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Desalting System for Excavated Metal Objects Using High Temperature, High Pressure Deoxygenated Water

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□ ABSTRACT : We propose a new method to remove salts that have permeated into excavated metal objects. This method cleans the excavated metal objects by using high temperature, high pressure deoxygenated water containing inhibitors for corrosion of metals. The method greatly reduces the washing time compared with previous methods. Waste water from the method does not need treatment, nor do chemicals need to be removed from the metal objects. Furthermore, this method is applicable to some kind of metals(for example iron objects, bronze objects). We measured quantitatively the soluble salts dissolved from actual metal objects and found that there was a large difference between soluble chloride ions and sulfate ions.

1. Introduction

If metal objects unearthed by excavations are left in the atmosphere without additional treatment, rusting occurs due to the dramatic change from the preservation condition and the metal objects are quickly destroyed. In order to protect the metal objects from destruction, preservation treatment must be conducted as quickly as possible. In the preservation treatment process, the most time-consuming process is the washing process in which soluble salts, which have permeated into the metal objects while buried, are removed. This washing process removes water-soluble such as $FeCl_2$, $FeCl_3$ and CuCl in the form of a solution. Depending on the metal properties, various methods are used in practice.

In the case of iron objects, various methods have been used such as immersing the objects in alkali solution at room temperature for a few weeks or months(Oddy 1970, Akiyama

1983), immersing in high temperature deoxygenated water(Scott & Seeley 1986, Aoki 1990), or, together with desalting, converting unstable iron rust on objects to a stable rust(Magnetite : Fe_3O_4) in an alkaline solution under reduction conditions(alkaline sulfite method)(Gilberg 1982, Aoki 1987). However, in the method of immersing in alkali solution, the washing usually takes several months and devices are needed for treating the waste and removing the remaining chemicals. Also, the method of immersing in high temperature deoxygenated water has various problems such as the need for large facilities and maintenance.

In the case of bronze objects, there is less destruction by rusting than with iron objects. However, sometimes corrosion products containing copper chloride, called "bronze disease", occur. For bronze objects, preservation methods include immersing in heated distilled water, and immersing in alkali solution such as sodium sesqui-carbonate : Na_2CO_3, $NaHCO_3$. In the water solution of sodium sesqui-carbonate, however, there is the danger of dissolving and discoloration of the patina(Plenderleith 1971). The method of immersing in 3% benzotriazole(BTA) in alcohol to stabilize the rust is widely used(Madsen, 1967).

We propose a method(Imazu, Koezuka, 1994, 1995, 1996) that greatly shortens the washing time by using a readily available autoclave for medical use and high temperature, high pressure deoxygenated water with the addition of inhibitors to prevent corrosion of various metals. This method shortens the washing time substantially and does not require the treatment of waste water or the removal of chemicals remaining in the metal. The method can be used for any kind of metal including iron, copper, silver and other metals.

2. Apparatus and Method

2.1 Apparatus

In order to perform the treatment safely using high temperature, high pressure deoxygenated water, a special washing apparatus is needed. This apparatus is basically a modified autoclave for medical use. The apparatus removes oxygen from the chamber and maintains the temperature as high as 121 ℃ and the pressure of $1.2kg/cm^2$. The chamber maintains the high temperature, high pressure deoxygenated condition and the apparatus can be operated automatically for the series of processes of removal oxygen by reduction of pressure while maintaining the high temperature, high pressure condition, ending in the deoxygenated state after one cycle of the unit(Fig. 1, 2, 3).

2.2 Method

The washing apparatus is operated in the deoxygenated state. However, as soon as the chamber is opened, oxygen in the air enters the

