Wooden Materials Suitable for Storage Boxes or Cellar Walls to Remove Nitrogen Dioxide and Ozone in Ambient Air

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Abstract

An investigation was made of wooden materials suitable for storage boxes or cellar walls to protect cultural properties from air pollution. An air sample containing nitrogen dioxide and ozone that can injure the properties was passed through individual columns packed with fine particles of wooden materials, such as pine, cypress, cedar, paulownia, zelkova, lauan, hemlock spruce and magnolia hypoleuca, and the concentrations of these gases were monitored. Cedar and zelkova displayed great abilities to reduce nitrogen dioxide to nitogen monoxide, and cedar and cypress were shown to decompose ozone. Boxes or cellars finshed with cedar inside may be the most favorable to conserve cultural properties for long periods without incurring the effects of air pollution in urban areas.

Key words : conservation of cultural properties nitrogen dioxide, ozone, remove of air pollutants, wooden material,

1. Introduction

Historical properties have often been reported to undergo extreme damage due to air pollution and acid rain from industrial and household activities, especially in urban areas, as seen in Rome, Italy ; Athens, Greece ; Beijing, China. Development of measures is urgently needed to conserve such valuable properties and save them for future generations. In Japan, cellars or boxes made of wooden materials are empirically known to be effective at conserving cultural properties for long periods. At Todaiji temple, a great number of ancient properties, such as sutras, fine arts, documents, Buddhist images, household articles, festival tools, swords, musical instuments, etc., have been preserved for 1200 years without serious degradation in cedar boxes in a cypress storage house. Constant temperature and humidity can be achieved in spaces surrounded by wooden material[1,2], and lower concentrations of air pollutants can be observed in wooden cellars or structures than outdoors[3-5]. On the other hand, wardrobes or cabinets made of sufficiently dried cedar, paulownia, etc., can produce highly airtight and insect-repellent spaces suitable for preserving paper, cloth, wood and metal goods. So far, these favorable qualities have not, however, been scientifically analyzed.

In this study, qualities were investigated of wooden materials popularly used for containers, storage cellars and interior designs or structures, such as pine, cypress, cedar, paulownia, zelkova, lauan, hemlock spruce and magnolia hypoleuca, to detemine if they are effective and economical to use for containers or storage cellars for historical properties. The results have indicated that cedar may be the most suitable for boxes or cellars for conserving historical properties over long periods in urban areas with serious air pollution.

2. Experimental Method

2.1 Apparatus and materials

The experimental tubes used were 200 mm × 7.6 mm i.d. U-shaped Pyrex glass tubes made by Sanwa (Osaka, Japan), and the nitrogen dioxide (NO_2) standard gas was a 99.6 ppm balanced nitrogen produced by Sumitomo-Seika (Osaka, Japan). Figure 1 and 2 show experimental systems for investigating the effect of wooden materials on NO_2 and ozone (O_3) concentrations in air, respectively. Sawdust particles of pine (*Pinus densiflora*), cypress (*Chamaecyparis obtusa*), cedar (*Cryptomeria japonica*), paulownia (*Paulownia tomentosa*), zelkova (*Zelkova serrata*), lauan (*Parashorea*), hemlock spruce (*Tsuga heterophylla*) and magnolia hypoleuca (*Magnolia obovata*) were perpared by sawing these materials into 0.71-1.00 mm diameter particles, drying at 70°C for more than 12

