様式Ｃ－１９

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研究課題名（和文）　文化財保存修復におけるナノテクノロジー

研究課題名（英文）　Nanotechnology in the conservation

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研究成果の概要（和文）：ナノライム（水酸化カルシウム）を合成した。楮紙、雁皮紙および木材パルプ紙の脱酸性処理を行ったところ、ナノライムと通常の水酸化カルシウム溶液処理は効果に差が無かった。モルタル、煉瓦、人工石材（砂岩、花崗岩、凝灰岩）の強化処置を通常の処理方法と比較した。ナノライムの炭酸化が処理後も表面の 3㎜ 程度に留まっていたため最終的な効果は現在のところ不明であるが、砂岩や凝灰岩には有効であり、市販の強化剤と同等（パラロイド）か、より効果的（ワッカー、アラルダイト）でありそうである。完全に炭酸化後に再度評価を行う。

研究成果の概要（英文）：Research has been focussed to the synthesis of calcium hydroxide nano-particles. Deacidification of kozo and gampi Japanese papers and western type acidic wood pulp paper with non-aqueous nano-lime is effective. Effectivity is about the same then that of common (normal) lime. The consolidation of mortar, brick and “artificial” stones (sandstone, granite and tuff), and comparison with traditional consolidants: Final evaluation can’t be given because carbonatation of nanolime was completed only in a 2-3mm thick surface layer in three month. As temporary result nano-lime is especially promisable for the consolidation of sandstone and tuff “artificial stones” used in the study. Consolidation (splitting tensile strength) is about the same than that of Paraloid and higher than that of Wacker and Araldite treated. After full carbonatation results will be re-evaluated.

交付決定額

（金額単位：円）

	直接経費	間接経費	合　計
２００９年度	4,600,000	1,380,000	5,980,000
２０１０年度	2,900,000	870,000	3,770,000
２０１１年度	1,700,000	510,000	2.210,000
総　計	9,200,000	2,760,000	11,960,000

研究分野：総合領域
科研費の分科・細目：文化財科学・文化財科学
キーワード：ナノ材料、脱酸性処理、強化剤、保存、石材、漆喰、モルタル

１．研究開始当初の背景

Applications of nanotechnology to conservation have provided clear evidences of the huge potentiality for cultural

heritage protection (Soft Matter 2006. 2. 293-303, Journal of Cultural Heritage 7, 2006. 110-115). The conservation nano-research in the world has focused to the use of nano calcium hydroxide particles in the field of consolidation and fixing deteriorated paint layers of wall paintings (Baglioni et al. 2006), consolidation of calcareous materials like limestone (Croveri et al. 2004), and deacidification of paper, canvas and wood (Baglioni et al. 2002, Sequeira et al. (2006).

２．研究の目的

(1)Successful synthesis of calcium hydroxide nanoparticles, study the reaction parameters and characterization of particles.

(2) Deacidification of kozo, gampi and wood pulp paper with calcium hydroxide nanoparticles.

(3) Consolidation of mortar, "artificial" stones (sandstone, granite and tuff), brick with $Ca(OH)_2$ nanoparticles and comparison with traditional consolidants

３．研究の方法

(1)Acquiring the synthesis of nano-lime in our laboratory

Characterisation of nano-limes: crystallite size and shape by XRD, HRTEM and particle size distribution by laser scattering particle size analyser

(2)Traditional sized Japanese paper (kozo, gampi) and acidic wood pulp paper were deacidificated by alcoholic nano-lime and commercial traditional lime. After moist heat ageing (80℃65%rh), the pH, colour, tensile index and folding endurance were measured.

(3) Consolidation:

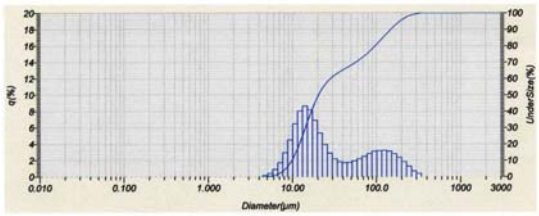
Preparation of samples and treatment with nano-lime and traditional consolidants

Measuring splitting tensile strength, P-wave velocity and Equotip surface hardness

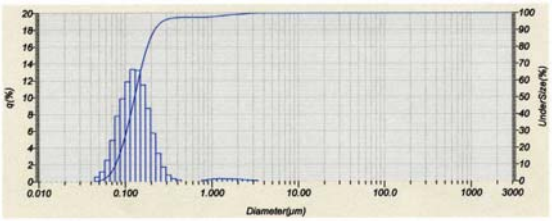
４．研究成果

(1) Synthesis: was successfully completed from aqueous solutions of $CaCl_2$ and NaOH at 90 °C under powerful mixing (rpm 10 000). After chloride removal and centrifugation, product was transferred (peptized)into alcoholic (mostly n-propanol) dispersions. The size of the particles of synthetized nano-lime (Fig.1) varied between about 50-400 nm.

