ALTERNATIVE GOLD REFINIG PROCEDURE USING “ORGANIC AQUA REGIA”

By

[1]Akihiro Yoshimura, [2] Pariya Torkaman, [1]Yasunari Matsuno, [2]Marcello M Veiga

[1]Chiba University, Japan
[2]University of British Colombia, Canada

Presenter and Corresponding Author

Akihiro Yoshimura
a.yoshimura@chiba-u.jp

ABSTRACT

Artisanal small-scale gold mining (ASGM) is one of the most important incomes for miners in developing countries. Mercury (Hg) is mainly used for the extraction of gold (Au) from ore in the ASGM process. The use and emission of Hg cause environmental impact and health damage, and the Minamata Convention on Mercury propose the reduce and elimination of the use and emission of Hg from ASGM. However, as mentioned above, ASGM is very important income for the miners including their families and the developing countries. An alternative procedure is required to balance the reduction or elimination of Hg use and income keeping.

The authors suggest the application of organic aqua regia (OAR) for the refining of Au. This OAR consists of an organic solvent containing copper halide (CuX_2, X= Br or Cl). In the organic solvent like dimethyl sulfoxide (DMSO) or propylene carbonate (PC), the cuprous ion (Cu^+) is stable while the cupric ion (Cu^{2+}) is stable in water. The OAR can dissolve Au because Cu^{2+} liberated from CuX_2 performs as a strong oxidant. And dissolved Au can be recovered by the addition of water to OAR. The authors used this solvent for the recycling of Au from secondary sources like a waste of electric and electronic equipment (WEEE) and successfully recovered Au.

In this research, the authors applied this OAR for the gold refining from ore, considering the utilization at ASGM sites. We used $CuBr_2$ or $CuCl_2$ as an oxidant and potassium bromide (KBr) or sodium chloride (NaCl) as a supplier of halogen elements. The simulated ore which is a mixture of sand and Au wire and ore containing 48 ppm of Au was treated by Br or Cl type OAR and the authors evaluated the extraction ratio from the ore under an ambient temperature or 40 °C. After the extraction, the authors evaluated the recovery of Au by the addition of acidic water to the solvent. Sulfuric acid (H_2SO_4) or lemon juice were used for this recovery.

As a result, the authors successfully extracted most of the Au from ore in every case. The ore used in this research was hard to treat by the conventional ASGM procedure using mercury. Thus, the OAR can be a candidate for the effective extractor of Au. In addition, extracted Au was recovered by adding acidic water like sulfuric acid or lemon juice. Considering the availability at ASGM sites, lemon juice is suitable for the precipitant media.

However, the cost of this procedure was much higher than the conventional ASGM process. Optimization is required for the spreading of the OAR process.

Keywords: Organic aqua regia, artisanal small-scale gold mining, Minamata Convention on Mercury

INTRODUCTION

Gold (Au) mining is an important industry for many countries especially developing countries of its high price. In such countries, artisanal small-scale gold mining (ASGM) is mainly operated for the extraction of Au from ore. Mercury (Hg) is mainly used for extraction in this procedure and this use causes environmental impact and health damage. In addition, cyanidation is also used together to extract Au and this causes mercury cyanide ($Hg(CN)_2$) which has strong toxicity for human health and the environment (1). Minamata Convention on Mercury was proposed for the reduction and elimination of Hg use in ASGM (2). However, as mentioned above, ASGM is a very important income for the miners including their families and the developing countries. An alternative procedure is required to balance the reduction or elimination of Hg use and income keeping.

Considering this situation, the authors suggest the application of organic aqua regia (OAR) for the refining of Au This OAR consist of organic solvent, e.g. dimethyl sulfoxide (DMSO) or propylene carbonate (PC) as a solvent and copper halide (CuX_2, X = Br, Cl) as an oxidant. The liberated cupric ion (Cu^{2+}) from CuX_2 can be a strong oxidant and dissolve Au. In addition, dissolved Au can be recovered by the addition of water to OAR (3). The authors used this solvent for the recycling of Au from secondary sources like a waste of electric and electronic equipment (WEEE) and successfully recovered Au (4).

