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Abstract

Liquid laboratory waste containing osmic acid and cacodylic acid was mixed with potter's clay or hydraulic cement. The clay-waste product was kneaded into blocks and baked in a klin (1,200-1,400 degrees C). The cement-waste product was allowed to harden into concrete blocks. Some of the baked clay blocks and concrete blocks were ground, and immersed in 1 N NaOH or 10% HCl solutions for 3-6 months. X-ray microanalysis of the dried samples of these solutions showed that no leakage of osmium and arsenic occurred in the baked clay embedding, and that some leakage of these agents occurred in the concrete embedding. The present study indicates that the baked clay embedding method is useful for safe storage of dangerous laboratory wastes. Additional experiments suggested that glass embedding is also useful for safe storage of laboratory wastes or harmful metals.

KEYWORDS: laboratory waste, osmic acid, cacodylic acid, clay-embedding, cement-embedding, baking

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Embedding of Laboratory Wastes in Clay or Concrete Blocks, with Special Reference to Baking Osmic Acid and Cacodylic Acid Wastes with Clay

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Liquid laboratory waste containing osmic acid and cacodylic acid was mixed with potter's clay or hydraulic cement. The clay-waste product was kneaded into blocks and baked in a kiln (1,200–1,400 °C). The cement-waste product was allowed to harden into concrete blocks. Some of the baked clay blocks and concrete blocks were ground, and immersed in 1 N NaOH or 10% HCl solutions for 3–6 months. X-ray microanalysis of the dried samples of these solutions showed that no leakage of osmium and arsenic occurred in the baked clay embedding, and that some leakage of these agents occurred in the concrete embedding. The present study indicates that the baked clay embedding method is useful for safe storage of dangerous laboratory wastes. Additional experiments suggested that glass embedding is also useful for safe storage of laboratory wastes or harmful metals.

Key words: laboratory waste, osmic acid, cacodylic acid, clay-embedding, cement-embedding, baking

H heavy metals and organic substances such as osmic acid and cacodylic acid are routinely used as fixatives, dyes or buffers in laboratories (1–4). Wastes of these agents must be stored, since they are harmful or contaminate the environment (5). We previously described a starch-embedding method for storage of such harmful wastes (6). In the present paper, we describe other embedding methods which involve baking the wastes with clay or mixing of the wastes with hydraulic cement and allowing the mixture to set.

Materials and Methods

Samples (25 ml) of liquid laboratory wastes containing 1–2% osmic acid and 3–4% cacodylic acid were mixed with 5 ml of 10% tannic acid solution. This product was then mixed with 1 kg of potter's clay (from Bizen, Okayama, Japan) which contained 30–35% water (Fig. 1). This clay-waste product was kneaded into blocks (flower vases and ashtrays). These kneaded specimens were dried in air for 1–2 months, and baked in an electric kiln (1,200–1,400 °C, 6 ampere) (Yaesu-Giken, Tokyo) overnight. Some of the kneaded and dried specimens were left unbaked.

Similar waste samples (30 ml) of osmic acid, cacodylic acid and tannic acid were diluted with 70 ml of water. This product was then mixed with 700 g of rapid-hardening (hydraulic) cement (Onoda Cement, Yamaguchi, Japan), and left to set in plastic boxes for 3 months.

Some pieces of commercially available colored (stained) glass containing cobalt or chromium were washed in distilled water, and dried in air.

The baked clay-waste, unbaked clay-waste, hardened cement-waste, and colored glass specimens were ground (pulverized) into powder. In each case, 10 g of the powdered samples were incubated in 100 ml of 1 N HCl or 10% NaOH solution for 3–6 months, and centrifuged at 7,000 rpm. The supernatant (0.01 ml or more) was placed on a nickel grid coated with a thin sheet of LR White resin, dried in air, mounted in copper mounts, observed with a transmission electron microscope, and analyzed under an X-ray microanalyzer (Kevex, DELTA plus) with a SEM (Scanning Electron Microscope) superdry

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Fig. 1 Injection of liquid laboratory waste (W) into clay (C).

detector, in order to detect osmium, arsenic and other metals. The sediment (0.01 ml or more) was also dispersed on the resin-coated nickel grid, dried in air, observed with the transmission electron microscope, and analyzed under the X-ray microanalyzer. Some supernatants and sediments were sometimes treated by arsine-silver-diethyldithiocarbamate-burcine-chloroform system (7) to check for the presence of arsenic alone.

