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THERMO-TRIBO-ACTIVATION METHOD FOR UTILISATION OF INDUSTRIAL PYRITE WASTES

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Abstract. Low-grade pyrite wastes from flotation process were used as a raw material for extraction of precious and rare metals. Pyrite wastes were treated using different equipment and conditions for tribo-mechanical activation. It has been confirmed that exothermic reactions took place during the activation process. As a result new crystal and phase structures were formed. X-ray diffraction method was applied to determine the new phases in the solid products obtained. Leaching of some metals from activated samples was subject of flow-up studies. The experimental data obtained show much higher rates of extraction of gold, silver, germanium, etc. Optimal conditions for leaching process are recommended. It is concluded that the use of thermo-tribo-activation process for preliminary treatment of pyrite wastes from mining industry is a promising way for obtaining different products from the wastes with better efficiency.

Keywords: solid waste, utilisation, pyrite, tribo-mechanical activation, clean technology.

AIMS AND BACKGROUND

Gold is found exclusively as free gold pieces with impurities of silver, copper, bismuth, etc. in minerals such as sphalerite, silvinite, petricide, nagatite, etc. It is found as small gold pieces in quartz, as well as in natural deposits resulting from quartz erosion.

About 1000 t of gold is available in Bulgaria. The biggest deposits are in the regions of Chelopech village (60 t), Topolovgrad town (30 t), Etropole town (15 t), Tran town (10 t), Haskovo town (15 t), Panagjuriste town (8 t), Burgas town (3 t), Chiprovtsi town (West Balkan Range) (95 t), Madjarovo town (East Rhodope Mountains) (250 t), etc. At present, less than 1 t of gold is extracted per year in Bulgaria. The main quantity of non-extracted gold is thrown away as flotation waste from mineral processing factories that produce copper concentrate ('Bimak', 'Asarel-Medet', 'Elatsire', 'Chiprovtsi', 'Burgaski medni mini').

The flotation waste is mainly pyrite concentrate that is not processed at present and is disposed in the tailings' ponds of the corresponding mineral processing enterprises. Considerable amounts of Bulgarian gold (1-10 g/t), as well as

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other valuable metals, such as Ag, Se, Te, Ge, Ta, Sb, Bi, and Pt are thrown away with the pyrite concentrate.

The goal of the presented work was to create possibilities for an effective and environmentally friendly gold extraction by means of thermal, tribo-chemical and thermo-tribo-chemical activation of pyrite concentrates.

The interest in hydrometallurgy of precious metals has considerably increased recently. This is demanded by the necessity to use clean technologies on the one hand, and to utilise effectively the solid waste – on the other hand.

The hydrometallurgy is a dominating method for precious metals extraction from their commercial ores, as well as from secondary or waste products of mineral processing and metallurgy. Hydrometallurgy domination is caused by the regularly fine dispersity of gold and other concomitant valuable and rare metals on the one hand, and the possibility to practice enough selective and profound extraction of valuable metals at acceptable cost – on the other hand[1-4].

Pyrometallurgical, thiocarbamide, cyanide, thiosulphate methods, and acidic decomposition with halogen elements, leaching with nitrate, chlorine and other solutions are the main methods used in world-wide practice for precious metals extraction[5,6].

Taking into consideration (a) the fact that the gold in Bulgarian ores, concentrates and wastes, as well as in the gold grains and aggregates, is entirely or partially covered by surface formations, and (b) the ability of the tribo-chemical and thermo-chemical methods to remove those surface formations, it can be expected that the thermo-tribo-chemical activation of ores, concentrates and wastes will lead to a practical realisation of effective hydrometallurgical methods for extraction of gold and other precious rare metals[7,8].

EXPERIMENTAL

Characterisation of the ores, concentrates and wastes. Investigations described in this work were carried out with pyrite concentrate from 'Bimak JSC' Mineral processing factory, village of Chelopech. The Chelopech deposit is unique for the Bulgarian mining industry, its balance reserves of gold-copper-pyrite ores come up to 53.5 millions of tons. The ore is rich in Cu, Au, Ag, S, Se, Te, As, as well as in Ga, Ta, Sb, Bi, Pt, and Ca. The average gold content is around 7 g/t.

Chelopech ores are classified as massive-sulphide ores, according to their mineralogical-technological parameters and are represented by two main types: chalcopyrite-tenantite-pyrite and enargite-lusonite-pyrite.

