A Method for Leaching or Dissolving Gold from Ores or Precious Metal Scrap

Nicolas Geoffroy and François Cardarelli

The hydrometallurgical leaching of native gold from gold-bearing ores or the dissolution of gold metal during the recycling of electronic and precious metal scrap is performed every day using hazardous chemicals such as sodium cyanide or aqua regia. These chemicals represent health and safety risks for workers and a serious threat for the environment. However, even if several other reagents are known to dissolve gold at the laboratory scale, none of these are used industrially. Hot mixtures of hydrochloric acid with strong oxidizing compounds are known to generate in-situ nascent chlorine which is capable of dissolving gold efficiently. In this study, the authors investigated the capability of a hot mixture of hydrochloric acid and ground manganese (IV) oxide to dissolve gold metal either under atmospheric or pressurized conditions. The best result was obtained under a pressure of 639 kPa at 90°C with a dissolution rate of 0.250 g·cm^{-2}h^{-1} and it was compared to that reported in the literature for other industrial reagents.

INTRODUCTION

In 2003, according to the *U.S. Geological Survey*, approximately 2,593 tonnes of gold (i.e., about 83.4 million troy ounces) were produced worldwide from various mining operations.[1] Moreover, about 943 tonnes of secondary gold were recovered from precious metal scrap and spent gold-bearing alloys coming from the electronic industry, jewelry, and dentistry sectors.[2] All the hydrometallurgical gold extraction routes utilize a leaching step to produce a gold-bearing solution as an intermediate product while the recycling of secondary gold from electronic and precious metal scrap is based on the selective and fast dissolution of the precious metal. Therefore,

either leaching or dissolution operations require highly corrosive media due to the well-known chemical inertness of the noble metal toward most acids and bases.[3]

Several reagents are known to leach native gold from gold-bearing ores. It has been known for more than a century that alkaline solutions of alkali-metal cyanides (e.g., NaCN, KCN) dissolve gold under aerated conditions. The dissolution of metallic gold is due to the strong complexing capabilities of cyanide anions combined with the oxidizing properties of the dissolved molecular oxygen. The dissolution of the metal is given by chemical Reaction 1.[4] (All reactions can be found in Table I.)

Upon dissolution, gold forms the stable dicyanoaurate (III) complex anion [Au(CN)$_2^-$]. In replacement of dissolved oxygen, other oxidizing compounds like cyanogen bromide (CNBr) can also be used, such as in the Diehl process.[5] Gold metal is also leached by aerated aqueous solutions of ammonium thiosulfate[6]

according to the overall reaction scheme given in Reaction 2.

Finally, gold metal is dissolved by an aerated solution containing thiourea[7] according to the overall reaction 3.

However, only the cyanidation process is used industrially in hydrometallurgical processes. The optimized leaching conditions are usually a concentration of lixiviant of 0.1 mol·dm^{-3} NaCN. Enough NaOH must be present as neutralizer to maintain alkaline conditions at a constant pH of 11.

Several reagents can be used in the dissolution of gold metal from electronic and precious metal scrap.[8] Among them, hot aqua regia is extensively used in small- and medium-scale operations. It is obtained by mixing three parts of concentrated hydrochloric acid (HCl) with one part of concentrated nitric acid (HNO$_3$). Moreover, it usually contains a halogen or even a certain amount of hydrogen peroxide to increase the dissolution rate. Upon dissolution in this media, gold forms the stable tetrachlo-