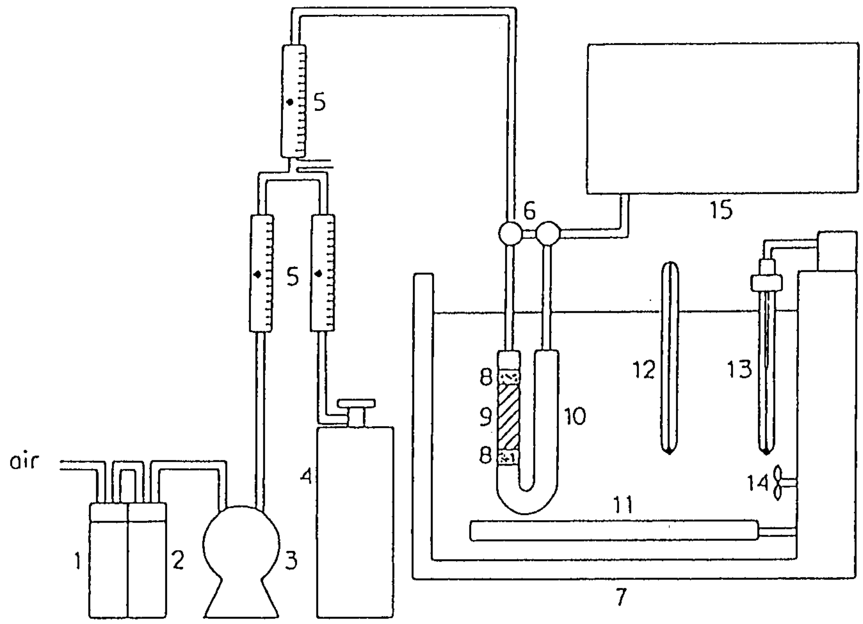

Fig. 1 Apparatus for investigating qualities of wood materials in removing NO_2 from air. 1 : silica-gel (500 g), 2 : activated charcoal (500 g), 3 : air compressor, 4 : NO_2 standard gas cylinder (99.6 ppm), 5 : flow meter (280 mL/min air), 6 : 3-way cock, 7 : thermostatic water-bath, 8 : glass wool, 9 : sawdust wood column (30-100 mm × 7.6 mm i.d.), 10 : U-shaped Pyrex glass tube (200 mm × 7.6 mm i.d.), 11 : temperature controller, 12 : thermometer, 13 : Beckman thermometer, 14 : stirrer, 15 : Kimoto (Osaka, Japan) Model-265 NO_X meter.

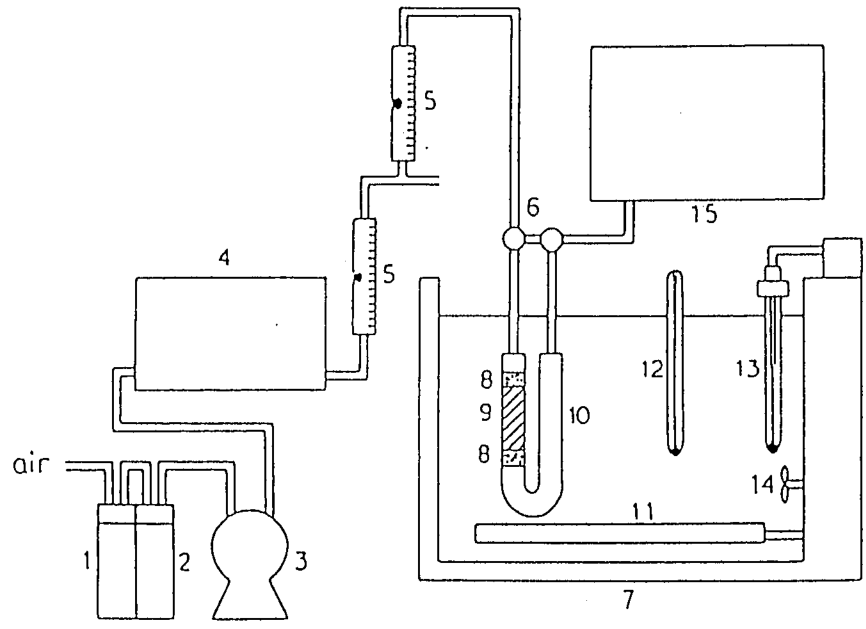

Fig. 2 Apparatus for investigating qualities of wood materials in removing O_3 from air. 1-3 : see Fig. 1, 4 : Yanako (Kyoto, Japan) OZ-2 O_3 generator, 5-8 : see Fig. 1, 9 : sawdust wood column (20-30 mm × 7.6 mm i.d.), 10-14 : see Fig. 1, 15 : Kimoto Model F 03-803 O_3 meter.

hours, and packing the individual wood sawdust samples intoa part of the U-shaped tubes. Glass wool was packed at both ends of the wooden sample.

