



Research article

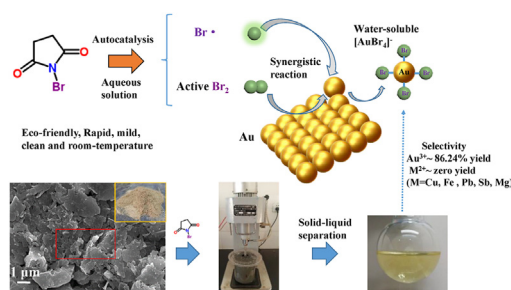
Eco-friendly and rapid extraction of gold by in-situ catalytic oxidation with N-bromosuccinimide

Xiang Liu^{a,b}, Yongliang Wang^{d,**}, Li Xiao^{a,b}, Licheng Ma^{a,c}, Peiwei Han^{a,c}, Shufeng Ye^{a,c,*}^a State Key Laboratory of Multiphase Complex Systems, Institute of Process Engineering, Chinese Academy of Sciences, 1 North 2nd Street, Zhongguancun, Haidian District, Beijing, 100190, PR China^b School of Chemical Engineering, University of Chinese Academy of Sciences, No.19A Yuquan Road, Beijing, 100049, PR China^c Innovation Academy for Green Manufacture, Chinese Academy of Sciences, Beijing, 100190, PR China^d Beijing Research Institute of Chemical Engineering and Metallurgy, CNNC, Beijing, 101149, China

HIGHLIGHTS

- Utilizing nitrogen heterocyclic to carry bromine and sustainably release Br• to in situ catalytically oxidize gold.
- One-pot conversion and high-efficient option to extract gold in a mild, clean and room-temperature chemistry.
- Bromine separates from NBS skeleton to generate Br• and active Br₂ and rapidly oxidized Au⁰ to Au³⁺ to form stable complex compound [AuBr₄]⁻.
- High Au leaching selectivity with 86.24% yield by 0.05 M NBS and nearly negligible yields of other coexisting metals.

GRAPHICAL ABSTRACT



ARTICLE INFO

Keywords:

Gold extraction
In-situ autocatalysis
Non-cyanide
NBS
Oxidative etching

ABSTRACT

Gold is a valued, critical element whose chemical activation or extraction is challenging. Non-cyanide extraction of gold is now the focus, and N-bromosuccinimide (NBS) is attracting attention. Herein, new insights into the possible mechanism are deeply revealed through comprehensive analysis and detection of the reaction by using elementary gold and gold bearing ore. Experiments on gold foil indicate that Au can be activated in NBS solution to perform a satisfactory dissolution. Application of NBS in gold extraction from ore show a high yield of 86.24% under optimal conditions of NBS dosage 0.05 M, liquid-solid ratio 4:1, stirring speed 400 rpm, pH 8, 25 °C and leaching for 20 h, while yields of other coexisting metals are nearly negligible. The process leads to direct, efficient, one-pot conversion of gold, into simple water-soluble salts. Characterizations show that the framework of NBS are not destroyed, only bromine separates from the framework. The oxidation of neutral gold atom to trivalent Au^(III) occurs in a mild, clean and room-temperature chemistry, which converts gold to [AuBr₄]⁻, and the framework to succinimide. The active bromine and radical Br (Br•) generated from in-situ autocatalysis of NBS are responsible for this. The systematic results herald a green procedure for preparation of gold derivatives and gold extraction industry.

* Corresponding author.

** Corresponding author.

E-mail addresses: jakese@163.com (Y. Wang), sfy@ipe.ac.cn (S. Ye).<https://doi.org/10.1016/j.heliyon.2022.e09706>

Received 27 March 2022; Received in revised form 6 May 2022; Accepted 7 June 2022

2405-8440/© 2022 The Author(s). Published by Elsevier Ltd. This is an open access article under the CC BY-NC-ND license (<http://creativecommons.org/licenses/by-nc-nd/4.0/>).

1. Introduction

The oxidative leaching of gold is the key step in gold metallurgy. Cyanidation has been the most viable technology and dominant means in the industry for the last 100 years [1, 2, 3]. However, cyanide is lethal to humans since it causes tissue hypoxia and asphyxiation [4]. Poisoning symptoms will appear within a few seconds and people died soon [5]. Cyanidation produces a large amount of wastewater and residue containing cyanide which are difficult to be disposed of, causing serious harm to the environment [6]. To replace cyanidation, a growing number of researchers have been focusing on developing new reagents [7]. In recent years, studies on non-cyanide gold extraction mainly focus on thiosulfate, thiourea, halogen and its compounds, polysulfide, lime sulphur, etc [8, 9]. Alternative lixivants have been studied and a great job has been done, such as thiosulfate [10, 11, 12, 13, 14, 15, 16], thiourea [17, 18, 19, 20], chloride [21, 22], bromine [21, 23] and iodine-iodide [24, 25, 26]. Table 1 is the comparison of conventional non-cyanide leaching gold technologies to describe the general situation. We can find that the methods commonly have certain limitations. As a halogen, Br₂ is a promising lixiviant for gold extraction with excellent advantages of low-toxic, rapid gold leaching, high yield and simple process. In fact, Br₂ had been utilized for gold extraction since the end of the XIX century [23]. However, the leaching environment is acidic and Br₂ is volatile, corrosive and toxic, which is not conducive to its development [9, 22, 27]. Its application as an alternative to cyanide has been downplayed due to its hazard and extreme difficulty in storing or transporting under safe conditions [23]. To solve the problem, bromide and oxidant are utilized to in-situ generate Br₂ for gold leaching. Bromide leaching system has many advantages, such as fast leaching, non-toxic, suitable for gold leaching in a wide pH range and even neutral solutions [23].

Generally, Figure 1a shows the conventional routes for converting Au into water-soluble complexes, and the methodologies based on harsh conditions. Au commonly requires harsh reaction conditions including aqua regia as a solvent for activation and dissolution to form soluble derivatives. Recently, Do et al. developed a mechanochemistry method of solvent-free conversion of palladium and gold by ball milling with oxidants [28]. This is a relatively environmentally friendly approach, albeit one that involves potentially high energy consumption and is not good to reducing carbon emissions. For chemical route, developing a simple, clean, efficient method is imperative and Figure 1b may show a promising one. We demonstrated an approach of in-situ generation of active Br₂ and bromine free radicals from NBS, synergistically and quickly converting gold to [AuBr₄]⁻, which is no heating, nearly no use of acids and bases, and significantly simpler, cleaner, and safer than conventional routes in Figure 1. So, the method in this paper may be a more eco-friendly move. NBS is a kind of multifunctional bromination agent commonly used in the anion bromination and free radical bromination of alkenes and other compounds in organic synthesis [29, 30] and the pharmaceutical industry for synthesis of antibiotics, such as benzyl cephalosporin [30, 31]. The application of it to gold etching has just begun to attract attention. Singh and Prasad reported that NBS was able to change the shape of organically dispersed gold nanoparticles and cause the oxidation of Au⁽⁰⁾ in hydrophobic gold nanoparticles to Au³⁺ ions at appropriate concentrations. Through comparative tests, they concluded that the bromine molecules released by NBS might be the substances oxidizing gold nanoparticles [32]. Zhang and Yang discovered gold oxidation from neutral Au⁽⁰⁾ to trivalent Au^(III) under certain oxidative environments provided by NBS and amino acids and proposed that Au^(III) could bind with DNA to decrease the redox potential, as a result, continuous dissolution of gold atoms is facilitated [33]. Subsequently, Yue et al. reported a strategy based on the use of NBS and pyridine (Py) to leach gold from gold ore and WEEE and convert it to Au(III) with a high yield and high selectivity. They believed that the exclusion of any reagent from NBS/Py would result in a poor gold leaching yield [7]. The downside is that Py has a foul odor and is carcinogenic to people.

Table 1. Comparison of conventional gold leaching technologies.

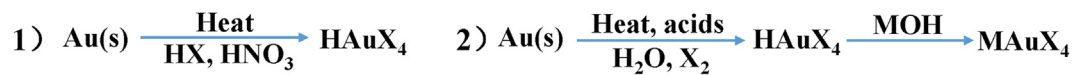
Immersion systems	Oxidants	Complexing agents	Advantages	Disadvantages
Cyanidation	O ₂	CN ⁻	Simple process, high yield, remarkable economic benefit, large-scale industrial production.	Slow, no anti-interference, extremely toxic, harmful to environment and human health.
Thiosulfate	O ₂ , Cu(NH ₃) ₂ ⁺	S ₂ O ₃ ²⁻	Rapid, high yield, strong anti-interference, slight equipment corrosion.	Large reagents consumption, complex gold recovery process.
Thiourea	Fe ³⁺ , H ₂ O ₂	SC(NH ₂) ₂	Rapid, high yield, strong anti-interference, preliminary industrialization.	Poor stability, large consumption, strong corrosiveness, high cost.
Chlorine	Cl ₂ , NaClO	Cl ⁻	High yield, cheap and readily available reagents.	Strong toxicity, easy to leak, poor security, strong corrosiveness
Bromine	Br ₂	Br ⁻	Rapid, cheap, good adaptability.	Volatile, difficult to transport.
Iodine-iodide	I ₃	I ⁻	Non-toxic, rapid, high yield, eco-friendly.	High cost, poor industrial application, harsh conditions.
Polysulfide	S _x ²⁻	S _x ²⁻ , S ₂ O ₃ ²⁻	Cheap, non-toxic, rapid.	Subsequent process is not perfect.
NBS (in this paper)	Br ₂ , Br [·]	Br ⁻	Less dosage, mild, rapid, high yield, eco-friendly.	Under laboratory stage, unverified by industry.

In this study, we focus on the mechanism of the associated oxidation process by NBS. Through comprehensive analysis and detection of the reaction, new insights into the possible mechanism are deeply revealed. The application and most relevant operating conditions that could affect the performance of NBS on gold extraction were also investigated. The results are very encouraging, as a high yield and selectivity of Au is in noticeable contrast to the conventional systems. The comparison of NBS with other non-cyanide technology is shown in Table 1. More noteworthy, without other reagents to assist, NBS has a great potential to serve as a simple, clean and high-efficient option, as well as a viable alternative to cyanide. It heralds a green procedure for gold extraction from gold-bearing raw materials.