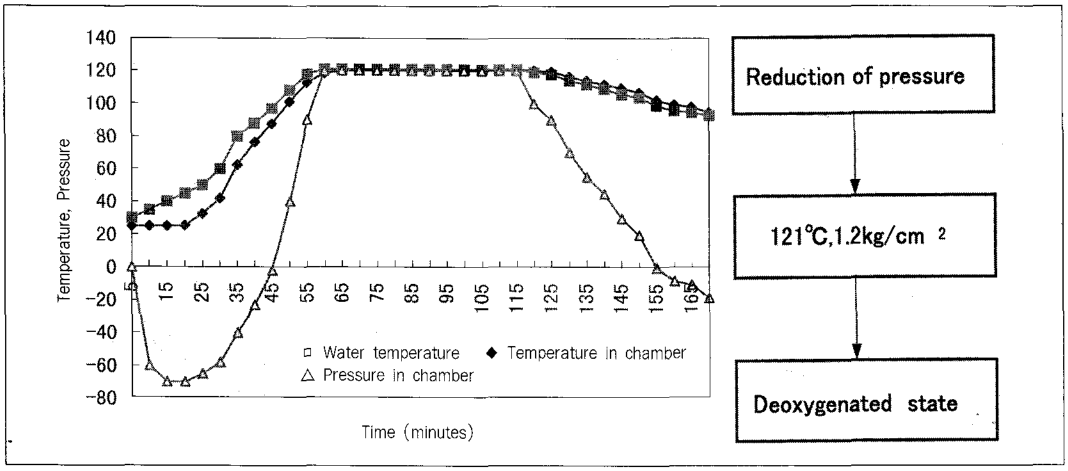

Fig. 1. Structural drawing of washing apparatus

high temperature water, so to prevent additional rusting, inhibitors for corrosion of metals are added. Various industrial chemicals are utilized as inhibitors, but often such corrosion-protective chemicals are toxic, so to ensure corrosion-protection and safety, for copper alloy we used a 0.2% water solution of benzotriazole(BTA : $C_6H_5N_3$), and for iron products, we used in addition to 0.2% BTA, highly purified deionized water containing 0.1% borax($Na_2B_4O_7$) or sodium benzoate($C_7H_5O_2Na$)(Table 1).

2.3 Analytical method(Fig. 4)

The washing process was operated at 121℃, 2.0 atmospheric pressure for 6 hours as one cycle. For each cycle, soluble salts dissolved in 10 times of water(highly purified deionized water containing 0.2% BTA and 0.1% borax) relative to excavated objects were analyzed using ion-exchange chromatography(DIONEX DX-100).

3. Measurement of washing efficacy

Table 1. Comparison of inhibitors for corrosion of metals(unit:mg/dm^2. day)

	Solution	Inhibitor none	Sodium sulfite	Sodium dichromate	Sodium benzoate	Borax	Na.MBT (BTA)
toxicity		none	poison	poison	LD50=2.7g		LD50=560mg
steel (Fe)	a b	140 510	0 0	0 1	〈 1 4	〈 1 365	〈 1 365
case iron (Fe)	a b	101 98	1 3	2 2	91 107	〈 1 144	36 109
copper (Cu)	a b	1 3	3 14	1 1	1 11	3 3	〈 1 1

a : Supply water b : Supply water+NaCl 2000ppm+$NaSO_4$ 1000ppm Ooyama 1983, p.182

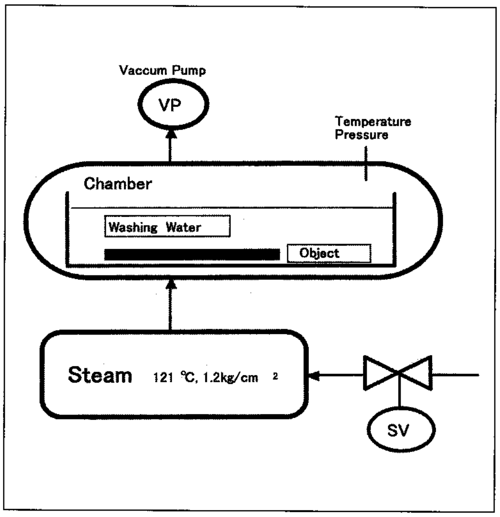

Fig. 2. Appearance of washing apparatus (effective dimension of chamber)

