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A TECHNIQUE FOR SELECTIVE EXTRACTION OF IONS OF GOLD AND SILVER FROM HYDROCHLORIC SOLUTIONS WITH TRIBUTYLPHOSPHATE

L.A. VOROPANOVA, N.B. KOKOEVA
North Caucasus Mining and Metallurgical Institute (State Technological University), Vladikavkaz, Russia

Extraction is studied by tributylphosphate (TBP) of ions of gold and silver from hydrochloric solutions during the portional and single time feed of extractant in dependence of the initial concentration of metal ions, temperature, concentration of hydrochloric acid, the ratio of organic (O) and water W phases O:W. The initial solutions contained soluble complex chlorides of gold and silver. When dissolving metal chlorides in the solution of common salt and hydrochloric acid, water soluble coordinate compound are formed that contain complex anions $[AuCl_2]^-$, $[AuCl_4]^-$, $[AgCl_2]^-$, $[AgCl_3]^{2-}$, $[AgCl_4]^{3-}$, et al. As an extractant we used the tri-butyl ether of phosphoric acid $(C_4H_9O)_3PO$ hat belongs to oxygen containing neutral extractants. The formation of coordinate (complex) compounds of TBP and metal polychlorides may be treated as the process of solvation of the extracted metal salt by the extractant. For selective extraction of ions of gold and silver from their hydrochloric solutions by tributylphosphate it is run feeding the extractant portionally to the solution at the minimal time of contact between the solution and the extractant; it helps extracting gold almost completely with the few first portions of the extractant at concentrations of 2n HCl 240 g/dm^3 NaCl and the temperature t = 60°C. Meanwhile the extraction of silver is kept to a minimum. Silver is extracted almost completely after the extraction of gold is over; it is done with tributylphosphate as well at concentrations of 3n HCl, 240 g/dm^3 NaCl and the temperature t = 20°C.

***Key words*:** extraction, gold, silver, tributylphosphate, solution, hydrochloric acid, common salt.

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Selective extraction of individual components from lean poly-metal ores and technogenic wastes appears to be a difficult task. Along with gold and silver such entities contain iron, nonferrous metals and other valuable components. In the course of complex processing of ores and technogenic wastes respective technologies aim at extracting not only gold and silver but other components as well. For example, to extract iron and zinc from solutions of complex composition the process is run using tributylphosphate (TBP). In such conditions it is also preferable to use TBP to extract gold and silver, provided they are present in such solutions [10, 11].

The technique that is in best agreement with the current study is that of separate extraction of gold and silver from thiocyanate solutions [3], during which gold is first extracted by the solution of tributylphosphate in kerosene, and then silver follows extracted by the mixture of tributylphosphate and diphenylthiocarbamide in kerosene. However optimal conditions for selective extraction of ions ofAu and Ag from hydrochloric solutions of mixtures of their salts by tributylphosphate alone were never looked into. Chloride hydrometallurgy is employed in the process of leaching poly-metal concentrates [1, 7, 8]. Because of increased capability of hydrochloric to form complexes, it would be interesting to consider its use in the schemes involving sorption extraction technology of separating metals [2-8, 12-14].

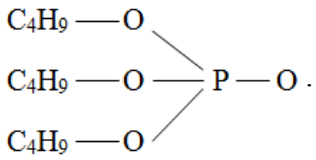
The current study was dedicated to extraction by tributylphosphate (TBP) of ions of gold and silver from hydrochloric solutions during the portional and single time feed of extractant in dependence of the initial concentration of metal ions, temperature, concentration of hydrochloric acid, the ratio of organic (O) and water W phases O:W.

Such extraction was done feeding the extractant portionally and single time to hydrochloric solutions of $V_{раст}$ = 100 cm^3 volume at concentration of common salt C^{NaCl} = 240 NaCl g/dm^3, concentrations of hydrochloric acid C^{HCl} = 2 and 3n, temperatures of 20 and 60°C and various volume ratios of the organic (O) and water (W) phases O:W. During the portional feed of the extractant, extraction was run in five stages, TBP volume during each stage being V_{TBP} = 20 cm^3, O:W = 1:5 (thus totally V_{TBP} = 100 cm^3 and O:W = 1:1), while single time feed of the extractant yielded V_{TBP} = 100 cm^3, O:W = 1:1. Each stage was conducted within 10 min.