2. Materials and methods

2.1. Reagents and materials

Pure gold foil (99.985% Au, thickness 0.025 mm) was purchased from Alfa Aesar and H₂SO₄ (98%), HCl (36%–38%), HNO₃ (68%) and Br₂ (3%) from Beijing Chemical Works. NBS (AR, 99%), Na₂S₂O₃·5H₂O (AR, 99%), CuSO₄ (AR, 99%), CCl₄ (AR, 98%), and NaOH (GR, 97%) were supplied by Macklin. KI (AR, 99%), I₂ (AR, 99.8%) and ammonia (GR, 25–28%) were bought from Sinopharm. Thiourea (AR, 99%), KOH (GR, 99.9%), acetone (HPLC) and ethanol (AR, 97%) were purchased from Aladdin. Deionized water was prepared by water purification systems (Millipore S.A.S.). Moreover, all these reagents were not further treatment before the experiments. The raw gold-bearing oxidized ore sample originated

(a) Traditional methods:

Recently:



⊗ = solvent-free, ball milling

X = Cl, Br, I M = K, NH₄

Ox = oxidant L = ligand

Harsh conditions, strong acids, and high-temperature

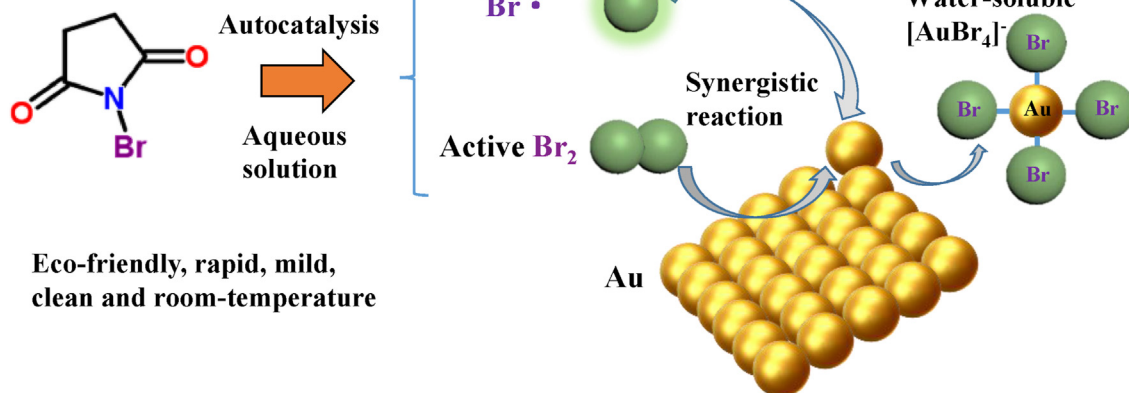
(b) In this work:

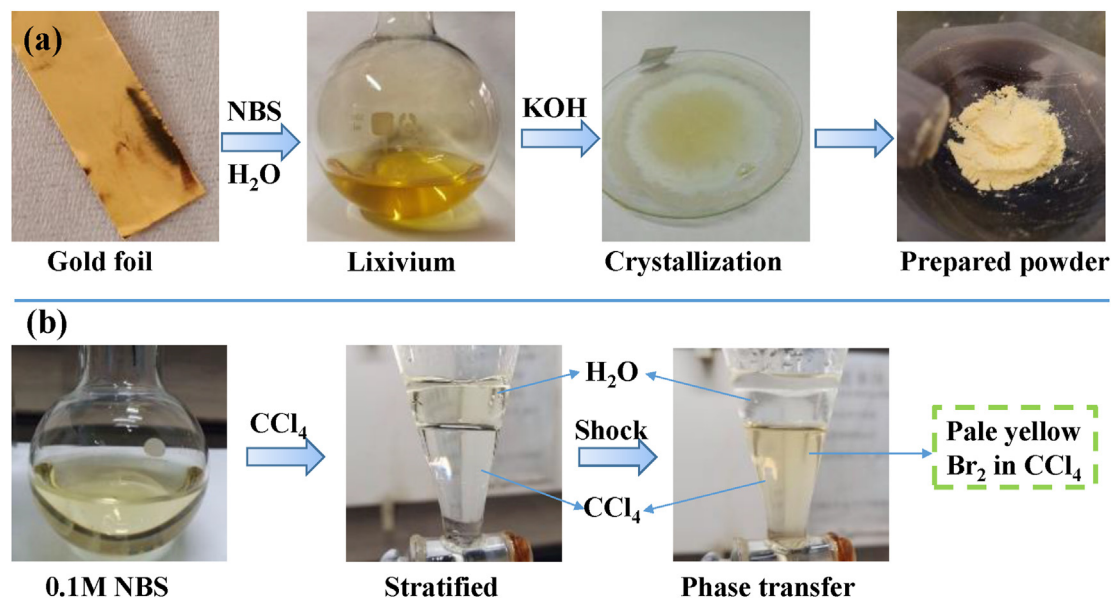
Figure 1. Comparison of routes for Au oxidation (a) conventional routes for converting Au into water-soluble complexes, (b) a lower environmental impact approach herein.

from the Republic of Kyrgyzstan, which belongs to a finely disseminated gold ore.

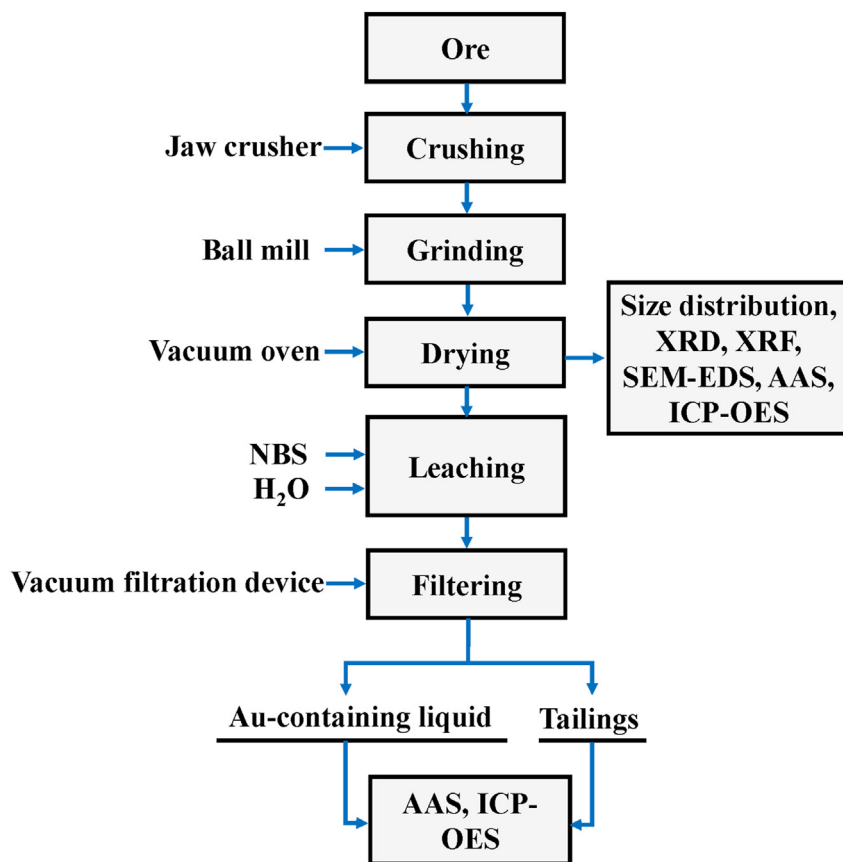
2.2. Characterization method

Scanning Electron Microscope with Energy Dispersive Spectrometer (SEM-EDS, JSM-7001F, JEOL, Japan) were applied to observe the morphology and microstructure of the samples. X-ray Fluorescence

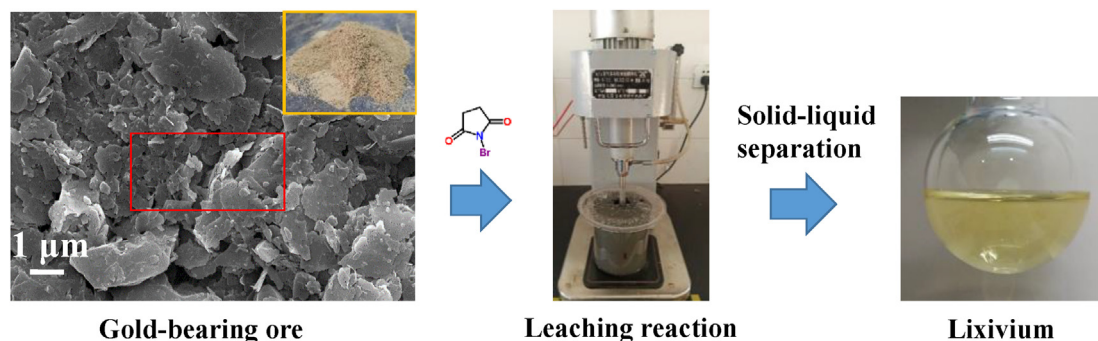
Spectrometry (XRF, AXIOS-MAX, PANalytical B.V.) was utilized to determine the elemental composition of the gold ore. X-ray Diffraction (XRD, Smartlab-201307, Rigaku Corporation, Japan) equipped with Cu-K α radiation and a scanning angle from 5° to 90° was performed to obtain the mineralogical characterization of samples. Fourier-transform infrared spectroscopy (FT-IR, iS50R) was used to examine the crystalline composition, chemical structure, and composition of the samples. X-ray Photoelectron Spectroscopy (XPS, ESCALAB 250Xi, Thermo Fisher



Scheme 1. Dissolution of gold foil in NBS aqueous, (a) preparation of powder, (b) phase transfer from water to CCl₄.



Scheme 2. Flow sheet of gold-bearing ore processed by NBS method.



Scheme 3. Extraction of gold from gold-bearing ore by NBS method.

Scientific, USA) with a monochromatic Al K α radiation was used to study of surface compositions and valence state of elements. The photoelectron energy drift due to charging effects was taken into account in reference to the position of C 1s at 284.8 eV, which is generated by adventitious carbon on the surface of the powder as-inserted into the vacuum chamber. The accurate concentrations of gold and other metals in the ore, residue or lixivium were analyzed by flame Atomic Absorption Spectrophotometry (AAS, WFX-130A, Beijing, China) and Inductively Coupled Plasma-Optical Emission Spectrometry (ICP-OES, Optima 8000, PerkinElmer, Waltham, MA).

