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Process Development for Refractory Gold Concentrates Treatment on Pokrovsky POX Hub

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The chemical composition and mineralogy of Malomir and Pioneer gold-bearing ores were discussed. The main gold forms in the ores were indicated: the preferential gold association with sulfide minerals was noted. The chemical composition of sulfide flotation concentrates was shown. The laboratory and pilot tests results of concentrates pressure oxidation were introduced. The influence of organic carbon content in the concentrate and chloride ion content in the liquid phase of pressure oxidation slurry on the gold extraction from materials were noted and researched. The effect of preliminary treatment stages on POX indicators was shown. The positive effect of hot autoclave slurry conditioning on gold recovery was noted. The process flow sheet for treating both Malomir and Pioneer ores was developed and advised.

Keywords: gold ores, separation of the pressure oxidation, pressure oxidation technology.

Introduction

Malomir and Pioneer mine sites are located in the Russian Far East in Amur region. Petropavlovsk PLC Group of Companies owns and operates both mines. Petropavlovsk is the second largest gold producer in Russia producing 710 400 ounces (22,1 tons) of gold in 2012.

Malomir and Pioneer gold ores are refractory due to the gold association with sulfides. Refractory materials constitute approximately half of the Group's current gold reserves. That makes processing of refractory ores a strategic priority for Petropavlovsk.

The prefeasibility study of POX, bio oxidation and roasting of Malomir and Pioneer ores revealed that POX is the most suitable pre-treatment technology.

Malomir and Pioneer ores will be subjected to flotation and upgraded to high-grade concentrates. Flotation concentrates will be trucked by existing roads to Pokrovsky mine site for processing in high-pressure autoclaves, which are currently being installed as well as oxygen plant and filtration site. POX hub on Pokrovsky site benefits from existing infrastructure and RIP facilities.

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This article provides the results of Malomir and Pioneer material analysis and POX process development, batch and pilot tests.

Ore chemical composition and mineralogy

The studied Malomir ore samples mostly consist of lithophile components with predominance of silica (55–63 %). Sulphur and arsenic are found mostly in the sulphidic form. The share of sulphidic iron accounts for 36 to 54 %. Malomir ore is also characterised by the presence of organic carbon in an amount of 0.10 to 0.16 %.

The Pioneer ore had a smaller content of metallic minerals components and insignificant levels of arsenic. The lithophile component content is slightly higher with predominance of silica (72.4 %).

The main valuable component of the ores is gold. Malomir ore assays at 1.45 to 2.0 g/t with Pioneer lower at 1.2 g/t.

The bulk of Malomir and Pioneer ore samples are rock-forming minerals with predominance of quartz (38–44 %). In addition, feldspar, hydromicaceous clay and carbonates are present in significant amounts. Sulphide minerals are mostly pyrite (2.2–3.8 % in Malomir and 2.0 % in Pioneer) and arsenopyrite (1.2–1.3 % in Malomir and insignificant amounts in Pioneer). In addition, iron hydroxides are present. Malomir ore is also characterized by the presence of carbonaceous matter.

Gold association

The following forms of gold occurrence are typical for the studied ore samples: leachable by direct cyanidation; leachable by cyanidation after treatment with hydrochloric acid (locked in iron hydroxides, carbonates, etc.), nitric acid (locked in sulphides), roasting (locked in carbonaceous matter and in sulphides finely distributed through rock-forming minerals); locked in rock-forming minerals.

The Table 1 data shows that Malomir and Pioneer ores are refractory to direct cyanidation. Gold available for cyanide leaching is 12–17 % in Malomir ore and 30 % in Pioneer ore. The primary reason for the refractory ore is gold association with sulphides.