Figure 3 shows a diffusion-type passive sampler[6] used for monitoring nitrogen monoxide (NO), NO_2 and sulfur dioxide (SO_2) in various places at an urban museum. A Daikin (Osaka, Japan) PA-5L polytrifluoroethylene (PTFE) filter was cut to 26 mm diameter and used. An Advantic Toyo (Tokyo, Japan) NO. 514 A filter paper cut to 18 mm diameter was used as the absorption disk for NO_2, NO_X and SO_2, washed in 1L of water at 50°C in an ultrasonic bath, than washed with water three times at 60-80°C and dried at 50°C for 12 hours under reduced pressure. Seventy-μL of 10 % triethanolamine (TEA) aqueous solution was dispersed onto the disk for NO_2 sampling, 70-μL of

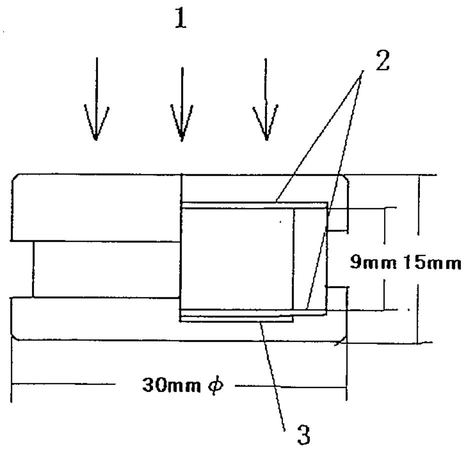

Fig. 3 Passive sampler for monitoring NO_2, NO_X and SO_2[6]. 1 : ambient air, 2 : PTFE filter, 3 : paper disk impregnated with absorbents.

10 % 2-phenyl-4,4,5,5-tetramethylimidazoline-3-oxide-1-oxyl (PTIO) and 10% TEA aqueous solution for NO_X sampling, and 70-μL of 5% sodium carbonate aqueous solution for SO_2 sampling.

2.2 Procedure of reduction tests by the sawdust woods

An air stream containing 800-900 ppb of NO_2 was prepared by flushing the NO_2 standard gas into a pure air stream at 280 mL/min. The air was passed through the U-shaped tube packed with a wooden material at 20, 30 and 40°C. The concentrations of NO_2 and NO were thus monitored both at the head and at the exit of the tube using a NO_X meter. A blank test was done in the same way using the tubes packed with glass wool.

For the O_3 test, an air stream containing 350-400 ppb of O_3 was prepared at 1800 mL/min by diluting ozone air from an O_3 generator with purified air. The experiment was done the same as that for NO_2.

The blank test was conducted by monitoring the NO_2 or O_3 concentrations at the entrance of the tube

Table 1 Sampling places in an urban museum.

place wooden material: wall	floor	ceiling	temp. °C	humidity %	ventilation rate times/hr	floor space (capacity) m²(m³)	air conditioner
storage cellar 1							
cedar	lauan	cedar	22	55	0.05	250 (700)	equipped
storage cellar 2							
cedar	lauan	cedar	22	55	0.05	27 (76)	equipped
display case							
glass	cloth	cloth	23-28	55-65	<0.5	5 (10)	equipped
exhibition room							
stucco	mortar	stucco	23-28	55-65	0.5	250 (900)	equipped
entrance hall							
stucco	mortar	stucco	—	—	5-6	—	no equipped
outdoor garden							
—	—	—	22-34	28-99	—	—	—

