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研究課題名（和文）Enhanced cementation of gold ions via synergistic effect using activated carbon and zerovalent aluminum: A novel approach to recover gold ions from ammonium thiosulfate system

研究課題名（英文）Enhanced cementation of gold ions via synergistic effect using activated carbon and zerovalent aluminum: A novel approach to recover gold ions from ammonium thiosulfate system

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研究成果の概要（和文）：The main achievement of this project is; successful recovery technique for gold ions from the eco-friendly solution, ammonium thiosulfate, with simple and high efficiency was newly developed to eliminate the challenges of poor recovery of the system.

研究成果の学術的意義や社会的意義
Currently in metallurgy, the focus is on green mining with non-toxic solution, but the application of the system to industrial mining is elusive so far due to the limited recovery technique. In the project, a simple recovery technique was newly developed and >99% of Au ions can be recovered.

研究成果の概要（英文）：The main achievements of this project are; (1) successful recovery technique with simple and high efficiency for gold ions from the eco-friendly ammonium thiosulfate solution was newly developed to eliminate the challenges of the limited industrial application by the poor recovery in the system, and (2) to widen the scope of the research, recovery of heavy metal ions from the waste/acid medium by the developed technique was also evaluated, not limited to only gold.

研究分野：Hydrometallurgy

キーワード：Ammonium thiosulfate　Gold　Cementation　Aluminum　Activated carbon　Galvanic interaction　Recovery of gold ions

１．研究開始当初の背景

Cyanide and/or halide leaching are the most commonly employed hydrometallurgical techniques to extract gold (Au) from both primary and secondary resources (Ha et al., 2010). Although effective, cyanide is toxic to human health, difficult to handle, and harmful to the environment while the halides (e.g., aqua regia) are strongly corrosive and unselective (Jeon et al., 2017). Because of these critical drawbacks, several alternative lixiviants for Au are being developed and among them, ammonium thiosulfate is the most promising because it is non-toxic, has high selectivity for Au and is less corrosive (Arima et al., 2002). Despite these advantages, the industrial application of ammonium thiosulfate is still limited primarily because of two reasons: (1) the recovery of dissolved Au from ammonium thiosulfate pregnant solutions remains elusive to date, and (2) conventional recovery techniques like adsorption and reductive precipitation (i.e., cementation) are ineffective in ammonium thiosulfate media. Jiexue and Qian (1991), for example, only recovered ~30% of dissolved Au using activated carbon in their thiosulfate system, which they attributed to the low adsorption affinity of the Au-thiosulfate complex ($Au(S_2O_3)_2^{3-}$) to activated carbon. Gallagher et al. (1990) compared the adsorption on activated carbon of the Au-thiosulfate complex with several Au-cyanide complexes and found that the adsorption of Au-thiosulfate complex was the least favorable because the affinity of Au-complexes to activated carbon strongly depended on the type of ligand and follows this order: $SCN^- > SC(NH_2)_2 > CN^- > S_2O_3^-$.

Aside from adsorption, dissolved Au in ammonium thiosulfate pregnant solutions could be recovered via reductive precipitation or cementation, an electrochemical process whereby Au ions are reduced and deposited as elemental Au onto the surface of metals like zinc (Zn) and copper (Cu) that acted as electron donors or reductants (Arima et al., 2002). Unfortunately, this approach suffers from the excessive amount of Zn and Cu needed for Au recovery because these metallic reductants easily dissolve in ammonium thiosulfate solutions (Arima et al., 2002; Aylmore and Muir, 2001; Jeon et al., 2018a). Aluminum (Al) could be another good candidate for Au recovery because of its low standard redox potential (Arima et al., 2002). Unfortunately, Al is easily oxidized in moist air, so its surface is rapidly covered with an aluminum oxyhydroxide film that protects the metal from reductively dissolving especially in solutions with pH between 6 and 10.

