svetloba, prekržani nikoli (foto: arhiv ZVKDS RC)

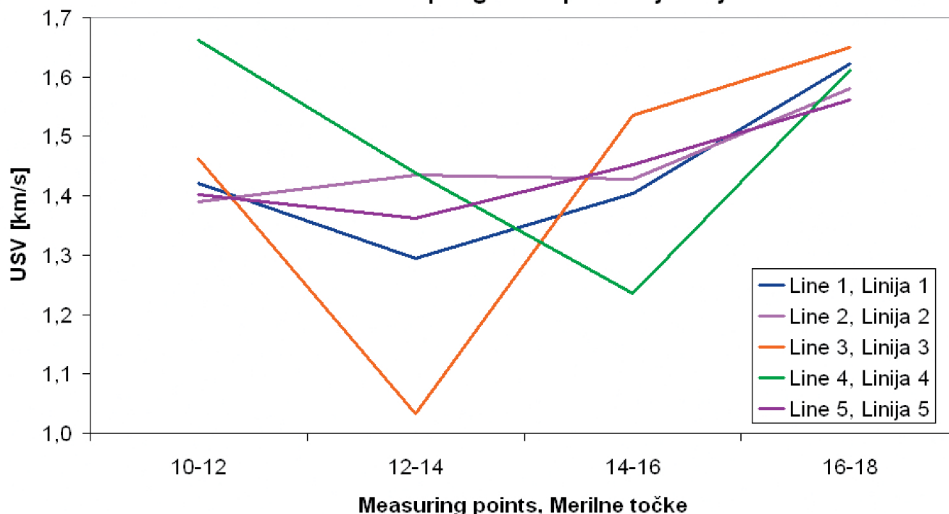
Image of arriccio seen through an optical microscope: the carbonate and silicate grains of the aggregate and the carbonated lime binder. Transmitted light, parallel polars (photograph: Archives of the ZVKDS RC)



7. Eden izmed štirih merilnih poligonov v kapeli sv. Pashala Bajonjskega. Številke označujejo merilna mesta.

One of the four test areas in the chapel of St Pascal Baylon. The numbers indicate the measuring points.

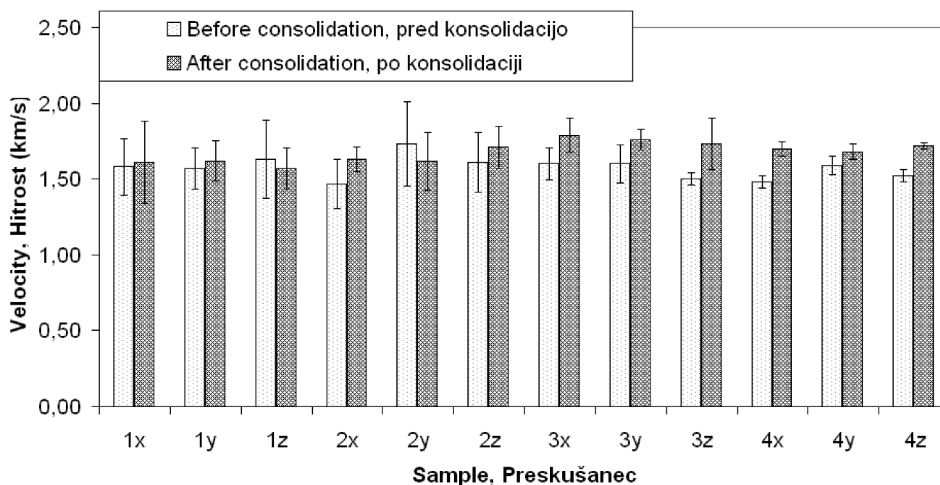
**Ultrasonic velocity in test area 1 before consolidation
Hitrost zvoka na poligonu 1 pred utrjevanjem**



8. Sprememba hitrosti vzdolž vzporednih linij na merilnem poligonu 1. Upad hitrosti nakazuje spremembo v koheziji podlage.