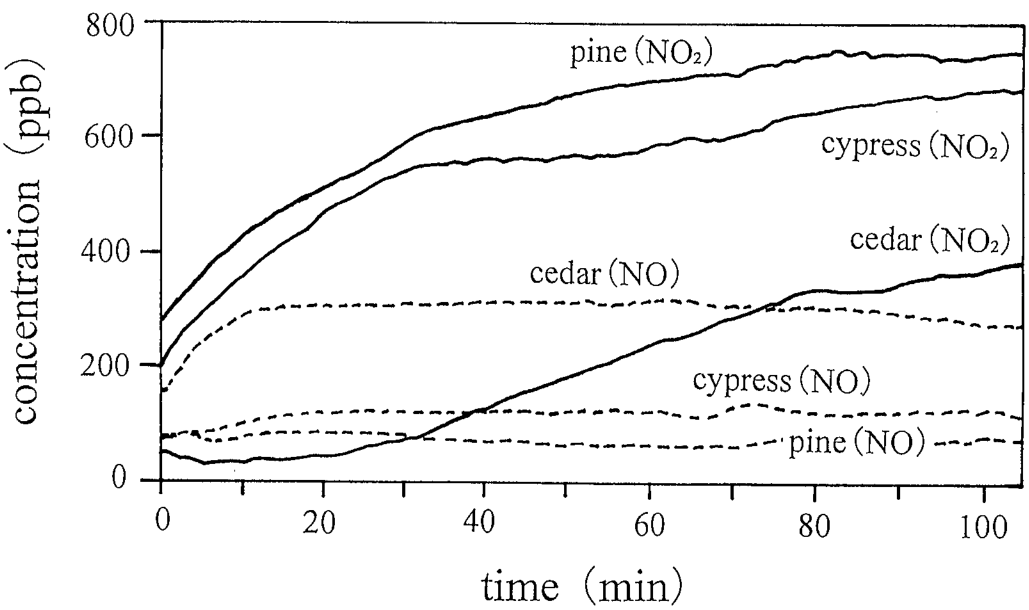

Fig. 4 Effects of wooden materials on NO_2 and NO in air. NO_2 concentration at column inlet : 600-750 ppb. Temperature : 30°C. Flow rate : 280 mL/min. Weight of wood sample : 0.56 -1.03 g.

and at the outlet in 1 min for NO_2 or in 10 min for O_3 after the tests started.

2.3 Monitoring for the air pollutants in an urban museum

Table 1 describes the sampling places. The storage cellars and the exhibition room were equipped with air conditioners. The entrance room was open to the outdoor. The ventilation rates were empirically 0.05 times/hr in the storage cellars, 0.5 times/hr in the exhibition room and 5-6 times/hr in the entrance hall. The passive samplers were placed for monitoring NO_2, NO_X and SO_2 for 2 weeks in the sampling places. The sampling disks were subjected to determination of NO_2, NO_X and SO_2[6]. The NO concentration was calculated as the difference between the concentration of NO_X and that of NO_2.

3. Results and Discussion

3.1 Reduction of NO_2 in air by the wood materials

Figure 4 shows the aspects of NO and NO_2 concentrations in air samples passed at 30°C through the experimental tubes packed with pine, cypress, and cedar sawdusts. The columns of pine and cypress indicated the same aspects. The NO_2 concentration was reduced at the initial stage, gradually increased and reached the concentration at the column head in 100 min. The NO concentration was at a nearly constant level during the experiment. This suggested that the initial reduction of the NO_2 concentration may be mainly derived from adsorption on the sawdust particles. The paulownia, lauan and hemlock spruce columns show the same aspects as those of pine and cypress.

In the cedar column, the NO_2 concentration remained at a substantially low level at the outlet for 20 min and then gradually increased. On the other hand, the NO concentration was remarkably high from the initial stage and nearly constant for more than 100 min. This suggested that besides adsorption the cedar may reduce NO_2 to NO. The zelkova showed the same aspect as that of cedar though the degree of the reduction was somewhat lower.

Table 2 Reduction of NO_2 by wooden materials at different temperatures.

wooden material	amount of reduced NO_2, μmol/g*		
	20°C	30°C	40°C
pine	0.26	15.5	3.28
cypress	0.38	15.5	7.41
cedar	0.38	66.2	17.1
paulownia	0.31	7.66	
zelkova	0.89	59.6	8.17
lauan	0.33	13.0	
hemlock spruce	0.23	2.79	
magnolia hypoleuca	0.89	1.21	

NO_2 concentration at column inlet : 600-930 ppb. Flow rate : 280 mL/min. Weight of wooden sample : 0.30-1.03 g. *Amount of reduced NO_2 : defference between amount of NO_2 totally integrated at the inlet until 50% of NO_2 concentration is attained at the outlet and that integrated at the outlet for that period.