In a previous study of the authors that investigated the ammonium thiosulfate leaching of Au from printed circuit boards (PCBs), it was reported that Au extraction efficiency was low especially at high solid-to-liquid ratios because extracted Au ions were readily re-deposited onto coexisting metals in PCBs during leaching (Jeon et al., 2018). This interesting phenomenon of enhanced Au cementation in ammonium thiosulfate solution was attributed by the authors to galvanic interactions of the various metals found in PCBs (e.g., Cu and Al) that made electron transfer to Au-thiosulfate complex easier. In other words, Al and Cu formed numerous galvanic cells composed of Al as the anode (i.e., primary electron donor) and Cu as the cathode (i.e., electron acceptor), a configuration that created an electron pathway between Al and Au-thiosulfate complex (Jeon et al., 2018). Cu-Al galvanic interactions interfered with and limited the extraction of Au from PCBs in ammonium thiosulfate solution but by looking at these results from another perspective, a promising way to recover Au ions from ammonium thiosulfate solution was discovered.

２．研究の目的

The main objective of the study is the development a novel recovery technique for gold ions from the eco-friendly lixiviant, ammonium thiosulfate solution. (1) Firstly, recovery of Au ions from the ammonium thiosulfate lixiviant was evaluated by batch-type experiments in single systems—AC or Al only—as well as binary mixtures of AC and Al. Secondly, (2) to establish the applicability of the recovery technique to industrial Au ore and/or E-waste recycling processing, the effects of various parameters (i.e., initial concentration of Au ions, time, oxygen, solid-to-liquid ratio, mixing ratio of AC and Al, temperature) as well as coexisting metal ions that could be present in the leached pregnant solution on Au recovery were also investigated. Furthermore, (3) the mechanisms were evaluated by characterization of the residue by scanning electron microscopy with energy dispersive spectroscopy (SEM-EDX) and electrochemical experiments including linear sweep voltammetry (LSV) and chronoamperometry. (4) Finally, to widen the scope of the research, removal of heavy metal ions from the waste/acidic solutions was also carried out whether the technique could also be employed to not only metallurgy field but also environmental filed or not.

３．研究の方法

Objective (1), (2), and (4): For research (1), (2), and (4) were mainly proceeded by batch-type experiments. The stock ammonium thiosulfate solution containing Au ions was prepared by dissolving Au powder (99.999%, Wako Pure Chemical Industries, Ltd., Japan) in ammonium thiosulfate solution using a 300-ml Erlenmeyer flask shaken in a thermostat water bath shaker at 25 °C for 24 h with constant shaking amplitude and frequency of 40 mm and 120 min−1, respectively. The concentration of Au in stock solution was measured by inductively coupled plasma atomic emission spectroscopy (ICP-AES) (ICPE-9820, Shimadzu Corporation, Japan) (margin of error = ± 2%). Subsequently, 0.15 g of ZVAl (99.99%, Wako Pure Chemical Industries, Ltd., Japan) and/or 0.15 g of AC (99.99%, Wako Pure Chemical Industries, Ltd., Japan) were mixed with 10 ml of Au-thiosulfate solution in 50-ml Erlenmeyer flasks at 25 °C (shaking amplitude of 40 mm and frequency of 120 min−1) under the nitrogen purging condition to remove the dissolved oxygen in the solution. After 1 h, the filtrate and residue were separated by filtration using 0.2 μm syringe-driven membrane filters (LMS Co., Ltd., Japan). The residues were washed thoroughly with deionized water, dried in a vacuum oven at 40 °C, and analyzed by scanning electron microscopy with energy-dispersive X-ray spectroscopy (SEM-EDX, Super scan SSX-550, Shimadzu Corporation, Japan). Meanwhile, the concentrations of Au ions remaining in the filtrates were analyzed by ICP-AES. For research (4), selective heavy metal ions (Co, Ni, Pb, and Zn) and sulfate/chloride solution were used. To investigate the removal/recovery efficiency of heavy metal ions from sulfate/chloride solutions, 10 mL of prepared solutions (initial pH of 1, 2, 3, 4, and 5) were poured into a 50-mL Erlenmeyer flask and then purged with ultrapure N_2 (99.9%) for 15 min to remove dissolved oxygen. Afterward, Al and/or AC powder was introduced into the flask.

