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54 Process for the recovery of silver from metallurgical intermediates.

57 An aqueous slurry of the silver-containing intermediate is chlorinated to dissolve platinum group metals and gold leaving the silver in the residue, from which it is dissolved with an aqueous thiosulphate solution. When the intermediate contains lead, the thiosulphate leach solution should have a pH of at least 7. Silver is recovered from the final solution by cementation or reduction.

Process for the Recovery of Silver
from Metallurgical Intermediates

. . This invention relates to the recovery of silver from metallurgical intermediate materials which also contain one or more other precious metals.

Many base metal ores, such as those of copper,
5 nickel, zinc, and lead also contain metals of the platinum group together with silver, gold, selenium, tellurium and other constituents. Such ores form important sources of the valuable metals which are known colloquially as "precious metals", that is to say the six platinum group
10 metals, gold and silver.

These metals occur in the various metal ores in small amounts and become concentrated during the working up of the base metals in the form of various metallurgical intermediates, including anode sludges, leach residues and
15 cements. The composition of these precious metal-containing materials thus vary widely depending upon the nature of the ore. Despite the differences in composition these materials tend to lend themselves to a more or less common scheme of treatment and tend to contain largely the
20 same ingredients, although the proportions of valuable metals therein can vary. Thus, metals which may be present in the precious metals intermediate products include all six members of the platinum group, gold, silver, selenium, tellurium, lead, arsenic, antimony, tin, bismuth, copper,
25 nickel, zinc, iron and sulphur. Once the materials are concentrated, e.g. in the form of anode sludges or leach residues, it then becomes important to recover the metal values as completely as possible and to produce metal concentrates of respectable purity. One known method, for
30 example, can involve decopperizing of the precious metal

intermediate by leaching with sulphuric acid and then
smelting in a Doré furnace in which silver may be
recovered in the form of Doré metal. Such a procedure
is expensive and can produce harmful emissions of
5 selenium, arsenic, lead and other heavy metals.

It is known also to recover precious metal from
intermediate products by dissolution in hydrochloric acid
with chlorination followed by ammonia extraction of
silver from the resulting residues and recovery of
10 platinum group metals, selenium, and tellurium from the
leach liquor. It is also known from the photographic art
that thiosulphate solutions can be employed to dissolve
silver from light-unaffected portions of film which is
employed for photographic purposes. Ammonium thiosulphate
15 leaching of gold and silver from ammoniacal leach residues
in the presence of cupric ion and free ammonia is also
known.

Publications relevant to this subject matter
include Tsvetnye Metally, 1963, Vol.36, No.11, pages 85-86;
20 the U.S. Patents Nos. 3,658,510; 4,070,182; 4,269,622 and
4,229,270.

The present method provides a hydrometallurgical
method for working up precious-metal-containing
intermediate materials to give selective and efficient
25 separation of silver therefrom.

According to the invention, silver present in a
metallurgical intermediate material that also contains
one or more other precious metals is concentrated and
recovered by slurrying the material with water,
30 chlorinating the aqueous slurry to dissolve platinum
group metals and gold present and to produce a residue
enriched in silver, dissolving silver from the residue
with an aqueous thiosulphate solution and recovering silver
from the resulting solution.

5 In carrying out the process, the silver-
containing precious metal intermediates to be treated
should be slurried with water in the proportion of
from 5 to 50% by weight solids. The resulting slurry is
then chlorinated for a time sufficient to convert the
10 silver content to silver chloride and to chlorinate most
of the remaining metal values as chlorides. In the course
of the chlorination a substantial quantity of
hydrochloric acid can be formed by reactions between
chlorine and elements such as sulphur, selenium,
15 tellurium, and arsenic or compounds thereof. A convenient
temperature range for chlorination is from 60 to 80°C.
Since chlorination is usually exothermic, cooling of the
solution may sometimes be required, and the rate of
addition of chlorine should be controlled to avoid
20 possible overheating and/or excessive chlorine consumption.

After completion of the chlorine leach, the
silver-containing residue is separated from the
supernatant solution, which now contains the other precious
metals.

25 The silver-containing residue can then be
leached, preferably at ambient temperature, with an
aqueous thiosulphate solution, e.g. sodium thiosulphate,
to dissolve silver selectively with regard to impurities
such as silica and ferrites which may also be present
30 in the silver-containing residue. The thiosulphate leach
may be conducted at a temperature of from 10 to 80°C.