In this research, the authors applied this OAR for the gold refining from ore, considering the utilization at ASGM sites. We used $CuBr_2$ or $CuCl_2$ as an oxidant and potassium bromide (KBr) or sodium chloride (NaCl) as a supplier of halogen elements. First, the authors used the simulated ore which is a mixture or sand and Au wire by Cl type OAR to establish a fundamental procedure. After that, ore containing 48 ppm of Au was treated by Br or Cl type OAR and the authors evaluated the extraction ratio from the ore under ambient temperature or 40 °C. After the extraction, the authors evaluated the recovery of Au by the addition of acidic water to the solvent. Sulfuric acid (H_2SO_4) or lemon juice was used for this recovery.

MATERIALS AND METHODS

Materials

In this research, the authors used simulated and actual ores. Figure 1 shows the samples used in this research.

The simulated ore consists of sand and Au wire (ϕ = 0.20 mm) for the confirmation of a fundamental procedure of Au extraction and recovery. 20 – 200 g of sand was added for approx. 100 mg of Au to simulate 500-5,000 ppm of ore.

The authors also used an actual ore from La Maria, Colombia. This ore consists of quartz (SiO_2), pyrite (FeS_2), chalcopyrite ($CuFeS_2$) and periclase (MgO) as rock contents. In addition, 48.9 ± 6.30 ppm of Au was contained. In the previous tests, 83.7% of Au was extracted by the cyanidation process (5).

The OAR of this research consists of DMSO as a solvent and CuX_2 as an oxidizing agent. In addition, potassium bromide (KBr) was added for $CuBr_2$ solution ($CuBr_2$-KBr OAR) and sodium chloride (NaCl) was added for $CuCl_2$ solution ($CuCl_2$-NaCl OAR), respectively.

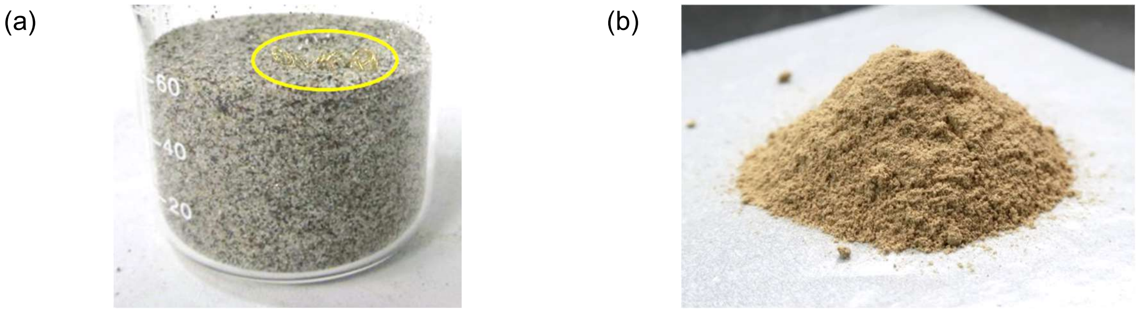

Figure 1: Used samples in this research, (a) the simulated ore and (b) the ore from La Maria

For the precipitation procedure, H_2SO_4, vinegar (CH_3COOH) and lemon juice (pure and half diluted) were selected precipitants.

Mechanism

In DMSO, the cupric ion (Cu^{2+}) and the cuprous ion (Cu^{+}) are stable. Dissolved CuX_2 in DMSO forms the complex of $[CuX_3]^-$ with halogen ion (X^-), while Cu^+ forms the complex of $[CuX_2]^-$. On the other hand, Au forms the complex of $[AuX_4]^-$ or $[AuX_2]^-$ in DMSO. Thus, Cu^{2+} ion can be a strong oxidant and dissolve Au by following reactions (6). In addition, as shown in Eqs. (1) and (2), an excessive amount of X- is required for the effective dissolution of Au. Thus, halogen compounds e.g. KBr or NaCl were added to the OAR.

$$Au + 3[CuX_3]^- + 4X^- \leftrightarrow [AuX_4]^- + 3[CuX_2]^- \qquad (1)$$
$$Au + [CuX_3]^- + 2X^- \leftrightarrow [AuX_2]^- + [CuX_2]^- \qquad (2)$$

On the other hand, reverse reactions will occur in water. Thus, after the Au dissolution, dissolved Au will be recovered by the addition of water to OAR. To prevent the precipitation of other metal compounds, especially Cu and Fe, acidic water like hydrochloric acid (HCl) or H_2SO_4 is preferable for the precipitation.