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The initial solutions contained soluble complex chlorides of gold and silver. When dissolving metal chlorides in the solution of common salt and hydrochloric acid, water soluble coordinate compound are formed that contain complex anions $[AuCl_2]^-$, $[AuCl_4]^-$, $[AgCl_2]^-$, $[AgCl_3]^{2-}$, $[AgCl_4]^{3-}$ and et al. [12].

As an extractant we used the tri-butyl ether of phosphoric acid $(C_4H_9O)_3PO$ hat belongs to oxygen containing neutral extractants, its structural formula being:



The formation of coordinate (complex) compounds of TBP and metal polychlorides may be treated as the process of solvation of the extracted metal salt by the extractant.

Extraction was done with continuous mixing of the solution. Extraction results were assayed by residual concentration of ions of metal in the raffinate in the process of extraction at a given moment, by the level of extraction (in mass % of the initial amount of metal) at each stage of the extraction, by concentration of metal in the extract, by the coefficient of distribution $D = C_{org} / C_{wat}$, where C_{org} and C_{wat} are concentrations of ions in the organic and water phases, respectively, and the separation coefficient $\beta_{Au/Ag} = D_{Au} / D_{Ag}$.

Re-extraction of gold and silver rom the organic phase was performed using 8 % solution of thiourea $CS(NH_2)_2$ and 10 % solution of HCl.

The effect was studied of macro-components, HCl and NaCl on the results of extraction from the mixture of hydrochloric solutions of salts of gold and silver, O:W = 1:1, extraction time 15 min, t = 20°C. It was found that for the salts of Au and Ag extraction results increase in dependence of concentrations of HCl and NaCl following the sequence: 4M NaCl → 3n HCl → 2n HCl + 2M NaCl.

Fig. 1 demonstrates the effect of volume ratio of water, W and organic, O phases W:O on the results of extracting gold and silver from their individual hydrochloric solutions, C^{HCl} = 2n, C^{NaCl} = 240 g/dm^3, extraction time 15 min, temperature t = 20°C. One may see that the best results of extraction were obtained for the ratio W:O ≤ 2:1.

The extraction was studied of ions of gold and silver from hydrochloric solutions in case of the portional feed of extractant for the initial concentrations, $C_{исх}$, q/dm^3: 282 Au and 254 Ag, 3n HCl, 240 g/dm^3 NaCl and temperatures of 20 and 60°C. Extraction was conducted in five stages, 20 cm^3 TBP added during each stage, O:W = 1:5 (totalling 100 cm^3 and O:W = 1:1). Extraction results are presented in Fig.2, *a*.

The extraction of gold reaches 99 % during the first stage at the temperature of 60°C and during the third stage at the temperature of 20°C. The extraction of silver reaches 99 % during the third stage at 20°C, while at 60°C even the fifth stage only yields 78 % extraction. The extraction of gold shows quite a weak temperature dependence and varies between 98.4-99.7 % mass at 20°C and 99.3-99.7 % mass at 60°C, while the extraction of silver depends significantly on the temperature: higher temperatures result in lower extraction from 98.4-98.8 % mass at 20°C to 52.8-78.4 % mass at 60°C. The highest values of distribution D_{Au} = 559 for gold was obtained during the first stage at 60°C, and that for silver, D_{Ag} = 68 was obtained during the second stage at 20°C. The highest separation coefficient between gold and silver $\beta_{Au/Ag}$ = 155 was obtained during the first stage at 60°C.