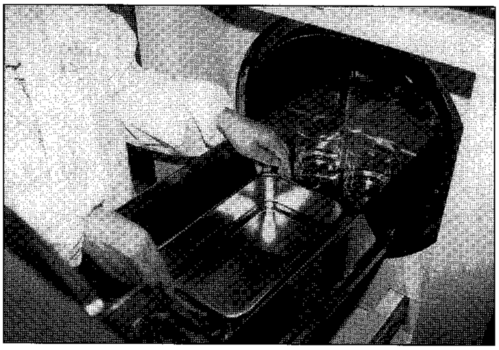

Fig. 3. Changes of temperature and pressure by washing apparatus

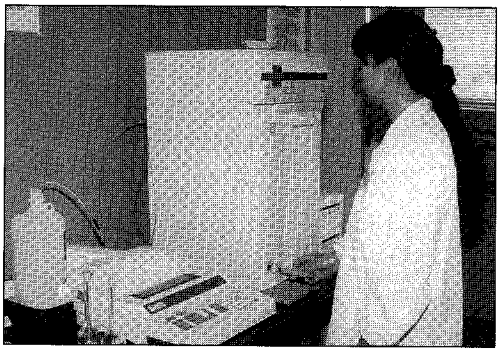

Fig. 4. Quantitative analysis of desalting efficacy by ion-chromatography

Fig. 5. Destroyed iron object used in the experiment

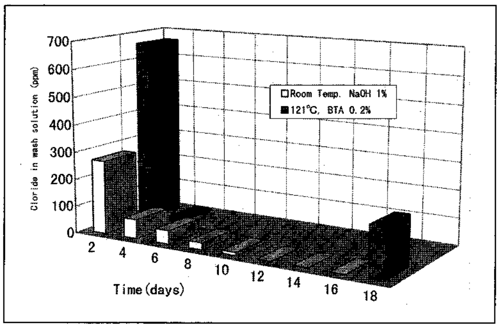

Fig. 6. Comparison of washing methods (NaOH method at ambient temperature and high temperature, high pressure deoxygenated water method)

3.1 Shortening of washing time(Fig. 5, 6)

In order to compare the washing efficacy, the method of immersing in sodium hydroxide solution(1% NaOH) at ambient temperature and replacing the solution every other day was compared with the method of using high temperature, high pressure deoxygenated water and replacing the water every 6-hour cycle(2 cycles per day). The washing process using high temperature, high pressure deoxygenated water was found to require just 1/6 of the time required by the method of immersing in sodium hydroxide solution at ambient temperature. Also, when using sodium hydroxide solution at ambient temperature, not all the soluble salts were extracted.

3.2 Desalting effect for destroyed iron object(Fig. 7, 10)

Using a fragment of an iron object that had been destroyed completely by being left in the atmosphere after excavation, the washing efficacy was measured. The fragment was pulverized, and the remaining ratio of soluble salts was measured, showing that 90% of soluble salts extracted by the washing process.

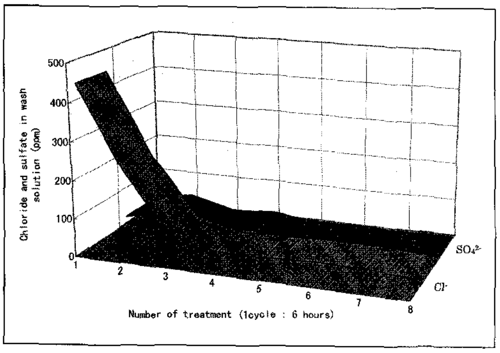

Fig. 7. Washing efficacy for completely destroyed iron object(sword)

Fig. 8. Element mapping by energy dispersion type fluorescence X-ray analysis before and after treatment

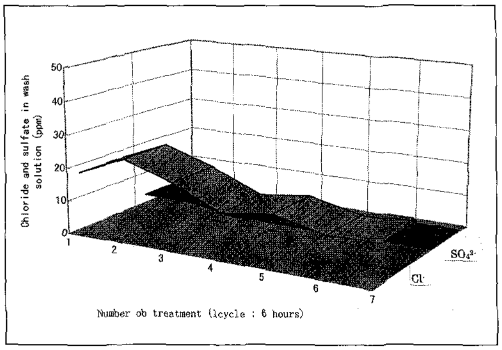

Fig. 9. Washing efficacy for iron object(arrowhead) that was not destroyed after excavation

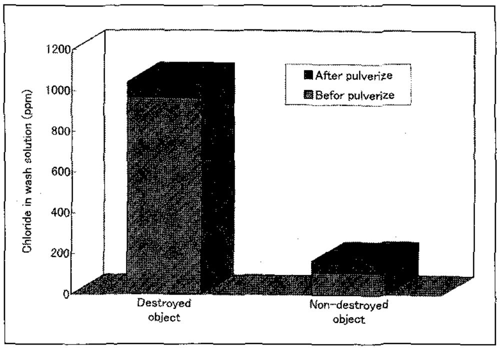

Fig. 10. Total extracted amount of soluble chloride ions(extracted from excavated object and then extracted from pulverized object)

3.3 Desalting effect for a non-destroyed iron object(Fig. 8, 9, 10)

Washing efficacy was measured using a fragment of an arrowhead that had not been destroyed even several tens of years after excavation. Element mapping was conducted by X-ray fluorescence analysis on a cross section of the iron object before and after the washing process. The results showed that about 65% of soluble chlorides was extracted by the washing process, but in the closed area where high temperature, high pressure water could not permeate, soluble salts were found remaining inside the sample.