Objective (3): LSV measurements were conducted using SI 1280B electrochemical measurement unit (Solartron Instruments, UK) attached to a computer and a conventional three-electrode system composed of an Al working electrode, Ag/AgCl in saturated KCl solution as the reference electrode, and platinum plate as the counter electrode. The 120 ml of ammonium thiosulfate solution with Au ions was poured into a glass cell with water jacket and purged with ultra-pure nitrogen gas (99.99%) for 45 min prior to the measurements to minimize the influence of dissolved oxygen in the solution. Furthermore, all electrochemical measurements were maintained at 25 ºC by a thermostat water recirculation system. Measurements were done after equilibrating the Al electrode to its open circuit potential (OCP). The cathodic scan was done at a rate of 30 mV/s from the OCP to –1.3 V. Chronoamperometry measurements were also conducted using SI 1280B electrochemical measurement unit (Solartron Instruments, UK) attached to a computer with a conventional three-electrode system composed of the Al working electrode, Ag/AgCl in saturated KCl solution as the reference electrode, and a platinum plate as the counter electrode. Preparation of the aluminum electrodes and solutions for the measurements were the same as outlined in previous paragraph. After equilibration of the Al working electrode to the OCP, it was polarized at –0.8 V and –1.0 V for 15 min, and then its surface was examined by SEM-EDX.

４．研究成果

The results showed that individually neither of these two materials could not recover Au effectively in ammonium thiosulfate lixiviant as reported in many previous studies, but when combined, over 99% of Au ions could be recovered from the ammonium thiosulfate solution, which means that there is a synergistic interaction between Al and activated carbon that promoted Au recovery (*published a paper to international journal (Q1)*). And in the Al-AC system, the highest Au recovery was obtained under the following conditions: 1 h recovery time without oxygen, 1:1 of Al and AC, and 0.3g/10ml at 25 ºC. The LSV results using an oxidized Al working electrode with AC showed two new cathodic peaks at –0.8 V and –1.0 V, indicating that AC acted as a reduction mediator that enhanced Au recovery. Chronoamperometry results at –0.8 V and –1.0 V showed that Cu and Au were recovered on AC even if Al oxide was present on Al (*submitted a paper to international journal (Q1)*). In the case of the study on the effects of various coexisting base metal ions on Au recovery, still high Au recovery was obtained when Cu ions (catalyst in the leaching system) are present in the solution with minimal effect of other competing base metal ions (*submitted a paper to international journal (Q1)*). When the recovery technique was employed to environmental filed, which is the removal of heavy metal ions from the sulfate/chloride solutions, the results showed that removal efficiency was higher in the AC/Al-mixture than those in AC or Al only experiments (*published 2 papers to international journals (both Q1)*). The results will have important industrial implications of the eco-friendly solvent in the mineral processing/resource recycling field.

The achievements in detail are as follows:

FY 2019

Journal papers

1. S. Jeon, C.B. Tabelin, H. Takahashi, I. Park, M. Ito, N., Hiroyoshi, Enhanced cementation

of gold via galvanic interactions using activated carbon and zero-valent aluminum: A novel approach to recover gold ions from ammonium thiosulfate medium. Hydrometallurgy 191, 2020, 105165.

Presentations

1. CINEST 2019, S. Jeon, S. Bright, I. Park, M. Ito, N. Hiroyoshi, The effects of co-existing metal ions on the recovery of gold from thiosulfate solutions using aluminum and activated carbon.
2. International Symposium on EARTH Science and Technology 2019, 10.13.-17., Fukuoka, Japan, S. Jeon, S. Bright, I. Park, S. Hong, M. Ito, N. Hiroyoshi, The effects of coexisting metal ions on the recovery of gold from ammonium thiosulfate solutions using aluminum and activated carbon.
3. 4th International Future Mining Conference, Sydney, Australia 2019, S. Jeon, H. Takahashi, C.B. Tabelin, M. Ito, N. Hiroyoshi, Recovery of gold ions from ammonium thiosulfate using synergistic effect of aluminum and activated carbon.
4. 15th International Symposium on East Asian Resources Recycling Technology, S. Choi, S. Jeon, I. Park, C.B. Tabelin, M. Ito, N. Hiroyoshi, Cementation of Cd and Pb ions from sulfate and chloride solutions using aluminum and activated carbon, Pyeongchang, South Korea.