Methods

The proposed flow is shown in Figure 2. Au in ore was extracted by OAR treatment for several hours. In some cases, the authors tried to recover the dissolved Au. The detailed conditions of each method are described below.

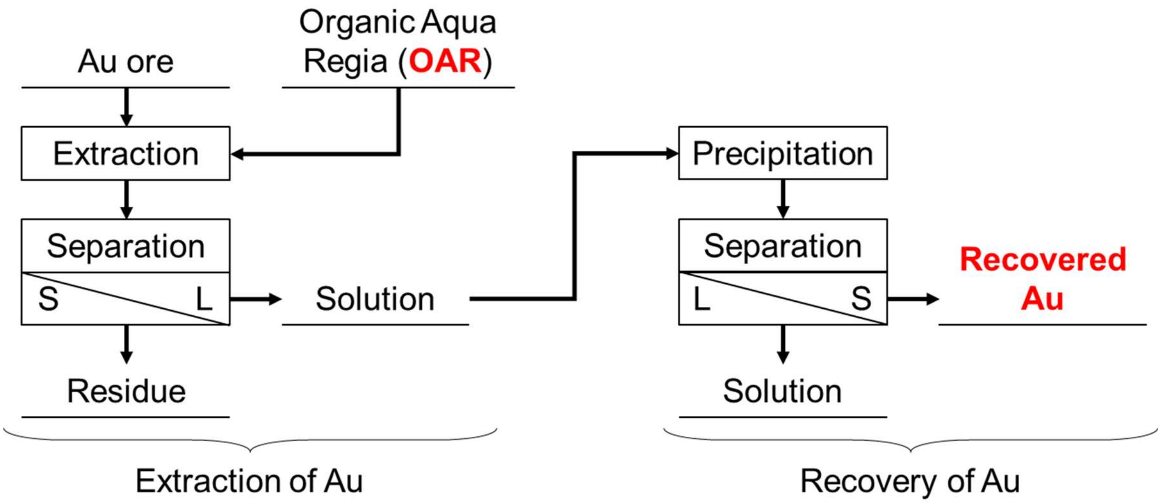

Figure 2: Experimental flow of this research

Treatment of the simulated ore

(1) Extraction of Au from ore
As described above, the authors used mixtures of 100 mg of Au wire and sand as samples. OAR volume was varied from 10 mL (for pure Au wire), 20 mL (for 5,000 ppm sample), 40 mL (for 2,500 and 1,000 ppm samples) to 80 mL (for 500 ppm sample), respectively. In every case, OAR contained 403 mg (3 mmol) of $CuCl_2$ and 117 mg (2 mmol) of NaCl.
As common conditions, the treatment temperature and time were set at 80 °C for 6.0 hours. The change of Au wire weight was checked on 0.5, 1.0, 1.5, 2.0, 3.0, 4.0 and 6.0 hours to confirm the dissolution amount by OAR treatment. The dissolution rate was compared with pure Au wire to evaluate the effect of the coexistence of sand.

(2) Recovery of extracted Au
After extraction, the OAR solution containing dissolved Au was separated from the Au sample residue. H_2SO_4 was added to this solution and obtained the precipitation. The recovery ratio of Au was calculated from Au content in the precipitation by SEM-EDS analysis and its weight.

Treatment of the ore from La Maria

(1) Extraction of Au from ore

In this research, the authors used $CuBr_2$-KBr or $CuCl_2$-NaCl OAR as the solvent. In the fundamental treatment, the authors used a high temperature (80 °C) to achieve the high-speed dissolution of Au, however, it causes an extra cost to keep the temperature at ASGM sites. Considering this, the treatment temperature was set as lower temperature.