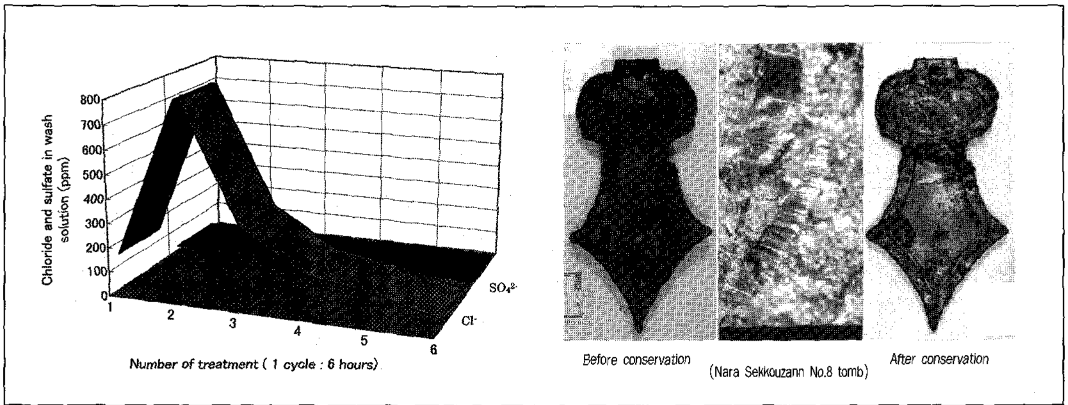

Fig. 11. Iron objects showing extraction of large quantity of soluble salts

3.4 Extracted amounts of soluble salts and relationship with destruction of excavated objects(Fig. 11-15)

Extracted amounts of soluble salts were measured for excavated objects in varying states of deterioration. For a sword that had been excavated more than 20 years ago and destroyed, the extracted amount of chlorides exceeded 1000ppm. On the other hand, the chlorides extracted from an arrowhead that had not been destroyed 20 years after excavation was less than 100ppm. For an iron ax that had been destroyed even after the preservation process by washing with alkali water at ambient temperature, sulfate ions of more than 1000ppm were detected.

4. Conclusion

We proposed a new method to extract soluble salts from excavated metal objects using high temperature, high pressure deoxygenated water. The special features of this method may be summarized as follows.