Thiosulphate should be used in approximately
the proportions of two to four mols of thiosulphate for
each mol of silver to be leached.

The pH of the thiosulphate solution should be at least 2, and when lead is present in the chlorine leach residue to an extent requiring selective removal of the silver, the pH of the thiosulphate leach solution should
5 be at least 7 and more preferably > pH 9 or pH 10. When the thiosulphate solution is sufficiently basic, the thiosulphate leach is highly selective for silver as compared with lead in the precipitate being dissolved. A further advantage of maintaining the thiosulphate
10 solution basic is that the stability of the solution is thereby increased. Small amounts of sulphite, e.g. sodium sulphite, added to the thiosulphate leach solution will also improve its stability.

The thiosulphate leach solution containing
15 silver from the residue may be treated in a variety of ways to recover the silver. For example, cementation with metals such as iron, zinc or magnesium at ambient temperature produces cements analyzing about 90% silver. Organic reducing agents, e.g. fructose, dextrose and
20 lactose, can be used to produce silver precipitates of high purity, e.g. containing at least 90% of silver. Electrolytic recovery means may also be used.

As noted hereinbefore, the composition of the silver-containing precious metal intermediates to be
25 treated in accordance with the invention can vary widely depending upon the ore from which they are obtained, and it may be convenient to subject them to preliminary treatment. For example, in working up copper refinery sludges to recover silver the sludge may be given a
30 decopperizing leach in sulphuric acid prior to treatment in accordance to the invention. Similarly, a lead removal step may be employed prior to treatment of the intermediate in accordance with the invention.

Some examples will now be given.

Example 1

66.2 kg of a precious metals-containing feed, analyzing (in per cent by weight) Pt 1.5, Pd 1.6, Au 0.40, Rh 0.16, Ru 0.09, Ag 7.6, Pb 7.1, Se 5.6, Te 0.67, Cu 0.34 was slurried in water at a solids density of 450 g solids per litre of slurry and heated to 60°C.

Gaseous chlorine was sparged into the agitated slurry for a total of 4 h at a flowrate of 100 litres/min. After filtration of the leached slurry about 46.5 kg of leach residue was obtained, which was found to analyze Pt 0.035, Pd 0.016, Au 0.005, Ag 10.1, Pb 3.2%. The following metal extractions were obtained (%): Pt 98, Pd 99.3, Au 99.1, Ag <1.

The chlorine leach residue was then leached with thiosulphate as follows: 33.8 litres of water was added to 15.5 kg of the above chlorine leach residue, which already contained 39% moisture. NaOH was added to the agitated slurry to bring the pH to 10.0 at 22°C. Then 3.75 kg of Na₂S₂O₃ was added (3.9 kg Na₂S₂O₃/kg Ag) and the slurry was agitated for 30 minutes at a pH of 10 (22°C). The residue was filtered off and washed with one cake displacement of water. Since the leach residue contained a large quantity of filter-aid, which tends to trap large amounts of leach liquor, the wet residue was subjected to a repulp leach using 11 litres of water and 0.4 kg of Na₂S₂O₃. Leaching was again conducted for 30 minutes at 22°C (pH 10). Finally, the leach residue was separated from the solution by filtration. The leach residue analyzed 0.11% Ag and 5.2% Pb. 99.1% of the silver was extracted with only 0.8% of the lead.

The thiosulphate leach liquor and the repulp leach liquor were combined, resulting in a solution analyzing (g/l) Ag 18.0 and Pb 0.07. Sulphuric acid was added to the solution to reach a pH of 4.0 at 22°C.

Then iron powder was added to cement the contained silver values. The pH was held at 4 by simultaneous addition of sulphuric acid. When a redox potential of -400 mV(SCE) was reached, the slurry was filtered. The silver cement
5 analyzed (%) Ag 87.1, Fe 9.3, Pb 0.38, S 1.4. More than 99.9% of the silver had been cemented and the barren solution analyzed 10 mg/l Ag.

Example 2

This example shows the effect of varying the
10 chlorine leaching conditions.

170 g of a moist (39.4% H₂O) precious metals containing feed analyzing (%) Pt 1.73, Pd 1.65, Au 0.33, Ag 2.00, Pb 3.43 and SiO₂ 52.0 was slurried with water alone and with various amounts of hydrochloric acid, as
15 shown in Table 1. The resulting slurries (30-35% solids) were agitated and heated to 80°C. Gaseous chlorine was bubbled into the slurry at a flowrate of 1 g/l slurry/min. for a total of 4 h. The slurry was then filtered and the leach residue and the leach liquor were analyzed.

