

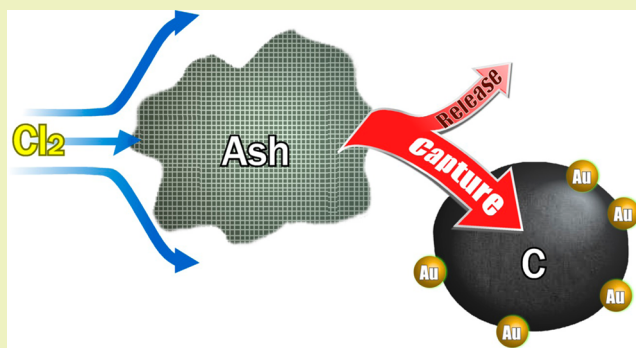
# Recovery of Gold from Incinerated Sewage Sludge Ash by Chlorination

Junichi Kakumazaki, Takahiro Kato, and Katsuyasu Sugawara\*

Faculty of Engineering and Resource Science, Akita University, 1-1 Teagta Gakuen-cho, Akita City 010-8502, Akita Prefecture, Japan

**ABSTRACT:** In a series of studies into the development of an efficient and selective recovery process for gold that eliminates the need for water, the release behavior of gold from an incinerated sewage sludge ash heated to between 100 and 1000 °C under a chlorine gas stream was investigated. A release of gold was observed above 600 °C, with all gold being transferred to the gas phase at 1000 °C. The addition of solid carbon to the incinerated ash reduced this initial release temperature to 400 °C, with all gold being released into both the gas phase and solid carbon at 700 °C. Subsequent optimization of the reaction conditions to maximize the amount of gold reporting to the solid carbon determined that the mixture of incinerated ash and carbon should first be heated to a terminal temperature of 800 °C under a nitrogen gas stream. Upon reaching this temperature, the gas stream should be switched from chlorine to nitrogen, and the mixture held at 800 °C for 1 h. Scanning electron microscopy and X-ray diffraction measurements confirm that this produces a distribution of fine metallic gold over the carbon surface.

**KEYWORDS:** Gold, Recovery, Chlorination, Carbon, Ash



## INTRODUCTION

The outstanding ductility, thermal/electrical conductivity, and chemical stability of gold have caused it to be utilized widely in a variety of products, most notably in jewelry and electronics. Its distribution, however, is unevenly spread in the sense that just 20 countries account for 90% of the world's known gold reserves. At present, the annual demand for gold is around 4000 t/y, 2500 t of which is produced by refining of ores and 1500 t by the recycling of spent industrial products.<sup>1</sup> Typically, these secondary resources such as electronic circuit boards and incinerated ash contain a higher content of gold than primary ores. For example, economic ore grades are typically within a range of 0.3–17 g/t, whereas the circuit board of a cellular phone contains 300–350 g/t.<sup>2,3</sup>

In Southeast Asian, African, and South American countries, the use of mercury in the recovery of gold has created serious human health and environmental problems. Indeed, about 40% of all mercury that is released to the atmosphere and aquatic environments comes from gold refineries.<sup>4</sup> The use of sodium cyanide has rendered the use of mercury largely obsolete and has been widely used for dissolving precious metals in ores due to the high yields that can be achieved. However, cyanidation processes do have their own disadvantages, such as the long treatment time required of multistep extraction and the discharge of harmful residue and effluents.<sup>5</sup> Because of this, a number of alternative leachants have been considered over recent years, including thiourea, thiosulfate, bromide, iodide, and sodium hypochlorite. Of these, thiourea is carcinogenic and requires high cost to recover the metals, thiosulfate exhibits low

solubility, and both iodide and bromide are highly volatile. The search for a more effective leachant than sodium cyanide is therefore still very much ongoing.<sup>6–8</sup>

The commercial recovery of gold is normally dependent on aqueous solutions; however, a suitable dry process would be expected to greatly simplify the process of separation and reduce the need for wastewater treatment. One such dry process is to volatilize target elements by heating with CO gas or solid carbon, but the reducing atmosphere this produces is not economically viable for elements with a high boiling point. On the other hand, chlorination provides a means to volatilize target elements as chlorides, with low melting and boiling points, by heating with a suitable chlorine source such as Cl<sub>2</sub> gas or vinyl chloride. Moreover, the volatilization temperature of the target elements can be lowered by incorporating both chlorinating and reducing reagents. In this way, the authors have previously reported on the release behavior of Pb and Zn from fly ash, Ta and Nb from sintered hard alloys, and rare metals such as La, Gd, Nb, and Ta from optical lenses using chlorination in conjunction with added carbon.<sup>9–12</sup>

In the present study, an incinerated sewage sludge ash from the Lake Suwa area in Nagano Prefecture, Japan, containing 0.83 wt % gold was used as the test subject for chlorination. In order to develop a selective dry separation process, the release behavior of gold from the incinerated ash was investigated

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**Table 1. Elemental Analysis of Incinerated Ash (wt %)**

P	K	Zn	Fe	S	Ca	Al	Au	Cu	Ag	Si	Ni	Ti	Pd
15.33	9.41	3.50	2.17	2.70	2.17	1.38	0.83	0.49	0.40	0.26	0.05	0.03	0.02

under a chlorine gas stream at temperatures from 100 to 1000 °C, both with and without the addition of solid carbon. By optimizing the reaction conditions, it is intended to propose a new method for the recovery of gold by chlorination with solid carbon.