Flotation concentrates

Malomir and Pioneer ores require flotation concentration before being fed to the POX stage. The main flotation product is sulfide concentrate comprising most of the gold from the ore. Moreover the

Table 1. Gold association in Malomir and Pioneer ores

Forms of gold	Malomir	Pioneer
Leachable by direct cyanidation	12-17 %	30 %
Locked in iron hydroxides, carbonates, etc.	12-18 %	20 %
Locked in sulphides	51-56 %	39 %
Locked in carbonaceous matter and in sulphides finely distributed through rock-forming minerals	10-13 %	н/д
Locked in rock-forming minerals	2-5 %	9 %

Table 2. Malomir and Pioneer sulfide concentrates chemical composition

Component	Malomir										Pioneer
	24d	21b	26a	24d	21b	26c	24d	21b	26d	24d	21b
	Component content (%)										
Fe tot.	—	24.6	—	—	22.5	—	25.7	25.9	—	27.0	19.7
S tot.	—	23.0	20.6	21.0	18.9	21.3	23.5	24.3	23.9	23.0	20.4
S sulfide	—	22.8	20.5	20.9	18.8	21.1	23.3	24.2	23.7	23.0	20.4
As tot.	—	7.81	—	—	—	—	9.19	8.53	—	7.10	0.66
C org.	0.31	0.41	0.55	0.65	1.10	1.14	1.20	1.48	2.04	2.40	н/д
Au (g/t)	21.2	22.0	28.6	24.4	24.3	24.6	24.3	23.8	25.7	23.5	26.5

carbon flotation is introduced to the Malomir flotation flowsheet in order to remove carbonaceous matter.

Chemical composition of the Malomir and Pioneer pilot flotation concentrates is shown in Table 2.

The Malomir concentrate samples were produced according to the different flotation flowsheets. The main difference in chemical composition of these concentrates is organic carbon content as shown in Table 2. The Pioneer pilot concentrate samples were relatively even in chemical composition. Hence, chemical composition for only one Pioneer sample is shown in Table 2.

Malomir sulfide concentrate yield, depending on ore sample origin and concentration flowsheet details, is 4.5–5.6 %. Gold recovery to the concentrate is 86–87 %. Pioneer concentrate yield is 2.9–3.6 %; gold recovery is 82–85 %.

POX process development

Initially POX technology was extensively tested in SRC Hydrometallurgy laboratory in St. Petersburg. Every flotation concentrate sample was subjected to batch tests in laboratory autoclaves. In order to test and confirm the laboratory batch tests results as well as to achieve a better understanding of the process, a series of continuous pressure oxidation tests on Blagoveshchensk Pilot Plant was also carried out.

Laboratory tests

Experimental methods. In all the laboratory tests, distilled water was used in order to eliminate the influence of chloride impurities contained in tap water. A sample of concentrate was ground and treated with sulfuric acid to remove carbonates. The resulting slurry was filtered, the cake was washed with water on the filter to remove chloride ion dissolved from concentrate during acid treatment. The washed cake was loaded into a titanium autoclave by Büchi Glas Uster with the capacity of 1100 cm³ equipped with a turbine stirrer with adjustable rotational speed. The temperature of the slurry was kept constant by the automatic control system with an accuracy of ± 0.5 degrees. A Bronkhorst flow and pressure meters was used to control and regulate total pressure and oxygen flow. Oxidized slurry was cooled and conditioned. The resulting slurry was then filtered. The filter cake was then washed and diluted with water, neutralized and treated

with cyanide using standard RIL methods. After RIL, the solids of the slurry were separated and subjected to gold assay.

Results. During initial POX testwork the influence of the following primary parameters was investigated:

- Temperature (190–230 °C),
- Oxygen overpressure (450–730 kPa),
- Regrinding (size of 90 % of particles less than 15, 40 and 70 microns).

The results (as predicted) showed that high POX temperature, high oxygen overpressure and fine particle size favor a high oxidation rate. As long as there was complete decomposition of sulphides high gold recovery was achieved. The following basic parameters were fixed for the rest of laboratory tests: temperature 225°C, oxygen overpressure 730 kPa, and particle size of 90 % of particles less than 40 microns.