20 As shown in Table 1, it was found that the extraction of the precious metals Pt, Pd and Au was essentially unaffected by the initial acidity. However, much less silver was extracted (only 0.2%) in the test where the feed was slurried with water. Thus, a better
25 separation of silver from Pt, Pd and Au was achieved.

Example 3

This example shows the effect of acidity on the extraction of silver by a thiosulphate solution.

A chlorine leach residue analyzing, in weight
30 per cent, Ag 17.3 and Pb 9.9, was subjected to thiosulphate leach tests at various pH values between 2 and 12.

TABLE 1

CHLORINE LEACHING OF PRECIOUS METALS CONTAINING FEED
- EFFECT OF INITIAL ACIDITY

Feed Assay (%): 1.73 Pt, 1.65 Pd, 0.33 Au, 2.00 Ag, 3.43 Pb, 52.0 SiO₂
 Conditions: 170 g of moist (39.4% H₂O) feed, 30-35% solids, 4 h at 80°C
 Cl₂ added at ~1 g Cl₂/l slurry/min, filter, wash (H₂O).

INITIAL ACIDITY (M/l HCl)	SOLUTION ASSAY (g/l)		EXTRACTION (%)			
	Pt	Ag	Pt	Pd	Au	Ag
6	3.40	0.25	99.9	99.9	99.6	5.7
4	3.40	0.16	99.9	99.9	99.7	3.6
2	3.40	0.07	99.9	99.9	99.7	1.6
0	3.35	0.01	99.6	99.9	99.7	0.2

The leach conditions were similar to Example 1 and are listed in Table 2, together with the results of duplicate tests. The extraction of silver was lowest (97%) at a pH of 2.0, and was generally 99% or higher between pH 4 and 12. The dissolution of lead was strongly influenced by the pH. At pH 6 and below, more than 75% of the Pb was dissolved, whereas at pH 8 less than 20% Pb was extracted and at a pH of 10 the dissolution of Pb was only 1%.

Table 2

LEACHING OF CHLORINE LEACH
RESIDUE WITH SODIUM THIOSULPHATE

Feed Assay(%): 17.3 Ag, 9.9 Pb

Conditions: Leaching of 102 g Cl₂ leach residue at 20% solids in water, 3.85 g Na₂S₂O₃/g Ag, 30 min. at 22°C. Repulp in 15 g/l Na₂S₂O₃ solution (30 min at 22°C) at the same pH.

<u>pH</u>	<u>RESIDUE ASSAY(%)</u>		<u>EXTRACTION(%)</u>	
	<u>Ag</u>	<u>Pb</u>	<u>Ag</u>	<u>Pb</u>
2.0	0.91	2.40	96.2	83.2
2.0	0.69	2.20	97.2	84.9
4.0	0.22	2.60	99.0	83.7
4.0	0.22	2.61	99.1	82.9
6.0	0.13	3.40	99.5	77.6
6.0	0.20	3.44	99.2	77.1
8.0	0.16	10.8	99.3	19.5
8.0	0.09	10.8	99.5	17.9
10.0	0.20	12.8	99.1	1.1
10.0	0.25	13.4	98.9	0.8
12.0	0.16	12.8	99.3	1.1
12.0	0.30	13.1	98.7	1.6

The next four Examples (Nos. 4-7) illustrate the recovery of silver from thiosulphate leach solutions obtained in the process of the invention.

Example 4

5 A thiosulphate leach liquor (1.0 litres)
analyzing (g/l) Ag 18.4 and $S_2O_3^{2-}$ 68 at pH 10 was
acidified to pH 4, and 3.8 g of Mg granules (0.177-0.21mm)
was added over 2 h with simultaneous addition of 151.5 ml
10 of 50 g/l H_2SO_4 solution to maintain pH 4. During this
period the temperature rose from 22 to 31°C and the redox
potential of the solution decreased from +70 mV to
-250 mV (Pt vs SCE). After filtration and drying, the
solids (20.14 g) analyzed (%): Ag 90.9, Mg 1.6 and S 3.15.
The filtrate (1.085 litres) contained 0.042 g/l Ag. Thus,
15 99.7% of the silver was recovered in the solids.