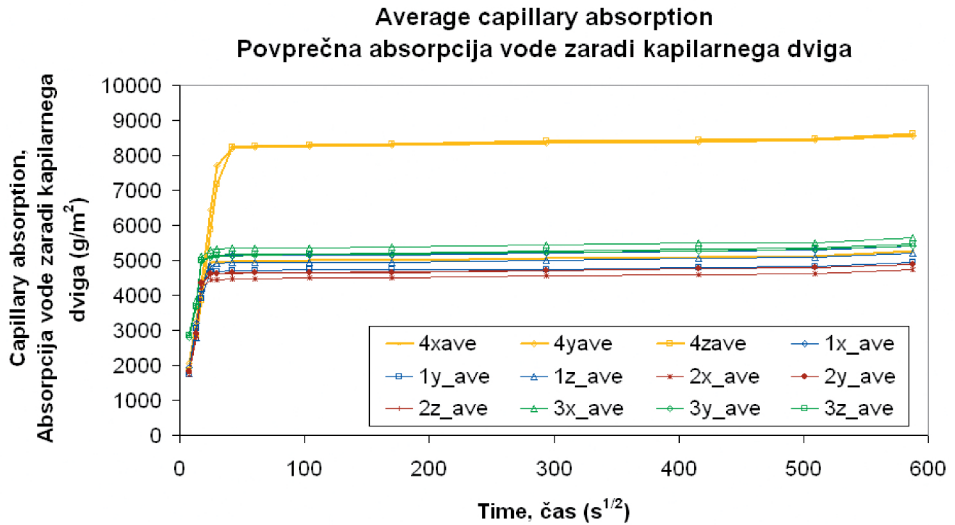
Change of speed along parallel lines in test area 1. A drop in speed indicates a change in the cohesion of the ground.

**Ultrasonic velocity before and after consolidation - laboratory measurements
Hitrost zvoka pred in po konsolidaciji - laboratorijske meritve**



9. Hitrost zvoka skozi laboratorijske preizkušance malte pred utrjevanjem in po njem

Speed of sound through laboratory samples of mortar before and after consolidation.



10. Sprememba povprečne absorpcije vode impregniranih preizkušancev zaradi kapilarnega dviga. Vzorci se razlikujejo glede na koncentracijo utrjevalca (oznaka 1 – utrjevalec : tekočina = 1 : 9, oznaka 2 – utrjevalec : tekočina = 3 : 7, oznaka 3 – utrjevalec : tekočina = 4 : 6, oznaka 4 – utrjevalec : tekočina = 10 : 0) in števila nanosov (x – 1-kratni nanos, y – 5-kratni nanos, z – 15-kratni nanos).

Change in the average absorption of water of impregnated samples as a result of capillary lift. The samples differ in terms of the concentration of the consolidant (1 – consolidant:liquid = 1:9, 2 – consolidant:liquid = 3:7, 3 – consolidant:liquid = 4:6, 4 – consolidant:liquid = 10:0) and the number of applications (x – 1 application, y – 5 applications, z – 15 applications).

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Selection of the most suitable consolidant in the restoration of Langus's wall paintings in the Church of the Annunciation in Ljubljana

Original scientific article

UDC

75.052Langus

75.025(497.451.1)

75:693.611

693.611:620.3

Keywords: consolidation of wall paintings, nanoparticles of calcium hydroxide, nanolime, nanotechnology, analysis of plasters.

Abstract

The comprehensive conservation-restoration intervention includes, among other things, a thorough review of previous restoration interventions, facts relating to the history of art, a historical account, previous scientific examinations and interpretation of the results of investigations, which logically continue with a definition of technologies, materials and execution. By execution we mean the devising and testing of procedures for consolidating paintings, testing procedures for removing unsuitable layers above the original painting, etc. The first part of the article presents a classification of the extent of damage to the Langus paintings in all the chapels as the result of unsuitable climatic conditions. In view of the type of damage, an inorganic approach of consolidation was chosen, where compatible materials such as calcium hydroxide, barium hydroxide and ammonium oxalate were used exclusively – materials that have a similar chemical nature to the other architectural artefacts, i.e. lime-based plasters. Further on there is a partial presentation of a conservation-restoration intervention involving the Langus paintings with an emphasis on developing and testing procedures for consolidating the plaster and paintings in the first chapel and testing the effectiveness of the selected method of consolidation using nanoparticles of calcium hydroxide in all subsequent chapels simultaneously *in situ* and in the laboratory.