Under these specified conditions a number of flotation concentrates samples were tested. As noted earlier, the main difference between various Malomir concentrates samples is organic carbon content.

Pioneer concentrate tends to be a relatively simple material to treat using POX. Maximum achievable gold recovery from Pioneer is 98 % (and higher). In order to achieve high gold recovery from Pioneer it is necessary to oxidize the sulfides (at least 98 % of them).

Gold recovery from Malomir strongly depends on carbonaceous matter content as well as chloride concentration in the autoclave slurry.

Malomir concentrates pressure oxidation with potassium chloride addition and subsequent cyanidation results were shown and discussed in the paper [1]. It is seen that with the increasing levels of organic carbon content in concentrate, gold recovery from the autoclave residues decreases proportionally. For low-carbonaceous concentrate T-24d gold recovery is 96.6 %, while for the concentrate T-16 recovery is 84.3 %. The concentration of chloride ion in all the experiments is similar: the range is 2 to 5 mg/dm³.

For all tested concentrates a significant decrease in gold recovery occurs with increasing of chloride content in the autoclave slurry. It is clear that the negative effect of chloride ion manifests itself to varying degrees. High-carbonaceous concentrates are more sensitive to increased amounts of chloride compared to low-carbonaceous concentrates. When the concentration of chloride in the autoclave slurry reaches 15 mg/dm³, gold recovery from low-carbonaceous concentrates (0.3-0.6 %) decreases to 90 %, from high-carbonaceous concentrate T-16 – to 65 %.

Gold recovery from Pioneer concentrate is 98 % (and higher) even with chloride ion concentration up to 10 – 20 mg/dm³. A noticeable decrease of recovery occurs only when chloride ion content reaches 100 mg/dm³ or higher.

Special testwork was carried out to investigate the influence of concentrate pre-treatment on gold recovery. It was found that water washing of concentrate before feeding to the autoclave allows washing out a water-soluble part of chlorides and chlorides contained in porous moisture. Furthermore acid pretreatment of concentrate, along with carbonate decomposition, allows further dissolution of chloride-containing minerals. The subsequent water wash results in chloride removal from the concentrates.

Water washing of acid pre-treated concentrate removes chloride, which in turn leads to increased gold recovery as shown in Fig. 1.

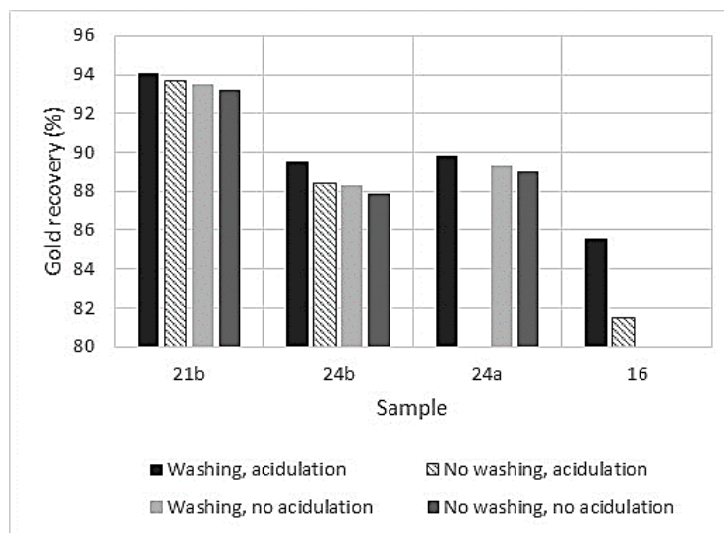


Fig. 1. Concentrate preliminary treatment effect on gold recovery

Pilot POX testwork

Experimental methods. Continuous pressure oxidation tests were carried out on a Pilot Plant in Blagoveshchensk Test Facility [2], a schematic of which is shown below in Fig. 2.