Table I. Reactions	
$4Au^0 + 8\,NaCN + 2H_2O + O_2 \rightarrow 4Na[Au(CN)_2] + 4NaOH$	(1)
$4Au^0 + 8(NH_4)_2S_2O_3 + 2H_2O + O_2 \rightarrow 4(NH_4)_3Au(S_2O_3)_2 + 4NH_4OH$	(2)
$4Au^0 + 8NH_2CSNH_2 + 2H_2O + O_2 \rightarrow 4Au[NH_2CSNH_2]_2^+ + 4OH^-$	(3)
$Au^0 + 4HCl + HNO_3 \rightarrow HAuCl_4 + NO + 2H_2O$	(4)
$2Au^0 + 3H_2O_2 + 8HCl \rightarrow 2HAuCl_4 + 6H_2O$	(5)
$MnO_2 + 4HCl \rightarrow MnCl_2 + 2H_2O + Cl_2$	(6)
$2Au^0 + 14HCl + 3MnO_2 \rightarrow 2HAuCl_4 + 3MnCl_2 + 6H_2O$	(7)
$2Cu^0 + 4HCl + O_{2(dissolved)} \rightarrow 2CuCl_2 + 2H_2O$	(8)
$2Ni^0 + 4HCl + O_{2(dissolved)} \rightarrow 2NiCl_2 + 2H_2O$	(9)
$Cu^0 + MnO_2(s) + 4HCl \rightarrow CuCl_2 + MnCl_2 + 2H_2O$	(10)
$Ni^0 + MnO_2(s) + 4HCl \rightarrow CuCl_2 + NiCl_2 + 2H_2O$	(11)
$2AuCl_4^-{}_{(aq)} + 3Fe^{2+}{}_{(aq)} \rightarrow 2Au^0(s) + 3Fe^{3+}{}_{(aq)} + 8Cl^-{}_{(aq)}$	(12)

EXPERIMENTAL PROCEDURES

All the tests were performed using disk-shaped coupons punched into a thick foil made of pure gold metal (i.e., 99.95 wt.% gold) purchased from Goodfellow Ltd., United Kingdom. Each coupon exhibited the following overall dimensions: an outside diameter of 19.05 mm, a thickness of 0.565 mm, and a weight of approximately 3.11 g (1/10 troy ounce or 2 pennyweights). Prior to each experiment, the coupons were first degreased by trichloroethylene in an ultrasonic bath, then etched with aqua regia, thoroughly rinsed with deionized water, and finally air dried.

The aqueous solution of hydrochloric acid 32 wt.% HCl (20°Be) was prepared by dilution from ACS-grade hydrochloric acid 37 wt.% purchased from Fisher Scientific and calibrated by acido-basic titrimetry using a 1 M NaOH solution and methyl orange as pH indicator. Pure manganese (IV) oxide certified grade was also purchased from Fisher Scientific and its MnO_2 content was measured by reacting it with sulfuric acid and hydrogen peroxide and measuring the oxygen evolved by gas analysis using a Lunge burette.[14] Reducing reactant for precipitating gold such as iron (II) sulfate and oxalic acid were all ACS grade and both purchased from Fisher Scientific.

For atmospheric experiments, a 250 cm³-Erlenmeyer flask made of thick-walled borosilicate glass and equipped with a condenser was used. The gold coupon was held in the solution by piercing a small hole into the disk and passing a twisted polytetrafluoroethylene (PTFE) tape through it and squeezing the extremities in the ground joint. For pressurized experiments, a 125 mL general-purpose Parr acid digestion bomb Model No. 4748 equipped with a thick-walled PTFE liner (Parr Instruments Company, Moline, Illinois) was used as pressure-leaching reactor. The bomb was immersed in a water bath for heating. The pressure exerted inside the bomb during the test was assumed to be roughly equal to the absolute vapor pressure of the acid plus the ideal pressure exerted by the stoichiometric quantities of chlorine gas evolved and contained in the free space, that is, the volume of the container (125 cm³) less the volume occupied by the solution (ρ_{HCl} = 1,160 kg.m⁻³), the gold coupon (ρ_{Au} = 19,300 kg.m⁻³), and the manganese dioxide (ρ_{MnO2} 5,234 kg.m⁻³). Note that this calculated pressure corresponds to the maximum theoretical pressure or peak pressure because the chlorine is consumed readily by the dissolution of gold. Therefore, the total pressure inside the vessel at a given temperature can be roughly assessed using Equation A.