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Introduction

A pilot project involving the Langus paintings in the first¹ of the six chapels in the Franciscan Church of the Annunciation in Ljubljana began in 2006. The project, run by the Restoration Centre of the Institute for the Protection of Cultural Heritage and headed by Martina Lesar Kikelj, is now in its fourth year. Renovation in the chapel of the Sacred Heart of Jesus was completed in 2010 and work has now moved to the chapel of the Magi. Analyses of plasters are an important aspect of the project and are presented in detail in the article. The first results of analyses of the plasters from the paintings were presented at RIPAM 3 (3rd International Meeting on the Architectural Heritage of the Mediterranean), which took place in Portugal in October 2009 (Lesar-Kikelj et al., 2009).

Attitudes towards the aesthetic artistic value of a work are constantly changing. The cyclical nature of critical attitudes towards works of art, always present at the various stages of respecting the authenticity of the original, means that they sometimes coincide with our position and other times are further away. Today's attitude, taking into account the ethics of the conservation-restoration profession, which places the integrity of the subject ahead of all other aspects, is an important one. The fact is, the general public only perceives the artistic/aesthetic side, while for the restorer it is usually the consolidation of the support and the paint layer which is of vital importance, and which places the aesthetic aspect in second place. Only when the foundation or support of the paint layer is adequately consolidated, can we deal with the question of reintegration of paint losses.

Identifying the technique used in Langus's paintings

In the case of wall paintings, the support is generally a masonry structure which is then covered with one or more layers of plaster. A cross section (stratigraphy) of an ideal fresco follows the following sequence: a stone wall with a binding mortar, followed by several layers of plaster – binder, leveller, *arriccio*, *intonaco* – then a smooth final layer and finally the paint layer. The advanced level of technology in medieval fresco painting is shown by the relatively good state of conservation of frescoes from this period. The oldest traces date back to the twelfth century, although in that period for the most part artists only painted on walls that had been whitewashed several times. The technique reached full maturity in the fifteenth century but after this period technological discipline slackened considerably. The components of the plaster that is used as a ground for paintings are lime, sand and water. In the golden age of fresco painting the quality, proportions and method of mixing these components were precisely known, as was the thickness of the individual layers (Hudoklin, 1955). In view of the fact that the true fresco (also known as *buon fresco*) technique began to lose quality, the faster degradation of more recent frescoes is entirely expected. The composition and quality of the painted plaster to which the painting is applied enables us to judge whether or not we are dealing with true fresco. As a rule, the materials for the painted plaster were carefully chosen; the plaster usually contained a large

1 Chapel of St Lucy, St Apollonia and St Agatha.

quantity of lime that had been aged for several years. The sand used to make the plaster contained no chance additives.² This is evidence of specific rules and knowledge acquired through experience that was passed from generation to generation in painters' workshops. In later periods, uniformity and care in the preparation of plasters for painting were lost, and the sand used to make plaster often contained clay additives that colour the lime and also reduce the lime content. Such plasters are of poorer quality and paintings on them are less durable (Butina, 2005). Langus's paintings are painted on poor-quality plaster and furthermore have spent most of their existence in highly unfavourable climatic conditions. Because of the considerable pulverisation of the pigments, it was initially difficult to affirm that Langus used the true fresco technique, even though this is confirmed by sources from various literature: "*Langus's main works are: in the fresco technique: the inside of the cathedral dome (1834) and the vaults and chapels of the Franciscan church (1845–55) [...]*" (Stele, 1935). Analyses of different kinds were carried out in order to determine the state of the paintings and the technique used. It was established that the analysed pigments are mixed with carbonated lime. The analytical finding is that the bulk of the cycle of paintings was completed in fresco technique, while some sections were done in fresco technique transitioning to fresco-secco. We talk about a mixed true fresco and fresco-secco technique when paint is applied to the ground in several layers. The first application is still true fresco, but subsequent applications no longer bind sufficiently strongly because the calcium hydroxide cannot impregnate several paint layers with equal thoroughness and carbonate evenly throughout. As a result, in such places the paint layer (particularly with some types of pigment) tends to fade. During the Romanesque and Gothic periods, the *intonaco* was smoothed using an iron trowel, which created an undulating effect, while in the baroque period it was levelled and smoothed using a wooden spatula. The surface of this plaster was grainy and rough. A basic drawing of the composition was impressed into the fresh plaster. Pigments were applied as glazes and pastose applications using a mixed true fresco and fresco-secco technique. Artists working in this technique in Slovenia included Quaglio, Jelovšek, Lerchinger and Langus, among others. These plasters are solid and tend to last well (Pirnat, 1972). The technique described here can only be suitable if materials of sufficient quality are used during the creation of the fresco. This was not the case with Langus's paintings in the chapels, since the quality of the plaster was extremely poor and the coarse and fine mortars were presumably not prepared with sufficient care. Viktor Steska mentions that "*the plaster for the frescoes in the chapel is not particularly good, because it contains too much sand; the plaster is therefore crumbly and the frescoes cannot survive for long.*"