In the extraction experiments, the solid-liquid (S:L) ratio, the concentration of solvents and treatment time were evaluated. The detailed conditions are following:

- $CuBr_2$-KBr OAR

  20 g of ore was treated with 50 mL or 100 mL of OAR. This OAR contained 0.82-3.27 g of $CuBr_2$ and 0.29-1.16 g of KBr. The treatment temperature was 40 °C and the treatment time was 4-24 h, respectively.

- $CuCl_2$-NaCl OAR

  10 g of ore was treated with 3- or 10-times volume of OAR. This OAR contained 1.34-2.7 g of $CuCl_2$ and 0.6-1.16 g of NaCl. The treatment temperature was ambient and the treatment time was 8 or 24 h, respectively.

(2) Recovery of extracted Au

In the case of $CuBr_2$-KBr OAR treatment, dissolved Au was recovered by the addition of acidic solvents referring to the existing research (6). As a fundamental procedure, enough amount of H_2SO_4 solution was added. However, it is hard to purchase and use such chemicals at ASGM sites. Considering this, the authors tried to use CH_3COOH and lemon juice which are easy to purchase and use for the precipitation of extracted Au.

EXPERIMENTAL RESULTS

Extraction of Au from Ore

$CuCl_2$-NaCl OAR for the simulated ore

Figure 3 shows the dissolution rate of Au from ore by $CuCl_2$-NaCl OAR for the simulated ore. As shown, the dissolution rate of Au from simulated ore decreased compared with pure Au wire. On the other hand, except 500 ppm sample, all or most of added Au were dissolved within 6 h. In addition, considering the result, all of Au can be dissolved by the continuous treatment from the 500 ppm sample.

From these results, the coexisting sand may not affect the Au dissolution in the case of pure Au exposed on the ore surface. And these results suggest the importance of pre-treatment of ore, e.g., grinding or crushing before the extraction by OAR.

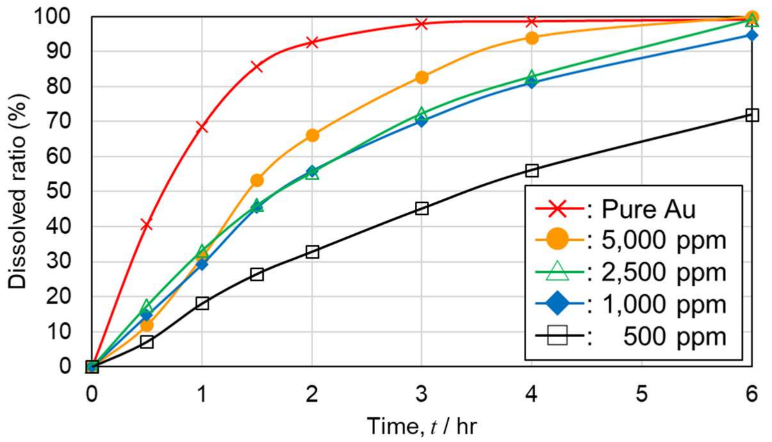

Figure 3: Dissolution rate of Au from the simulated ore by $CuBr_2$-KBr OAR

$CuBr_2$-KBr OAR for the Ore from La Maria

Figure 4 shows the extraction ratio of Au by $CuBr_2$ (3.27 g) - KBr (1.16 g) OAR treatment for the ore from La Maria. As shown, approx. 100% of Au was extracted by over 12 h treatment at 40 °C.
Au dissolution speed decreased compared with the simulated ore, however, all of the Au content was extracted even the concentration of Au was significantly smaller than the simulated ore.
In addition, all of Au was extracted from the ore in the case of 100 mL of OAR, even if the concentration of $CuBr_2$ and KBr was 1/2 or 1/4, while 50 mL of OAR could extract only 40%.