2.3. Experimental techniques

2.3.1. Experiments of dissolution of gold foil in NBS aqueous solution

The pieces of pure gold foil (2 × 2 mm, 1 × 2 mm) were rinsed with deionized water, soaked and washed with ethanol and acetone and then

polished with 0.1 μm monocrystalline diamond paste, washed with acetone twice, rinsed with distilled water and swept with lint-free paper. Experiments for pure gold leaching were performed in a 250 mL reactor using a magnetic stirrer. The stirring speed was maintained at 200 rpm. Put the gold foil in 100 mL of 0.1 M NBS aqueous solution under room temperature and observe the change of the gold foil in 10 days. Lixivium was adjusted by KOH, placed on an evaporating dish, and slowly evaporated under 30 °C to get the prepared powder for XRD, FT-IR and XPS in Scheme 1a. The same experiment by 0.05 M bromine water was also performed. Phase transfer experiment of NBS was performed by CCl $_4$ in Scheme 1b.

2.3.2. Pretreatment and measurement of chemical compositions of gold ore

The raw oxidized gold ore was crushed to -2mm by a jaw crusher (Wuhan Prospecting Machinery Co., China), and then ground to a particle size of about 92% passing 300 mesh (50 μm) through a ball mill

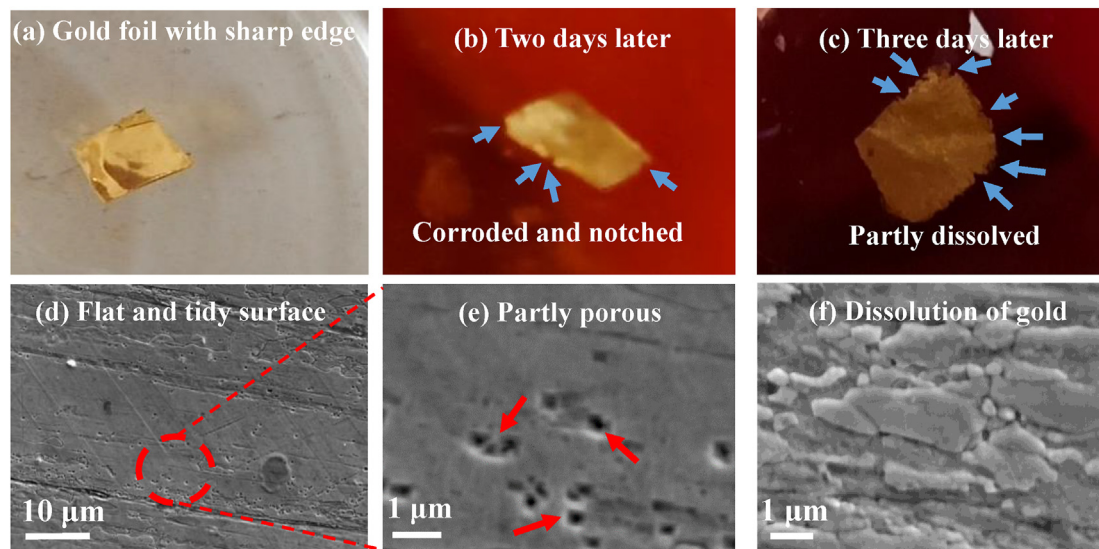


Figure 2. The change of gold foil in 0.1 M NBS aqueous solution (a) gold foil after cleaning, (b) change of gold foil after 2 days, (c) change of gold foil after 3 days, (d) SEM images before etching, (e) local magnification of (d), and (f) SEM image after etching.

(Wuhan Prospecting Machinery Co., China). After the as-received ore was thoroughly comminuted and blended by rolling, grinding and then dried at 100 °C for 24 h, samples were collected for size distribution, XRD, XRF, SEM-EDS and leaching (Scheme 2).

Elemental analysis of samples was performed. For the measurement of Au, aqua regia was used for the digestion of samples. Typically, put a 250 mL Teflon beaker on a hot plate, add 5 g of samples and 50 mL of aqua regia. After boiling to 5 mL, add 30 mL deionized water. Slowly

pour the solution through an activated carbon layer to filter the solution and adsorb gold. Calcine the activated carbon layer at 750 °C for 50 min and redissolve in boiled dilute aqua regia. For the measurement of Ag, Cu, Pb, Zn, Fe, As and Sb, add 5 g of samples and 50 mL of aqua regia. Then, boil to 5 mL and add 30 mL deionized water. After completely filtered by a sand core funnel with a 0.22 μm membrane, the filtrate was diluted and the content of each metal component was quantified via ICP-OES and AAS. Total sulfur was measured by a sulfur element analyzer.

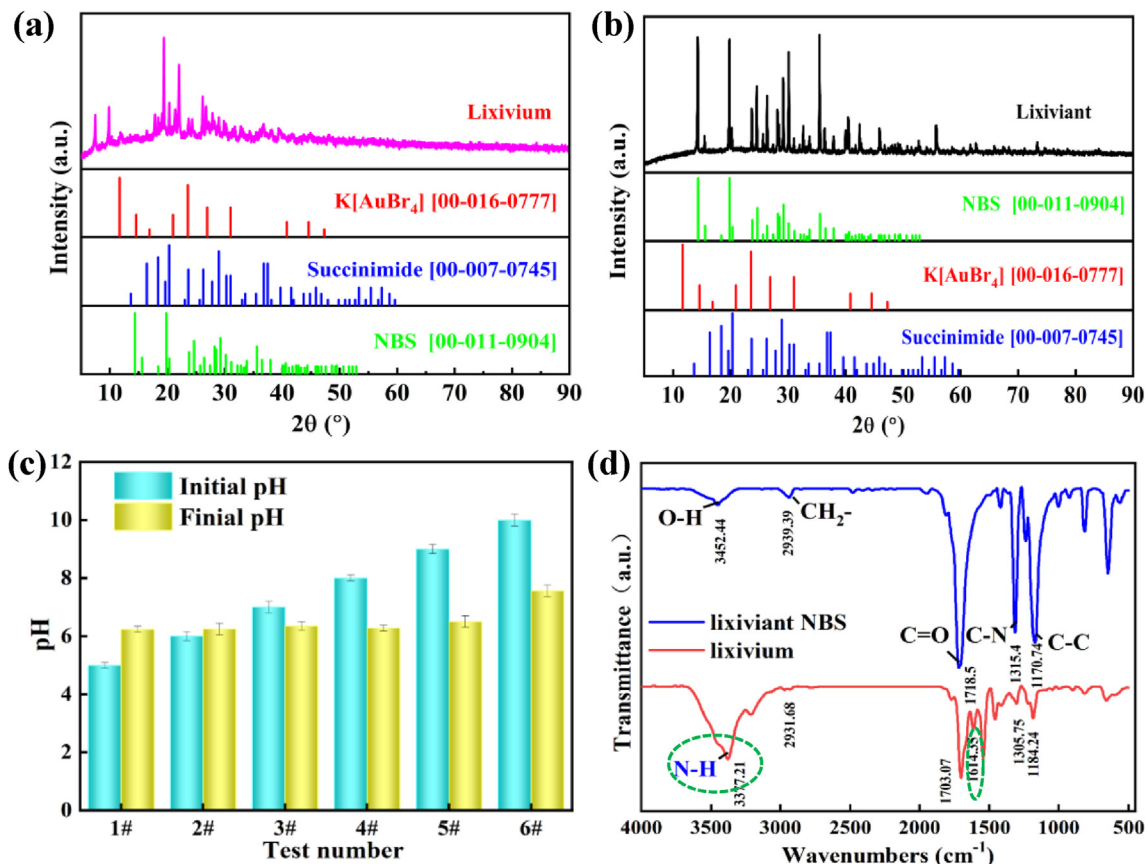


Figure 3. XRD pattern of (a) lixivium and (b) lixiviant, (c) the change of pH in the leaching of ore, (d) infrared spectra analysis of lixiviant NBS and lixivium