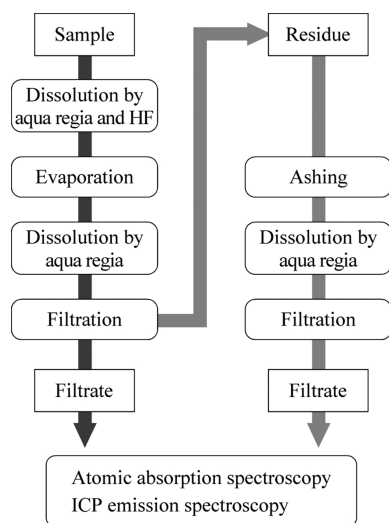
## EXPERIMENTAL PROCEDURE

**Samples.** A gold-bearing incinerated ash derived from sewage sludge was used as the basis of this study; its elemental analysis is provided in Table 1. The average particle size of the sample is 24.2 μm, with a gold and sulfur content of 0.83 and 2.70 wt %, respectively. The solid carbon used as a reducing agent was prepared by the pyrolysis of phenolphthalein at 500 °C for 10 min in a nitrogen stream. Phenolphthalein was chosen here to obtain the solid carbon without impurities. The particle size of the resulting solid carbon was 73 μm.

**Chlorination.** The solid carbon was added to the incinerated ash with a mixing ratio of 1:1 by weight. The sample was then placed in the center of a fixed bed reactor with a fused silica tube (26 mm i.d.) and heated at 10 °C/min to a terminal temperature of between 100 and 1000 °C. The exhaust gas was trapped by a sodium hydroxide solution.

In all, three types of experiments were carried out. In experiment Type I, a 100 mL NTP/min flow of chlorine gas was supplied to the reactor during heating to the desired final temperature, after which the sample was cooled by a nitrogen gas flow. In the Type II experiment, nitrogen gas was supplied to the reactor during heating. Upon reaching the final temperature, chlorine gas was supplied, and the temperature was maintained for 1 h, with the samples then cooled by nitrogen gas. Finally, in the Type III experiment, the samples were heated and cooled in a nitrogen atmosphere, without being held at their final temperatures.

**Analysis of Gold.** The sequential leaching scheme proposed by Terashima et al.<sup>13</sup> and depicted in Figure 1 was applied for the quantitative determination of gold. In this method, the sample was first dissolved by a combination of aqua regia and hydrofluoric acid at 115 °C. The resulting solution was then evaporated at 150 °C to remove the hydrofluoric acid, with the obtained solid dissolved again in aqua regia and hydrochloric acid at 115 °C. After cooling, the obtained solution was separated into a filtrate and solid residue, the former



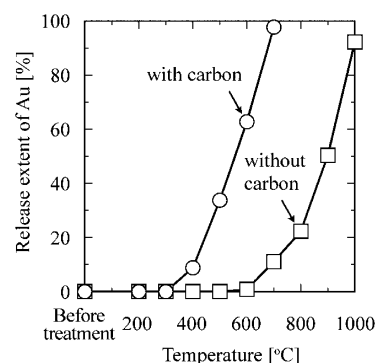
**Figure 1.** Procedure of quantitative analyses of gold and coexisting elements.

containing any gold that remained in the incinerated ash sample. The solid residue, which consisted of the added solid carbon, was then combusted at 500 °C for 2 h in air. The residue obtained was then dissolved by aqua regia and hydrochloric acid. This dissolved solution contained gold that was released from the incinerated ash and subsequently captured by the added carbon.

The concentrations of gold and other elements in the dissolved solutions were determined by inductively coupled plasma emission spectroscopy (Shimadzu ICPE-9000) and atomic absorption spectroscopy (Shimadzu AA-6800). X-ray diffractometry (Rigaku, Ultima IV), scanning electro-microscopy SEM (Hitachi, S-2000), and wavelength dispersive X-ray fluorescence spectrometer (Shimadzu XRF-1700) were also used to confirm the form and distribution of gold in the carbon.