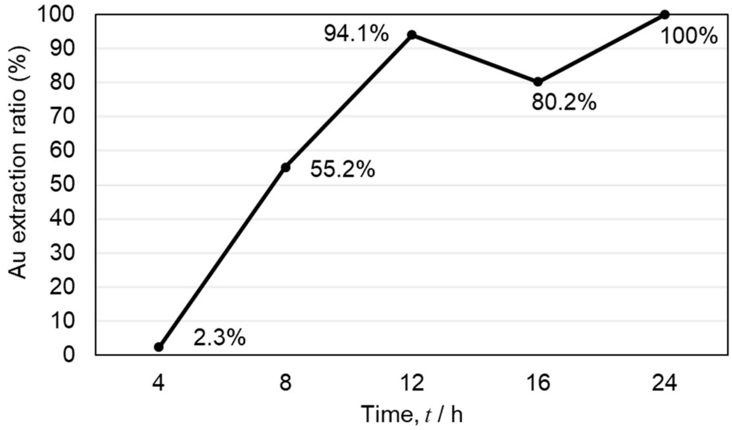

Figure 4: Extraction ratio of Au from the La Maria ore by $CuBr_2$-KBr OAR

$CuCl_2$-NaCl OAR for the Ore from La Maria

Figure 5 shows the extraction ratio of Au by $CuCl_2$-NaCl OAR treatment for the ore from La Maria. (a) shows the effect of the solid-liquid ratio and (b) shows the effect of treatment time. As common conditions, the treatment time was 24 h in the case of (a) and the S:L ratio was 10% in the case of (b), respectively. These experiments were carried out at ambient temperature.
Considering these results, the S:L ratio and treatment time are the important factors for the Au extraction from ore, while the concentration of $CuCl_2$ and NaCl didn't affect significantly.
In addition, the treatment at ambient temperature could extract all of the Au content. This can be a strong feature for the OAR refining procedure because of the easy operation conditions and the low costs.

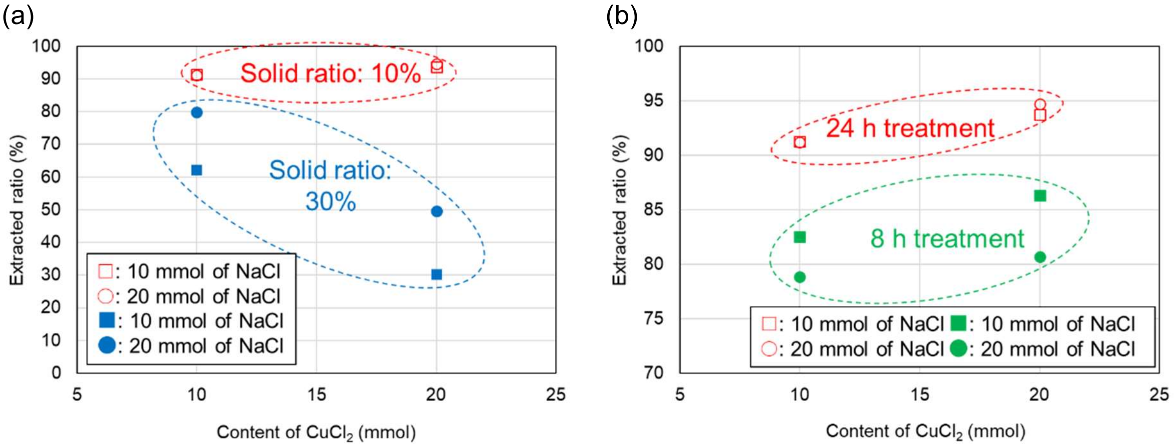

Figure 5: Extraction ratio of Au from the La Maria ore by $CuCl_2$-NaCl OAR

As described above, $CuBr_2$-KBr and $CuCl_2$-NaCl OAR can extract all of Au from ore in the optimized conditions, while cyanidation could extract only 84%. In addition, the contact of OAR with ore is a more important factor for the Au extraction than the concentration of the extractant. Considering this, the pulverizing to obtain a fine ground ore as shown in Figure 1 is an effective pre-treatment for the extraction.
Through these experiments, the authors confirmed the availability of OAR for the Au extraction from ore.