Extent and type of damage to the paintings

The biggest factor in the disintegration of walls, mortar³ and plaster, and therefore of wall paintings, is moisture. This is the direct cause of the disintegration of the lime binder in the mortar and plaster, and a condition for the appearance of a variety of soluble salts (nitre, epsomite, gypsum), fungi, algae and rust. Most often moisture gets into mortar and plaster

² Sifted river sand with a grain size ranging from 0.5 mm to 1 mm, crushed marble or pure limestone.

³ "Mortar" denotes a binding material made of sand, water and lime; "plaster" means mortar that is applied evenly to masonry (definition taken from Slovar slovenskega knjižnega jezika, 1995, Ljubljana).

from the ground below the structure by means of capillary rise,⁴ although it can enter with construction materials or hygroscopically from the air.⁵ The disintegration of Langus's paintings in the chapels has also been accelerated by precipitation, which for years has infiltrated through the dilapidated roof covering where the chapels join the church. At points where water has infiltrated through the masonry of the vault, the lime binder has disintegrated.

Previous conservation-restoration interventions

Besides overpaintings and retouchings that in the meantime have darkened or otherwise altered, we can also observe damage to the pictorial layer that has occurred as the result of unsuitable mechanical cleaning; in places the painting must have been aggressively cleaned using unsuitable agents or tools, which gives it a bruised appearance (Fig. 1).

All the chapels and vaults were restored following an earthquake in 1887. Archive information unearthed to date indicates that four major restoration interventions have been carried out on the paintings in the chapels. In 1882, barely four decades after it was built, Janez Wolf repainted the chapel of St Francis of Assisi, one of the first two chapels to have been painted by Langus. Owing, however, to the excessive protein content in the binder (the egg tempera technique), Wolf's technique did not prove to be particularly durable either.

The second restoration intervention was carried out by two painters from Vienna, Kastner and Kleinert, immediately after the earthquake (Stele, 1935). These restorers did not limit themselves to repairing damage but permitted themselves to overpaint a considerable part of the original in the sanctuary and nave. They were slightly more considerate when it came to renovating the paintings in the chapels. They did, however, use unsuitable oil paints. This can be observed today from the uneven reaction of the painted surface to the cleansing and consolidating agents employed. The presence of oil in the paintings is also demonstrated by analysis of the paint layers.

Between 1925 and 1933 the paintings in the chapels were restored by Matej Sternen, considered a restorer with a great ability to adapt to the characteristics of the original and the period. He also had a good mastery of the true fresco technique. Sternen's reconstructions, of which there are quite a number in the chapel, are in technological terms of better quality than the original. Sternen probably replaced the original painting with a reconstruction in places where the *intonaco* and *arriccio* had separated from the ground. In places the plaster had completely fallen away or was hanging onto the support in the form of a blister. From Sternen's intervention onwards, the detaching of the remaining plaster from the ground has continued. The process of disintegration was therefore not halted, something which is evident today as repeated blistering and the detaching of large pieces of plaster. Sternen's different-sized fillings with reconstructions are well preserved and are not detaching from the ground. The plaster in these places is still very solid and durable today.

The last restoration intervention on the paintings in the chapel of St Francis of Assisi was car-

⁴ Capillary moisture.

⁵ Condensation moisture.

ried out in 1972 by Franc Kokalj and colleagues from the Monument Protection Institute.

Disintegration and detaching of plaster

Excessive moisture in the wall causes a slow softening and disintegration of the lime binder in the mortar and of the binder on the inner side of the plaster (the surface against the wall). As a result of the decomposition of the binder (lime), the mortar loses cohesion and the wall gradually disintegrates. The plaster, in which moisture has disintegrated the binder holding it to the wall, gradually detaches, crumbles and falls away. The very thin layer of fine lime plaster called *intonaco*, to which the artist applied the pigment, falls away together with the paint layer. The damage goes even deeper and the *arriccio*, the thicker layer of coarser plaster, also falls away.