## RESULTS AND DISCUSSION

**Release of Gold from Incinerated Ash.** Figure 2 shows the behavior of the gold released during heating of the



**Figure 2.** Release behavior of gold from ash during heating in a chlorine gas stream (Type I experiment).

incinerated ash in a Cl<sub>2</sub> gas stream (Type I experiment). The extent of this release is defined by the following equation

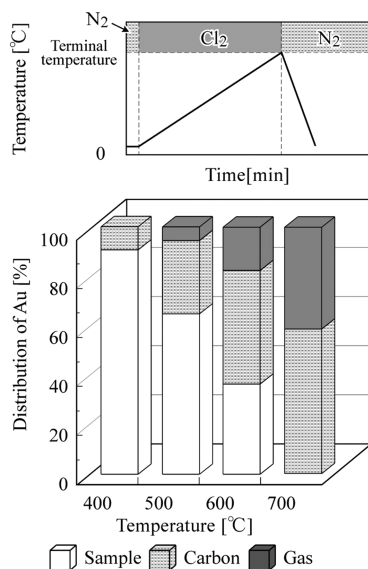
$$Au_{rel} [\%] = \{(Au_0 - Au_{Cl})/Au_0\} \times 100$$

where  $Au_{rel}$  is the extent of gold released,  $Au_0$  is the initial amount of Au, and  $Au_{Cl}$  is the amount of Au after chlorination.

When the incinerated ash sample is heated in a Cl<sub>2</sub> gas stream without the addition of carbon, gold begins to release starting at a temperature of 600 °C. A more drastic release of gold is observed above 800 °C, with 90% of the gold volatilized by 1000 °C. On the other hand, an appreciable release of gold is observed at temperatures from 400 to 700 °C when carbon is added to the incinerated ash. Indeed, all of gold in the incinerated ash is released to the gas phase by 700 °C. Furthermore, the addition of solid carbon lowers the volatilization temperature from 700 to 400 °C, thus accelerating the rate of gold volatilization. This is in direct contradiction to the calculated thermodynamic equilibrium, which suggested that the presence of carbon should not have any influence on the change in gold form. However, the presence of complexes between gold and other elements within the ash could explain this observed behavior, with the release of gold potentially being accompanied by the volatilization of chlorides of other elements.<sup>14–17</sup>

X-ray fluorescence analysis of the volatiles produced during low temperature chlorination indicates that they contain Au, Fe, and Cl; thus, the release of Au at low temperatures seems likely to occur in the chemical form of  $\text{AuCl}_3 \cdot \text{FeCl}_3$ .<sup>15</sup> It has previously been reported that the chlorination of metal oxides in the presence of carbon is accelerated via complexes of four elements: carbon, oxygen, chlorine, and various metals.<sup>18</sup> Future theoretical considerations on the data are now going on.

**Distribution of Gold.** Figure 3 shows the distribution of gold following the Type I experiment, in which “Sample”

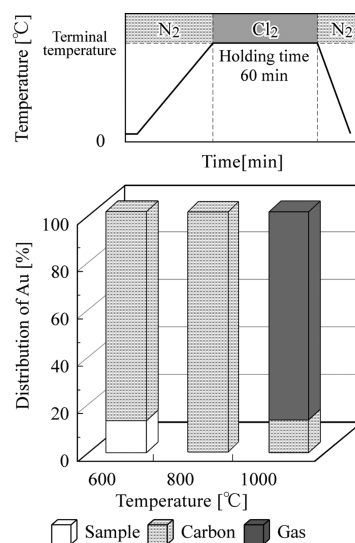


**Figure 3.** Distribution of gold during heating in a chlorine gas stream (Type I experiment).

indicates the unreactive and residual gold, and “Carbon” represents the gold captured by the carbon particles. “Gas” denotes the gold that transitioned to the gas phase and subsequently flowed out of the reactor; this being obtained by the difference between the initial gold content and the combined gold content of the Sample and Carbon. These results demonstrate that the released gold is distributed to both the gas and carbon phases, with the gold in Gas first observed above 500 °C and increasing to 40% at 700 °C. Similarly, the gold distributed to Carbon also increases with temperature from 10% at 400 °C to 60% at 700 °C.

According to the results of Figures 2 and 3, even though gold chloride is released rapidly above 400 °C, its deposition on the carbon is reliant on its capture, with the remaining gold lost to the gas phase. Because these competing reactions of carbon capture and volatilization exhibit different tendencies in relation to temperature, a 60:40 split is obtained at 700 °C.