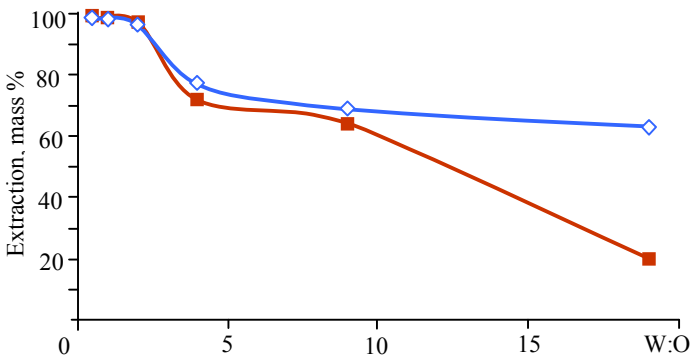


Fig. 1. Dependence of extraction of gold and silver by TBP on volume ratio W:O from individual hydrochloric solutions
C^{HCl} = 2n, C^{NaCl} = 240 g/dm^3, extraction time 15 min, t = 20°C

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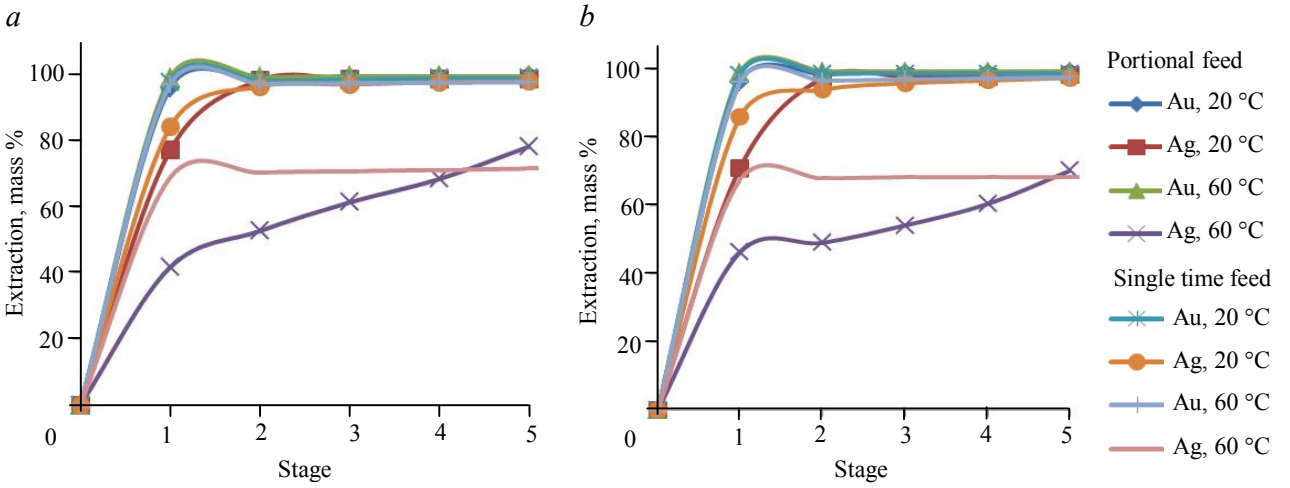


Fig.2. Comparative results of extracting ions of gold and silver from hydrochloric solutions during portional and single time feeding of extractant at concentrations $C_{исх}$, g/dm^3:

a – 282 Au and 254 Ag, 3n HCl, 240 g/dm^3 NaCl, temperatures of 20 and 60°C;
b – 282 Au and 254 Ag, 2n HCl, 240 g/dm^3 NaCl, temperatures of 20 and 60°C

The extraction was studied of ions of gold and silver from hydrochloric solutions in case of single time feed of extractant for the initial concentrations, $C_{исх}$, g/dm^3: 282 Au and 254 Ag, 3n HCl, 240 g/dm^3 NaCl and the temperatures of 20 and 60°C. The extraction was done in single stage, feeding 100 cm^3 TBP in single portion, O:W = 1:1. Extraction results are presented in Fig. 2, *a*.