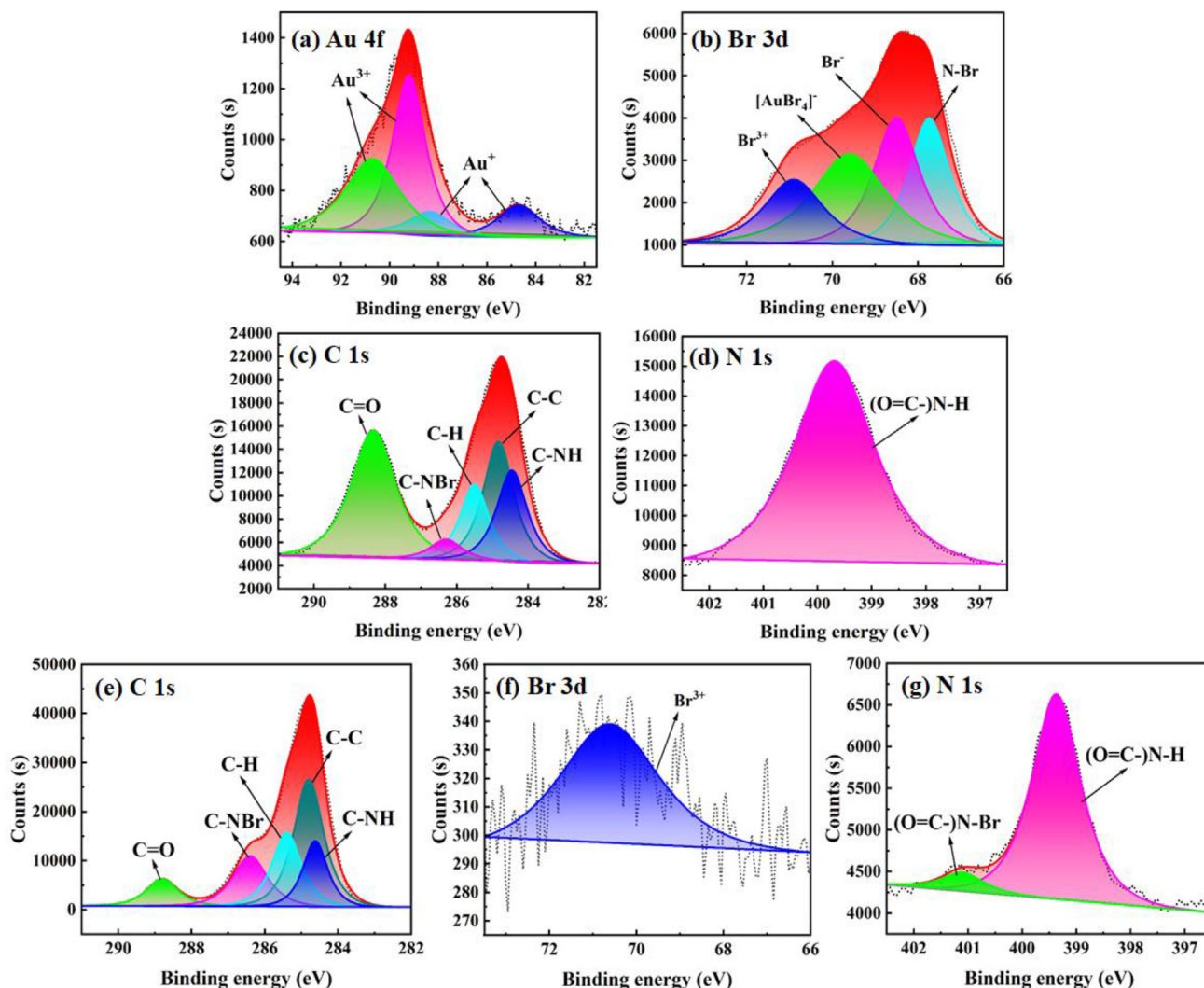


Figure 4. XPS spectra of powder of lixivium after reaction (a) Au 4f (b) Br 3d (c) C 1s (d) N 1s, and NBS before reaction (e) C 1s (f) Br 3d (g) N 1s.

Screen analysis was performed by sieving the pulp containing 500 g ore with standard industrial sieves. After drying and weighing all the size grades, the content of Au was measured.

2.3.3. Extraction of gold from gold ore by NBS method

Leaching experiments were performed by a leaching equipment (XJTII, Jilin Prospecting Machinery Co., China) in Scheme 3. The parameters were changed every series of leaching experiments to determine the optimal conditions. Typically, put 100 g ore sample into a 2 L leaching tank, and add water to the set liquid-solid ratio. After testing and recording pH, add a predetermined dosage of NBS. If necessary, adjust pH with NaOH or dilute H₂SO₄. Then, the leaching began at a predetermined stirring speed and temperature. Maintain the temperature with a water bath if necessary. Samples during the reaction were sucked by a straw, and centrifuged for the supernatant. After reaction, measure and record the pH of pulp. The residue was separated from the filtrate by a vacuum filtration device (SHB-IIIS, Hengyan Instrument Co., China), rinsed repeatedly with deionized water for three times and dried in a vacuum oven at 100 °C for 3 h. Finally, the content of each metal in the lixivium and residue was quantified via ICP-OES and AAS. The leaching yield of gold was calculated, as presented in Eq. (1).

$$X_m = W_s / (W_s + W_r) \quad (1)$$

Where, X_m is the leaching yield of gold, W_s is the final gold content in liquid, and W_r is the gold content in residue [34].

2.3.4. Extraction of gold from gold ore by conventional systems

Leaching experiments were performed the same as NBS method except conventional reagent combinations with the dosage referred to optimized concentration reported in other groups. The reactions were conducted at different pH. The yield for each metal was then calculated based on Eq. (1).

3. Results and discussion

3.1. The dissolution of gold foil in NBS aqueous

The change of the gold foil in 0.1 M NBS aqueous solution in a period time strongly proves the excellent ability of NBS to dissolve gold under room temperature. The pieces of gold foil after cleaning looks bright with sharp edges in Figure 2a. Microscopic appearance in the SEM images show that the surface is flat and tidy in Figure 2d. It is worth mentioning that the surface is microporous in Figure 2e (local magnification of Figure 2d), which is conducive to the adsorption of reagents to etch gold. After reacting for 2 days, the surface of gold foil looks not that bright and the edge is obviously corroded and notched in Figure 2b. SEM images

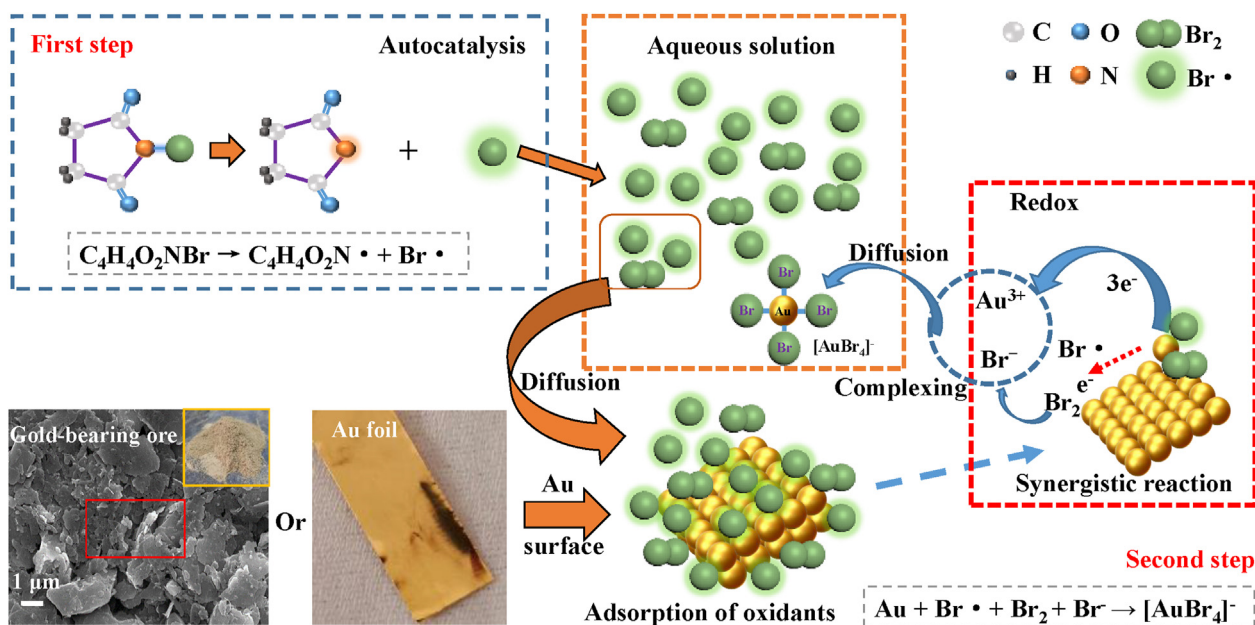


Figure 5. Mechanism for gold conversion by NBS.

show that the surface on the edge of gold foil has been dissolved in Figure 2f, exposing the inside of the gold. After reacting for 3 days, the corrosion of gold foil increases, and as more and more gold dissolves, the notches become bigger in Figure 2c. Most important of all, when the reaction time is extended to 10 days, the whole gold foil is completely dissolved. This test has shown a visual and pronounced effect of gold dissolution by NBS.

3.2. Mechanism of gold conversion by NBS method

XRD patterns of samples were performed to detect chemical compositions. It indicates that the lixivium contains $K[AuBr_4]$ and succinimide. In Figure 3a, the peaks located at 11.66, 14.56, 20.99, 23.58, 26.91, 31.03, 40.80 and 44.60° are assigned to $K[AuBr_4]$ while 13.65, 16.40, 18.40, 19.62, 20.31, 23.64, 26.27, 27.77, 28.97, 30.27, 31.03, 36.81 and 37.44° to succinimide. In Figure 3b, the diffraction peaks and the standard PDF cards show that the lixiviant is pure NBS with no $K[AuBr_4]$ and succinimide contained. That's to say, when gold comes in connect with NBS solution, the gold surface is activated and the oxidation of neutral gold atom to trivalent $Au^{(III)}$ occurs, which convert gold into $K[AuBr_4]$. In the gold leaching experiments from ore, no matter acidic or alkaline the initial pH is adjusted to, the final pH will be close to 6 in Figure 3c, as the same pH of pure succinimide in solution. This may be related to the production of a large amount of succinimide in gold leaching reaction. Thus, it can be preliminarily proposed that $K[AuBr_4]$ and succinimide are formed through gold conversion reaction which will be further confirmed below.

For further study, FT-IR of NBS and lixivium were carried out. In Figure 4b, as for NBS, the peak at 3452.44 cm^{-1} is O-H in H_2O , and 2939.39 cm^{-1} is the stretching vibration peak of methylene C-H. The peak of carbonyl C=O is 1718.5 cm^{-1} , which is very strong. The absorption peak at 1315.4 cm^{-1} is indexed to amine C-N and 1170.74 cm^{-1} to C-C single bond skeleton vibrates. According to comparison with infrared characteristic peaks, if succinimide, a secondary amine, is generated in the reaction, N-H stretching vibration will produce a characteristic absorption peak with moderate intensity among wavenumber $3400 - 3300\text{ cm}^{-1}$ and the N-H bending vibration will produce an absorption peak with weak intensity at $1650 - 1550\text{ cm}^{-1}$, which is confirmed by the absorption peak at 3377.21 cm^{-1} and 1614.35 cm^{-1} of the lixivium. Figure 3d displays typical results. The strong N-H

absorption peak appears in the lixivium proves that the gold leaching reaction resulted in the formation of succinimide. The peak positions of other functional groups remain basically the same except a strong N-H absorption peak appearing in the lixivium. This indicates that the ring framework of NBS is not destroyed by Au, only N-Br bond breaks and bromine separates from the framework to react with Au, while a large number of succinimide was generated.