Example 5

A thiosulphate leach liquor (1.0 litres)
analyzing (g/l) Ag 18.5, Pb 0.11 and $S_2O_3^{2-}$ 69 at pH 10
was heated at 80°C and 14.3 g of D-fructose was added.
20 The solution was maintained at pH 10 by addition of
72.9 ml of a 150 g/l NaOH solution. After 15 minutes the
redox potential of the solution had decreased from 0 mV
to -660 mV (Pt vs SCE) and the silver mirror, originally
plated on the sides of the beaker, disappeared leaving a
25 flocculant precipitate (18.23 g) which analyzed (%):
Ag 97.5, Pb 0.55, and S 0.66. The filtrate (1.044 litres)
analyzed <5 mg/l Ag. Thus, 99.97% of the silver was
recovered in the solids.

Example 6

30 A thiosulphate leach liquor (1.0 litres)
analyzing (g/l) Ag 17.9, Pb 0.10, and $S_2O_3^{2-}$ 67 at pH 10
was heated to 80°C and 14.3 g of D-glucose was added.

The solution was maintained at pH 10 by addition of 265 ml of a 38 g/l NaOH solution. After 30 minutes the redox potential of the solution had decreased from +30 mV to -660 mV (Pt vs SCE) and the silver mirror, originally plated on the sides of the beaker, disappeared leaving a flocculant precipitate (17.45 g) which analyzed (%): Ag 97.9, Pb 0.52, and S 0.56. The filtrate (1.26 litres) contained 40 mg/l Ag. Thus, 99.7% of the silver was recovered in the solids.

10 Example 7

A thiosulphate leach liquor (1.0 litres) containing 17.9 g/l Ag and 67 g/l $S_2O_3^{2-}$ was adjusted to pH 13 at 24°C by adding 16 g NaOH. Then 14.3 g of D-fructose was added. After 2 hours the redox potential had decreased from +60 mV to -225 mV (Pt vs SCE) and 8.85 g of precipitate was filtered off. After standing overnight, an additional 8.30 g of precipitate was recovered. The combined precipitates analyzed 99.6% Ag while the solution contained only 70 mg/l Ag. Thus, 99.6% of the silver was recovered in the solids.

20 Example 8

The compositions of five other precious metal-containing materials susceptible to treatment in accordance with the invention are shown in Table 3. Each of these materials was chlorine leached under the conditions and for the times shown in Table 4. It will be seen from Table 4 that excellent extractions of platinum-group metals and gold were achieved with all the materials treated although the compositions thereof varied widely. On the other hand, extractions of silver were low. The compositions, in weight per cent, of the chlorine leach residues are shown in Table 5. All of the chlorine leach residues were susceptible to thiosulphate leaching, in accordance with the invention, to dissolve silver.

TABLE 3
PM CONTAINING FEEDS TO CHLORINE-WATER LEACHING
- ASSAYS (%)

Feed No.	1	2	3	4	5
Cu	0.09	0.75	1.42	1.86	38.6
Ni	0.28	5.65	3.90	1.30	13.7
Fe	---	---	0.74	0.13	4.45
S	---	---	---	---	19.4
Se	0.96	8.40	---	16.0	1.86
Te	0.14	0.60	---	4.00	0.14
Pb	3.7	5.90	11.8	2.75	3.08
Sb	0.05	0.08	---	0.05	0.15
Sn	0.39	0.75	---	0.30	0.20
Bi	0.04	0.15	---	0.13	0.07
As	0.73	0.75	---	0.25	0.26
Pt	2.32	1.18	8.0	0.21	2.04
Pd	3.12	1.81	8.0	0.52	2.22
Au	0.47	0.36	2.70	0.25	0.55
Rh	0.29	0.17	1.55	0.06	0.40
Ru	0.13	0.10	0.30	0.10	0.14
Ir	0.1	0.05	---	0.03	0.10
Ag	2.5	9.5	34.3	13.1	7.32
SiO ₂	67	41.0	---	---	---

TABLE 4

CHLORINE-WATER LEACHING OF PM FEEDS

Conditions: Pulp density 250-400 g/l in water
1.0-2.5 g Cl₂/min/l slurry

<u>Feed</u>	<u>1</u>	<u>2</u>	<u>3</u>	<u>4</u>	<u>5</u>
Leach Temperature (°C)	60	60	80	80	80
Leach Time (h)	6	6	5	6	5

EXTRACTIONS (%)