1. High temperature, high pressure deoxygenated water reaches the tiny gaps

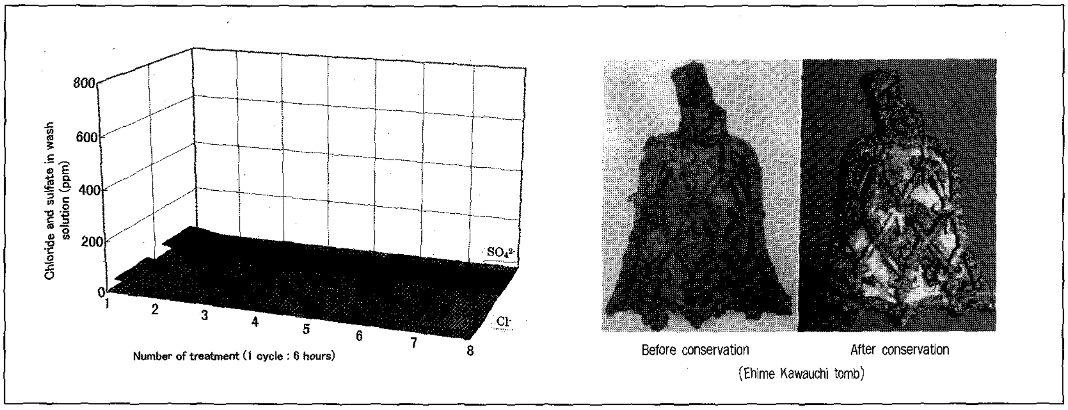

Fig. 12. Iron objects showing extraction of small quantity of soluble salts

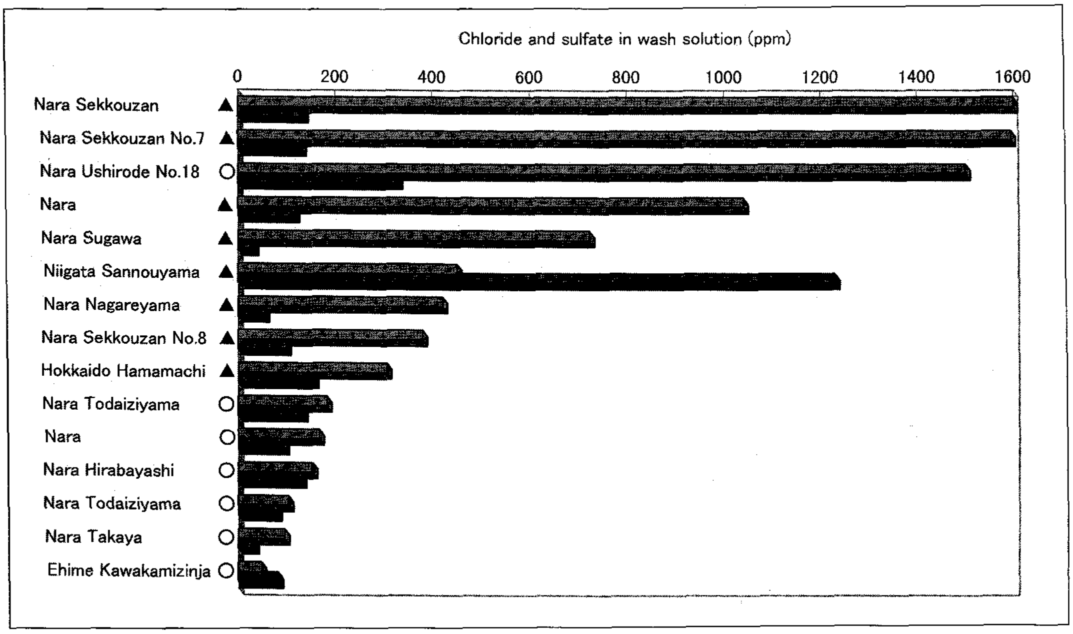

Fig. 13. Extracted quantity of soluble salts and relationship with destruction of excavated objects
(▲ degree of destruction was large, ○ degree of destruction was small)

in rust by the reduction of surface tension and coefficient of viscosity and dissolves the soluble salts contained the excavated objects.

2. Because hot water is used, excavated objects that are processed with resins can be treated without additional processing, so the method can be used for objects that were impregnated with resins without pre-treatment.
3. The processing time and hence preservation treatment time is greatly shortened.
4. Inhibitors against metal corrosion such as BTA act as stabilizing agents for rust after