The nano-limes investingated by HRTEM showed a wide variety in particle sizes. Mostly the samples contained particles in nano-region, but rarely micron-sized particles could be also observed because of aggregation. Particles below 50 nm were rare, 100-300 nm common, over 500 nm only in several cases.



Commercial "dry" hydrated lime powder in water



Synthetized nanolime in ethanol

Fig.1 Comparison of commercial "dry" hydrated lime powder in water (mean particle size: 52.9 μm, bimodal distribution) (upper) and synthetized nano-lime in ethanol (mean particle size: 173.3 nm, unimodal distribution)(lower). Particle size was determined by Horiba laser scattering particle size analyser.

Aggregation was present in all samples. We found both randomly oriented (non-oriented) reversible (crystals redisperse in water or under ultrasonic mixing)) and chrystallographically oriented irreversible aggregation (such crystals do not revert back to smaller crystals when reintroduced to water or under ultrasonic mixing). The dominant crystallographically oriented self-assemble of Portlandite nanocrystals happened along the basal planes (001).

On Fig.2 a HRTEM direct lattice imaging of an aggregate composed of three crystallites, showing the lattice layers (fringes) corresponding to the (001) planes of oriented (face-to-face) nanocrystals in a synthetized nano-lime can be seen. The pairs of arrows indicate the contacts between the nanocrystals. The observed d-spacing is 5.1 Å (0.51nm). This value is about the same as the d_{001}-spacing = 4.956

Å, given in the International Centre for Diffraction Data's PDF Card). This distance indicates, that the $Ca(OH)_2$ forms a one layer monotype.

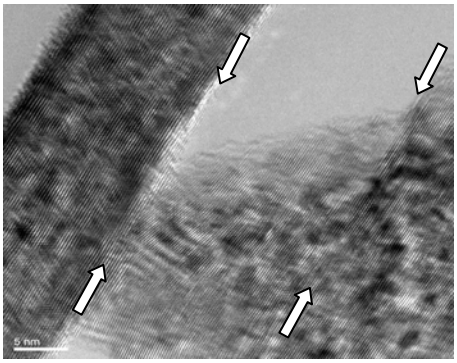


Fig.2 Direct lattice image

Estimating crystallite size and shape

Crystallites are single crystals of different sizes, which are built up from the same type of unite cells. A particle can be composed of one crystallite (in this case crystallite size is equal to particle size), but usually it is built up from more crystallites because of aggregation. Particle size is equal or larger than crystallite size. The study of both is important.

The crystal structure, crystallite size and shape of the synthetized calcium hydroxide colloidal crystals were investigated by X-ray diffractometry (XRD) (Fig.3).

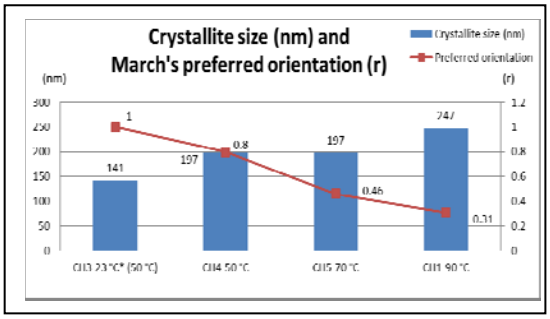
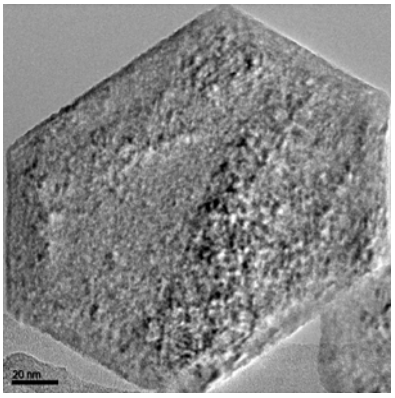


Fig.3 Results for crystallite size and preferred orientation for synthetized nano-limes obtained by XRD

Calcium hydroxide (Portlandite) crystals are of hexagonal character. They can form flat plate-like or tall column-like crystals. The shape of the synthetized Portlandite particles was dominantly hexagonal plate (Fig.4). We could not observe hexagonal prisms (columns) by HRTEM. If originally there were any immediately after the synthesis, may be they were transferred into plates under the storage-time by interlayer (basal) cleavage. Plate-like crystals have larger specific surface area therefore their chemical reactivity is higher, than that of column-like crystals.