More information has been gained to prove the above inference by XPS of the powder of lixivium and NBS in Figure 4. A conclusive proof for the oxidation of gold to Au^{3+} comes from Figure 4a. The Au^{3+} was evidenced by peaks at 89.2 eV and 90.7 eV. A small amount of Au^+ was also detected, and identified by the $4f_{7/2}$ and $4f_{5/2}$ bands centered at 84.7 eV and 88.35 eV, respectively. The presence of Au^+ can be attributed to a partial reduction of Au^{3+} , as it is easily reducible by exposure to ambient atmospheric conditions [28]. In Figure 4b, Br 3d after reaction consists of four peaks while only one weak peak before reaction in Figure 4f. It should be noted that the main peaks located at 69.54 eV and 68.5 eV are in accordance with Br $3d_{3/2}$ and Br $3d_{5/2}$ of Br^- . The species at 69.54 eV can be assigned to the $[AuBr_4]^-$ complexes and 68.5 eV to Br^- . The peak at 67.74 eV is assigned to a covalent N-Br bond. In Figure 4c, the XPS spectrum of C 1s after reaction is assigned to five peaks located at 284.62, 284.8, 285.4, 286.4 and 288.8 eV, which are matched with C-NH, C-C, C-H, C-NBr and C=O, respectively. Fig. 4c and Fig. 4e show that C 1s peaks almost remain the same after reaction, which confirm that the ring framework of NBS is not destroyed. The difference that's worth paying attention to is that the peak of C-NH after reaction is much stronger with a higher FWHM than that before reaction and C-NBr turns to be very weak. This is because N-Br bond breaks to release bromine and generate C-NH. In Figure 4d, only one N 1s peak, and the location is 399.69 eV, which is the peak of (O=C-)N-H. In Fig. 4g, N 1s XPS spectrum consists of two peaks, and the location of 399.37 eV, 401.1 eV are assigned to (O=C-)N-H and (O=C-)N-Br, respectively. The XPS spectrum of C and N coincided with the conversion of NBS to succinimide. Therefore, these XPS results indicate that $K[AuBr_4]$ and succinimide are formed in the conversion reaction of gold due to the release of active bromine by the N-Br bond fracture.

Au can be activated in NBS solution, and the activation of Au by NBS makes it dissolve. The above results confirm that the oxidation of neutral gold atom to trivalent $Au^{(III)}$ occurs in a mild condition, which convert gold into $K[AuBr_4]$. To find the reason why Au is easy to dissolve in NBS,

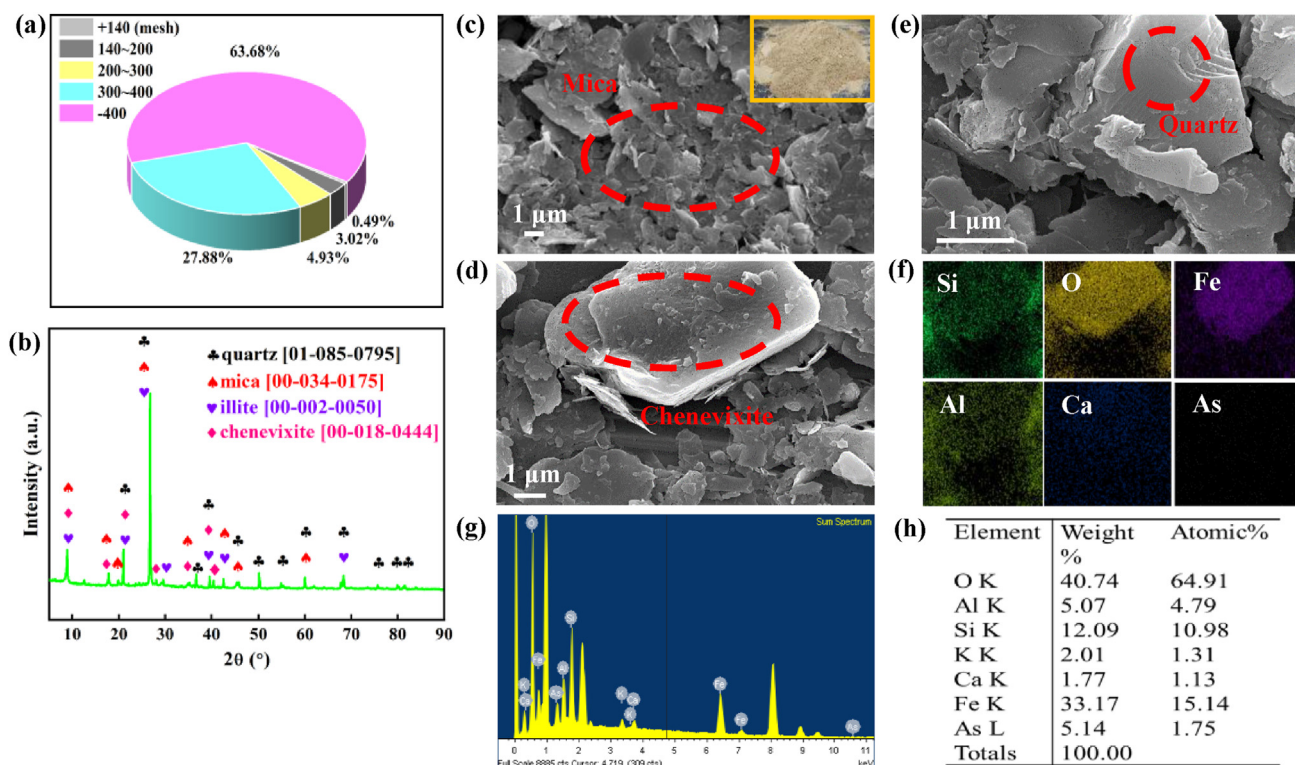
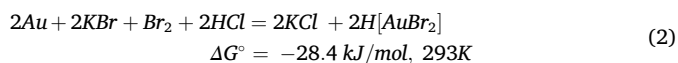


Figure 6. Analysis of gold ore (a) the particle size distribution of the sample, (b) XRD pattern of the ore sample, (c)–(e) SEM images of raw ore surface, inset in (c) shows the prepared ore, (f)–(h) EDS spectra of (d).

a phase transfer experiment was performed by CCl_4 , since NBS is hardly soluble in CCl_4 . Obviously, a phase transfer from NBS to CCl_4 can be seen, which is the phase of Br_2 . The concentration is very low, so the solution looks pale yellow in Scheme 1 b. The Br_2 in-situ generated and released by NBS is very activated and easy to react with Au. The leaching of gold by active Br_2 in this study is a redox reaction. And the formation of AuBr_2^- , given as follows in Eq. (2) [24], can be thought as a first step in the overall leaching mechanism [23].



For gold–halide species in solution, the standard redox potentials of Au/Au^+ , $\text{Au}/\text{AuCl}_2^-$, $\text{Au}/\text{AuBr}_2^-$, and Au/AuI_2^- are 1.83, 1.15, 0.96, and 0.576 V/SHE at 25 °C, respectively. The gold–bromide complex can form at a low potential, which makes gold easy to dissolve. The second step is purely chemical: this monovalent gold bromide decomposes into gold and more stable $[\text{AuBr}_4]^-$ given in Eq. (3) [1].



The total reaction is given in Eq. (4) [23].



However, active Br_2 is not the only reason for oxidation of neutral gold atom to trivalent Au(III). The release of bromine is slow and continuous since that NBS can only be slightly soluble in aqueous solution and keep dissolving during the reaction. To confirm whether the Br_2 in-situ generated by NBS is the only reason for gold dissolution, the experiment of gold foil etching is performed by 0.05 M bromine solution. The result shows that dissolution rate of gold foil is far away from that in NBS. The gold foil begins to dissolve at day 3 and only partly dissolved at day 10. What's more, the yield of gold leaching from ore by bromine solution is 53.5% lower than that of 86.24% by NBS. That is to say, Br_2 may not be the only factor to make gold dissolved. Through previous

studies, in NBS solution, autocatalysis of NBS can slowly and sustainably provide oxidizing power and complexing ligands by in-situ generating low concentration of active Br_2 and Br^\bullet in a mild, clean and room-temperature [35, 36]. The in-situ autocatalysis of NBS is as shown in Eq. (5) (6) and (7) [37]. Eq. (5) (6) and (7) are the main reactions in NBS solution. Otherwise, the oxidation of NBS also comes from HBrO by Eq. (8). HBrO is unstable and easy to decompose. See Eq. (9) and Eq. (10). HBrO and HBrO_2 are species with oxidizability, but their contents are very low due to the secondary reaction of Eq. (8) (9) and (10), thus, the oxidation of gold may be minimal. To sum up, it's more convincing that radical Br^\bullet may be an essential role and reaction of Eq. (11) may occur that active Br_2 and Br^\bullet synergistically and quickly oxidize the gold.

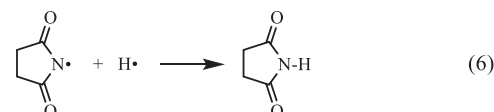
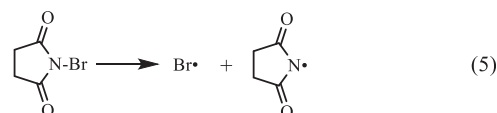


Table 2. Screen size and gold content analysis of gold ore.

Size (μm)	Weight		Au	
	(g)	(%)	(g/t)	(%)
+106	2.44	0.49	1.39	0.11
-106 + 74	15.03	3.02	2.16	1.08
-74 + 50	24.54	4.93	4.52	3.70
-50 + 38	138.80	27.88	5.61	25.94
-38	317.02	63.68	6.55	69.17
Total	497.83	100.00	6.03	100.00

Table 3. Chemical composition of the ore sample by XRF.

Element	O	Si	Al	Fe	K	Ca	Mg	Ti	S	Na
Content (%)	47.77	29.48	10.41	4.28	3.84	1.72	0.81	0.63	0.20	0.25
Element	As	P	Mn	Sb	Cr	Ni	Zr	Rb	Sr	Zn
Content (%)	0.24	0.12	0.07	0.04	0.03	0.03	0.01	0.01	0.01	0.01

Table 4. Element content of the ore sample by AAS and ICP-OES.