Gold content (in g per ton) and distribution (in %) among the different phases in the Chelopech pyrite concentrate is the following:

- free gold → 2.7 g/t, 40.91%;
- able to be extracted by cyanidation → 3.0 g/t, 45.45%;

- in oxide coating → 0.3 g/t, 4.55%;
- in sulphides → 0.4 g/t, 6.06%;
- fine-dispersed → 0.2 g/t, 3.03%;
- totally → 6.6 g/t, 100 %.

Surface formations of gold 'grains and aggregates' that are over 65% of the total number are divided into two main groups:

– sulphides and sulpho-salts – gold is genetically bound to them;

– surface coatings, resulting from ore processing.

Granularity of the gold-bearing pyrite concentrate is <0.02 mm – 3.4%; 0.02÷0.04 mm – 7.9%; 0.04÷0.063 mm – 58.5%; 0.063÷0.071 mm – 17.4%; 0.071-0.08 mm – 2.9%; 0.08÷0.10 mm – 6.9%, >0.10 mm – 3.0%.

Thermo-tribo-chemical activation of pyrite concentrate and leaching with ammonium thiosulphate. The tribo-chemical activation of the pyrite concentrate was carried out in two tribo-reactors with the following parameters:

- 'Planetary mill' tribo-reactor:

– reactors with volume of 250 cm^3;

– ratio 'concentrate: grinding bodies' = 20 g : 600 g (steel balls with ∅20 mm, 20 balls, 600 g);

– intensity of the mechanical influence – 288 rev./min;

– time of activation – 0÷30 h.

- 'Vortical installation with rotating magnetic field (VIRMF)' tribo-reactor:

– reactor with ∅82 mm and length of 160 mm;

– grinding particles with ∅2 mm and length of 24 mm;

– magnetic induction – 0.168 T;

– synchronous frequency of the dipolar magnetic field – 3000 rev./min;

– ratio 'pyrite concentrate: grinding bodies' = 150:100 g;

– time of activation – 3÷10 min.

After the tribo-chemical activation, the pyrite concentrate was taken out of the tribo-reactor, and was oxidised in air for 30 min, at continuous stirring and temperature of about 600°C.

Tribo-chemically activated material, in a planetary mill and in VIRMF reactor, being subsequently oxidised, was subjected to leaching with ammonium thiosulphate solution containing 60 % solution of $(NH_4)_2S_2O_3$, NH_4OH, $CuSO_4.5H_2O$, and $Ca(OH)_2$. The ratio 'concentrate: leaching solution' was from 1:30 to 1:90 and the treatment time was 0 ÷120 min.

RESULTS AND DISCUSSION

Results for gold recovery from initial and tribo-chemically activated pyrite concentrate in a planetary mill are presented in Table 1.

Table 1. Data on gold recovery from tribo-chemically activated pyrite concentrate by leaching with ammonium thiosulphate at ratio 'solid:liquid' = 1:2 and treatment time of 90 min

No	Gold content in pyrite concentrate, C_{Au} (g/t)	Time of tribo-chemical activation, τ_{TchA} (h)	Gold recovery, α_{Au} (%)
1	1	0	12.18
2	1	4	20.36
3	1	8	43.82
4	1	12	76.80
5	7	0	10.60
6	7	8	39.70
7	7	12	54.20
8	10	0	7.20
9	10	4	16.16
10	10	8	30.32
11	10	12	46.29
12	438	0	2.65
13	438	12	18.20
14	438	30	26.80

Data presented in the table show the favourable effect of tribo-chemical activation on the gold recovery which effect generally comes to the following:

- Recovery increases from less than 10% for non-activated concentrate to 75% (for the same concentrate) after 12 h of tribo-activation;
- Gold recovery increases with the tribo-activation time;
- The tribo-activation is more effective, and the recovery is higher at lower gold content in the initial concentrate;
- The ratio 'leaching solution : pyrite concentrate' and the leaching time do not influence considerably the gold recovery degree;
- Most probably, the positive influence of the tribo-chemical activation is due to opening-up of surface coatings on the gold grains and aggregates and the change in the structure of pyrite concentrates. This is confirmed by the data from X-ray analysis of initial and activated concentrate, with different gold concentration, as shown in Figs 1 and 2.

Data on gold recovery from pyrite concentrate passed through tribo-activation in VIRMF reactor and subsequent oxidation are presented in Table 2.