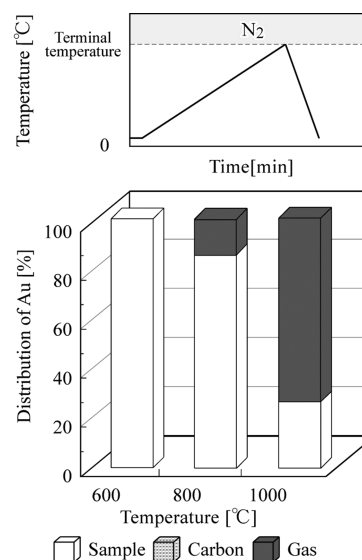
**Optimum Conditions for Gold Recovery.** The Type II experiment was utilized in optimizing the carbon capture of gold in relation to the volatilization rates of the various metal chlorides, with the use of a nitrogen atmosphere intended to inhibit the volatilization of the gold. From the distribution of gold obtained in this way (Figure 4), we can see that 80% of the gold is transferred to the carbon when the ash is heated to 600 °C, with no release of gold to gas phase observed. In contrast, 7% and 20% of the gold was released to the gas phase at 500 and 600 °C, respectively, by the Type I experiment shown in Figure 3. Furthermore, by heating the incinerated ash and carbon to 800 °C in a Type II experiment, all of the gold can be



**Figure 4.** Distribution of gold during heating in nitrogen and chlorine gases stream (Type II experiment).

captured by solid carbon. Further heating to 1000 °C, however, results in 80% of the gold being lost to the gas phase.

The distribution of gold resulting from the Type III experiment, in which the samples were not held at temperature, is shown in Figure 5. From this, it is clear there is no release of



**Figure 5.** Distribution of gold during heating in a nitrogen gas stream (Type III experiment).

gold at 600 °C, with 10% and 70% of the gold released to the gas phase at 800 and 1000 °C, respectively. No transfer of gold to carbon was observed, and because the incinerated ash and carbon were rapidly cooled when the sample reached its terminal temperatures, the gold released at 1000 °C is believed to be that released during the heating period in the nitrogen gas atmosphere. In order to separate and capture all of the gold from incinerated ash, it should be mixed with carbon and heated to 800 °C in a nitrogen atmosphere and then held for 1 h in a chlorine gas stream.

The form of gold produced on the carbon at 800 °C during the Type II experiment was analyzed by XRD, and the results are shown in Figure 6. The small peaks observable at 38°, 45°,

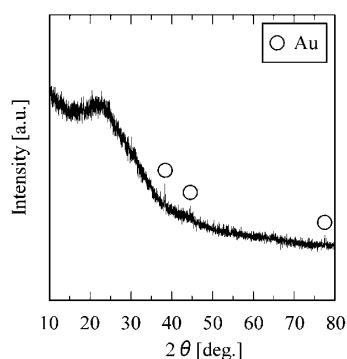


Figure 6. XRD pattern of solid carbon.

and  $76^\circ$  are all attributable to metallic gold. The SEM-EDX images shown in Figure 7 confirm that very fine gold particles

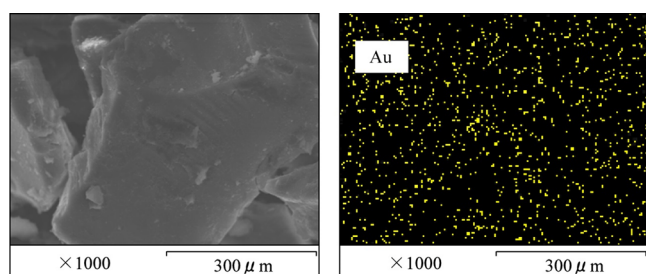


Figure 7. SEM-EDX image of solid carbon.

are distributed in the carbon. Consequently, although gold in the ash is volatilized as gold chlorides during chlorination, it is fine particles of metallic gold that are precipitated on the carbon surface by reduction. Sutter et al. have previously investigated the interaction between carbon and gold nanoparticles, identifying that gold is incorporated into carbon with a high degree of solubility above  $500^\circ\text{C}$ . Moreover, nanoparticles of gold in carbon exhibit grain growth by coalescence,<sup>19,20</sup> which is likely to have had some influence over the selective capture and precipitation of gold by solid carbon observed in this study.

## CONCLUSIONS

In order to develop a process of selective separation of gold by a dry process, release behavior of Au from the incinerated ash was investigated. Through this study, it has been demonstrated that the addition of carbon to an incinerated sewage sludge ash reduces the temperature at which gold is volatilized by chlorine from  $700$  to  $300^\circ\text{C}$ ; however, such behavior contradicts predictions based on thermodynamic equilibrium calculations of the Au-Cl<sub>2</sub> system. The released gold was effectively captured by the solid carbon, with the proportion recovered in this way increasing with temperature. In this way, it is possible for all of the gold contained in the incinerated ash to be recovered by solid carbon by heating to  $800^\circ\text{C}$  in a nitrogen gas stream and then holding at that temperature for 1 h in a chlorine gas stream. The gold captured by the carbon is reduced to form fine metallic particles, evenly distributed over the carbon surface.

## AUTHOR INFORMATION

### Corresponding Author

\*E-mail: katsu@ipc.akita-u.ac.jp.

## Notes

The authors declare no competing financial interest.

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