

Petr VODVÁŘKA *

LEACHING TESTS USING THIOUREA

The lixiviation of hardly dressable gold- and silver-bearing materials using acid thiourea solutions represents a progressive leaching method. Thiourea minimally dissolves Cu, Fe, Zn, As, Sb and Pb, in contrast to cyanide leaching solutions in which these metals and their sulphides are easily soluble. To achieve a perfect recovery of precious metals with thiourea, a considerably shorter leaching time is necessary. In this paper we discuss literature data along with 21 leaching tests with thiourea.

Introduction

The leaching of gold- and silver-bearing ores with thiourea was first developed in 1960 in the Soviet Union. In contemporary literature this method is considered a method of ore-dressing equal to direct cyanidation. Direct cyanidation of hardly dressable ores is not economical because of a low recovery of precious metals. Among non-conventional leaching agents, thiourea seems to be the most effective. In comparison to cyanidation, leaching with thiourea is more advantageous because:

1. It hardly dissolves Cu, Fe, Zn, As, Sb and Pb and sulphides, while in cyanide solutions these elements and compounds are easily dissolved into more or less complicated cyanocomplexes which reduce gold and silver dissolution and increase reagent consumption.
2. No pretreatment is necessary before leaching with thiourea, while

* Ore Research Institute, 252 10 Mnisek pod Brdy, Czechoslovakia

hardly dressable ores must be pretreated before cyanidation. Such pretreatment involves oxidation roasting, bioleaching and pressure leaching, acid leaching, etc. Thus, the cost of dressing grows.

The toxicity of thiourea leaching solutions has not been completely explained. According to some sources, thiourea presents low toxicity [1,2] while older medical books [3,4] describe thiourea as highly toxic matter which influences mental health. Repeated intoxication can cause permanent consequences (white blood-corpuscle wastage). In recent years thiourea has postulated as a carcinogen. Thus it is necessary to keep safety and hygiene at a high level when working with thiourea.

The leaching process using thiourea was tested on various materials. Satisfactory results were achieved with pyrite, arsenopyrite and chalcopyrite, antimony-gold concentrates, etc., where an extraction of 99% was reported. These materials are, however, very specific; so the leaching results cannot be generalized. A technique for the stationary leaching of gold from broken porcelain was elaborated in GDR. The composition of the leaching solution was thiourea, ferric sulphate, sulphuric acid and hydrogen peroxide. It was noted that leaching time increases with decreasing concentrations of Fe (III) ions, which were reduced to Fe (II) during the reaction. A dynamic thiourea leaching of gold and silver was performed in Taiwan [5]. A rotating pure gold and silver disk was used to determine the effect of the concentration of oxidant on gold and silver dissolution. Hydrogen peroxide was not used as the oxidant. It was found that the rate of gold and silver dissolution was 10 times higher than that in a solution of 0.5% sodium cyanide. Copper dissolution was negligible. The cyanidation of antimony-gold flotation concentrates was studied in New Zealand [6]. Recovery of gold reached only 35%. This result was improved considerably using thiourea. The recovery of gold varied with the pH and red-ox potential, and the Fe (III) ion concentration in leaching medium. The leaching time was 15 minutes and the extraction of gold reached 80%.

The aim of this study was to maximize the gold recovery by optimizing the most important parameters of leaching with thiourea, i.e.: pH, red-ox potential, and the Fe (III) ion concentration in the leaching solutions.

Experimental

The sulphide flotation concentrate in question was of the following composition:

Element or compound	Content %	Element or compound	Content %
SiO ₂	25.86	As	11.38
Fe	21.48	Bi	0.16
MnO	0.019	Au	37.11g/t
Al ₂ O ₃	1.63	S _{comb.}	21.75
CaO	0.76	Ni	0.015
MgO	4.88	Co	0.012
Cu	2.82	W	0.18
Zn	0.52	K ₂ O	0.62
Pb	0.202	Na ₂ O	0.082
Sb	1.67		

Direct cyanidation of this concentrate was not effective due to the high content of As, Sb, and Fe. At extreme leaching conditions (NaCN concentration 8,0 g/l, leaching time: 48 hrs), the recovery was 74,4%. No improvement was observed when the concentrate was roasted before cyanidation.

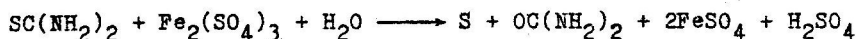
Description of the equipment

The tests with thiourea were conducted in a leaching vessel with a glass stirrer and a cooling jacket. A thermometer, a combined glass electrode and a Pt - calomel cell for red-ox potential measurements and for pH were installed in the vessel. The electrode walls were coated with PVC foil. Water cooling was necessary to hold the temperature of the leaching medium (during hydrogen peroxide additions mainly) below 35°C because gold dissolution is then reduced [2].