$$P_{vessel} = \pi_{HCl}(T) + \{(m_{MnO2}/M_{MnO2})RT/[V_{vessel} - V_{HCl} - (m_{MnO2}/\rho_{MnO2}) - (m_{Au}/\rho_{Au})]\} \quad (A)$$

with

P_{vessel}	total absolute pressure inside the pressure reactor vessel in Pa
$\pi_{HCl}(T)$	vapor pressure of HCl solution at temperature T in Pa
V_{vessel}	inside volume of the pressure reactor vessel in m³
V_{HCl}	volume occupied by the HCl solution in m³
m_{MnO2}	initial mass of manganese dioxide in kg
m_{Au}	initial mass of the gold coupon in kg
M_{MnO2}	molar mass of the manganese dioxide in kg.mol⁻¹
ρ_{MnO2}	mass density of the manganese dioxide in kg.m⁻³
ρ_{Au}	mass density of gold metal in kg.m⁻³
R	ideal gas constant in J.K⁻¹mol⁻¹
T	absolute thermodynamic temperature in K

Note that the vapor pressure of the acid corresponds to the sum of the vapor pressure of HCl and water above the solution taken from tabulated data found in the literature.[15] For instance, according to the previous reference, at an operating temperature of 90°C the partial pressure of HCl above the solution is 970 mmHg (129.3 kPa) and the partial pressure of the water vapor is 184 mmHg (24.5 kPa), giving a total vapor pressure of 153.8 kPa above the solution.

The dissolution of gold was measured gravimetrically weighing accurately the gold coupon before and after each test and reporting the final concentration of gold in the solution by dividing mass difference of gold per unit volume of solution:

$$C_{Au} = (m - m_0)/V_{soln} = \Delta m/V_{soln} \quad (B)$$

To confirm that the concentration of gold in the solution can be simply calculated from the weight loss of the coupon, the gold concentration was also measured once by atomic absorption spectrometry.

roaurate (III) complex anion [$AuCl_4^-$] according to Reaction 4.

The main drawback of the treatment with aqua regia is the nitric oxide (NO) gas that evolves when the metal is digested. This noxious gas represents a major threat for the health and safety of the workplace. Apart from aqua regia, other corrosive reagents have been used or tested. For example, in the Plattner process, gold was dissolved into chlorine water (i.e., water saturated by chlorine gas) while bromine water was also mentioned. It was the first hydrometallurgical process to recover gold.[9] Svistunov et al., studying the action of chlorine water onto gold, suggested that the dissolution mechanism is based on the reaction of molecular chlorine in water followed by a decomposition of a fraction of the hydrochloric acid, yielding nascent chlorine.[10] On the other hand, strong halohydric acids HX (e.g., HCl, HBr) in which the corresponding halogen X_2 (e.g., Cl_2, Br_2) is dissolved have been known and used from several centuries. Actually, gold metal dissolves in the presence of both a strong oxidant and a halide anion under highly acidic solutions. Moreover, a hot solution of hydrochloric acid mixed with a hydrogen peroxide (H_2O_2) also dissolves gold according to the chemical reaction (see Reaction 5).

Nesbitt et al. demonstrate that the dissolution of gold in these media is always attributed to the formation of the highly reactive nascent chlorine.[11]

Quite surprisingly, either in the hydrometallurgical leaching of gold ores by cyanidation or in the aqua regia process used for the recovery of secondary gold from electronic and precious scraps, the lixiviant and the reagent are both highly hazardous chemicals. These chemicals pose health and safety risks as well as a serious threat for the environment. However, they are generally considered a necessary evil because they are widespread commercially and inexpensive. Also, and probably more importantly, the two processes have a proven record for decades and they require less capital investment than the other competing technologies.

Therefore, in order to find a healthier and environmentally friendly process for either leaching and/or dissolving gold, it was decided to find a safer, cleaner
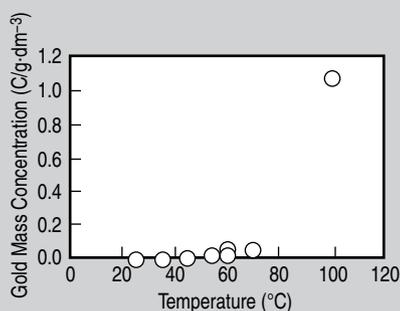
Figure 1. The dissolution of gold in hot HCl with MnO_2 under atmospheric pressure as a function of temperature. (Conditions: the initial mass of gold was 2.8249 g; the mass of MnO_2 was 5.1112 g; 150 cm³ of 32 wt.% HCl; reaction time 15 min.)