FY 2020

Journal papers

1. S. Choi, S., Jeon, I., Park, C.B. Tabelin, M. Ito, N., Hiroyoshi, Enhanced cementation of Cd2+, Co2+, Ni2+, and Zn2+ on Al from sulfate solutions by activated carbon addition. Hydrometallurgy 201, 2021, 105580.
2. S. Choi, S., Jeon, I., Park, M. Ito, N., Hiroyoshi, Enhanced cementation of Co2+ and Ni2+ from sulfate and chloride solutions using aluminum as an electron donor and conductive particles as an electron pathway. Metals 2021, 11(2), 248.
3. C.B. Tabelin, I., Park, S. Jeon, Copper and critical metals production from porphyry ores and E-wastes: A review of resource availability, processing/recycling challenges, socio-environmental aspects, and sustainability issues. Resources Conservation & Recycling 2021 [Accepted on April 06, 2021], RECYCL_105610
4. S. Jeon, S. Bright, I. Park, C.B. Tabelin, M. Ito, N. Hiroyoshi. A simple and efficient gold ion recovery technique from ammonium thiosulfate medium by galvanic interactions using zero-valent aluminum and activated carbon: A parametric and mechanistic study. Submitted to Hydrometallurgy (Q1).
5. S. Jeon, S. Bright, I. Park, C.B. Tabelin, M. Ito, N. Hiroyoshi. Recovery of gold ions from ammonium thiosulfate solution by enhanced cementation technique using galvanic interactions between zero-valetn aluminum (ZVAl) and activated carbon (AC): Identification of the effects of coexisting metal ions on Au recovery. Submitted to Metals (Q1).

Presentations

1. MMIJ, Chiba, Japan, March 15-17, 2020, Removal of d and Pb ions from sulfate and chloride solutions by cementation using aluminum and activated carbon.
2. MMIJ, Sendai, Japan, September 8-10, 2020, Enhanced cementation of Co, Ni, and Zn from sulfate and chloride solutions using aluminum and activated carbon powders.
3. [Best speaker award], S. Bright, S. Jeon, M. Ito, N. Hiroyoshi, Eco-friendly recovery of gold ions from thiosulfate solutions using aluminum (Al) and activated carbon (AC): Characterization of gold loaded Al/AC for development of gold stripping method. XVI International Forum-Contest of Students and Yong Researchers “Topical Issues of Rational Use of Natural Resources”, Virtual Event. 2020.

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５．主な発表論文等

〔雑誌論文〕　計6件（うち査読付論文　0件／うち国際共著　6件／うちオープンアクセス　2件）

１．著者名 S. Jeon, C.B. Tabelin, H. Takahashi, I. Park, M., Ito, N. Hiroyoshi	４．巻 191
２．論文標題 Enhanced cementation of gold via galvanic interactions using activated carbon and zero-valent aluminum: A novel approach to recover gold ions from ammonium thiosulfate medium	５．発行年 2020年
３．雑誌名 Hydrometallurgy	６．最初と最後の頁 105165
掲載論文のDOI（デジタルオブジェクト識別子） 10.1016/j.hydromet.2019.105165	査読の有無 無
オープンアクセス オープンアクセスではない、又はオープンアクセスが困難	国際共著 該当する

１．著者名 S. Choi, S. Jeon, I. Park, C.B. Tabelin, M. Ito, N. Hiroyoshi	４．巻 201
２．論文標題 Enhanced cementation of Cd2+, Co2+, Ni2+, and Zn2+ on Al from sulfate solutions by activated carbon addition	５．発行年 2021年
３．雑誌名 Hydrometallurgy	６．最初と最後の頁 105580
掲載論文のDOI（デジタルオブジェクト識別子） 10.1016/j.hydromet.2021.105580	査読の有無 無
オープンアクセス オープンアクセスではない、又はオープンアクセスが困難	国際共著 該当する

１．著者名 S. Choi, S. Jeon, I. Park, M. Ito, N. Hiroyoshi	４．巻 11(2)
２．論文標題 Enhanced cementation of Co2+ and Ni2+ from sulfate and chloride solutions using aluminum as an electron donor and conductive particles as an electron pathway	５．発行年 2021年
３．雑誌名 Metals	６．最初と最後の頁 248
掲載論文のDOI（デジタルオブジェクト識別子） 10.3390/met11020248	査読の有無 無
オープンアクセス オープンアクセスとしている（また、その予定である）	国際共著 該当する