Controls consisted of a mixture of Bizen pottery clay (containing no laboratory wastes) and distilled water. Supernatant and sediment from this mixture were placed on the LR white resin-coated nickel grid, dried in air, mounted in copper mounts, and analyzed under the X ray microanalyzer.

Results

The clay-laboratory waste mixture was readily kneaded into blocks (flower vases and ashtrays). They were sufficiently dried in air and baked in a kiln. The resulting baked flower vases and ashtrays could be used as household objects (Fig. 2). Transmission electron microscopy confirmed that the supernatants prepared by 7,000 rpm centrifugation contained no grains, and that the sediments were of fine grains (data not shown).

Successive X-ray microanalysis indicated that the supernatants from the NaOH or HCl solution incubated with the baked clay-waste samples contained neither osmium nor arsenic (Fig. 3). No silicon was detectable in these supernatants (Fig. 3). In contrast, the sediments of these samples showed strong osmium, arsenic and silicon reactions (Fig. 4).

The supernatants from the NaOH or HCl solution incubated with unbaked clay-waste samples showed clear osmium and arsenic reactions in the X-ray microanalysis (data not shown). No silicon was detected in these supernatants. The sediments from these unbaked samples showed clear and strong osmium, arsenic and silicon reactions (data not shown).

The cement-laboratory waste mixture hardened quickly. X-ray microanalysis indicated that the supernatants from the NaOH or HCl solution incubated with concrete-waste blocks contained some osmium and arsenic (Fig. 5). No silicon was detected in these supernatants (Fig. 5). The sediments from the concrete-waste samples showed strong osmium, arsenic and silicon reactions in the X-ray microanalysis (data not shown).

In the sediments from the colored glass specimens, clear cobalt or chromium reactions were noted. In the supernatants from these glass specimens, no such cobalt or chromium reactions were noted (data not shown). No silicon was detected in the supernatants.

Neither osmium nor arsenic was detected in the control specimens or in the supernatants and sediments from the mixture of Bizen pottery clay (containing no laboratory wastes) and distilled water (Figs. 6, 7). Silicon was not detected in the supernatants from the control mixture of Bizen pottery clay and distilled water (Fig. 7).

Nickel, copper, gold and niobium were detected in all specimens, including the sediments from baked clay-waste samples and supernatants from the controls (data not shown).