The extraction of gold reaches 97-98 % 10 min after starting the extraction at the temperatures of 20 and 60°C. The extraction of silver reaches 97 % 20 min after starting the extraction at the temperature of 20°C, while at 60°C the extraction remains 72 % only even 50 min after starting the extraction. The extraction of gold shows quite a weak temperature dependence and varies between 98.42-98.9 % mass at 20°C and 97.3-97.9 % mass at 60°C, while the extraction of silver depends significantly on the temperature: higher temperatures result in lower extraction from 96.5-98.0 % mass at 20°C to 70.5-71.7 % mass at 60°C. The highest value of distribution $D_{Au} = 93$ for gold was obtained 40 min after starting the extraction at 20°C, and that for silver, $D_{Ag} = 50$ was obtained 50 min after starting the extraction at 20°C. The gold and silver separation coefficient $\beta_{Au/Ag} = 15\text{-}18$ maintains its value through the full time of extraction at 60°C.

The extraction was studied of ions of gold and silver from hydrochloric solutions in case of portional feed of extractant for the initial concentrations, $C_{исх}$, g/dm^3: 282 Au and 254 Ag, 2n HCl, 240 g/dm^3 NaCl and temperatures of 20 and 60°C. Extraction was conducted in five stages, 20 cm^3 TBP added during each stage, O:W = 1:5 (totalling 100 cm^3 and O:W = 1:1). Extraction results are presented in Fig. 2, *b*.

The extraction of gold reaches 99 % during the first stage at the temperature of 60°C and during the third stage at the temperature of 20°C. The extraction of silver reaches 98 % during the third stage at 20°C, while at 60°C even the fifth stage only yields 70 % extraction. The extraction of gold shows quite a weak temperature dependence and varies between 98.6-99.5 % mass at 20°C and 99.5 % mass at 60°C, while the extraction of silver depends significantly on the temperature: higher temperatures result in lower extraction from 97.6-98.4 % mass at 20°C to 49.2-70.5 % mass at 60°C. The highest values of distribution $D_{Au} = 542$ for gold was obtained during the first stage at 60°C, and that for silver, $D_{Ag} = 56$ was obtained during the second stage at 20°C. The highest separation coefficient between gold and silver $\beta_{Au/Ag} = 126$ was obtained during the first stage at 60°C.

The extraction was studied of ions of gold and silver from hydrochloric solutions in case of single time feed of extractant for the initial concentrations, $C_{исх}$, g/dm^3: 282 Au and 254 Ag, 2n HCl, 240 g/dm^3 NaCl and temperatures of 20 and 60°C. The extraction was done in single stage, feeding 100 cm^3 TBP in single portion, O:W = 1:1. Extraction results are presented in Fig. 2, *b*.

The extraction of gold reaches 99 % 10 min after starting the extraction at the temperatures of 20°C and 97 % 20 min after starting the extraction at 60°C. The extraction of silver reaches 97 %

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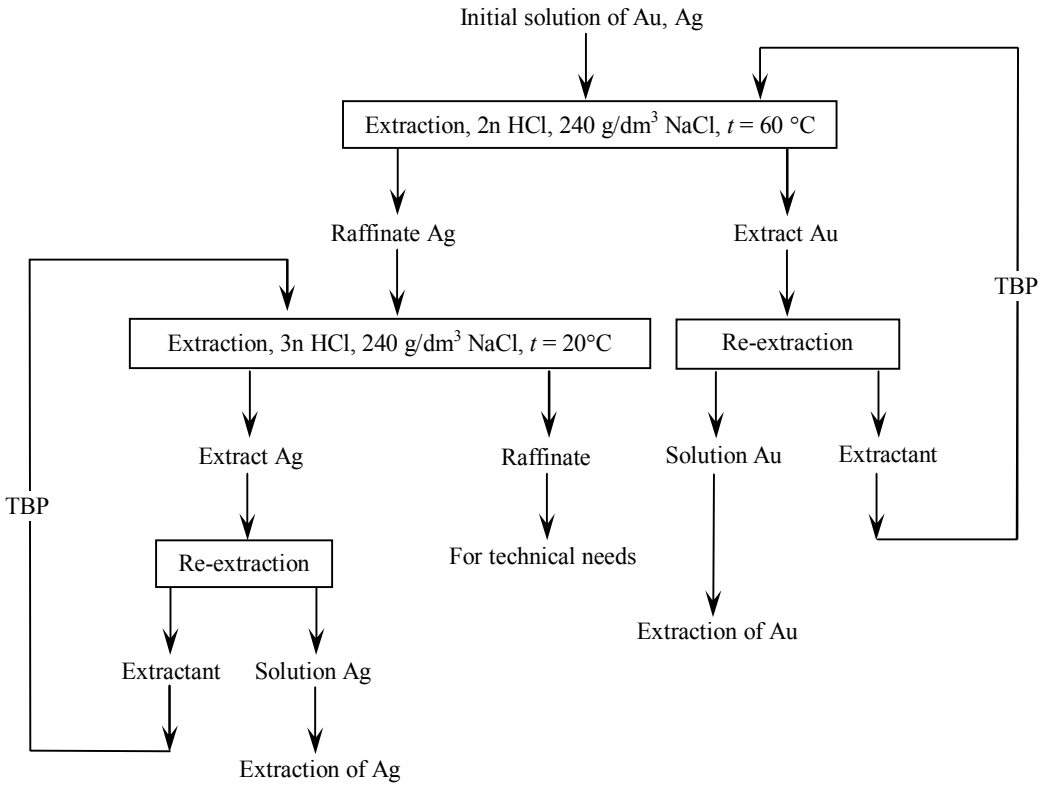