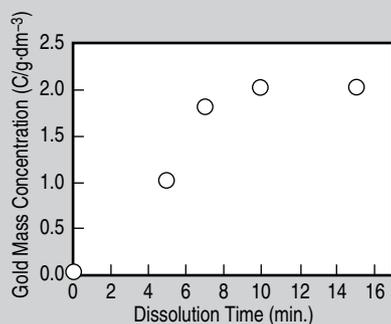Figure 2. The dissolution of gold in hot HCl with MnO_2 under pressure at 90°C as a function of time. (Conditions: the initial mass of gold was 1.72 g; the mass of MnO_2 was 1.00 g; 50 cm³ of 32 wt.% HCl; and the peak internal pressure was evaluated at 639 kPa.)

dissolving reagent. Based on the fact that nascent chlorine dissolved into hydrochloric acid is a powerful solvent for gold, the aqueous solutions of hydrochloric acid with the generation of nascent chlorine in-situ were especially investigated.

Several options were available to produce a hydrochloric solution containing nascent chlorine. The first straightforward option consists of saturating the hydrochloric acid solution with chlorine gas initially pressurized or liquefied and contained in a gas cylinder. However, the chemical reactivity of the dissolved molecular chlorine is known to be much lower than that of its nascent equivalent. The second option relies on the fact that nascent chlorine can be produced efficiently in-situ by the oxidation of an aqueous solution of hydrochloric acid by a powerful oxidant such as hydrogen

peroxide (H_2O_2), manganese dioxide (MnO_2), and ammonium peroxodisulfate ($(NH_4)_2S_2O_8$). A third option consists of producing it by the electrolysis of hydrochloric acid, the nascent chlorine being formed at the anode (+) in the anodic compartment of the electrolyzer. Finally, a fourth option is to prepare nascent chlorine by photolysis, which is irradiating the hydrochloric solution by far ultraviolet radiation. This study focused on the second option, using an inexpensive oxidizing chemical, namely, manganese dioxide (MnO_2). Manganese dioxide is extensively found in manganese-bearing ore deposits as pyrolussite and cannot decompose unexpectedly when heated, as is the case for the other mentioned compounds. Moreover, every chemist will remember the simple experiment for preparing pure chlorine gas by heating hydrochloric acid with powdered manganese (IV) oxide in a Kipp apparatus according chemical Reaction 6.

It is known that gold can be efficiently leached from gold-bearing ores using a mixture of hydrochloric acid, ferric chloride, and manganese dioxide.[12] The chemical reaction involved during the dissolution of gold in this media is shown in Reaction 7.

Despite the fact that this method was already applied for the dissolution of gold for analytical purposes,[13] it was never investigated nor mentioned for the metallurgical extraction of gold from ores or precious metal scrap. For all of these reasons, if this technique is successful, it would offer numerous advantages over existing processes. See the sidebar for experimental procedures.

RESULTS AND DISCUSSION

The dissolution of the gold was conducted under atmospheric pressure in an open vessel equipped with a condenser to minimize loss of water. The final gold concentration of the solution, recorded as a function of the operating temperature, is presented in Figure 1.

Figure 1 shows clearly that for an operating temperature below 70°C no major dissolution occurs while above 80°C a significant amount of gold is dissolved with a dissolution rate of 0.128 g·cm^{-2}·h^{-1}. However, above this temperature the strong evolution of chlorine gas combined with the high vapor pressure of the hydrochloric acid solution leads to important losses of reactants. This is not compliant with the task of reducing health and safety risks described in the introduction. Therefore, it was decided to perform the dissolution under pressure using the pressure vessel. The temperature was fixed at 90°C and the quantities of reagents decreased in order to comply with the safety guidelines provided by the manufacturer of the acid digestion bomb. The final concentration of gold into the solution was recorded as a function of the dissolution time and presented in Figure 2.

Figure 2 shows that above 10 min., no major dissolution takes place. It is important to note that at least 10 min. of immersion in the water bath are required to reach a thermal equilibrium of the bomb, ensuring that the solution is at the right temperature. Therefore, below these dissolution times, no reliable results can be obtained.