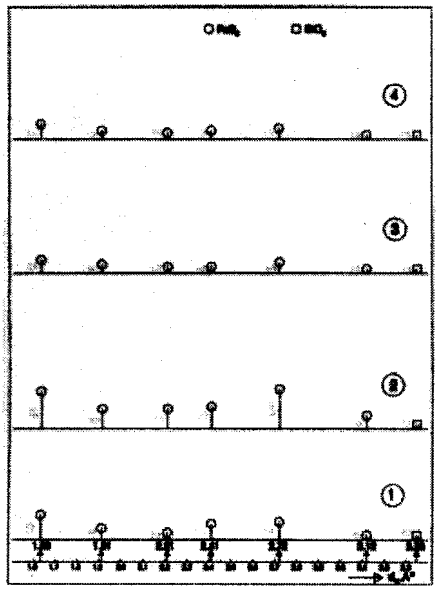

Fig. 1. X-ray analysis of non-activated pyrite concentrate
1 – C_{Au} = 1 g/t, 2 – C_{Au} = 7 g/t, 3 – C_{Au} = 10g/t, 4 – C_{Au} = 438 g/t

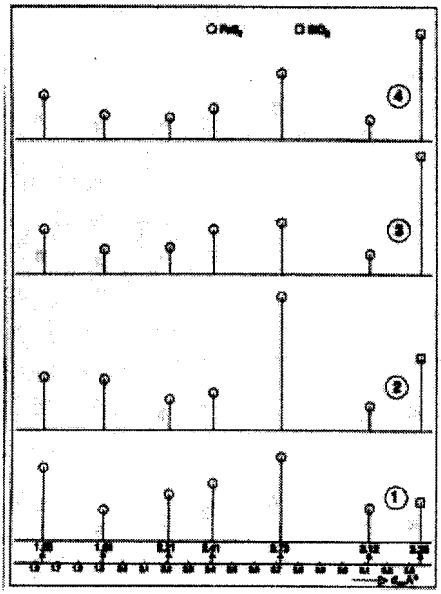

Fig. 2. X-ray analysis of pyrite concentrate, activated in a planetary mill for 12 h
1 – C_{Au} = 1 g/t, 2 – C_{Au} = 7 g/t, 3 – C_{Au} = 10g/t, 4 – C_{Au} = 438 g/t

Table 2. Data on gold recovery from pyrite concentrate undergone tribo-chemical activation in VIRMF, subsequent oxidation and leaching with ammonium thiosulphate

Tribo-chemical activation		Thermal treatment		Oxidation		Leaching		α_{Au} (%)
ratio 'material: grinding bodies'	τ_{TChA} (min)	T (°C)	τ (min)	T (°C)	τ (min)	ratio 'solid: liquid'	τ (min)	
–	–	700	300	–	–	2	60	38.2
1.5	3	–	–	–	–	2	60	46.4
1.5	3	–	–	600	30	2	60	83.4
1.5	6	–	–	600	30	2	60	92.4
1.5	10	–	–	600	30	2	60	95.1

Data shown in Table 2 again confirm the positive influence of the tribo-activation – in this type of tribo-reactor and at considerably less time of mechanical influence – up to 10 min.

The combination of tribo-chemical and thermal activation undoubtedly leads to a new 'tribo-thermal effect' manifesting itself in reaching gold recovery

over 95%. Along with that, the combination of mechanical-chemical and thermal influence leads to decomposition of pyrite concentrate with sulphur dioxide release, which complicates the use of the 'tribo-thermo-chemical method' for treating pyrite ores, concentrates and wastes with the aim to extract the gold, or to achieve a profound utilisation of the above mentioned materials.

Results on the recovery of other elements accompanying the gold were analysed simultaneously with the gold recovery. The results confirmed the positive influence of the tribo-chemical activation and showed the necessity of additional investigations for finding the optimum conditions for thermo-chemical and tribo-chemical treatment aimed at better extraction of all precious and rare metals, available in pyrite ores and their secondary products and wastes.

CONCLUSIONS

The possibility is proved for nearly entire extraction of gold available in pyrite ores, concentrates and wastes by use of preliminary tribo-chemical and thermal activation and subsequent leaching with ammonium thiosulphate.

Use of the tribo-thermal method for treating pyrite concentrates will lead to their complex processing with a maximum utilisation of the valuable components available in the raw material.

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