Flotation concentrate sample was ground in a ball mill to 90 % of particles passing 40 microns. The ground sample was then diluted with water to 30 % of solids and treated with concentrated sulfuric acid or recycled acid solution to remove carbonates.

The resulted slurry was then filtered. The cake was diluted with water to 45 – 55 % solids content and loaded into autoclave feed reactors. The slurry was fed to the autoclave by high pressure pump by Netzsch. The slurry was continuously oxidized in a titanium four-compartment autoclave with a capacity of 50 dm³. The autoclave is equipped with five agitators with adjustable rotational speed. Slurry temperature was maintained at 225 °C by feeding cooling water to the autoclave compartments. An oxygen flow rate was controlled and measured by Bronkhorst flow meters. A working pressure was maintained at 3 250 kPa by continuous autoclave gas venting. Oxidised slurry was then discharged from the autoclave last section, cooled to the temperature of 95 °C and conditioned for two (2) hours. The resulting slurry was filtered. The filter cake was washed and then diluted with water, neutralized and treated with cyanide using standard RIL method. After RIL cyanidation the solids in the slurry were separated and subjected to gold assay.

In the process of continuous pressure oxidation each autoclave compartment was also slurry sampled and the solids were treated in the same way as the autoclave discharge. The retention time was calculated in each autoclave compartment by dividing the volume of a compartment and a sum of feed slurry and cooling water fed to the compartment.

Results and discussion. Chemical composition of the concentrates produced on flotation Pilot Plant and corresponding gold recovery achieved after POX are shown in Table 3.

In total, over 50 pilot autoclave runs lasting 10 to 15 hours each were made to oxidize Malomir concentrates and 15 more runs for Pioneer concentrates. Various pressure oxidation parameters