The dissolution rate obtained during the experiments and the figures reported in the literature for other reagents are presented in Table II.

Although the kinetics of the dissolution of gold were extensively studied,[18] it was not the aim of the this work to study the dissolution mechanism. A

Table II. Comparison of Dissolution Rates Obtained with Figures in the Literature

Reagent or Mixtures	Operating Conditions	Dissolution Rate (/g·cm^{-2}·h^{-1})	References
HCl 32 wt.% + MnO_2 (s)	100°C atm	0.137	Present work
HCl 32 wt.% + MnO_2 (s)	90°C 639 kPA	0.250	Present work
NaCN 0.006M + Ca(OH)$_2$ 0.004M + air	30°C atm	0.700	5
NaCN 0.45M + NaOH 0.2M + air	30°C atm	1.50	5
HCl 6M + H_2O_2 0.22M	50°C	4.0	16
HCl 6M + Cl_2 (satd.)	40°C atm	180	17
3HCl + HNO_3 (6M)	80°C atm	1,800	5

comparison of the results obtained with other industrial reagents indicates that the dissolution rate is still too slow but working both at higher temperature and pressure or with a higher concentration of reactants is expected to increase the kinetics of the dissolution. Until now, no tests were performed on gold alloys but the dissolution rate is expected to be similar or greater due to the fact that the corrosion resistance of gold alloys decreases rapidly for a gold content below 75 wt.% (i.e., below 18 kt). Also, tests performed using pure copper and pure nickel under approximately 639 kPa of pressure showed dissolution rates of 0.290 $g \cdot cm^{-2} \cdot h^{-1}$ and 0.170 $g \cdot cm^{-2} \cdot h^{-1}$, respectively. Neither pure nickel nor pure copper metals dissolve into deaerated, hot, and concentrated hydrochloric acid solutions. The dissolution rate observed can be explained by several factors acting separately or jointly. First, the presence of dissolved oxygen in the solution promotes the dissolution of the two metals according to chemical Reactions 8 and 9. Second, the highly positive Nernst standard electrode potential of the Mn(IV)/Mn(II) redox couple $[E^0_{298}(MnO_2/Mn^{2+}) = +1.230$ V/SHE] compared to that of pure copper $[E^0_{298}(Cu^{2+}/Cu^0) = +0.340$ V/SHE] or pure nickel $[E^0_{298}(Ni^{2+}/Ni^0) = -0.257$ V/SHE] could explain the possible anodic dissolution of the two metals due to a galvanic corrosion occurring between the immersed copper or nickel metals (i.e., anodic sites) put in electrical contact with the slurry of semiconductive particles of MnO_2 (i.e., cathodic sites) according to electrochemical Reactions 10 and 11.

However, as in the case of dissolution using aqua regia, alloys containing high proportions of silver can cause problems because of the formation of an inert layer of silver chloride (AgCl) on the surface of the metal.

On the other hand, the relatively important concentration of the manganous cation (Mn^{2+}) in the leach liquor at the end of the dissolution is not a significant problem during the precipitation stage for the recovery of gold from precious metal scrap. Actually, the electropositive Nernst potential of the Mn^{2+}/Mn^0 redox couple $[E^0_{298K}(Mn^{2+}/Mn^0) = -1.180$ V/SHE] strongly indicates that it should not interfere with the precipitation of the more noble $AuCl_4^-$/Au^0 couple $[E^0_{298K}(AuCl_4^-/Au^0) = +1.002$ V/SHE]. To confirm this, a mass of approximately 0.200 g of gold was dissolved using 1.00 g of manganese dioxide and virtually all the precious metal was precipitated using ferrous sulfate according to the reduction Reaction 12.

One can assume that the other common reducing compounds used as precipitating agents for gold (e.g., oxalic acid, sulfur dioxide) could also be used with the same degree of success.

CONCLUSION

The best results of these experiments were obtained under a pressure of 639 kPa at 90°C with a dissolution rate of 0.250 $g \cdot m^{-2} h^{-1}$. Despite this slow dissolution rate compared to other industrial reagents commonly used, the authors expect to further improve the yield by modifying the operating conditions, especially increasing the operating temperature and pressure and increasing the amount of reactants.