Element	Cu	Pb	Zn	Fe	S	As	Au ^a	Ag ^a
Content (%)	0.01	0.01	0.01	5.02	0.12	0.44	6.03	5

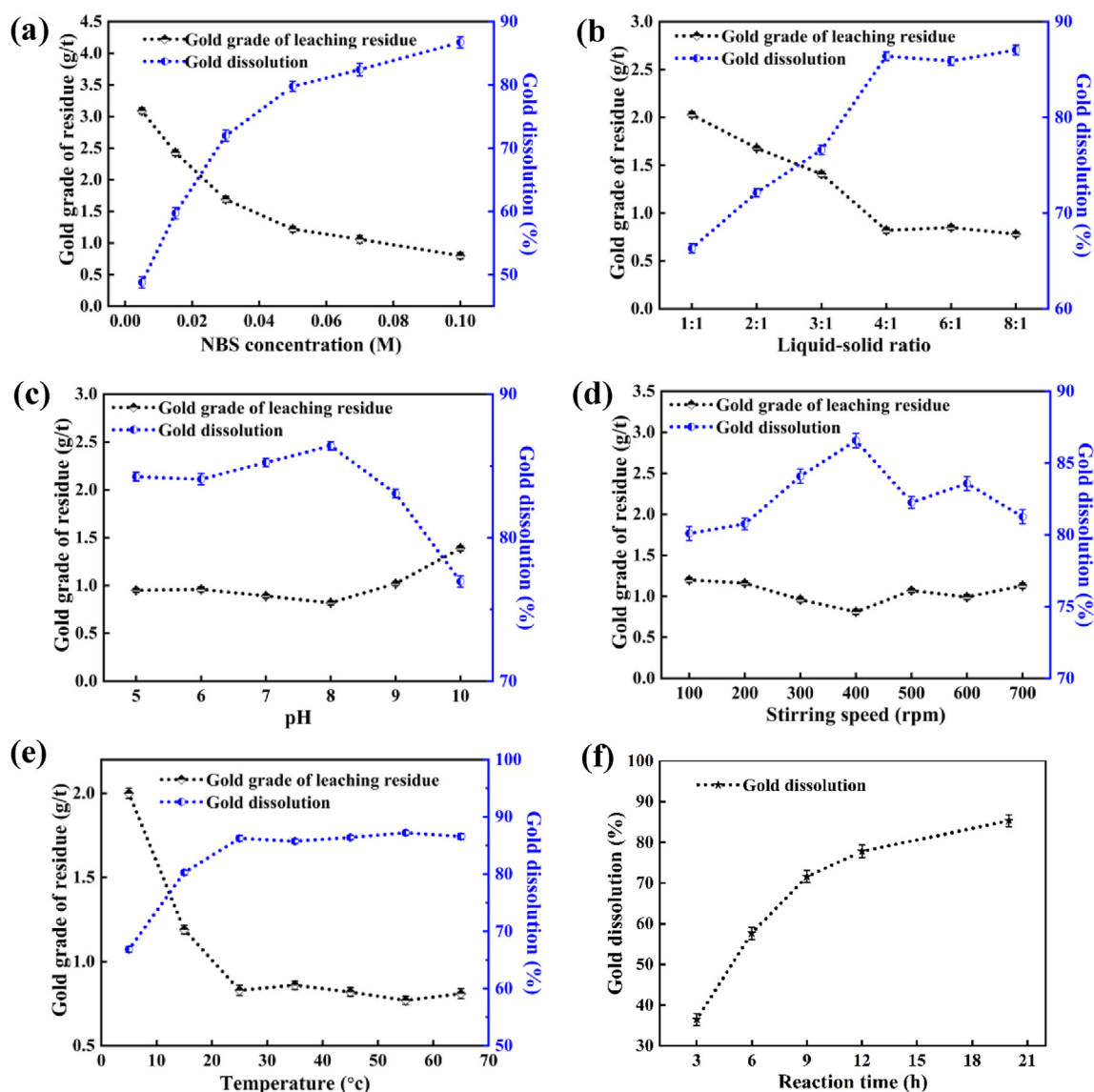
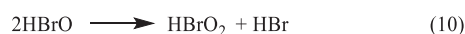
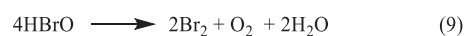
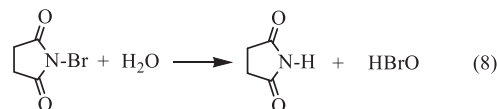
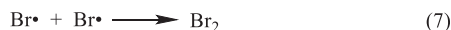
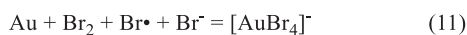
^a Unit g/t.

Figure 7. (a) Effect of NBS concentration on gold leaching with temperature at 25 °C, stirring speed 400 rpm, liquid-solid ratio 2:1, pH 7, and leaching for 20 h; (b) Effect of liquid-solid ratio on gold leaching with 0.05 M NBS, 25 °C, stirring speed 400 rpm, pH 7, and leaching for 20 h; (c) Effect of pH on gold leaching with 0.05 M NBS, liquid-solid ratio 4:1, 25 °C, stirring speed 400 rpm, and leaching for 20 h; (d) Effect of stirring speed on gold leaching with 0.05 M NBS, liquid-solid ratio 4:1, pH 8, 25 °C, and leaching for 20 h; (e) Effect of temperature on gold leaching with 0.05 M NBS, liquid-solid ratio 4:1, pH 8, stirring speed 400 rpm, and leaching for 20 h; (f) Effect of time on gold leaching with 0.05 M NBS, liquid-solid ratio 4:1, pH 8, 25 °C and stirring speed 400 rpm.



The results obtained make it possible to postulate an important mechanism in Au transfer to soluble complexes and an essential role for $\text{Br}\cdot$, as can be seen in Figure 5. In the suggested process, possible reaction mechanism may contain two steps. Firstly, NBS slightly dissolves in aqueous solution and in-situ autocatalysis of NBS occurs, among which bromine separates from NBS skeleton to form $\text{Br}\cdot$ as shown in the first step and bromine radicals go on to form active Br_2 . Secondly, $\text{Br}\cdot$ and active Br_2 diffuse and adsorb on the surface of Au and synergistically oxidize neutral gold atom to Au^{3+} which is binded by Br^- to form a stable compound $[\text{AuBr}_4]^-$ dissociated into the solution to promote the continuous dissolution of gold. This study offers new insights into the reaction mechanism and heralds a green procedure for gold recovery from gold-bearing raw materials and preparation of gold derivatives. Follow-up experiments were carried out to verify the feasibility of NBS in extracting gold from gold ores.

3.3. Gold leaching from gold-bearing ores by NBS

3.3.1. Characterization of gold ore

For better leaching of gold, the mineral would better be crushed and ground up to 300 mesh. Figure 6a show that the particle size of ore sample is main 63.68% passing 400 mesh (38 μm) and 27.88% passing 300 mesh (50 μm). By screen analysis, the occurrence and distribution of Au in size grades is reported in Table 2. Au mainly distributes in particles smaller than 200 mesh (74 μm) and lower in hard, non-breakable and big particles. XRD in Figure 6b shows that the major gangue minerals in the gold mine include quartz $[\text{SiO}_2]$, mica $[(\text{K}, \text{Na}) \text{Al}_2(\text{Si}, \text{Al})_4\text{O}_{10}(\text{OH})_2]$, chenevixite $[\text{Cu}_2\text{Fe}_2(\text{AsO}_4)_2(\text{OH})_4\text{H}_2\text{O}]$ and illite $[2\text{K}_2\text{O}\cdot 3\text{MgO}\cdot \text{Al}_2\text{O}_3\cdot 4\text{SiO}_2\cdot 12\text{H}_2\text{O}]$. XRF in Table 3 presents the high contents of Si, Al, Fe, K, Ca, Mg and As in ore sample, which supports the results of XRD. SEM was carried out to gain the information of the microscopic appearance and dissociation of the ore. The mineral appearance of the fracture surface structure can be clearly seen under electron microscopy in Figure 6c ~ e, most of which are lamellar and a few of which are cubic, in line with the dissociation characteristics of mica and quartz. EDS spectra in Figure 6f ~ h show that the main elements in the ore are Si, O, Fe, Al, Ca and As which are corresponding to XRF and XRD results. The accurate measurements of the content of gold and other elements were performed as shown in section 2.3.2. As shown in Table 4, the gold content is 6.03 g/t, and arsenic is 0.44%, and S content is 0.12% in this oxidized ore. Based on the above analysis, the ore sample was directly used to leach gold without pretreatment.

3.3.2. Effect of NBS concentration on gold leaching

The concentration of lixiviant is an important factor of gold leaching reaction. Some investigators have determined that there is a critical reagent concentration for the leaching reactions [2]. When the reagent concentration is less than this critical value, the reaction was limited by reagent diffusion from the solution to the gold surface. On the other hand, as it is greater than this critical value, the reaction will be independent of the reagent concentration. In this section, the influence of NBS concentration from 0.005 M to 0.1 M on gold dissolution was investigated, as shown in Figure 7a. In the low NBS concentration, active Br_2 and $\text{Br}\cdot$ produced by NBS is insufficient so that the oxidant diffusion to the surface of gold is deficient, and it results in low oxidation efficiency. When concentration increases, diffusion and mass transfer will accelerate and the oxidant adsorbing on the surface of gold increase to promote oxidation and dissolution of gold. The leaching yield increase significantly and the grade of gold in the corresponding residue show a sharp downward. The trend begins to flatten out when NBS is more than 0.05 M. When the NBS concentration is 0.1 M, the leaching yield reaches 86.73%, and 0.05 M with a yield of 79.77%. When NBS reduces to 0.03 M, the yield is 71.97%. Therefore, 0.05 M is selected as the optimization considering the cost of the reagent and the characteristics of the reaction.

3.3.3. Effect of liquid-solid ratio on gold leaching

The solution with low viscosity is favorable to the effective diffusion of reagents and products. The chemical substance is easy to diffuse, so that the reaction efficiency is high, and the gold ore can be quickly leached, which is conducive to the increase of leaching yield [7]. The liquid-solid ratio not only affects the consumption of reagent, but also affects the viscosity of pulp. Thus, it has an important influence on gold leaching effect and subsequent treatment. Improving the liquid-solid ratio is conducive to mixing, which will accelerate the partial turbulence to reduce the pulp viscosity and promote the internal diffusion of solution. In this section, effect of liquid-solid ratio from 1:1 to 8:1 was investigated, and the results are shown in Figure 7b. The experimental results show that the leaching rate increases with the increase of liquid-solid ratio. When the liquid-solid ratio is 4:1, yield is 86.4%, and gold content in residue decreases to 0.82 g/t. When the liquid-solid ratio is larger than 4:1, the leaching reaction is no longer affected by the pulp concentration. However, if the pulp concentration is too lower, it will increase the consumption of NBS and reduce the processing capacity of minerals. Thus, the optimal liquid-solid ratio is 4:1 with yield of 86.4%.