Leaching solution

The leaching solution was of the following composition: thiourea 10 g/l H₂O, sulphuric acid 3 ml/l H₂O (red-ox: 75 mV), and ferric sulphate 5 g/l H₂O (red-ox: 567 mV). In a comparative leaching test the concentration of Fe (III) ions was 2,5 g/l H₂O (red-ox: 574 mV). The components were mixed together just before testing because red-ox potential decreases during aging (after 24 hours of standing red-ox drops by 52 mV). Meanwhile, the color of the solution changes from yellow (Fe (III) ions) to green-yellow (Fe (II) ions). Also, a secondary

reaction takes place:



in which thiourea decomposes and Fe (III) ions reduce (elementary sulphur precipitates at the bottom of the vessel). The pH decreases as the concentration of H_2SO_4 increases. Therefore, hydrogen peroxide is added to oxidize Fe (II) ions back to Fe (III):



Leaching tests

The process of gold leaching goes through two stages:

1. gold oxidation:



2. complex formation:



The first leaching test

The influence of the initial concentration of H_2SO_4 and leaching time on the recovery of gold is shown in the table:

Number	$c_{\text{H}_2\text{SO}_4}$ (ml/l)	Leaching time (min.)	Recovery (%)
1	3	10	0.31
2	3	15	0.52
3	10	10	3.83
4	10	15	5.82

It can be seen from the table that the concentration of H_2SO_4 in the solution influences gold recovery. The recovery, however, is small. Furthermore, a high pH causes the decomposition of the active leaching medium.

The 2nd leaching test

The influence of H_2O_2 on gold recovery (pH value is kept between 0.85 and 1.20 with H_2SO_4).

Number	Leaching time (min)	H ₂ O ₂ addition (ml)	Potential Redox (mV)		Recovery (%)
			Initial	Final	
5	20	-	174	156	38.56
6	20	5	170	281	40.19
7	20	10	148	284	34.25
8	40	5	142	289	44.04

The 3rd leaching test

The influence of Fe (III) concentration in the leaching solution on gold recovery ($c_{\text{Fe(III)}} = 2,5 \text{ g/l H}_2\text{O}$).

Number	Leaching time (min)	H ₂ O ₂ addition (ml)	Redox (mV)		Recovery %
			Initial	Final	
9	20	-	172	140	38.75
10	20	5	163	260	46.10
11	20	10	128	256	36.37
12	40	5	107	271	51.63
13	40	10	118	237	43.47
14	60	10	112	251	55.38
15	60	15	105	302	24.85

Some conclusions can be formulated from the results of the 2nd and the 3rd leaching test:

- Fe (III) ions concentration influences the recovery of gold. At a lower concentration, higher recoveries are obtained but a longer leaching time must be used.
- Small amounts of H₂O₂ in the leaching solution increase the recovery of gold. The recovery is reduced, however, when more H₂O₂ is added.
- The recovery of gold is also influenced by the leaching time (in the solution containing H₂O₂). A longer leaching time increases the gold recovery.
- Red-ox potential values are raised by additions of H₂O₂.

The 4th leaching test

The influence of leaching time on recovery at pH ranging from 0.85 to 1.20.

Number	Leaching time (min)	H ₂ SO ₄ addition (ml)	Potential Redox (mV)		Recovery %
			Initial	Final	
16	20	6.00	142	136	25.03
17	40	5.40	143	159	42.58
18	60	1.45	150	143	34.20
19	120	1.60	147	160	47.26
20	180	2.25	155	189	69.59
21	240	2.70	130	179	71.21

The results show the unambiguous influence of leaching time on gold recovery even without H₂O₂ additions. The 4th leaching test can be rated as the most positive. It can be stated that leaching time has an essential influence on the tested flotation concentrate.

Conclusions

Effective leaching of the studied material was achieved at a longer leaching time (than presented in literature) and a lower concentration of Fe (III) ions. In comparison with cyanidation, nearly the same recovery is reached in a shorter leaching time, and without difficulties with toxic waste solutions.

The basic defect is in the limited amount of delivered concentrate. To obtain more information about this material it would be necessary to test the following parameters influencing the recovery of gold:

1. the age of the leaching solution (i.e., the influence of the initial red-ox value),
2. long leaching times at an Fe (III) concentration of 5,0 g/l (i.e. similar to the 4th leaching test),
3. the time of leaching at a lower Fe (III) concentration than 5,0 g/l,
4. the lowest Fe (III) concentration in the leaching solution,
5. the influence of various initial thiourea concentrations in the leaching solution.

Literature

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STRESZCZENIE

Vodvářka P., 1987. Ługowanie roztworami tiomocznika. Fizykochemiczne Problemy Mineralurgii 19; 275-281.

Przedstawiono nowoczesny sposób ługowania trudnowzbogacalnych materiałów zawierających złoto i srebro za pomocą kwaśnych roztworów tiomocznika. Tiomocznik rozpuszcza minimalnie Cu, Fe, Zn, As, Sb i Pb oraz ich siarczki w przeciwieństwie do roztworów cyjankowych, w których są łatwo rozpuszczalne. Wysokie uzyski metali szlachetnych otrzymuje się przy znacznie krótszych czasach ługowania niż przy ługowaniu cyjankami. W pracy przedstawiono rezultaty 21 testów ługowania tiomocznikiem i przedyskutowano dane literaturowe.

СОДЕРЖАНИЕ

П.Водважка, 1987. Выщелачивание растворами тиомочевина. Физикохимические вопросы обогащения, 19; 275-281.

Представлен современный способ выщелачивания труднообогатяемого сырья, содержащего золото и серебро, при помощи кислых растворов тиомочевина. Тиомочевина минимально растворяет Cu, Fe, Zn, As, Sb и Pb, а также их сульфиды в противоположности к цианистым растворам, в которых легко растворяются. Высокие извлечения благородных металлов получаются при значительно коротком времени выщелачивания, чем при выщелачивании цианидом. В работе представлены результаты 21 теста выщелачивания тиомочевинной и обсуждены литературные данные.