3.2 Effects of temperature on reduction of NO_2

Table 2 shows the amounts of NO_2 reduced in air by the wood sawdusts at 20, 30 and 40°C. The reduction of NO_2 was low at 20°C, noticeably increased at 30°C and decreased at 40°C in all the materials. The reduction of NO_2 was highest by the cedar and the zelkova at 30°C, while the NO concentration remarkably increased. This suggested that NO_2 was reduced to NO on these material.

3.3 Reduction of O_3 in air by the wood materials

Figure 5 describes the aspects of O_3 concentrations in air samples passed at 30°C through the experimental tubes packed with pine, cypress, and cedar particles.

In the pine column, the O_3 concentration was at zero level at the initial point, soon steeply increased and reached a gentle slope in 40 min. This suggested that

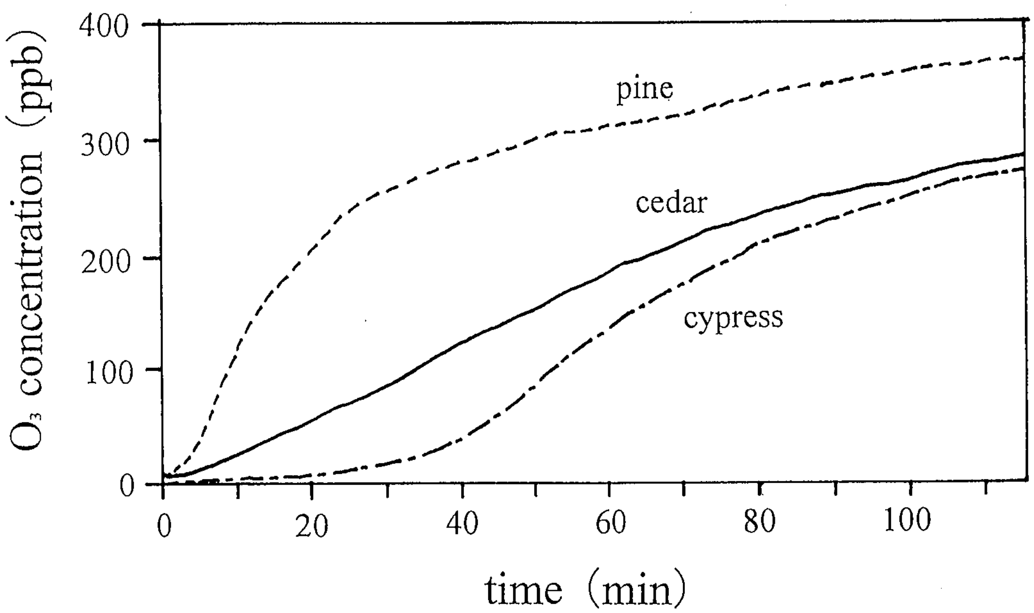

Fig. 5 Effects of wooden materials on O_3 in air. O_3 concentration at column inlet : 370-390 ppb. Temperature : 60°C, Flow rate : 1,800 mL/min. Weight of wood sample : 0.22-0.30 g.

Table 3 Reduction of O_3 by wooden materials at different temperatures.

wooden material	amount of reduced O_3, μmol/g*		
	20°C	40°C	60°C
pine	0.65	0.99	1.13
cypress	3.34	5.79	6.33
cedar	1.73	3.78	5.96
paulownia	0.73	0.37	1.07
zelkova	0.40	0.53	0.83
lauan	0.61	0.74	0.91
hemlock spruce	0.11	0.55	0.57

O_3 concentration at column inlet : 360-400 ppb. Flow rate : 1,800 mL/min. Weight of wooden sample : 0.19-0.37 g.
* Amount of reduced O_3 : defference between amount of O_3 totally integrated at the inlet until 50% of O_3 concentration is attained at the outlet and that integrated at the outlet for that period.

a breakthrough may occur on adsorption of O_3 on the column. The other wood material columns indicated the same aspects as that of pine except for cypress and cedar.