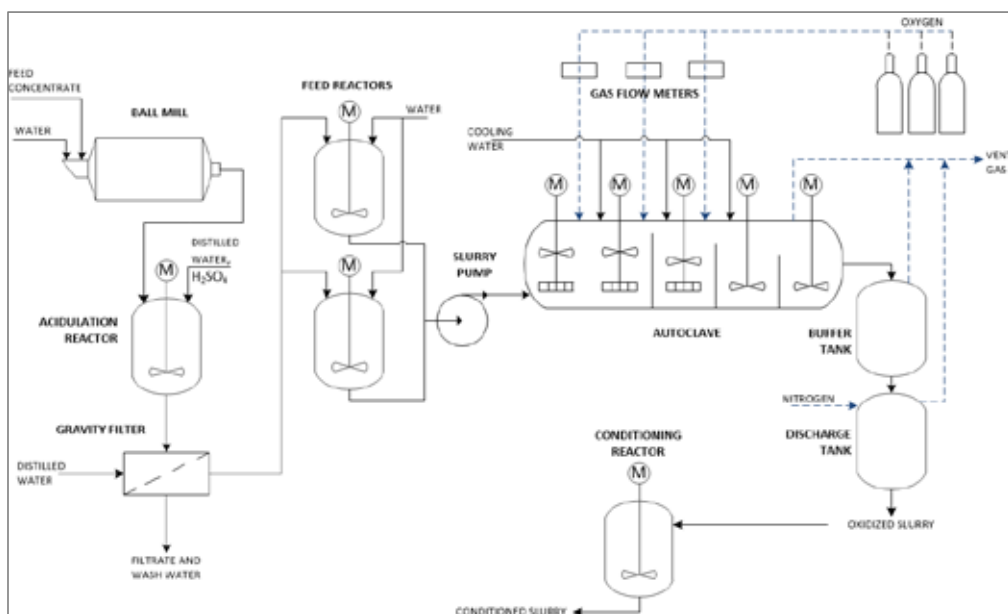


Fig. 2. POX Pilot Plant schematics

Table 3. Concentrates and POX results on Pilot Plant

Date of flotation	Sample	Chemical composition					Gold recovery (%)
		Au (g/t)	Deviation from design (%)	S (S ²⁻) (%)	Deviation from design (%)	C _{org} (%)	
Malomir							
Design		24.3	0	24.9	0	0.6	
April 2011	TS-1	23.3	-4 %	19.8	-20 %	1.7	90-93
December 2011	TS-1	27.9	15 %	23.5	-6 %	0.6	89-96
March 2012	TS-2	36.1	49 %	19.8	-20 %	0.6	90-94
September 2012 (1)	TS3-4	24.8	2 %	19.8	-20 %	1.7	78-83
September 2012 (2)	TS3-4	26.4	9 %	21.4	-14 %	1.0	85-89
September 2012 (3)	TS3-4	29.9	23 %	25.6	3 %	0.7	92
December 2012	TS-5	34.0	40 %	24.8	0 %	0.3	91-93
Pioneer							
Design		27.9		21.0			
2010 – July 2012		27.0-32.0		23.0-28.0			98-99

were tested, such as feed concentrate type, autoclave throughput, oxygen overpressure, concentrate pretreatment method, etc. In general, the dependencies observed in batch laboratory tests were confirmed by the results of continuous pilot tests.

Gold recovery from Pioneer concentrate was 98 to 99 % provided there was adequate level of sulfide oxidation (more than 98.5 %). Autoclave residence time was close to 30 minutes.

A brief description of the factors affecting the gold recovery after POX of Malomir is shown below.

Organic carbon and chloride-ion. The combined negative effect of carbonaceous matter and chloride on gold recovery from Malomir concentrates was observed and confirmed.

With the organic carbon content increase from 0.3 % to 1.7 %, gold recovery decreases by 8–10 % with the chlorides amount in the autoclave slurry was 2-5 mg/dm³ (Fig. 3). Chloride concentration increase leads to significant gold losses (Fig. 4). The mentioned negative effect is more pronounced for higher carbonaceous materials.

Preliminary treatment of flotation concentrates. During the pilot tests, it was confirmed that preliminary acid treatment and water washing of concentrates to remove dissolved chlorides improves gold recovery. Graphically this effect is shown in Fig. 5.