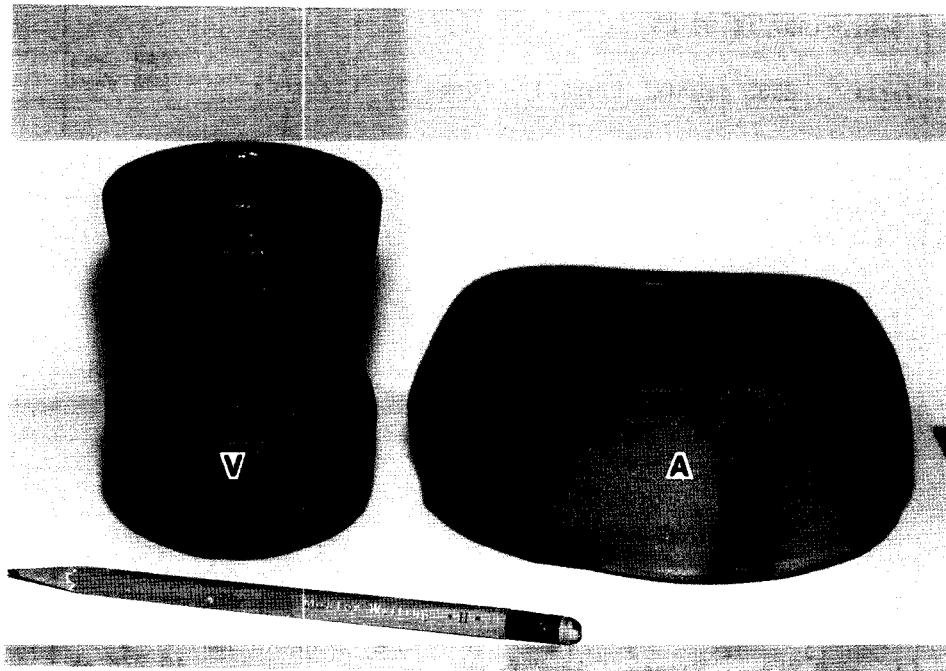


Fig. 2 Flower vase (V) and ashtray (T) prepared from the clay-osmic acid-cacodylic acid mixture. They were baked at a temperature of 1,200°C.

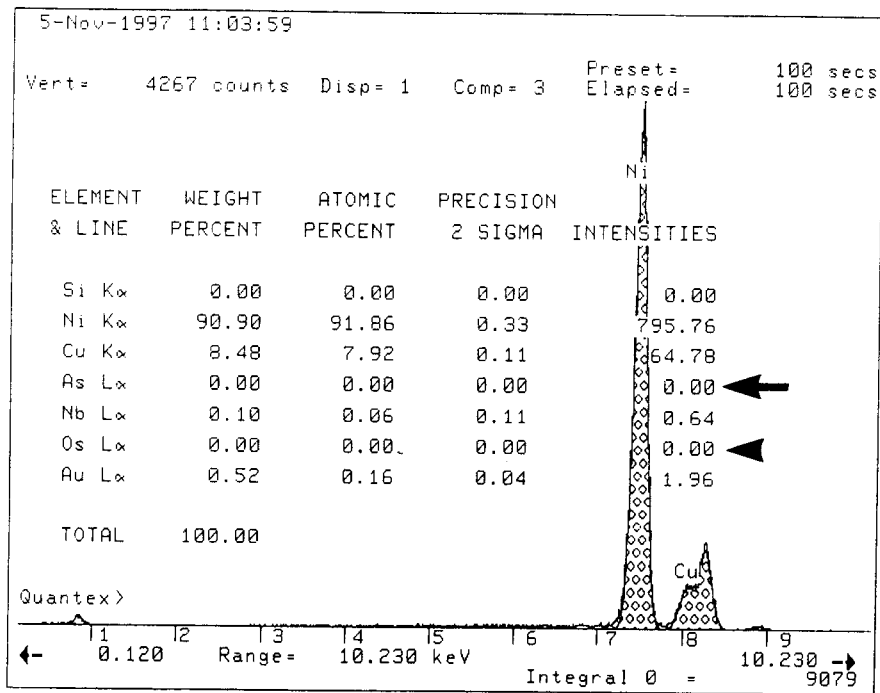


Fig. 3 X-ray microanalysis of dried supernatant from the mixture of '1N HCl' and baked clay-osmic acid-cacodylic acid block. Neither osmium (arrowhead) nor arsenic (arrow) is detectable.