(bar 20nm)

Fig.4 HRTEM micrograph of nano Ca(OH)2 (Portlandite crystals) having hexagonal plate shape, size: about 150 nm

Larger specific surface area has larger reactivity (better performance), therefore plate-like crystals have larger reactivity, than column shaped crystals of the same material. Limes with small plate-like crystals have faster carbonatation reaction (setting) and give more consolidation. In Conservation Science, the size and shape of the hexagonal Portlandite crystals are of main importance.

The crystallite size was estimated by the Scherrer formula (FWHM (Full Width at Half Maximum) of XRD peak is inversely proportional to crystallite size). The shape was studied by the March coefficient and profile fitting of the XRD spectra (Fig.3 and 5).

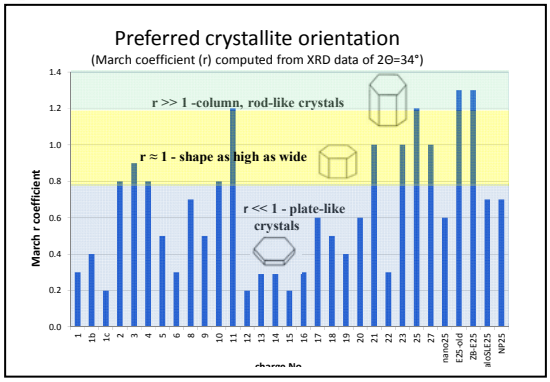


Fig.5 Result of preferred crystallite orientation (r) of synthetized nanolimes. If r<<1 - shape is plate, if r~1 – shape is as high as width, if r>>1 – shape is column.

(2) Deacidification of kozo, gampi and wood-pulp paper can be done successfully by nano and common $Ca(OH)_2$ particles.
Acidification of papers causes acid catalysed hydrolysis and consecutive chain breaking of cellulose and the loss of strength and flexibility of paper. Acidic paper discolours more easily than pH neutral or alkaline one. Therefore pH is the most important factor in the degradation of papers.

Papers mentioned before were treated by 30 min. soaking in 10g/L nano-lime and commercial (non-nano) dry slaked lime powder dispersed in alcohol. Later a moist heat accelerated aging (80°C and 65%rh for 8 weeks) was completed. After aging pH, colour change, tensile index, folding endurance were tested.

The **pH** of paper after the treatment and aging is determined by three factors: 1. the introduced $Ca(OH)_2$ increases, 2. the amount of acids developed before treatment (common aging) and under accelerated aging decreases, and 3. the transformation reaction of $Ca(OH)_2$ into $CaCO_3$ decreases pH. As a sum value pH was risen to 10.6-12.1 (after treatment and before accelerated aging). The maximum pH theoretically can rise up to 12, which corresponds the pH of the saturated aqueous $Ca(OH)_2$ solution. After accelerated aging, pH went down to 8.6-9.6. Values higher than 8.3 (which is the pH of the saturated aqueous calcium carbonate solution) are suggesting that the carbonatation reaction has not been fully completed inside the paper. pH between 8-9 is optimal for long term preservation of papers. $CaCO_3$ also serves as an alkaline reserve and binds future acids.
Nano and normal lime behaved similarly. In the case of nano-lime the pH went down slightly faster, probably due to the higher reactivity of the smaller sized crystals.

Kozo and gampi proved to be of good quality and rather stable papers against aging. Pulp paper was always inferior. Sizing of papers caused strong **colour change.** Due to the test unsized kozo and gampi treated with nano- and common lime proved generally not so effective in preventing colour change, sometimes the change exceeded the change of untreated samples. Nano- and common lime treatments can control effectively the colour change of sized papers, especially European type acidic wood pulp paper (Fig.6).

Nano-and common lime treatments of kozo and gampi were not effective in **tensile index**. For pulp paper the treatment is valuable, it kept nearly the original tensile index through the whole aging.

