# Int.3

# Earthenware remains used for salt cementation of parting gold and silver at Sado in early seventeenth century Japan

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## 1. Introduction

Sado Island is famous for rich in gold and silver (Fig. 1). Placer gold mining in Sado, probably at Nishimikawa, was documented in a book of the twelfth century. Hard rock mining started at Tsurushi and Niibo in the mid-sixteenth century extracting silver by cupellation, and mining area was expanded further north to Aikawa. However it is not certain whether gold was extracted besides silver from quartzose ore in the sixteenth century. In 1600 Sado Island came under the direct control of the Tokugawa shogunate and Sado Bugyosho (magistrate office) was constructed at Aikawa in 1603-1604.

Primary ores of gold-silver deposits in Sado Island consist of quartz with silver sulfide minerals and electrum (natural gold-silver alloy containing about 60 % gold and 40 % silver<sup>1)</sup>) (Fig. 2). Careful ore dressing and smelting of gold rich concentrates will result in silver dominated bullion and consequently, parting of silver from the bullion was essential to produce pure gold. A document of 1617 refers furnaces for gold and silver separation using sulfur<sup>2)</sup>. Cementation process, however, was introduced to Sado after the Sado koban office was attached to Sado Bugyosho in 1621.

During the excavation of the Sado Bugyosho site, in 1996, gold refining remains were found below the 1647 fire horizon<sup>3)</sup>. The subject of this report is the observation and analysis of the earthenware remains used for salt cementation of gold refining at Sado in the early seventeenth century.









### 2. Excavated materials and analytical methods

#### (1) Furnaces

In the southern part of the Sado Bugyosho site, a total of 29 furnaces were found in an area of east-west 17 m by north-south 8 m (Fig. 3). The largest furnace is an elongated shallow tray-like furnace (4 m long, 66 cm wide and 18 cm deep), which resembles closely the cementation furnace illustrated in eighteenth- and nineteenth-century picture scrolls of the Sado gold-silver mine. The furnace had purplish red color and charcoal dust stuck on the fire-hardened floor.

There were fourteen furnaces (average 80 X 50 cm and 25 cm deep) with a dividing wall. The abovementioned elongated furnace cut one of the furnaces. The circular furnaces (average 65 cm and 24 cm deep) and other furnaces were fourteen in number and some are different from the cementation furnaces. Eiji Izawa (Kyushu University Museum, E-mail: izawa@mine.kyushu-u.ac.jp)





Fig. 3 Left: replicated remains of unearthed refining furnaces. Center: a full-size replica of the elongated furnace, about 4 X 0.7 m and 18 cm deep, with purplish red color. Right: the cementation furnace illustrated in early nineteenth century picture scroll.

## (2) Earthenware

Interesting finds are a large number of fragments of earthenware such as clay dishes, clay plates and clay rods (Fig. 4). Raw materials of these bisques are hydrothermally altered siliceous volcanic rocks (dacitic composition) and rather rich in iron oxide. Although the earthenware was originally of an orange color and with reddish tint on the surface, many were discolored and cracked by the furnace work.

The number of clay dishes is over 1500 pieces and in addition furnace walls were reinforced with many small pieces of clay dishes<sup>3)</sup>. The original diameter of the clay dish seems to be more than 20 cm, the edge-height is about 5 cm and the depression is 0.6-1.6 cm.

Clay plates are quadrangle and round-shaped, 1.1-1.9 cm thick and original diameter seems to be more than 15 cm. All the clay plate occurs as fragments and are discolored.

There are many clay rods of prism- and cylinder-shape, 2-3 cm in diameter and originally more than 12-13 cm long. Some rods were less reacted and has reddish color but many were highly reacted and discolored. (3) Analytical methods

The chemical compositions of earthenware samples were determined with a Rigaku RIX 3100 X-ray fluorescence spectrometer (XRF), using pressed powder pellets. The constituent minerals were examined using a Rigaku Rint 2000 and Ultima IV X-ray diffractometer (XRD) with a Cu target.



Fig. 4 Clay dish (pen is 14.4 cm long).



Fig. 5 Clay plate.



Fig. 6 Clay rods.

## 3. Results and discussion

Obtained chemical compositions are shown in Table 1. Data were recalculated to water-free basis. The composition of discolored samples are characterized by increase in soda (Na<sub>2</sub>O), potash (K<sub>2</sub>O), sulfur (S), chlorine (Cl) and silver (Ag), and decrease in silica (SiO<sub>2</sub>) and iron (Fe<sub>2</sub>O<sub>3</sub>) in comparison with red colored less reacted samples.

XRD data are shown in Figures 7 and 8, which indicate decrease in silica minerals (quartz and cristobalite) and increase in sodium feldspar (albite).