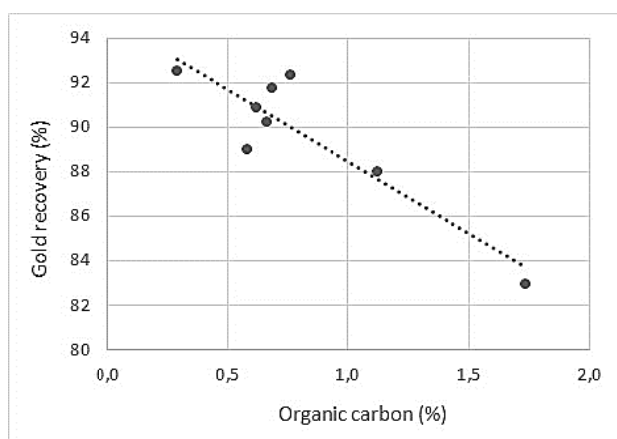


Fig. 3. Gold recovery versus organic carbon content in the concentrate

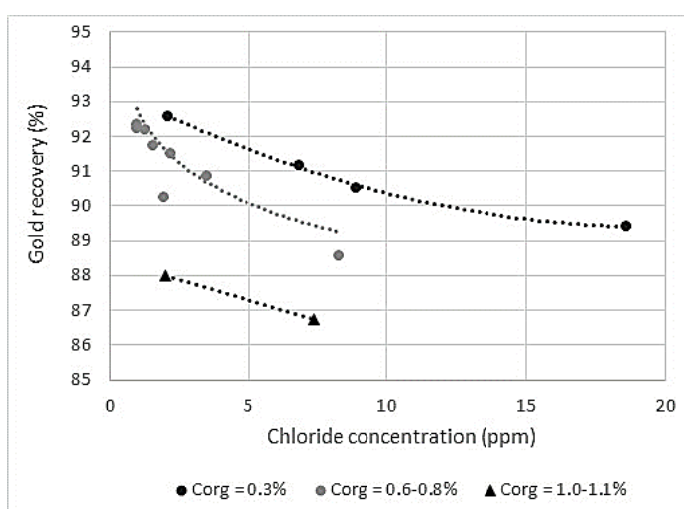


Fig. 4. Gold recovery versus chloride concentration in autoclave slurry for the concentrates with various organic carbon content

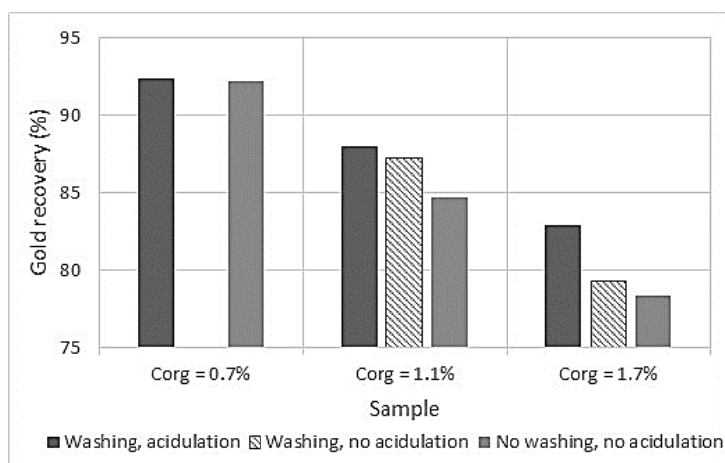


Fig. 5. Concentrate preliminary treatment effect on gold recovery

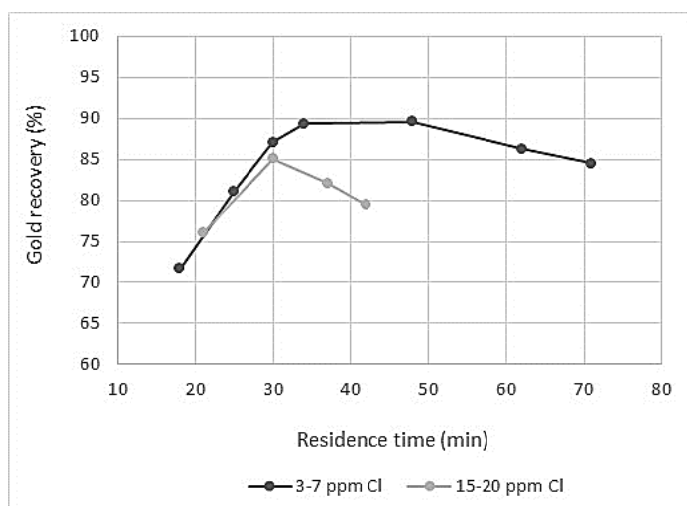


Fig. 6. Gold recovery versus retention time of low-carbonaceous Malomir concentrate (Corg = 0.6 %) in the autoclave

It was observed that as the organic carbon content in Malomir concentrates increases, gold recovery decreases; but also the positive effect of washing increases.

POX retention time. The very special effect of continuous oxidation in multi-compartment autoclave was noted. The continuous process revealed the need to limit the retention time. Oxidation duration should be sufficient to liberate most of the gold from sulfides and concurrently to prevent “over-oxidation” of the material. Graphically gold recovery versus retention time of low-carbonaceous Malomir concentrate is presented in Fig. 6.

It is seen that the curves strongly depend on the chloride content in the autoclave slurry. Gold recovery gradually increases with increasing oxidation duration. Obviously, this is due to the continued oxidation of sulphides and liberation of gold.