Crystallisation of soluble salts

Soluble salts present in the ground at the level of the foundations or in the materials in the wall travel with an aqueous solution through the wall into the plaster, and through the plaster to the surface of the painting (Fig. 2). The phenomenon of sulphation – the crystallisation of sulphate salts – was very widespread in the wall paintings in the chapels and present in all the samples taken from various sections of painting. Sulphate corrosion, identified in all the samples taken, had gradually penetrated from the surface towards the interior of the painted material. The reaction was very probably caused by high levels of air pollution in 1980s and 1990s.

The interior of the Franciscan church was not painted until the mid-19th century. Between 1845 and 1855 Matevž Langus painted the side chapels, the sanctuary and the nave. Langus recorded the progress of his work on the west wall – in the choir gallery – in two parallel inscriptions in German and Slovene (Stele, 1935). Because the interior was not painted, the plaster was directly exposed to soot from candles, exhaust gases from outside, dust, other forms of dirt, insects and microorganisms. The old walls are therefore impregnated with organic effluvia, sulphur dioxide and other substances. The support of the wall paintings in the Franciscan church was damaged even before painting. Although the old plasters were removed and the support thoroughly washed, substances remained in the gaps that contributed to the more rapid decay of the frescoes. As already noted, Langus did not paint the interior until the middle of the 19th century. When looking for factors to blame for the decay of frescoes, we should not limit ourselves merely to the interior: in fact, an incorrectly executed and poorly maintained façade is another very important factor. This has been exposed for many years to the action of acid rain, smoke, fumes and the exhaust gases of motor vehicles, the aggressive components of which have corroded all the materials in the façade. Their effect on the wall paintings has been particularly unwelcome. Although these are in the interior of the building, the external impact of the harmful factors is also transferred into the interior via the support, although the consequences are somewhat different. The facade was renovated in 1992, which slowed the operation of threat factors for some time.

Given the results of the samples taken before intervention (Ropret, 2008), which showed that the paint layer contains a high percentage of sulphur, a cleaning and consolidation method using ammonium carbonate was employed. Comparison of the mass fraction of sulphur shown by the majority of samples taken in various areas before cleaning, with the

mass fraction of sulphur in the samples taken following application of ammonium carbonate, revealed that the mass fraction of sulphur in the majority of samples had fallen by more than 50% (Ropret, 2008).

Pulverisation, reduction of the adhesive properties of the binder of the painted layer

The calcite surfaces of works of art such as wall paintings and stone sculptures are more often than not very exposed to decay. The most harmful natural factors causing the decay of the paint layers of wall paintings inside churches include fluctuations of temperature and relative humidity, the consequence of which is the condensation of moisture on the surface of the artworks. As a result of the sulphur dioxide in the air, which is water-soluble, the condensation on the surface is slightly acidic and dissolves the surface layer. As it dries, a first phase of deposition of calcium sulphite occurs. With oxidation, this then becomes calcium dihydrogen sulphate (gypsum). The mineralogical conversion of calcite into gypsum is manifested in a reduction of adhesiveness and pulverisation of the surface (Ropret, 2008) (Fig. 3).

Widespread brittleness of the painted surface is also the result of migration of moisture. Moisture in the wall usually travels towards the painted surface and causes pulverisation of the paint layer; before cleaning, we consolidated the detaching and pulverised paint layer. In doing so, we had to ensure that there were no significantly altered physical parameters such as the chromatic character, porosity and tension of the original pigments.

Cracks

The majority of cracks appeared at the time of the earthquake in 1887. A thick layer of dirt, soot and black smoke has slowly but surely combined with the paint layer and, through the cracks, also penetrated into the plaster. Some cracks are very deep; as a result of the force produced during the earthquake, it was not only the paint layer that ruptured but also all the layers of plaster right down to the support, i.e. the wall. In places we have established by means of microinjection that the lime injection compound drains away in uncontrolled fashion between the walls, meaning that the intervention had no effect in ensuring that the solidity of the surface of the paint layer was re-established.

Darkening of the painted surface

In the past the interior of the church was heated using unsuitable sources of heat. The substance that forms during combustion in these sources of heat was deposited on the surface of the paint layer for several years. Soot from candles also settled on the paint layer and between cracks. The layer of dirt or sooty dust gave the painting an altered, dim and indistinct appearance that in places was reminiscent of a negative (Fig. 4). As a result of the darkening, some parts of the painting lost their original depth and had a very two-dimensional effect. All later overpaintings were a shade or several shades darker. They may have darkened because of changes in the pigments but it is more likely that the process of decay and the falling away of microparticles of the paint layer continued in the unrestored sections, consequently giving the painting a lighter appearance because the light colour of the *intonaco* shone through onto the surface. Because condensation on the surface dissolved the surface layer, dust particles from the air were also caught in the structure of the paint layer on the surface, causing the darkening of the entire surface.