Complex reactions of cementation proceed under moderate temperatures (less than  $800^{\circ}C$  = melting point of common salt)<sup>4,5)</sup>. Sodium chloride reacts with water (H2O) from charcoal burning, which resulted in formation of sodium ion and hydrogen chloride (gas). This reaction will be accelerated by silica and in the case of Sado, quartz and cristobalite, and probably meta-kaolin (Al<sub>2</sub>Si<sub>2</sub>O<sub>7</sub>) exist in original earthenware. Then albite-forming reaction occurred:

2NaCl + H<sub>2</sub>O + 4SiO<sub>2</sub> + Al<sub>2</sub>Si<sub>2</sub>O<sub>7</sub> = 2NaAlSi<sub>3</sub>O<sub>8</sub> + 2HCl

Under the oxidizing and high temperature conditions, ferric component in earthenware reacts with hydrogen chloride and form ferric chloride (gas).

 $3HCI+1/2 Fe_2O_3 = FeCI_3 + 3/2 H_2O$ 

Table 1 Chemical composition of earthenware (XRF analysis).

	Weakly altered (red color)			Reacted (discolored)			
No.	D11-105	D11-94R	D11-31R	D11-671W	D11-56	D10-12	D11-6
Sample	Clay dish	Clay rod (cylinder)	Clay rod (prism)	Clay dish	Clay rod (prism)	Clay plate	Clay plate
SiO <sub>2</sub> (%)	68.9	68.7	68.5	63.7	63.2	63.7	60.0
TiO₂	0.92	0.80	0.90	0.80	0.90	0.80	0.89
Al <sub>2</sub> O <sub>3</sub>	22.1	21.6	21.0	20.6	21.5	20.6	21.5
$Fe_2O_3^*$	4.56	4.30	4.91	3.25	3.83	3.25	4.73
MnO	0.02	0.04	0.02	0.02	0.03	0.02	0.04
MgO	0.80	0.87	1.17	1.00	0.93	1.00	1.20
CaO	0.66	0.95	0.77	2.07	1.38	2.07	3.72
Na₂O	0.60	0.54	0.82	5.13	1.92	5.13	3.23
K₂O	1.19	1.24	1.61	1.79	5.23	1.79	2.62
$P_2O_5$	0.05	0.75	0.16	0.82	0.34	0.82	0.79
S	0.03	0.05	0.02	0.12	0.13	0.12	0.47
CI	0.02	0.01	0.02	0.48	0.30	0.48	0.44
Ag	0.004	0.002	0.004	0.099	0.042	0.099	0.201
Cu	0.001	0.002	0.001	0.002	0.005	0.002	0.005
Zn	0.012	0.002	0.004	<0.002	<0.002	<0.002	<0.002
Pb	0.004	0.004	0.006	0.028	0.007	0.028	0.006
As	0.002	0.006	0.002	0.007	0.009	0.007	0.011
Total	99.9	99.9	99.9	99.9	99.8	99.9	99.8
Total**	100.2	99.4	100.1	98.4	99.8	98.7	0.1
H <sub>2</sub> O(+)	5.66	5.02	2.58	4.52	7.72	4.80	5.98

 $Fe_2O_3^* = Total iron as Fe_2O_3, LOI^{**} = H_2O(+) + H_2O(-).$ 

Total\*\* = Before recalculation.

Au<0.005, Sb<0.01, Sn<0.01, Bi,0.01, Hg<0.001, Cd<0.001, Mo<0.003.



Fig. 7 X-ray powder-diffraction patterns for less-reacted clay rod showing intensities of silica minerals and feldspar.



Fig. 8 X-ray powder-diffraction patterns for highly reacted clay rod showing decreased intensities of silica minerals and increased intensity of albite (sodium feldspar).

Ferric chloride attacks silver and this forms silver chloride (melt) and ferrous chloride (melt).

 $FeCl_3 + Ag = FeCl_2 + AgCl$ 

Craddock (2000: p. 180-181)<sup>5)</sup> argued that chlorine (gas) was the important agent in the attack on silver. If iron or copper (transition metals) exist, chlorine will be formed under the condition of water-vapor existence in 700-800°C.

 $2\text{FeCl}_3 = 2\text{FeCl}_2 + \text{Cl}_2$ 

and

 $1/2 \operatorname{Cl}_2 + \operatorname{Ag} = \operatorname{AgCl}$ 

## 4. Conclusions

The changes in chemical composition of the earthenwares fit well in reactions of cementation process. It is an interesting problem to compare results of this seventeenth century process with the process described in picture scrolls and documents<sup>6)</sup> in the eighteenth century and after.

### References

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