The maximum gold recovery in the low-chloride test (3–7 ppm of chloride ion) is 90 % when retention time is 30 to 35 minutes. The further increase in retention time causes a gradual decrease of gold recovery. With increasing retention time, the proportion of decomposed sulfides as well as the amount of liberated gold also increases. This leads to subsequent elevated gold extraction to cyanide solution. Simultaneously oxidizing conditions in the autoclave favor the increasing proportion of ferric iron in solution also favoring conditions for reaction of gold complexation with chloride [3]. The gold complex is then adsorbed on the organic carbon and becomes inaccessible to recovery by conventional RIL.

Gold recovery from autoclave residues subjected to oxidation with excessive amount of chloride in the slurry (15 to 20 ppm of chloride ion) is lower. The maximum of gold recovery is also reached when retention time is near 30 minutes, but it is not higher than 85 %. Further “over-oxidation” of 14 concentrate leads to decrease of gold recovery. However, the negative effect of chloride is more pronounced due to elevated chloride concentration.

Thus, the optimal residence time for continuous process is reached when the most of sulfides are oxidized but no “over-oxidation” is allowed.

POX slurry conditioning. At the end of the pressure oxidation process the ferric ion is a subject to a hydrolysis forming basic ferric sulfate and mixed arsenates and sulfates. The hydrolysis reactions occur under high temperature and could be reversed: the hydrolysis products are dissolved when slurry is cooled. The general practice is to condition slurries under 90 to 100 °C [4].

Conditioning allows (a) decreasing solids yield due to basic iron sulfate decomposition and thus (b) decreasing reactants consumption (mainly lime for neutralization of cake before RIL). Moreover, as shown in Fig. 7, POX slurry conditioning leads to gold recovery increase.

The hydrolysis products formed lock gold and prevent it from being dissolved by cyanide. The subsequent conditioning liberates the gold which is then leached by cyanide. The conditioning of POX slurries consistently leads to gold recovery increase (2.0–4.5 %).

Flowsheet development

The laboratory and pilot tests data evaluation made by SRC Hydrometallurgy resulted in the following recommendations for the Pokrovsky POX technology design:

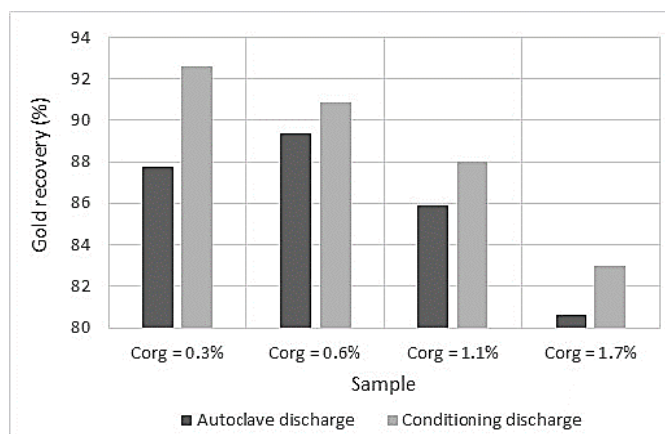


Fig. 7. Conditioning effect on gold recovery

1. Malomir ore flotation flowsheet and reactants addition should be aimed to minimize organic carbon recovery to sulfide concentrate. As a result of the testwork, organic carbon content was reduced from 2.4 % to 0.5 %. This allows increasing gold recovery and significantly reducing recovery sensitivity to the presence of chlorides during POX.
 2. Malomir and Pioneer concentrates should be processed separately. This allows organizing a relatively complex pretreatment stages (acidulation and counter-current decantation washing) necessary to achieve a high gold recovery from carbonaceous materials to process Malomir only.
 3. Only fresh chloride-free water should be fed to Malomir pretreatment and POX stages. The entire amount of neutralized recycle solution (both from Malomir and Pioneer process lines), containing significant amount of chloride, should be used to process Pioneer.
 4. POX parameters should be the following: temperature 225 °C, oxygen overpressure 700 kPa. Pilot tests results along with mathematical modeling of the oxidation process allowed calculation of the effective volume of POX equipment.
 5. POX slurry should be conditioned under 95°C for at least 2 hours to decompose hydrolysis products (basic iron sulfate, mainly) and unlock gold for subsequent cyanidation.
- A simplified block flowsheet is shown in Fig. 8.

