REVIEW OF THE AVAILABLE GLOBAL TECHNOLOGIES FOR GOLD AND SILVER REFINING

KRASTSVETMET

CPM Group

Krastsvetmet is making this Review of the Available Global Technologies for Gold and Silver Refining available to the world for free, at no cost. As one of the world's leading refiners of precious metals, we have compiled this Review to allow interested parties around the world to be able to find detailed discussions about the available refining technologies in one Review.

Krastsvetmet, founded in 1943, produces eight precious metals (Au, Ag, Pt, Pd, Rh, Ir, Ru, Os), processes mineral and secondary raw materials of any complexity, and makes fine metals out of it with a purity of up to 99.99%. Apart from fine metals, we do chemical compounds and catalysts for petrochemical, chemical, pharmaceutical industries, as well as industrial appliances for ammonia oxidation and glass making, and jewelry.

Company's main production facility is located in Krasnoyarsk, the capital of Russia's second-largest region. The Krasnoyarsk Territory is the country's leader in precious metal mining and the location of the richest deposits of gold and platinum group metals.

On a separate note, Krastsvetmet runs R&D Park, a facility for technology development and its transfer to industrial companies, that supports innovations and startup companies with funding, infrastructure and technology validation.

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List of abbreviations:

PM – precious metals

PGM – platinum group metals

BM – base metals

BE – base elements

WIP – work-in-progress

ORP – oxidation-reduction potential

INTRODUCTION

This review is based on materials of scientific publications and on long-term experience of Krastsvetmet. It provides a description of world refining technologies: the preparatory stage, dissolution of raw materials and reduction of pure precious metals.

The objective of the review is to analyse the existing methods of refining of gold and silver group metals and to provide guidance on technology selection.

The demand for precious metals (PM) is increasing annually. This stimulates the search for new sources of raw materials and improvements of the existing refining technologies.

There is a large variety of raw materials sent to refineries to produce gold. Most of raw materials come in the form of gold-zinc precipitation alloys, alluvial gold recovered from the enrichment process of placer deposits and ores, cathode unrefined gold from thiourea solution and alkali reclaims, domestic and industrial scrap, coins, dentistry waste, e-scrap, and other materials.

The main silver reserves are concentrated in complex polymetallic ores deposits. That is why: Silver is often a by-product of mining for other metals. Metallic silver is produced during the processing of various types of technogenic materials. Silver bearing raw materials used at refineries mostly come in the form of Dore, zinc precipitates, chloride slags, and other products. Additionally, secondary raw materials come in the form of e-scrap, silverware, etc.

Listed materials have a complex chemical composition. Apart from gold and silver, they contain copper, lead, mercury, arsenic, antimony, tin, bismuth and other impurities. The content levels of impurities and byproducts can reach 20% and more.

There are about 150 refineries all over the world. Electro-refining and solvent extraction processes are the most widely used processes in modern gold refineries. The Miller process, the hydrochlorination process and acid refining also are commonly used as standard processes in refineries.

The line between secondary metallurgy plants and refineries blurs, mostly because of competition over the sources of raw materials. The modern refineries are plants processing different types of raw materials and producing bars and billets as well as finished products for jewellery and dental industries, electronics and electronics, etc.

Due to an increasing volume and the simultaneous reduction in the quality of raw materials, special attention must be placed on the development and implementation of highly efficient processes that allow production of refined metals, to decrease in the volumes of the work-in-progress, to ensure a reduction in energy consumption, to reduce precious metals losses, to automate processes, and to improve working conditions.

The final election of refining technology for each specific plant depends on many factors such as the content and the quality of raw materials it will source, the types of impurities, the existing infrastructure, as well as environmental and financial considerations. The main criteria in the choice of refining technologies are the lowest levels of negative impacts on the environment and economic effectiveness.

Initial raw materials first undergo primary melting and testing to ensure a reliable result for purchase and acceptant purposes. After the melting and testing, alloys refined on the different methods depend on the PM content.

Based on the conducted analysis of gold refining technologies the following methods were distinguished:

1. Pyrometallurgical methods:
   - processing of the fused metal with chemical reagents to separate from impurities (Miller Chlorination Process);
   - removal of impurities by smelting with fluxes in order to improve the gold product quality;
   - vacuum distillation.
2. Electrolytic methods.
3. Hydrometallurgical methods (including dissolution in different acids).
4. Extraction methods.