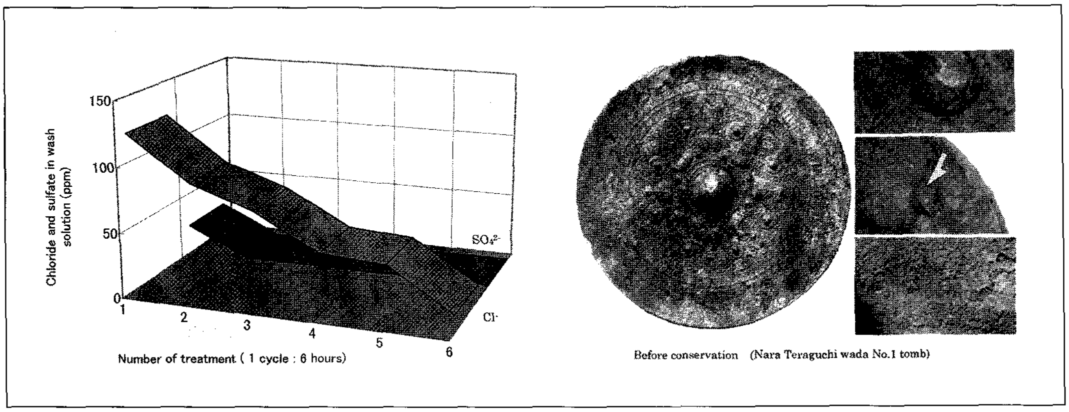

Fig. 14. Bronze objects showing extraction of large quantity of soluble salts

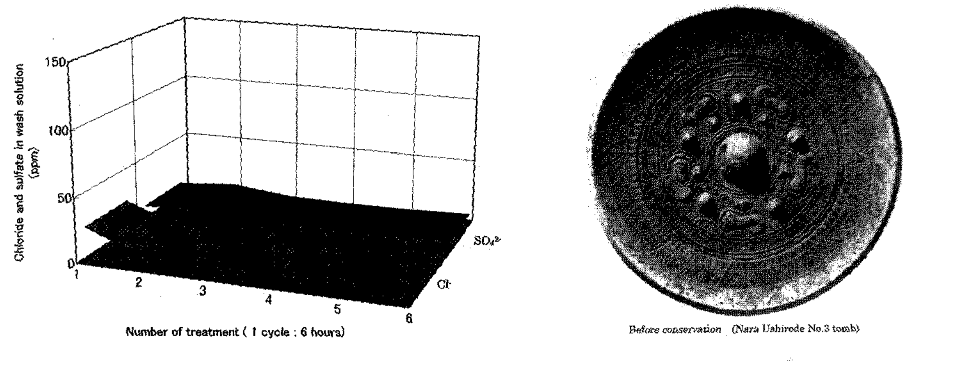

Fig. 15. Bronze objects showing extraction of small quantity of soluble salts

drying.

5. BTA is a relatively safe corrosion inhibitor(LD50=560mg) and exhibits an anticorrosion effect for copper, silver, iron, etc. Quantitative analysis of the soluble salts extracted from actual excavated objects revealed the following.
6. There was a large difference between the extracted amount of soluble chloride ions and sulfate ions from excavated objects showed less than 50ppm. Almost all the excavated objects that showed more than 400ppm of chloride ions were destroyed within a few years after excavation.
7. The excavated objects extracted amount of soluble chloride ions of less than 200ppm

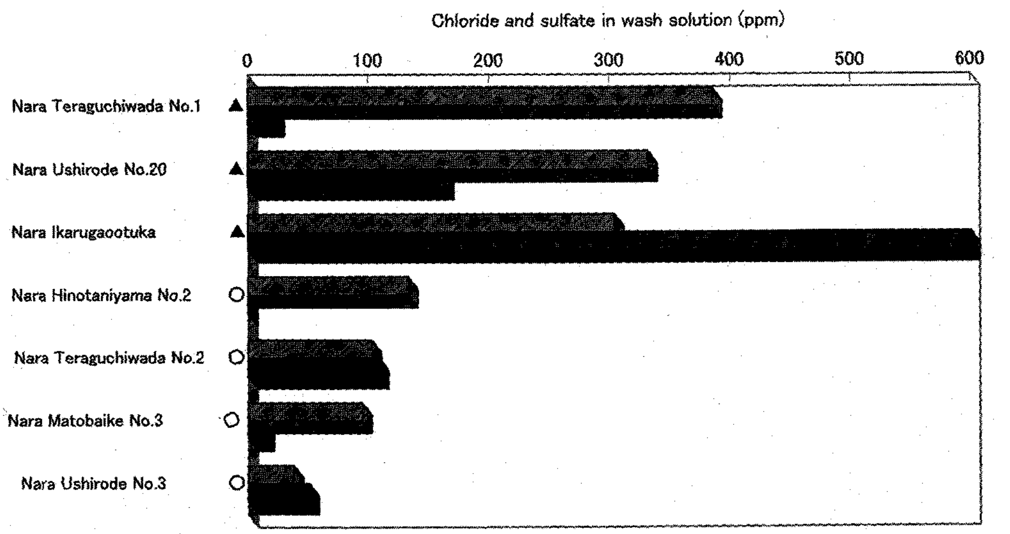

Fig. 16. Extracted quantity of soluble salts and its relationship with destruction of excavated objects (▲ degree of destruction was large, ○ degree of destruction was small)

are not destroyed even several decades after excavation.

8. The excavated objects that showed more than 1000ppm of sulfate ions were also destroyed. Sulfate ions can not fully removed by the treatment at ambient temperature.

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The concept of this system is based on more than ten years of research by Mr. Ri Sansu of the Korean National Central Museum on "Treatment by saturated steam pressure" using a high pressure pot. We came to know of the existence of this apparatus through research exchange activities with Korea(Representative Dr. Masaaki Sawada) and we then started research also in Japan. The results were thus produced by collaborative research exchange activities between Korea and Japan.

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