Recovery of Extracted Au

From the simulated ore

Figure 6 shows the recovered material from the simulated ore by $CuBr_2$-KBr OAR treatment and its SEM image. As shown, the recovered material was brown colored and uniform size and shape particles were recovered. The recovered material consists of almost pure Au without other elements. This was because of H_2SO_4 which can evade the precipitation of other elements, especially Cu. In addition, the content in sand e.g. SiO_2 or other oxides were not dissolved by the OAR treatment. As mentioned in the authors' previous research, pretreatments like oxidation or carbonization were effective in the prevention of the dissolution of other elements (4).
Table 1 shows the recovery ratio of Au from each condition. As shown, the existence of sand did not affect the precipitation of Au particles in most cases.

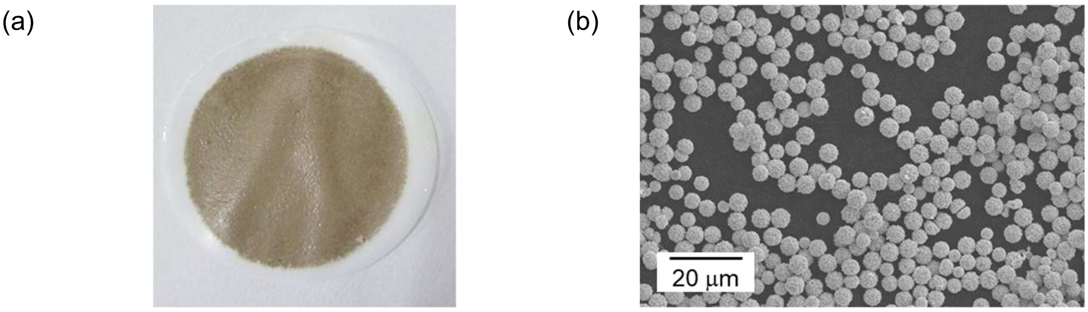

Figure 6: (a) Recovered material from the simulated ore and (b) its SEM image

Table 1: Recovery ratio of Au from the simulated ore

Au content (ppm)	Dissolved ratio (%)	Recovery ratio (%)
Pure Au	100	94.0
5,000	100	79.1
2,500	94.7	87.4
1,000	87.8	52.9
500	72.0	87.8

Figure 7 shows the shape difference of recovered materials between the dissolution conditions. As shown, the shapes of recovered particles differed from spherical or confeito-like by the recovery condition. These shapes are the same as in the previous research in which authors confirmed the particle growth mechanism using pure Au wire as the material (7).

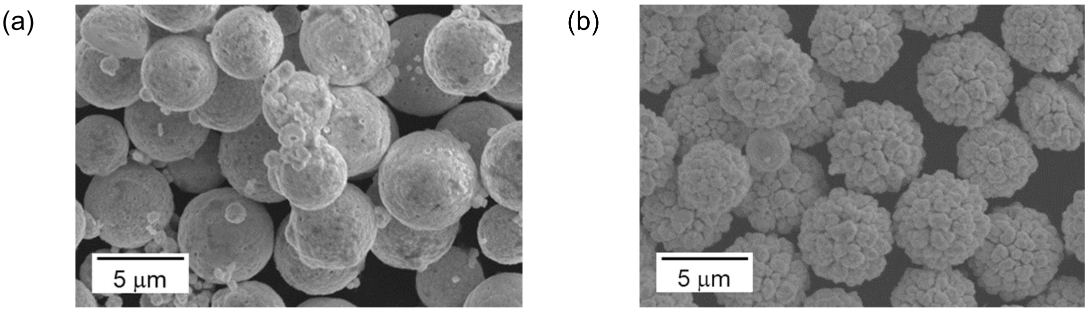

Figure 7: SEM images of recovered materials from (a) 1,000 ppm sample and (b) from 500 ppm sample

The same tendency between these results and the previous research suggests the possibility of Au recovery by the addition of acidic water to Au containing OAR.

From the La Maria ore

Figure 8 shows the recovered material and its SEM image from the La Maria ore by $CuBr_2$-KBr OAR treatment. In this precipitation, the authors added H_2SO_4 solution to prevent the precipitation of some elements e.g. Cu, Fe and S. As a result, this material contained approx. 1.5% of Au and consists of mainly Cu compound. As mentioned above, the ore contains $CuFeS_2$ and this OAR can dissolve $CuFeS_2$ (8). Thus, dissolved $CuFeS_2$ was precipitated by the addition of an acidic solution.