Previous attempts at consolidation and cleaning of the paintings in the first chapel

In the first chapel – dedicated to St Lucy, St Apollonia and St Agatha – a whole series of attempts were made on very differently damaged sections of the painting to identify the correct methodology for cleaning and consolidating the paintings.⁶ Following the initial research it was established that the entire painted layer had become darker, something that had not happened with the other cycles of paintings by the artist. The painting in the chapel of ease dedicated to the Virgin Mary on Šmarna Gora is entirely unchanged; Langus's original chromatic scale survives (Fig. 5). Optical microscopic analyses have shown that the material is turning to powder, which is most probably the consequence of strong sulphation. Thermographic research was carried out to identify the areas where the plaster was separating from the ground. Subsequently, chromatic disunities were identified with the help of ultraviolet light. These were proof of the presence of foreign material on the surface of the fresco. Using this knowledge, research was carried out with a selection of samples in order to identify the painting technique and the type of materials that had caused the change in the painting. After this, the methodology used to consolidate the paintings and the plaster was identified.

First results of cleaning and consolidation

When seeking a methodology for consolidation and cleaning, structural damage within the painted layer that has occurred as a result of natural ageing (decomposition of mineral and organic paint binders), as a result of changes of temperature and humidity in the location (different tensions within painted layers), and also as a result of damage caused by previous restoration interventions (the consequence of which is poorer adhesiveness and cohesiveness) is of essential importance. In the case of the Langus paintings, this process was supported to a large extent by the technical weaknesses of fresco painting at that time. Cleaning with ion-exchange resins did not give satisfactory results because it did not result in complete desulphation of the paint layer. The desired result was achieved with a combination of ionic resins and ammonium bicarbonate which not only brings about almost complete desulphation of the surface (with an application of at least half an hour), it also softens dirt. This can then be removed using a moist natural sponge through Japanese paper so as not to damage the paint layer. Barium hydroxide was only used in urgent cases. When cleaning with ammonium carbonate, a whitish surface appeared in some sections. In such cases, TBP (tributyl phosphate) was first applied to the painted surface.

Subsequently it was agreed on the basis of already collected data that an area of one square metre of the painting would be attempted to be cleaned and consolidated using compresses of 10% ammonium bicarbonate in a cellulose pulp of Arbocel 1000 and Arbocel 200. It should be emphasised that the painting in the selected area was in good condition. The results were satisfactory. The colours acquired the lustre that we can see in other well-conserved frescoes by Langus. Preliminary consolidation was essential in the worst-conserved sections of the frescoes, where parts of the painted layer had become detached. For this intervention we selected a type of consolidant the function of which was not only deep-down consolida-

⁶ Marta Bensa was involved in previous attempts at cleaning and consolidation in the first chapel (St Lucy, St Apollonia and St Agatha).

tion but also adhesiveness acting on the surface of the painting. The consolidant used was tylose dissolved in water (approx. 1% solution). Subsequently a mixture of ethyl silicate in white spirit was used, applied with a brush in a measured quantity so as not to reach saturation of the porous plaster and in this way bring about a change to the chromatic scale. The quantity of consolidant applied was limited to approximately 500 g/m² (Bensa, 2008).

Several months of research to determine a methodology of consolidation and cleaning of the paint layer had been successful. In the majority of cases, only inorganic materials were used to consolidate the painted surface. It turned out that with the methods of consolidation used to date, when it comes to the problem of deep-down disintegration of the plaster of the Langus paintings, the results we obtain are satisfactory but not optimal. We therefore invited to Slovenia a group of Italian experts who at that time were researching the field of consolidation of wall paintings on a lime base with inorganic consolidants, nanoparticles of calcium hydroxide,⁷ and also testing their effectiveness on original paintings.