ACKNOWLEDGEMENTS

References

1. E.B. Amey, "Gold," *USGS Mineral Yearbook 2004* (Washington, D.C., USGS, 2004), pp. 34.1–34.9.
2. Anonymous, "Gold," *Mining Journal,* (June 11, 2004), pp. 19–24.
3. F. Cardarelli, *Materials Handbook. A Concise Desktop Reference* (New York: Springer, 2001), pp. 196–203.
4. N.N. Greenwood and A. Earnshaw, *Chemistry of the Elements,* 2nd. ed. (New York: Pergamon Press, 1997), p. 1175.
5. H. Renner, "Gold," *Handbook of Extractive Metallurgy, Vol. III*, ed. F. Habashi (Weinheim, Germany: Wiley-VCH, 1997), pp. 1183–1213.
6. P. Pascal, *Nouveau Traité de Chimie Minérale. Tome III—Groupe Ia: Rubidium, cesium, francium; Groupe Ib: Généralités, cuivre, argent, or.* (Paris: Masson & Cie, 1957).
7. N. Gönen, "Leaching of Finely Disseminated Gold Ore with Cyanide and Thiourea Solutions," *Hydrometallurgy*, 69 (2003), pp. 169–176.
8. J.W. Mellor, *A Comprehensive Treatise of Inorganic and Theoretical Chemistry* (London: Longmans Green & Co., 1923), p. 499.
9. F. Habashi, *Principles of Extractive Metallurgy, Vol. 2,* 2nd ed. (New York: Gordon and Breach, 1980), p. 39.
10. N.V. Svistunov, "Mechanism for the Dissolution of Gold in Chlorine Water," *Tsvetnaya Metallurgiya*, 13 (5) (1970), pp. 69–71.
11. C.C. Nesbitt, J.L. Hendrix, and J.H. Nelson, "The Effect of Nascent Chlorine and Multivalent Chloride Salts in the Dissolution of Gold by Chlorine," *EPD Congress 1992,* ed. J.P. Hager (Warrendale, PA: TMS, 1992), pp. 313–326.
12. A.D. Brokaw, "The Solution of Gold in the Surface of Alterations of Ore Bodies, *J. Geology*, 18 (1910), p. 322.
13. P. Chattopadhyay and M. Mistry, "Novel Dissolution Procedure Using a Mixture of Manganese Dioxide and Hydrochloric Acid for the Matrix-Independent Determination of Gold," *Fresenius J. Anal. Chem.*, 357 (1997), pp. 308–313.
14. A.I. Vogel, *A Textbook of Inorganic Quantitative Inorganic Analysis*, 3rd ed. (London: Longman, 1961), p. 1091, paragraph XXI.13.
15. R.H. Perry and D.W. Green, *Perry's Chemical Engineers' Handbook,* 7th ed. (New York: McGraw-Hill, 1997), pp. 2–76.
16. R.W. Stanley, G.B. Harris, and S. Monette, "Process for the Recovery of Gold from a Precious Metal Bearing Sludge Concentrate, U.S. patent 4,670,052 (2 June 1987).
17. R.K. Lea, J.D. Edwards, and D.F. Colton, "Process for the Extraction of Precious Metals from Concentrates Thereof," U.S. patent 4,397,689 (9 August 1983).
18. J. Vinals, C. Nunez, and O. Herreros, "Kinetics of the Aqueous Chlorination of Gold in Suspended Particles," *Hydrometallurgy*, 38 (1995), pp. 125–147.

Nicolas Geoffroy is a student in the Department of Mining, Metals, and Materials Engineering at McGill University in Montreal, Canada. François Cardarelli is principal chemist, materials at Rio Tinto Iron & Titanium Inc. in Sorel-Tracy, Canada.

For more information, contact Nicolas Geoffroy, McGill University, 3610 University Street, Montreal, (QC) PQ H3A 2B2, Canada; e-mail nicolas. geoffroy@mail.mcgill.ca.