The gold (Fig. 1) and silver (Fig. 2) refining processes have the following stages:

1. Removal of impurities.
2. Gold-silver dissolution.
3. Precious metal reduction.
4. Melting finished products in the form of bars and granules.

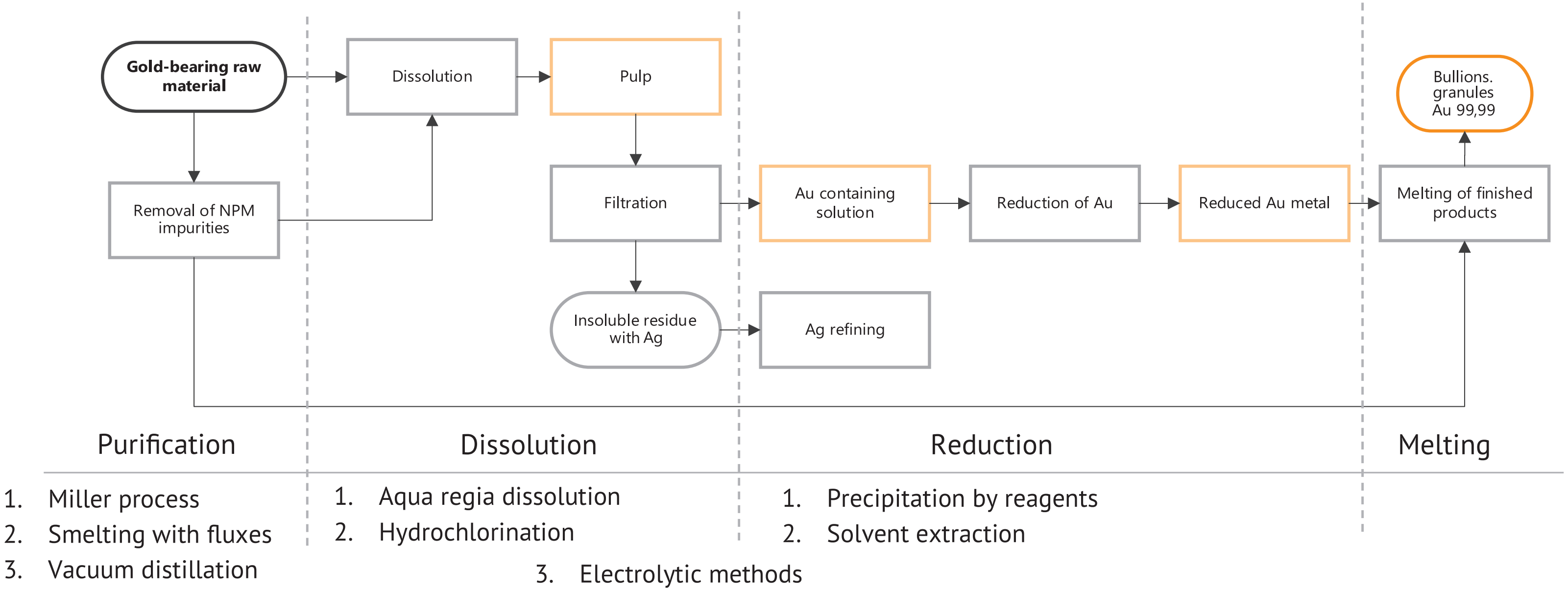
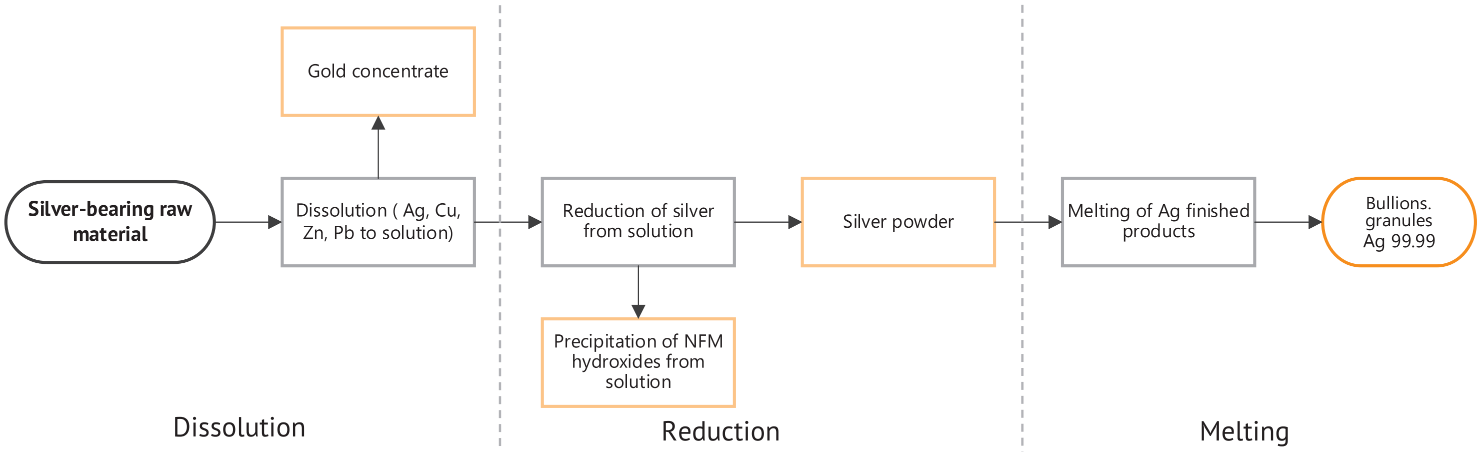