In the cypress column, the initial concentration of O_3 was nearly zero for 10 min and steeply increased in 40 min. Because this was different from an S-shaped curve indicating adsorption, a chemical decomposition of O_3 was suggested to occur in addition to adsorption on the material. In the cedar column, the O_3 concentration was increased at a constant rate from the start and reached a gentle slope in 80-100 min. This curve of O_3 concentration also suggested chemical decomposition of O_3 on the cedar particles for the reason described above.

3.4 Effects of temperature on reduction of O_3

Table 3 shows the reduction amount of O_3 in air by the wood sawdusts at 20, 40 and 60°C. The amount of reduced O_3 was defined as the difference between the amount of O_3 totally integrated at the column inlet until the O_3 concentration reached 50% of the inlet concentration at the outlet and that intergrated at the outlet for that sample period.

In the pine column, the amount of O_3 was slightly reduced as the temperature decreased. The other wood meterial showed the same aspect as that of the pine except for cypress and cedar.

In the cypress column, the amounts of O_3 reduction were at extremetly high levels at 40 and 60°C. The difference was minute between the amount of O_3 reduction at 40°C and that at 60°C. In the cedar column, the amounts of O_3 reduction were rather high and became higher as the temperature increased. As a result, usage of cypress and cedar are effective to remove O_3 from air for boxes or cellars conserving historical properties.

3.5 Aspects of air pollutants in a cellar finished with cedar plates

Air pollutants, such as SO_2, NO and NO_2, were monitored in storage cellars, a display case, an exhibition room, an entrance hall and an outdoor graden at an urban museum. The former experiments indicated that SO_2 from outdoor air was well adsorbed by wooden materials and reduced in concentration in a wooden enclosure[3-5]. Table 4 shows the monitoring results. Little SO_2 and NO_2 were observed in the storage cellars finished with cedar plates while minute or rather high concentrations of them were detected in the display case finished with cloth inside and the exhibition room finishied with stucco. The NO concentrations are much higher in the cedar cellars than those in the other places. The NO concentrations in the cedar cellars could correspond to the total concentrations of NO and NO_2 in the entrance hall or outdoor garden. This also suggested that NO_2 is converted to NO in the cedar cellar. The concentrations of SO_2 and NO_2 seemed to be inversely proportional to number of air change in the rooms. The SO_2 could be easily absorbed in the walls, made of wooden materials, cloth and stucco, within 10-12 minutes. On the other hand, the reduction of NO_2 could need for 20-200 hours in the storage cellars finished with cedar plates.

Table 4 Monitoring of air pollutants at an urban museum.

place	concentration of air pollutant, ppb*		
	NO_2	NO	SO_2
storage cellar 1	n.d.	31	n.d.
storage cellar 2	2.0	18	n.d.
display case	5.6	12	0.1
exhibition room	10	10	0.1
entrance hall	16	10	0.1
outdoor garden	26	7.0	4.4

* Average concentration of air pollutant for 2 consecutive weeks in August, 1995.
n.d. : not detectable (< 0.1 ppb for NO_2 and SO_2).

In general, high concentrations of organic acids (for example, formic acid : 8.2 ppb, acetic acid : 62.1 ppb) and aldehydes (for example, formaldehyde : 28.8 ppb, acetaldehyde : 1.1 ppb) are observed in the storage cellars finished with cedar plates[7]. This phenomenon could be related to the reduction of NO_2 and the decompositoion of O_3, though the NO_2 reduction and the O_3 decomposition mechanisms are not still clarified.

4. Conclusions

As the features indicate, cedar seems to be one of the best materials for boxes or cellars for protecting valuable properties from air pollution caused by acid precipitation and hazardous gases. Additionally, cedar is known to retain constant humidity and anti-insect effects for years. So far, a number of Japanese temples and shrines have empirically selected cedar for storage boxes and cellars to successfully conserve valuable properties with minimum damage for 600-1300 years. Boxes or cellars finished with cedar may be best to conserve valuable properties for long periods especially in urban areas.

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