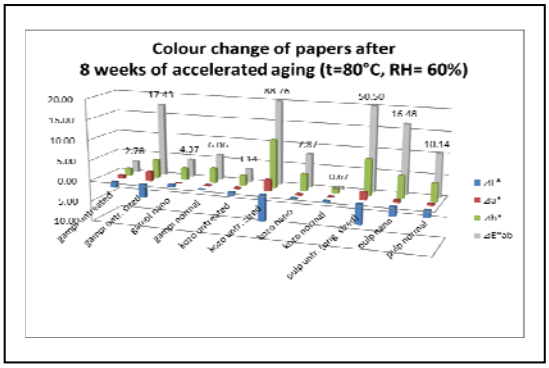


Fig.6 Colour change of papers after 8 weeks of accelerated aging. ΔL* = *lightness* (black to white), Δa*= *red to green*, and Δb*= *yellow to blue*, and ⊿ E*ab = overall colour change. See data in Table….(Abbreviations: ave.= average values, untr. = untreated, orig. = originally)

Untreated-unsized nano- and common (normal) lime treated kozo and gampi samples, all performed well in keeping the **folding endurance** of papers under the aging test nearly unchanged. Untreated-sized kozo lost nearly totally its original folding endurance. Nano- and normal-lime treatment of wood pulp paper performed excellently in keeping the folding endurance, while untreated lost markedly.
In most tests common and nano-lime behaved about the same, as normal lime without any important difference.

As a conclusion, nano- and common lime treatments especially suited for the preservation of acidic wood pulp papers, which are sized under the manufacture. Beside that they should have excellent performance in the case of sized kozo and gampi too, but it should be tested in a future study.

(3) Consolidation of cement mortar, "artificial" stones (sandstone, granite and tuff), brick, and real stones with $Ca(OH)_2$ nanoparticles and comparison with traditional consolidants:

We used for the study grits and powders mixed with cement binder and modelled the degraded materials with formulations

poor in binder. We prepared about 500 cylindrical (diameter and height 50 mm) samples of "artificial" stones (sandstone (Daigo, Ibaraki pref.), granite (Inada, Kasama, Ibaraki pref.) and tuff (pumice tuff- Ooya, Tochigi pref)), cement mortar and brick. All the grits and powders were compounded with Rapid hardening Portland cement (Sumitomo Osaka Cement Co) in volume-ratio 15+1. Impregnations were done by modern consolidants: a non-aquaeous collodial nano-lime ($Ca(OH)_2$) sol (mean particle size was around 160 nm), a well-known oligomeric tetraethoxysilane product (Wacker SILRES® BS OH 100), an extremely low viscous epoxy resin (Araldite 2020) and for cultural heritage the most frequently used thermoplastic acrylic resin (Paraloid™ B-72 or also called Acryloid™ B-72) which is known from its good durability, high transparency and non-yellowing film-properties. All consolidants were solved in n-propanol, except Araldite which was diluted by toluene. Concentrations were 25g/L, at Wacker it was 78.1 g/L which is relevant to 25g/L silica concentration after reaction.
n-Propanolic suspension of common lime (dry hydrated lime powder) having micronsized particles was also tried, but it had very limited penetration and the particles accumulated on the surface forming a thick white layer, therefore this consolidant was abandoned in the study.
Consolidants were applied by 10 minutes vacuum-impregnation once and three-times. It caused total impregnation throughout the crosscut. The depth of impregnation for nano-lime was proved by phenolphthalein staining method on the sample broken in half.
Mechanical tests were completed: splitting tensile strength, p-wave (ultrasonic pulse velocity) and Equotip dynamic surface hardness tests.

The reaction of $Ca(OH)_2$ into $CaCO_3$ causes the dominant strength change after the treatment. Reaction takes time and it is dependent on CO_2 concentration and humidity of the surrounding air. To speed up the carbonatation reaction, the nano-lime treated samples were kept for three months in a carbon dioxide rich environment, in a plastic tent, where CO_2 was generated by the reaction of marble and diluted (1:2) nitric acid.

Mechanical tests of nano-treated samples showed sometimes very low mechanical values. We were searching for the reason and cut or broke several samples and stained the crosscut by phenolphtalein which gives a purple colour with unreacted $Ca(OH)_2$. It was proved, that only a thin surface layer of the sample, about 2-3 mm in depth was carbonated in three month, while the inner bulk of the samples was still uncarbonated, indicated by purple colour (diameter of cylinder samples were 50 mm).