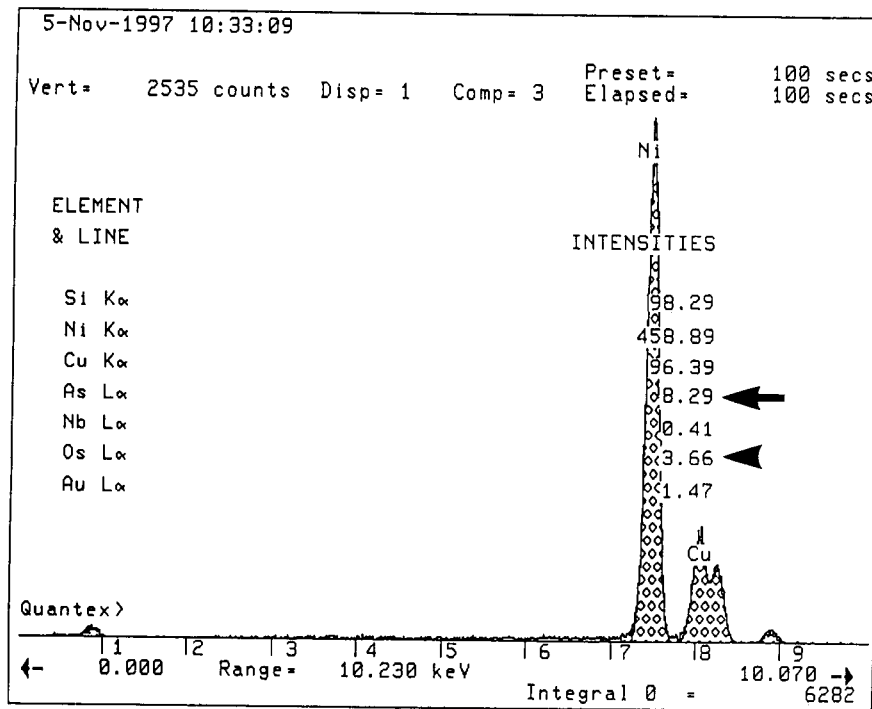


Fig. 4 X-ray microanalysis of dried sediment from the mixture of '1N HCl' and baked clay-osmic acid-cacolylic acid block. The sediment shows intense osmium (arrowhead) and arsenic (arrow) reactions.

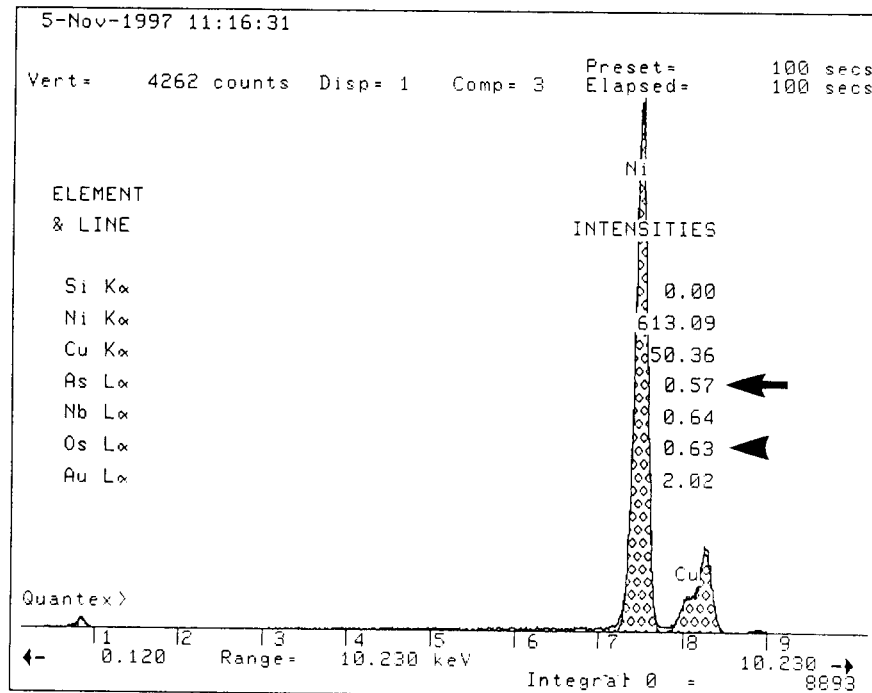


Fig. 5 X-ray microanalysis of dried supernatant from the '1N HCl' and concrete-osmic acid-cacolylic acid block. Osmium (arrowhead) and arsenic (arrow) are detectable.