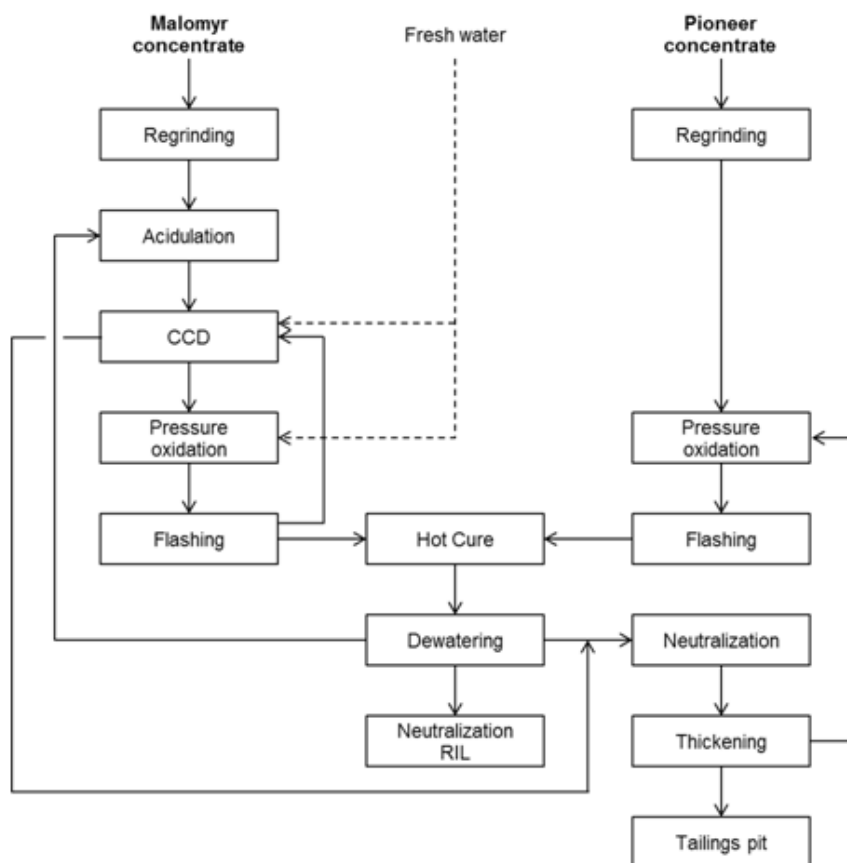


Fig. 8. Pokrovskiy POX flowsheet

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Разработка технологии переработки упорных золотосодержащих концентратов на Покровском автоклавно-гидрометаллургическом комплексе

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Рассмотрен химический состав и минералогия маломирских и пионерских золотоносных руд. Указаны основные формы золота в рудах: отмечено преимущественное соединение золота с сульфидными минералами. Показан химический состав сульфидных флотационных концентратов. Представлены результаты лабораторных и полупромышленных испытаний окисления концентратов под давлением. Отмечено и исследовано влияние содержания органического углерода в концентратах и содержания ионов хлорида в жидкой фазе суспензии окисления под давлением на извлечение золота из материалов. Показано влияние предварительных стадий обработки по показателям технологии автоклавного окисления. Отмечено положительное влияние обработки горячей автоклавной суспензией на извлечение золота. Разработана и рекомендована технологическая схема процесса обработки маломирских и пионерских руд.

Ключевые слова: золотоносные руды, суспензия окисления под давлением, технология автоклавного окисления.