１．著者名 S. Jeon, S. Bright, I. Park, C.B. Tabelin, M. Ito, N. Hiroyoshi	４．巻 -
２．論文標題 A simple and efficient gold ion recovery technique from ammonium thiosulfate medium by galvanic interactions using zero-valent aluminum and activated carbon: A parametric and mechanistic study	５．発行年 2021年
３．雑誌名 Hydrometallurgy	６．最初と最後の頁 -
掲載論文のDOI（デジタルオブジェクト識別子） なし	査読の有無 無
オープンアクセス オープンアクセスではない、又はオープンアクセスが困難	国際共著 該当する

1．著者名 C.B.Tabelin, I. Park, T. Phengsaart, S. Jeon, M.V. Tabelin, D. Alonozo, K. Yoo, M. Ito, N. Hiroyoshi	4．巻 170
2．論文標題 Copper and critical metals production from porphyry ores and E-wastes: A review of resource availability, processing/recycling challenges, socio-environmental aspects, and sustainability issues	5．発行年 2021年
3．雑誌名 Resources Conservation & Recycling	6．最初と最後の頁 105610
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オープンアクセス オープンアクセスではない、又はオープンアクセスが困難	国際共著 該当する

1．著者名 S. Jeon, S. Bright, I. Park, C.B. Tabelin, M. Ito, N. Hiroyoshi	4．巻 -
2．論文標題 The effects of co-existing copper, iron, cobalt, nickel, and zinc ions on gold recovery by enhanced cementation via galvanic interactions between zero-valent aluminum and activated carbon in ammonium thiosulfate system	5．発行年 2021年
3．雑誌名 Metals	6．最初と最後の頁 -
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オープンアクセス オープンアクセスとしている（また、その予定である）	国際共著 該当する

〔学会発表〕　計6件（うち招待講演　0件／うち国際学会　4件）

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2．発表標題 Cementation of Cd and Pb ions from sulfate and chloride solutions using aluminum and activated carbon
3．学会等名 EARTH2019（国際学会）
4．発表年 2019年

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2．発表標題 Recovery of gold ions from ammonium thiosulfate using synergistic effect of aluminum and activated carbon
3．学会等名 Future Mining 2019（国際学会）
4．発表年 2019年

１．発表者名
S. Jeon, S. Bright, I. Park, M. Ito, N. Hiroyoshi

２．発表標題
The effect of co-existing metal ions on the recovery of gold from thiosulfate solutions using aluminum and activated carbon

３．学会等名
CINEST 2019（国際学会）

４．発表年
2019年

１．発表者名
S. Choi, S, Jeon, M. Ito, N. Hiroyoshi

２．発表標題
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３．学会等名
MMIJ

４．発表年
2020年

１．発表者名
S. Choi, S, Jeon, M. Ito, N. Hiroyoshi

２．発表標題
Enhanced cementation of Co, Ni, and Zn from sulfate and chloride solutions using aluminum and activated carbon powders

３．学会等名
MMIJ

４．発表年
2020年

１．発表者名
S. Bright, S. Jeon, M. Ito, N. Hiroyoshi

２．発表標題
Eco-friendly recovery of gold ions from thiosulfate solutions using aluminum (Al) and activated carbon (AC):
Characterization of gold loaded Al/AC for development of gold stripping method

３．学会等名
XVI International Forum-Contest of Students and Yong Researchers “Topical Issues of Rational Use of Natural Resources”（国際学会）（国際学会）

４．発表年
2020年

〔図書〕　計0件

〔産業財産権〕

〔その他〕

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６．研究組織

	氏名 （ローマ字氏名） （研究者番号）	所属研究機関・部局・職 （機関番号）	備考

７．科研費を使用して開催した国際研究集会

〔国際研究集会〕　計0件

８．本研究に関連して実施した国際共同研究の実施状況

共同研究相手国	相手方研究機関			
オーストラリア	Curtin University	The University of New South Wales		