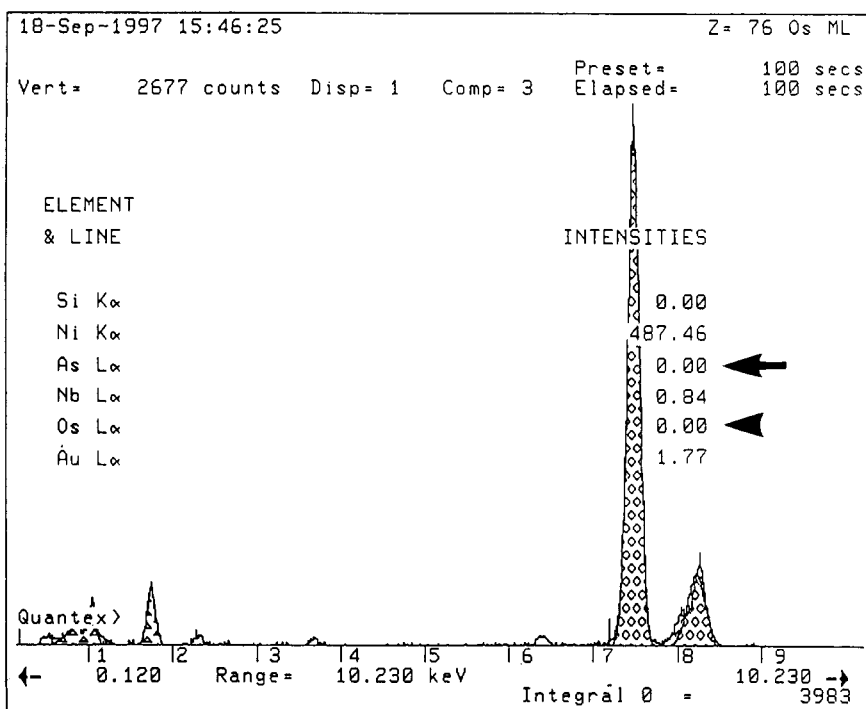


Fig. 6 Dried supernatant from the control (mixture of distilled water and unbaked clay containing no laboratory wastes). No reactions of osmium (arrowhead) or arsenic (arrow) are noted.

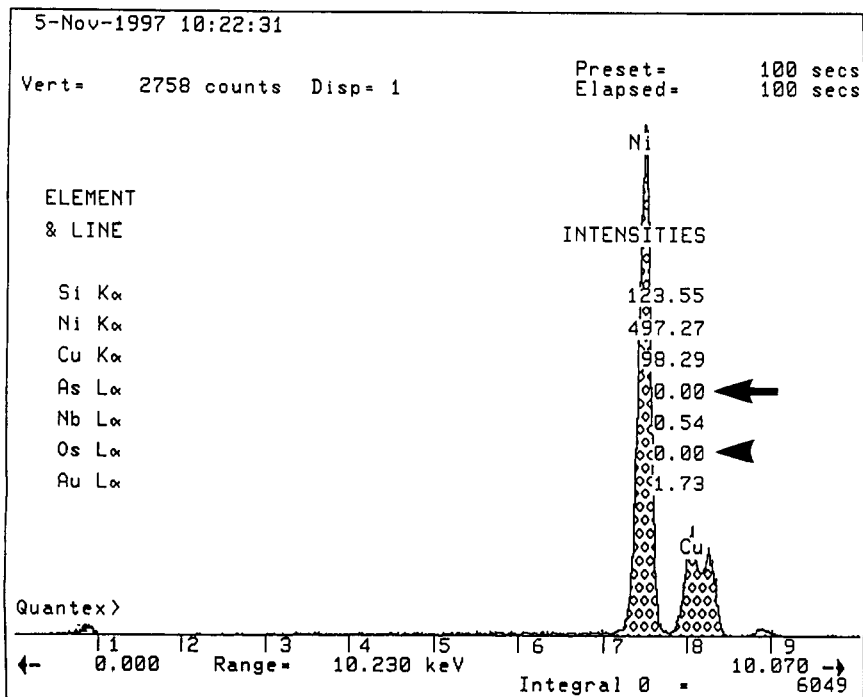


Fig. 7 Dried sediment from the control. No reactions of osmium (arrowhead) or arsenic (arrow) are noted.