International specialist seminar; the technique of consolidating wall paintings with nanoparticles of calcium hydroxide

Two international seminars took place in 2007 at the Wall Painting Department of the ZVKDS Restoration Centre: one on the topic *Methodology of the use of ammonium carbonate and barium hydroxide* led by the Italian restorer Sabino Giovannoni, and one on the topic *The technique of consolidating wall paintings with nanoparticles of calcium hydroxide* led by Luigi Dei, a professor of chemistry and physics.⁸

At the workshop Dr Dei presented the complete study and the results of consolidation using nanoparticles of calcium hydroxide.⁹ Restorers were also given a detailed presenta-

7 Nanoparticles of calcium hydroxide, hereinafter referred to as nanolime. Nanolime is a colloidal suspension of calcium hydroxide. A colloid is a substance dispersed in another substance (dispersion agent) in such a way that the particles of the first substance are between 1 nanometre and 1 micrometre in size.

8 Organisation of the international seminar: Marta Bensa, Martina Lesar Kikelj.

9 The article is limited above all to the selection of a suitable consolidant – nanolime – and therefore only that part of the seminar relating to the technique of consolidation using nanoparticles of calcium hydroxide is presented. The purpose of the study (L. Dei, B. Salvadori, 2006), which was carried out in June 2006, was to assess the effectiveness of procedures using inorganic compatible materials based on particles of calcium hydroxide (slaked lime) in nano sizes dispersed in an alcoholic medium as a consolidant for limestone/stone and painted surfaces that have decayed as a result of various causes. In recent times synthetic polymers have been convincingly substituted by inorganic materials. Until recently, calcium hydroxide was unsuitable for the consolidation of painted surfaces because an aqueous solution/lime water is too weak a consolidant because of the poor solubility of lime (approx. 1.6–1.7 g/l), and furthermore the aqueous dispersion of commercial slaked lime (lime milk) is too unstable -- sedimentation of particles causes the whitening of the treated surface and does not fix the decayed layers of wall paintings. The study presents an innovative way of preparing particles of slaked lime measuring approximately 100 nm or less. This is 10 times smaller than in the best commercial lime. Several trials were carried out on damaged/pulverised lime surfaces. The best solvent proved to be isopropyl alcohol mixed with deionised water in a ratio of 98:2. This mixture enabled an ideal evaporation speed. Several concentrations of nanolime were also prepared. In this way the best formulation for the application of consolidant to original wall paintings was determined. The visual effect following application of the nanolime dispersion was extremely good. This was also proved by scientific measurements confirming the good properties of the new material and technique. The use of an inorganic material allows the conserved object to retain the high durability and chemical stability characteristic of inorganic substances.

tion of the correct dispersion ratio and the method of preparing nanolime. Nanolime¹⁰ has been prepared for several years in the laboratory of the Science Department of the Restoration Centre, although a commercial form of nanolime called Nanorestore is already available on the market. Since every wall painting needs a unique approach, despite the good references of the inorganic consolidant we carried out our own analyses of the plaster before and after consolidation of the paintings using nanoparticles of calcium hydroxide.

Consolidation of Langus's paintings with nanoparticles of calcium hydroxide

Composition of plasters in the chapels of the Franciscan church

In the majority of cases the plasters of wall paintings represent "sacrificial" material which is often removed or replaced. Consolidation of wall paintings is a very important task in which we restore or recreate the cohesion of the material and in this way increase its mechanical solidity (Paradise *et al.*, 2008). Although consolidation is a fairly widespread practice, the choice of the right consolidant is still quite a difficult matter.

On the basis of examination of the plasters in two chapels of the Franciscan church using optical (Fig. 6) and electron microscopes, we can conclude that the original plaster is lime-based. The aggregate consists of rounded carbonate grains (calcite and dolomite) and lithic grains of magmatic rock. The rounded particles indicate the origin of the aggregate as river sand. Later fillings done in true fresco technique can also be observed. These differ from the original plaster above all in terms of the aggregate used, which in this case consists of sharp-edged grains of calcite. Crystallisation of salts is evident on the surface of the plasters – gypsum is present, the consequence of decay processes. Using Fourier transform infrared spectroscopy, we identified the presence of epoxy-based resin and proteins in the plaster (Kramar and Kavkler, 2009). Although a range of organic additives for improving the properties of plasters are known (Kučková *et al.*, 2009), the deliberate addition of proteins is not confirmed in our case. The presence of proteins is in all likelihood the consequence of previous consolidation of the wall paintings using ammonium caseinate, which was and still is frequently used in conservation-restoration interventions. This theory is also supported by the fact that the proteins were present both in primary and secondary layers.