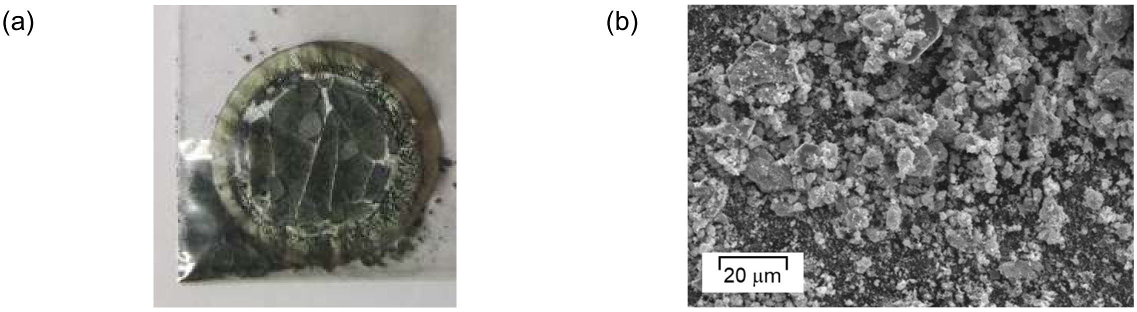

Figure 8: Recovered material from the La Maria ore by H_2SO_4 addition, (a) the precipitated material, and (b) its SEM image

Figure 9 shows the recovered material from the La Maria ore by $CuBr_2$-KBr OAR treatment. Small and dispersed particles were recovered from H_2SO_4 addition, while large and agglomerated particles were from lemon juice addition. In both cases, the Au content in particles was approx. 0.6-1.0% and all of extracted Au was recovered.

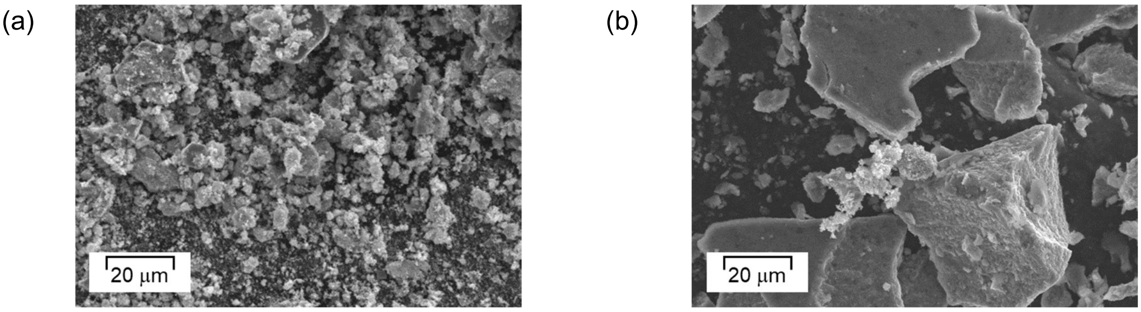

Figure 9: SEM images of recovered material from the La Maria ore, precipitated by (a) H_2SO_4 addition and (b) lemon juice addition

Table 2 summarizes the recovery ratio by the type of added acidic solutions. In the cases of H_2SO_4 or lemon juice, most or all of Au was recovered while vinegar could recover only 25%. As mentioned above, the accessibility of chemicals is an essential factor for spreading ASGM, and lemon juice is appropriate as a precipitant of extracted Au.