Similar results were obtained by arsine-silver-diethylthiocarbamate-burcine-chloroform system. Even with this system, no (negative) arsenic reaction was noted in the supernatants from the NaOH or HCl solution incubated with the baked and ground clay-waste blocks. Nor were arsenic reactions observed in the supernatants of the control clay samples containing no wastes (data not shown), or in those from the NaOH solution or HCl solutions incubated with concrete-waste blocks or with unbaked clay-waste blocks.

Discussion

The present experiments supplement our previous starch-embedding method (6), and introduce a baked clay embedding method for storage of laboratory wastes. No reactions of osmium and arsenic in the supernatants from the baked clay-waste specimens treated with NaOH or HCl indicate that osmic acid and cacodylic acid remain in the baked blocks without leaching. In our preliminary experiments, no leakages of osmium and arsenic were noted even when the samples were immersed in solvents: 4% acetic acid and 0.1N H₂SO₄ (unpublished data). Thus, our baked clay embedding method satisfies a Japanese environmental law which states that the arsenic content of leached material from chemical waste must be less than 0.1mg/l (8). We were unable to find mentions of osmium in this and other laws, including those relating to food and table wares (9).

Marked reactions of osmium and arsenic in the supernatants from the unbaked clay-waste samples show that the baking is essentially important for the stable storage of laboratory wastes in clay. No detection of osmium and arsenic in the control sediments confirms that Bizen pottery clay does not contain these metals. No detection of silicon in the supernatants, including that of the control clay, confirms that the supernatants obtained in each centrifugation were pure and free from clay elements.

Air pollutions (gaseous emissions of osmium and arsenic) from the baked clay-laboratory waste mixtures were not examined due to the difficulty in sampling the air in the kiln (10). However, the X-ray data or the intense osmium and arsenic reactions in the sediments from the baked clay-waste samples suggest that osmium and arsenic embedded in clay do not evaporate during baking. Neither air pollution nor production of dioxin has been reported in the electric pottery baking (personal communication with a pottery specialist in Bizen municipal office).

Many kinds of clay are useful for electric baking with laboratory wastes. In our preliminary experiments, such crude and cheap clays as used for tiles and bricks were sufficiently useful for our baked clay embedding method. If these cheap clays are used, 100ml of osmic acid or arsenic waste can be converted into baked clay-waste blocks at a cost of 1,000 yen. Thus, our baked clay-embedding method has some advantages over other methods, including the glass-embedding method, in that our method is handled more easily and cheaply.

Tannic acid in our method was used for reduction of metals, especially osmic acid, in the wastes. This tannin-treatment is not necessary when the wastes contain no metals. Our previous experiments have shown that osmium and other heavy metals, except copper and platinum, in laboratory wastes are precipitated as tannin-metal-protein complexes which are easily separated as filter cakes by paper filtration (6).

In this series of experiments, we also tried a method of embedding wastes in concrete. This method, however, is not always recommended since the embedded waste elements leaked out. This leakage indicates that the concrete blocks are eroded or corroded by acids and alkalis.

It is well known that X-ray microanalysis is useful for a reliable detection of metals, including heavy metals, and also for an accurate determination of their concentrations. The present experiments prove that determining the presence and concentration of metals in dried samples is easily done by X-ray microanalysis. The present experiments, thus, point up the usefulness of X-ray microanalysis as a substitute for the complicated chemical colorimetry and absorption spectrophotometry methods for the qualitative analysis of metals in the wastes (7, 9). Quantitative analysis was omitted in the present experiments, because the exact volumes of the mounted supernatants and sediments were not calculated. Detections of copper, gold and niobium in the present X-ray microanalysis may be due to the presence of these metals in the glids and holders used to mount the supernatants since these metals were detected even in the X-ray microanalysis of the control supernatants.

The present experiments further show that metals embedded in glass do not leach out in the solutions of strong acid or alkali, suggesting that the glass embedding method is also useful for the safe storage of metals.

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Bizen pottery clay and facilitated the use of the electric kiln.

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