***In situ* consolidation with nanolime; verifying the effectiveness of the consolidant**

The wall paintings in the chapel of the Franciscan church were consolidated using nanoparticles of calcium hydroxide (known as nanolime). Nanolime is highly suitable for the consolidation of lime plasters because of its good physical-mechanical suitability (compatibility), its suitability in the sense of the technology that is used to create wall paintings and, last but not least, the good penetration enabled by the small particles (Baglioni and Giorgi, 2006; Dei *et al.*, 2006).

10 There is currently no Slovene equivalent for the English nanolime, the German Nanokalk and the Italian nanocalce; for the time being the German expression is used as a loan word, although in future the Slovene word nanoapno may be adopted.

A suspension of the product in a non-aqueous medium (2-propanol) was applied between 10 and 20 times by brush through Japanese paper placed on the painted surface.

The effectiveness of consolidation on wall paintings was assessed on the basis of measurements of the propagation of ultrasound waves taken before the intervention and after it (after five months) in the chapel dedicated to St Pascal Baylon. The method for measuring the speed of sound through the wall painting (ultrasound waves) was chosen on the assumption that the greater solidity of the underlying layer following application of the consolidant leads to a greater speed of sound. To this end we selected four test areas (Fig. 7). We established the speed of sound by measuring the time taken for sound to travel from the transmitter to the receiver and the distance between them. We used a transmitter with a frequency of 60 kHz. A total of 246 measurements were taken.

In the measurements before consolidation, the method enabled us to identify places where the mechanical solidity of the underlying layer was reduced. In test area 1 we were thus able to see an area of detachment of the painting between points 12 and 14, where the speed of sound was very low (Fig. 8).

Although the method used is to a large extent dependent on the conditions of measurement (for example the humidity of the underlying layer and, consequently, temperature), the results show that following application of the consolidant, the speed of sound generally increased (Fig. 9). In order to evaluate the results we carried out further measurements in laboratory conditions.

Evaluation of consolidation with nanolime on laboratory samples

We also verified the effectiveness of consolidation with nanolime using laboratory samples. Various concentrations of the mixture and various applications were used. Research is currently under way to establish the depth of penetration of nanolime and changes in the physical-mechanical properties of the composite after consolidation, where different analytical techniques are used. The project has been set up in conjunction with the Building and Civil Engineering Institute of Slovenia, the University of Granada (Spain) and the Institute of Science and Technology for Ceramics in Faenza (Italy), part of Italy's National Research Council. The results of the analyses, i.e. measurements of ultrasound waves and capillary lift, are presented below.

To carry out the analysis, we first made laboratory samples of lime mortars. Following carbonation, nanolime mixtures were applied to the samples in various concentrations (1:9, 3:7, 4:6, 10:0) and with different numbers of applications (1, 10, 15).

We measured the samples using ultrasound waves before application of nanolime and again five months later, once carbonation had taken place. As can be seen from Fig. 10, there is a clear increase in speed following consolidation in almost all the samples. The speed increases with the concentration of the mixtures, while the number of applications does not influence the speed according to any rule.

It is also evident from the results of capillary rise that the number of applications does not significantly affect capillary absorption in the case of mixtures 1, 2 and 3. A typical difference in the number of applications is, however, evident in the case of mixture 4, which represents the maximum concentration. In this case a difference is evident between a single application, tenfold application and fifteenfold application. We would have expected a higher concentration and a greater number of applications to cause less capillary absorption, but it turned out that this correlation is inversely proportional (Fig. 10).

Conclusion

The research presented and the results produced during work on the Langus paintings are part of wider research in the field of wall painting and are extremely important from the point of view of obtaining the most suitable consolidants for painted surfaces on a lime base. It is important to be aware that with the results obtained in one structure we are still far from reaching the optimum point, and that it is necessary to keep searching for even better solutions. A conservation-restoration intervention must be planned in an open and sensitive manner that is always ready to accept new possible improvements. Interdisciplinary cooperation has once again proved to be essential from the point of view of obtaining complex solutions to a specific conservation-restoration problem. Once we understand why wall paintings are so badly damaged, we are also able to ask questions that can only be answered through correctly chosen and planned research. The awareness that a work of art, under the influence of natural factors or restoration interventions over the years, is constantly changing its composition is of key importance for the constant search for new and better methods of minimal intervention. Nanolime is without a doubt a product that may be included among those consolidants that contain the possibility of improvement and that are able to keep pace with the times; it can connect the present to the past.

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