Fig. 3. Principal technological flow-chart of selective extraction of ions of gold and silver from hydrochloric solutions of mixtures of their salts

40 min after starting the extraction at 20°C, while at 60°C the extraction reaches 68 % only by the end of the extraction process. The extraction of gold only shows a weak temperature dependence and yields 98.6-98.9 % mass at 20°C and 96.5-97.9 % mass at 60°C, while the extraction of silver depends on temperature quite strongly: it drops off at higher temperatures from 86.2-97.6 % mass at 20°C to 67.7-68.5 % mass at 60°C.

Conclusions to be drawn from the data in Fig. 2:

1. Temperature increase results in a drop-off of silver extraction by the factor of ~2 at each stage while that of gold remains unchanged.

2. The portional feed of extractant increases the extraction of silver 1.1 times at C^{HCl} = 3n during stage five of extraction for a given initial concentration.

3. The portional feed of extractant reduces its expenditure: to achieve identical results of extraction during stage-by-stage feed of extractant one needs O:W = 1:5 over 10 min, while single time feed of the extractant would need O:W = 1:1 over the same time period. Regenerating each portion of the extractant might reduce the extractant expenditure even more.

4. The best results of extraction were obtained during portional feed of the extractant to hydrochloric solutions at the concentration of 2n HCl, 240 g/dm^3 NaCl and temperature of 60°C for gold and the concentration of 3n HCl, 240 g/dm^3 NaCl and temperature of t = 20°C for silver.

Fig. 3 presents the principal technological flow-chart of selective extraction of ions of gold and silver from hydrochloric solutions of mixtures of their salts.

Conclusions

For selective extraction of ions of gold and silver from their hydrochloric solutions by tributylphosphate it is run feeding the extractant portionally to the solution at the minimal time of contact between the solution and the extractant; it helps extracting gold almost completely with the few first

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portions of the extractant at concentrations of 2n HCl 240 g/dm^3 NaCl and the temperature t = 60°C. Meanwhile the extraction of silver is kept to a minimum. Silver is extracted almost completely after the extraction of gold is over; it is done with tributylphosphate as well at concentrations of 3n HCl, 240 g/dm^3 NaCl and the temperature t = 20°C.

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Authors: **L.A.Voropanova**, *Doctor of Engineering Sciences*, *Professor*, *lidia_metall@mail.ru* (*North Caucasus Institute of Mining and Metallurgy* (*State University of Technology*), *Vladikavkaz*, *Russia*), **N.B.Kokoeva**, *Candidate of Engineering Sciences*, *Engineer*, *lidia_metall@mail.ru* (*North Caucasus Institute of Mining and Metallurgy* (*State University of Technology*), *Vladikavkaz*, *Russia*).
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