3.3.4. Effect of pH on gold leaching

To investigate the effect of pH on gold leaching, the pH of pulp was adjusted from 5 to 10 by H_2SO_4 or NaOH . The optimal gold leaching yield is about 86% during pH of 7–8, basically in the weakly alkaline range in Figure 7c. Although the gold leaching reaction occurs with a yield of 83% at pH 5 and 76% at pH 10, the yield drops obviously at alkaline. Destruction of active Br_2 in alkaline may be the reason. It can be seen that no matter the initial pH is adjusted to acidic or alkaline, the final pH will be close to neutral. That is to say, leaching reaction with NBS has an applicability over a wide range of pH. The most suitable pH is near 8, and the yield is 86.4%. At pH of approximately 8, metal oxides or sulfides usually have poor solubility, which makes gold leaching with NBS selective.

3.3.5. Effect of stirring speed on gold leaching

The dissolution of gold involves a series of heterogeneous reactions whose dynamics are greatly affected by diffusion. In the process of leaching, stirring can prevent the settlement of mineral particles, and enhance the diffusion effect by reducing the thickness of diffusion layer and increasing the diffusion coefficient, so as to improve the leaching speed [38]. However, when particle size is too fine, the mineral particles are easy to be absorbed by the vortex flow of the leaching liquid, so that the renewal of liquid on surface of mineral particles does not improve with increase of stirring speed. When the speed increases to a certain value, a certain particle begins to move synchronously with the leaching liquid, which lose effect on reducing the thickness of the diffusion layer. Thus, continue to increase the stirring speed may reduce the leaching effect [23] as shown in Figure 7d. The experimental results show that the stirring speed between 300 - 400 rpm is better. When the stirring speed increases from 400 to 700 rpm, the yield decreases from 86.57% to 82.32%. According to the experiments, the optimum stirring speed is 400 rpm with a yield of 86.57%.

3.3.6. Effect of temperature on gold leaching

Improving the leaching temperature can help to obtain a higher leaching efficiency due to the increase of diffusion coefficient and velocity constant. In this section, a series of leaching tests were carried out with variation of temperature from 5 °C to 65 °C to investigate the effect of temperature on the gold leaching with NBS. The results in Figure 7e suggest that at 5 °C, the yield drops to 66.83%. When the temperature varies from 25 °C to 65 °C, the leaching yield is steady and does not obviously change with the increase of temperature. The gold leaching reaction with NBS maybe exothermic [7], so heating is not conducive to the reaction. Furthermore, high temperature will greatly increase energy consumption, and make the solvent water evaporation, which is not conducive to leaching. Therefore, gold leaching reaction with NBS is no need of heating, and the optimum temperature is 25 °C with a yield of 86.24%.

Table 5. Extraction of gold from gold ore by conventional systems.

System	pH	Leaching yield	reference
0.05 M NBS	8	86.24% (25 °C, 20h)	In this paper
4 kg/t NaCN	11	71.32% (25 °C, 20h)	From production line
0.13 M thiourea, 0.09 M Fe ₂ (SO ₄) ₃	1.25	78.35% (25 °C, 20h)	[40]
0.5 M Na ₂ S ₂ O ₃ , 0.2 M CuSO ₄ , 1 M NH ₃	9.5	80.16% (25 °C, 20h)	[40]
20 g/L KI, 4 g/L I ₂	8.2	88.67% (25 °C, 20h)	[7]

3.3.7. Effect of time on gold leaching

In order to investigate effect of time on gold leaching, the pulp was sampled at 3 h, 6 h, 9 h, 12 h, 20 h and the gold content in the lixivium was measured by AAS. The gold concentration in lixivium after leaching for 12 h is 1488.96 µg/L and 1633 µg/L after 20 h in Figure 7f, which indicates that approximate 90% of the leaching is achieved in the first 12 h, and more leaching time after 12 h has little significance for the gold leaching. The almost linear figure in first 9 h shows that the reaction conducts stably at a high, basically constant speed [23]. The reason may be that NBS is sufficient at initial stage, and the reaction conditions are suitable after optimization. As reaction goes on, the reagent has been seriously consumed, which makes the concentration on the gold surface decreases obviously so as to deteriorate gold leaching [9]. Therefore, appropriate leaching time for NBS gold leaching was 12h. The NBS leaching process takes only 12 h to dissolve 90% of gold while cyanide leaching requires 30–40 h to obtain a similar yield.

Experiments of the most relevant operating conditions that could affect the performance of NBS show that extraction of gold could be enhanced by optimizing the conditions with a lower consumption of NBS. It can be concluded that: (a) with an applicability over a wide range of pH values, no pH adjustment is needed; (b) room-temperature is enough, no need of high temperature; (c) gold leaching mainly occurs in the first 12 h; (d) a higher liquid-solid ratio increases the gold recovery.

3.3.8. Comparison of NBS with conventional systems

NBS used alone to extract gold from gold ores performs a very outstanding performance. A high gold yield of 86.24% was achieved under optimal conditions of NBS dosage 0.05 M, liquid-solid ratio 4:1,

stirring speed 400 rpm, pH 8, 25 °C and leaching for 20 h. In contrast, the classical cyanide method exhibited a maximum leaching yield of only 71.32% at a high pH of 11 and a 78.35% leaching yield for thiourea required a pH of 1.25 in Table 5. For thiosulfate, yield of 80.16% at pH 9.5 with a complex leaching system. As for KI/I₂, the maximum yield for KI/I₂ is 88.67% at pH 8.2, which is similar as NBS. However, the reagent cost of KI/I₂ to achieve such a yield is nearly 20 times higher than that of NBS.

Adsorption and recovery of gold ions in solution are greatly affected by the symbiotic metals. The excellent gold selectivity of the leaching process means a corresponding cost advantage with simple adsorption and recovery process and lower reagent consumption [39]. The leaching selectivity for Au of NBS was evaluated by simultaneous conducting gold extraction experiments with conventional systems. The results are very encouraging, as high yield of Au is in noticeable contrast to the low yields of other metals in Figure 8a, though contents of coexisting metals are 1.7–1.8 × 10⁴ times than gold. In contrast, no significant Au leaching preference over other metals is observed in cyanide, thiourea and thio-sulfate methods. For cyanide and thiourea, the simultaneous leaching of Cu, Pb, Sb seriously interfere with Au leaching. Only KI/I₂ method has a similar selectivity for Au as NBS method, but the cost is higher. The high Au leaching selectivity over other coexisting metals is a key advantage of NBS approach, since extra purification steps and consumption of corresponding reagents are effectively diminished.

As shown in Figure 8b, the regeneration of NBS by the reaction of succinimide and bromine for recycling is very promising and can undoubtedly further reduce the cost of this method. This is easy to achieve and needs to be further studied. NBS used for gold extraction is promising. It can be more safely stored and transported than bromine and greatly decreases the environmental impact. The use of NBS for mammalian cytotoxicity assessment and toxicological tests on mice as mammalian models and aquatic organisms showed a low environmental impact and NBS is more eco-friendly than traditional methods [7].

4. Conclusions

Effect of NBS on gold conversion and extraction are investigated. A high gold yield of 86.24% was achieved under optimal conditions of NBS dosage 0.05 M, liquid-solid ratio 4:1, stirring speed 400 rpm, pH 8, 25 °C and leaching for 20 h. The reaction process has been confirmed that the ring framework and functional groups of NBS have not been destroyed, and bromine separates from the framework to in-situ generate active Br₂ and Br• and interact with gold to form [AuBr₄]⁻ under a mild condition. Gold can

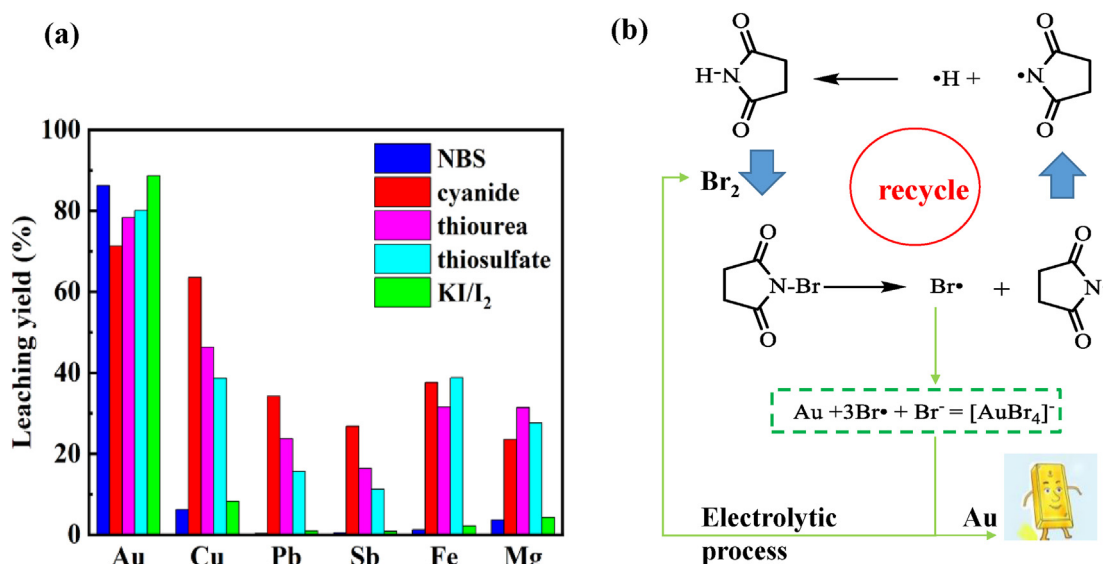


Figure 8. (a) Comparison of NBS with four hydrometallurgical approaches, (b) an implementable cyclic system of NBS.

be selectively leached by NBS without serious environmental pollution and high energy consumption. The systematic results are believed to offer new insights into the reaction mechanism and demonstrated that NBS has great potential to develop a simple, eco-friendly and high-efficient option to convert and extract gold, as well as a viable alternative to cyanide.

Declarations

Author contribution statement

Xiang Liu: Conceived and designed the experiments; Performed the experiments; Analyzed and interpreted the data; Wrote the paper.

Yongliang Wang: Performed the experiments; Analyzed and interpreted the data; Contributed reagents, materials, analysis tools or data.

Li Xiao: Conceived and designed the experiments; Analyzed and interpreted the data. </p>

Licheng Ma; Peiwei Han & Shufeng Ye: Analyzed and interpreted the data; Contributed reagents, materials, analysis tools or data.