According to the recent evaluation the three-times vacuum-impregnation with nano-lime caused small procentual **splitting tensile strength** increase at mortar (14.2%), brick (-3.5%) and granite (2.6%) samples (values are given as percentage of untreated). Unfortunately nano-lime caused marked increase in the case of sandstone (73.3%) and tuff (98.9%). Other consolidants increased the splitting tensile strength in order: Wacker, Araldite and Paraloid) at mortar 67.4; 46.8; 65.2%, brick 11.6; 64.0; 34%, sandstone 38.1; 47.6; 85%, and tuff 60.0; 61.7; 106.1%. All consolidants performed badly in the increase of splitting tensile strength at granite (between 1.9-3.1%) (Fig.7).

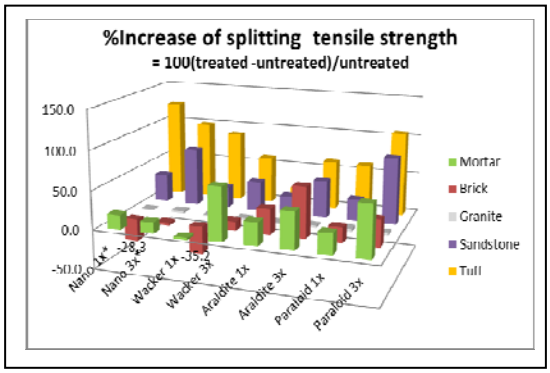


Fig.7 Percentual increase of splitting tensile strength

Ultrasonic pulse velocity (UPV) (or P-wave velocity) depends on density, pore structure, compactness, cracks, fractures and inner continuity or discontinuity of the stones. It is an inner integrity testing method. Internal loss or coherence forces the sound waves to follow a longer way or to pass through a layer of air and as a consequence the transition time increases and the UPV decreases.
As the consolidant fills the pores of stone, it makes the stone more compact, indicated by the increase of UPV.

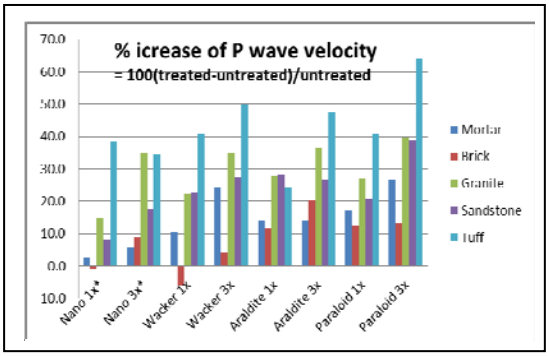


Fig.8 Percentual increase of p-wave velocity

In all sample materials nano-treated (3x) showed the lowest %increase of UPV values, ranging between -5.6% (mortar) to 34.9% (sandstone) (Fig8), therefore it can be concluded, that nano-lime caused the least change in porosity between all of the consolidants used. Not filling the pores is a big advantage under a possible drying because absorbed rainwater or moisture can escape easily from the inside of the consolidated stone.

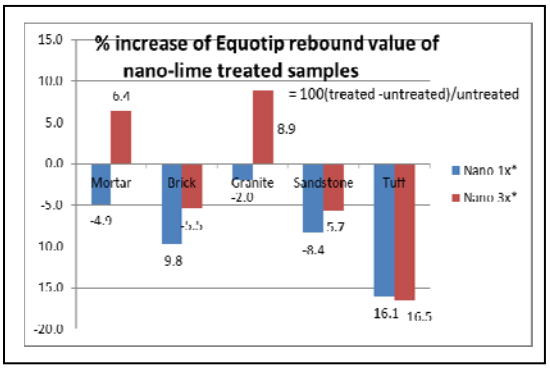


Fig.9 Percentual increase of Equotip surface hardness

The %increase of the Equotip surface hardness (Fig9) of nano-lime treated samples gave the lowest values for mortar, brick, sandstone and tuff treated with consolidants three-times, but it gave in the case of granite the second highest value. This low increase of surface hardness proves, firstly that the hardness of the consolidated surface is about the same as before consolidation, and secondly that nano-lime hardens in the crosscut uniformly and does not form a more consolidated surface shell, which is common for high molecular size polymers. Surface shell is always detrimental and cause speeded up weathering and peeling.

The values measured for nano-lime will change with progressing carbonatation. Therefore at moment a real final comparison of the nano-lime treatment can't be given. We have to wait for full carbonatation. May be it will take a year. We will measure the mechanical properties again after the completion of the carbonatation reaction on the remaining samples and re-evaluate the recent temporary consolidation results.

５．主な発表論文等

〔学会発表〕（計５件）

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６．研究組織

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