Cu	78	75	99	96	>99.9
Ni	7	15	99.2	89	99.9
Fe	--	--	--	21	99
S	--	--	--	--	--
Se	95	99.5	--	99.7	80
Te	99.9	99	--	99.7	99.3
Pb	60	98	89	93	99
Sb	23	59	--	72	94
Sn	4	49	--	82	95
Bi	72	94	--	94	92
As	88	72	--	88	99
Pt	99.2	99.2	99.4	99.3	98.8
Pd	99.9	99.4	99.6	99.8	99.6
Au	99.9	98.2	98.9	99.0	99.4
Rh	99.7	97	96	98	97
Ru	--	98	97	99.4	96
Ir	99.7	97	--	96	88
Ag	0.6	1.7	--	1.4	3.3
SiO ₂	<0.2	0.02	--	--	--

TABLE 5
CHLORINE-WATER LEACH RESIDUE ASSAYS (%)

	<u>1</u>	<u>2</u>	<u>3</u>	<u>4</u>	<u>5</u>
Cu	0.02	0.37	0.035	0.25	0.05
Ni	0.29	6.35	0.065	0.41	0.08
Fe	--	--	--	0.25	0.18
S	--	--	--	--	50.5
Se	0.07	0.07	--	0.15	2.43
Te	<0.01	0.01	--	0.03	<0.01
Pb	1.8	0.17	2.90	0.53	0.08
Sb	0.06	0.04	--	0.04	0.05
Sn	0.51	0.46	--	0.15	0.05
Bi	0.01	0.01	--	0.02	0.04
As	0.11	0.28	--	0.11	0.02
Pt	0.002	0.013	0.10	0.005	0.14
Pd	0.002	0.013	0.075	0.004	0.051
Au	<0.001	0.010	0.064	0.007	0.018
Rh	<0.001	0.007	0.14	0.004	0.057
Ru	--	0.004	0.020	0.002	0.033
Ir	<0.001	0.003	--	0.003	0.067
Ag	3.43	12.0	74.0	30.6	33.8
SiO ₂	74.6	57.0	--	--	--

Claims

1. A hydrometallurgical method for treating a metallurgical intermediate material that contains silver and also one or more other precious metals to concentrate and recover silver therefrom, characterised by the steps
5 of slurring the material with water, chlorinating the aqueous slurry to dissolve platinum group metals and gold and produce a residue enriched in silver, dissolving silver from the residue with an aqueous thiosulphate solution, and recovering silver from the resulting
10 solution.
2. A process according to claim 1, characterised in that the thiosulphate solution has a pH of at least 2.
3. A process according to claim 2, characterised in that the silver-enriched residue also contains lead and
15 the thiosulphate solution has a pH of at least 7.
4. A process according to claim 3, characterised in that the thiosulphate solution has a pH of at least 9.
5. A process according to any preceding claim, characterised in that the thiosulphate leach is conducted
20 at ambient temperature.
6. A process according to any preceding claim, characterised in that the silver is recovered from the final solution by cementation.
7. A process according to any preceding claim,
25 characterised in that the silver is recovered from the final solution by reduction with an organic reducing agent.



DOCUMENTS CONSIDERED TO BE RELEVANT			
Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (Int. Cl. 3)
Y	US-A-1 071 791 (F.W. PUGSLEY) * Claim 1 *	1	C 22 B 11/06
P,A	DE-A-3 145 006 (SUMITOMO METAL MINING) * Claim 1 *	1	
Y	Chemical Abstracts, vol. 75, no. 14, 4 October 1971, Columbus, Ohio, USA V.V. SAFONOV "Chlorination of copper-nickel anode slimes in a medium", page 395, column 2, Abstract 93960z & Tr. Mosk. Khim.-Tekhnol. Inst. 1969, pages 161-164	1	
Y	AT-B- 140 214 (J. EDER) * Page 2 *	1	TECHNICAL FIELDS SEARCHED (Int. Cl. 3)
A	GB-A- 151 952 (AMALGAMATED ZINC)		C 22 B 3/00 C 22 B 11/04 C 22 B 11/06
A,D	US-A-3 658 510 (J.E. HOFFMANN et al.)		
A,D	US-A-4 269 622 (B.J. KERLEY)		
The present search report has been drawn up for all claims			
Place of search BERLIN		Date of completion of the search 16-06-1983	Examiner SUTOR W
CATEGORY OF CITED DOCUMENTS			
X : particularly relevant if taken alone Y : particularly relevant if combined with another document of the same category A : technological background O : non-written disclosure P : intermediate document		T : theory or principle underlying the invention E : earlier patent document, but published on, or after the filing date D : document cited in the application L : document cited for other reasons & : member of the same patent family, corresponding document	