Funding statement

This work was supported by the Innovation Academy for Green Manufacture, Chinese Academy of Sciences (No. IAGM-2019-A05) and the National Key R&D Program during the 13th Five-year Plan Period (2019YFC1908405).

Data availability statement

Data included in article/supplementary material/referenced in article.

Declaration of interests statement

The authors declare no conflict of interest.

Additional information

No additional information is available for this paper.

Acknowledgements

The authors are thankful for the Material Chemistry and Engineering Group, Institute of Process Engineering, Chinese Academy of Sciences.

References

- [1] L.F. Kozin, V.T. Melekhin, Extraction of Gold from ores and concentrates by leaching with the use of cyanides and alternative reagents, *Russ. J. Appl. Chem.* 77 (2004) 1573–1592.
- [2] M.I. Jeffrey, P.L. Breuer, W.L. Choo, A kinetic study that compares the leaching of gold in the cyanide, thiosulfate, and chloride systems, *Metall. Mater. Trans. B* 32 (2001) 979–986.
- [3] X.M. Zhang, G. Senanayake, A review of ammoniacal thiosulfate leaching of gold: an update useful for further research in non-cyanide gold lixivants, *Miner. Process. Extr. Metall. Rev.* 37 (2016) 385–411.
- [4] D.M. Beasley, W.I. Glass, Cyanide poisoning: pathophysiology and treatment recommendations, *Occup. Med. (Oxf.)* 48 (1998) 427–431.
- [5] M.C. Reade, S.R. Davies, P.T. Morley, J. Dennett, I.C. Jacobs, Review article: management of cyanide poisoning, *Emerg. Med. Australasia (EMA)* 24 (2012) 225–238.
- [6] F. Halet, A.R. Yeddou, A. Chergui, S. Chergui, B. Nadjemi, A. Ould-Driss, Removal of cyanide from aqueous solutions by adsorption on activated carbon prepared from lignocellulosic by-products, *J. Dispersion Sci. Technol.* 36 (2015) 1736–1741.
- [7] C. Yue, H. Sun, W.J. Liu, B. Guan, X. Deng, X. Zhang, P. Yang, Environmentally benign, rapid, and selective extraction of gold from ores and waste electronic materials, *Angew. Chem.* 56 (2017) 9331–9335.
- [8] X.Y. Chen, X.Z. Lan, Q.L. Zhang, J. Zhou, Y.H. Song, Behavior of $S_2O_3^{2-}$ and SO_3^{2-} in sulfur-bearing aqueous solution system for gold leaching, *Trans. Nonferrous Metals Soc. China* 20 (2010) s46–s49.
- [9] S. Syed, Recovery of gold from secondary sources—a review, *Hydrometallurgy* 96 (2010) 30–51.
- [10] C. Abbruzzese, P. Fornari, R. Massidda, F. Vegliò, S. Ubaldini, Thiosulphate leaching for gold hydrometallurgy, *Hydrometallurgy* 39 (1995) 265–276.
- [11] B. Xu, W. Kong, Q. Li, Y. Yang, X. Liu, A review of thiosulfate leaching of gold: focus on thiosulfate consumption and gold recovery from pregnant solution, *Metals* 7 (2017) 222.
- [12] D. Feng, J.S.J.V. Deventer, Ammoniacal thiosulphate leaching of gold in the presence of pyrite, *Hydrometallurgy* 82 (2006) 126–132.
- [13] D.M. Muir, M.G. Aylmore, Thiosulfate as an alternative lixiviant to cyanide for gold ores, in: M.D. Adams, B.A. Wills (Eds.), *Developments in Mineral Processing*, Elsevier, 2005, pp. 541–560.
- [14] P.L. Breuer, M.I. Jeffrey, Thiosulfate leaching kinetics of gold in the presence of copper and ammonia, *Miner. Eng.* 13 (2000) 1071–1081.
- [15] H. Yu, F. Zi, X. Hu, J. Zhong, Y. Nie, P. Xiang, The copper–ethanediamine–thiosulphate leaching of gold ore containing limonite with cetyltrimethyl ammonium bromide as the synergist, *Hydrometallurgy* 150 (2014) 178–183.
- [16] G. Senanayake, The role of ligands and oxidants in thiosulfate leaching of gold, *Gold Bull.* 38 (2005) 170–179.
- [17] H. Zhang, I.M. Ritchie, S.R.L. Brooy, Electrochemical oxidation of gold and thiourea in acidic thiourea solutions, *J. Electrochem. Soc.* 148 (2001) D146–D153.
- [18] J. Li, J.D. Miller, Reaction kinetics of gold dissolution in acid thiourea solution using ferric sulfate as oxidant, *Hydrometallurgy* 89 (2007) 279–288.
- [19] T.L. Deng, M.X. Liao, M.H. Wang, Y.W. Chen, N. Belzile, Enhancement of gold extraction from biooxidation residues using an acidic sodium sulphite–thiourea system, *Miner. Eng.* 14 (2001) 263–268.
- [20] J. Li, J.D. Miller, Reaction kinetics for gold dissolution in acid thiourea solution using formamidine disulfide as oxidant, *Hydrometallurgy* 63 (2002) 215–223.
- [21] M. Hojo, M. Yamamoto, T. Maeda, H. Kawano, K. Okamura, Pure gold dissolution in dilute chloric, bromic or iodic acid solution containing abundant halide ions, *J. Mol. Liq.* 227 (2017) 295–302.
- [22] S. Seisko, M. Lampinen, J. Aromaa, A. Laari, T. Koiranen, M. Lundström, Kinetics and mechanisms of gold dissolution by ferric chloride leaching, *Miner. Eng.* 115 (2018) 131–141.
- [23] R. Sousa, A. Futuro, A. Fiúza, M.C. Vila, M.L. Dinis, Bromine leaching as an alternative method for gold dissolution, *Miner. Eng.* 118 (2018) 16–23.
- [24] S.S. Konyratbekova, A. Baikunurova, G.A. Ussoltseva, C. Erust, A. Akcil, Thermodynamic and kinetic of iodine–iodide leaching in gold hydrometallurgy, *Trans. Nonferrous Metals Soc. China* 25 (2015) 3774–3783.
- [25] M. Baghalha, The leaching kinetics of an oxide gold ore with iodide/iodine solutions, *Hydrometallurgy* 113–114 (2012) 42–50.
- [26] P.H. Qi, J.B. Hiskey, Dissolution kinetics of gold in iodide solutions, *Hydrometallurgy* 27 (2015) 47–62.
- [27] M.G. Aylmore, Chapter 27 - alternative lixivants to cyanide for leaching gold ores, in: M.D. Adams (Ed.), *Gold Ore Processing*, second ed., Elsevier, 2016, pp. 447–484.
- [28] J.L. Do, D. Tan, T. Friscic, Oxidative mechanochemistry: direct, room-temperature, solvent-free conversion of palladium and gold metals into soluble salts and coordination complexes, *Angew. Chem. Int. Ed. Engl.* 57 (2018) 2667–2671.
- [29] J.D. Roberts, E.R. Trumbull, W. Bennett, R. Armstrong, The reaction of norbornylene with N-bromosuccinimide. Norbornylene and its derivatives, *J. Am. Chem. Soc.* 72 (1950) 3116–3124.
- [30] K.N. Prashanth, K. Basavaia, M.S. Raghu, Utilization of N-bromosuccinimide as a brominating agent for the determination of sumatriptan succinate in bulk drug and tablets, *Int. J. Anal. Chem.* (2013) (2013). Article ID 934357.
- [31] Z.G. Zhao, Z.X. Wang, Halogenation of pyrazoles using N-halosuccinimides in CCl_4 and in water, *Synth. Commun.* 37 (2007) 137–147.
- [32] S. Singh, B.L.V. Prasad, Nearly complete oxidation of Au^0 in hydrophobized nanoparticles to Au^{3+} ions by N-bromosuccinimide, *J. Phys. Chem. C* 111 (2007) 14348–14352.
- [33] X. Zhang, P. Yang, Nucleic acid-mediated gold oxidation: novel biolithography for surface microfabrication and new insight into gold-based biomaterials, *Chem. Commun.* 48 (2012) 8787–8789.
- [34] L. Xiao, Y.L. Wang, Y. Yu, G.Y. Fu, P.W. Han, Z. Sun, S.F. Ye, An environmentally friendly process to selectively recover silver from copper anode slime, *J. Clean. Prod.* 187 (2018) 708–716.
- [35] R.H. Mitchell, Y.H. Lai, R.V. Williams, N-Bromosuccinimide-dimethylformamide: a mild, selective nuclear monobromination reagent for reactive aromatic compounds, *J. Org. Chem.* 44 (1979) 4733–4735.
- [36] V.L. Heasley, T.J. Louie, M.D. Millar, H.B. Moore, D.F. Nogales, A.M. Sauerbrey, A.B. Shevel, T.Y. Shibuya, D.K. Luttrull, Effect of N-bromosuccinimide (NBS) and other N-brominating agents on the bromination of α , β -unsaturated ketones in methanol, *ChemInform* 19 (1988) 2199–2204.
- [37] L. Horner, E.H. Winkelmann, Neuere Methoden der präparativen organischen Chemie II 14. N-Bromsuccinimid, Eigenschaften und Reaktionsweisen Studien zum Ablauf der Substitution XV, *Angew. Chem.* 71 (1959) 349–365.
- [38] L. Xiao, Y. Wang, Y. Yu, G. Fu, S. Ye, Enhanced selective recovery of selenium from anode slime using MnO_2 in dilute H_2SO_4 solution as oxidant, *J. Clean. Prod.* 209 (2018) 494–504.
- [39] L. Xiao, Y. Wang, Z. Sun, P. Qian, P. Han, B. Yu, S. Ye, A novel, solvent-free mechanochemistry approach for gold extraction from anode slime, *ACS Sustain. Chem. Eng.* 7 (2019) 11415–11425.
- [40] C.R. Adams, C.P. Porter, T.J. Robshaw, J.P. Bezzina, V.R. Shields, A. Hides, R. Bruce, M.D. Ogden, An alternative to cyanide leaching of waste activated carbon ash for gold and silver recovery via synergistic dual-lixiviant treatment, *J. Ind. Eng. Chem.* 92 (2020) 120–130.