Table 2: Recovery ratio change by acidic solutions from the La Maria ore

$CuBr_2$ - KBr (g)	Added acidic solution	Precipitation amount (mg)	Au content (%)	Recovery ratio (%)
1.64 - 0.58	Sulfuric acid (H_2SO_4)	69.9	1.60	100
0.82 - 0.29	Sulfuric acid (H_2SO_4)	61.2	1.41	89.6
3.27 - 1.16	Vinegar (CH_3COOH)	10.9	2.20	25.0
1.64 - 0.58	Lemon juice	261	0.58	100
1.64 - 0.58	Diluted lemon juice	163	0.61	100

For the spreading of the Au refining procedure using OAR

As described above, the authors confirmed the availability of OAR for Au refining. However, the process cost of OAR treatment is much more expensive than the conventional amalgamation process. In this research, the authors used 100 mL of DMSO for approx. 1 mg of Au extraction. This means 100 L of DMSO is required to extract 1 g of Au, while only 1.07 g of mercury was required (9). In addition, the use of acidic water caused the denaturation of OAR and used OAR should be refreshed by evaporation or other treatment. Considering these factors, optimizing the OAR process, including reducing or reusing chemicals, is essential for spreading this process.

CONCLUSIONS

In this research, the authors applied the “organic aqua regia” (OAR) for Au refining from the ore, especially which is refractory for the conventional extraction procedure.
For the application to the simulated ore which consists of Au wire and sand, all or most of added Au wire was successfully dissolved and most of dissolved Au was successfully recovered by the addition of H_2SO_4 solution as pure Au particles.

For the application to the actual ore from La Maria, contained Au was successfully extracted by ambient or low-temperature treatment. In addition, the extracted Au was recovered by the addition of acidic solutions, e.g., H_2SO_4 or lemon juice. Simple operation procedures, easy treatment conditions and easy accessibility of materials enable the operation of the OAR process at ASGM sites.

Through this research, the authors confirmed the availability of OAR for the Au refining. However, the cost of this OAR process is much higher than the conventional ASGM procedure because this procedure requires a large amount of chemicals, especially DMSO. Process optimization, which can reduce the cost, is essential for spreading OAR in developing countries.

ACKNOWLEDGMENTS

Our Group would like to express deep appreciation for the following:
-Gaylord Chemical Company, L.L.C., for providing DMSO for our experiments and sharing their valuable experience with us.
- Newlox Gold Ventures Corp. and their President & C.E.O. Mr. Ryan Jackson for their support and partial funding of our research.
- The Environment Research and Technology Development Fund (JPMEERF20195R52) of the Environmental Restoration and Conservation Agency of Japan for their partial funding of our research.

REFERENCES

1. Hinton, J. J., Veiga, M. M., Veiga, A. C. T., 2003. Clean artisanal mining: a utopian approach? J. Clean Prod., 11, pp. 99-115

2. United Nations Environment Programme, 2020. Minamata convention on mercury.

3. Yoshimura, A., Takai, M., Matsuno, Y., 2014. Novel process for recycling gold from secondary sources: Leaching of gold by dimethyl sulfoxide solutions containing copper bromide and precipitation with water. Hydrometallurgy, 149, pp.177-182.

4. Yoshimura, A., Takatori, K., Matsuno Y., 2020.Environmentally Sound Recovery of Gold from Waste Electrical and Electronic Equipment Using Organic Aqua Regia. Int. J. Automation Technol., 14 (6), pp. 999-1004.

5. Veiga, M. M., Goncalves, A., Aguilar, Y., Li, H., Liu, S., Zhang, D., LA MARIA PROJECT METALLURGICAL TESTWORK

6. Yoshimura, A., Matsuno, Y., 2016. A Novel Process for the Production of Gold Micrometer-Sized Particles from Secondary Sources. Materials Transactions, 57 (3), pp.357-361.

7. Matsuno, Y., Okonogi, E., Yoshimura, A., Sato. M., C. Sato., In-Situ Observation for Formations of Gold Micrometer-Sized Particles in Liquid Phase Using Atmospheric Scanning Electron Microscopy (ASEM). Materials Transactions, 59 (1), pp. 146-149.

8. Takatori, K., Kato, H., Yoshimura, A., Matsuno, Y., 2021. Chalcopyrite Leaching in a Dimethyl Sulfoxide Solution Containing Copper Chloride. Mining, Metallurgy & Exploration, 38, pp.1477-1485.

9. Gonçalves, O. A., 2016. Analysis of gold extraction processes of artisanal and small-scale gold mining In Portovelo-Zaruma, Ecuador, Thesis of University of British Columbia.