Fig. 1 – General layout of gold refining operations.



Dissolution
1. Dissolution in nitric acid
2. Dissolution in sulphuric acid
3. Electrolytic method

Reduction
1. Electroextraction
2. Precipitation by reagents

Fig. 2 – General layout of silver refining operations.

AVAILABLE GLOBAL TECHNOLOGIES FOR GOLD REFINING

1. Removal of impurity elements

1.1 Miller process

Separation of silver and other metals from gold by treating with gaseous chlorine was known in the early 1800's. The process was suggested in 1838 by Louis Thompson, but was first patented and implemented in 1865 by Francis Bowyer Miller at the Sydney Mint in Australia. Since then it has been known as the Miller process. The process involves purging gaseous chlorine through molten metal to be refined.

The feedstock may contain 80–90% Au, 7–11% Ag, and admixtures of copper, lead, iron, and zinc. The process is performed in alumina-lined graphite crucibles in induction electric furnaces. Crude metal that has passed incoming smelting is loaded as bars into a crucible with a capacity of up to 500 kg by gold. A mixture of sodium borate, quartz and sodium chloride is loaded into the crucible to form slag. The forming thin layer of slag reduces gold evaporation and preserves crucible walls from corrosion.

After the metal melts, one or two porcelain tubes are introduced via the crucible lid to supply gaseous chlorine. The process is performed at 1150°C. According to thermodynamics, zinc, lead and iron are the first to interact with chlorine. Low-boiling iron and zinc chlorides pass into gas phase. A partial evaporation of lead chloride also takes place. This step of the process is accompanied by vigorous bumping of the melt, and therefore chlorine is supplied to the melt slowly.

Copper and silver start reacting with chlorine only after the bulk of iron, zinc and lead has been chlorinated. The boiling points of copper and silver chlorides are higher than the process temperature, thus they remain in the crucible, forming a layer of molten chlorides at the surface of gold.

The molten chlorides and slag accumulating at the metal surface are periodically removed, and fresh flux is added. The end of the process is determined by the appearance of a yellow golden film on the chlorine-supplying tubes and the appearance of red fumes over the melt, the colour being determined by the presence of gold chloride. After completing the chlorination, the remaining chlorides and slag are removed from the metal surface, and the purified gold is transferred to the mixer and cast into bars.

The removed chlorides contain a rather substantial amount of entangled dore beads. To recover gold, these are smelted with soda, with part of the silver being reduced and entraining most of the gold present in the chlorides as it sinks to the bottom. Calcined soda decreases the amount of silver chloride in the salt, while metallic silver picks up incidental gold particles into a metal bead that is separated from the remaining salt upon cooling. The obtained silver-gold alloy is recycled to the chlorination step. Chlorides serve as the feedstock to obtain silver.

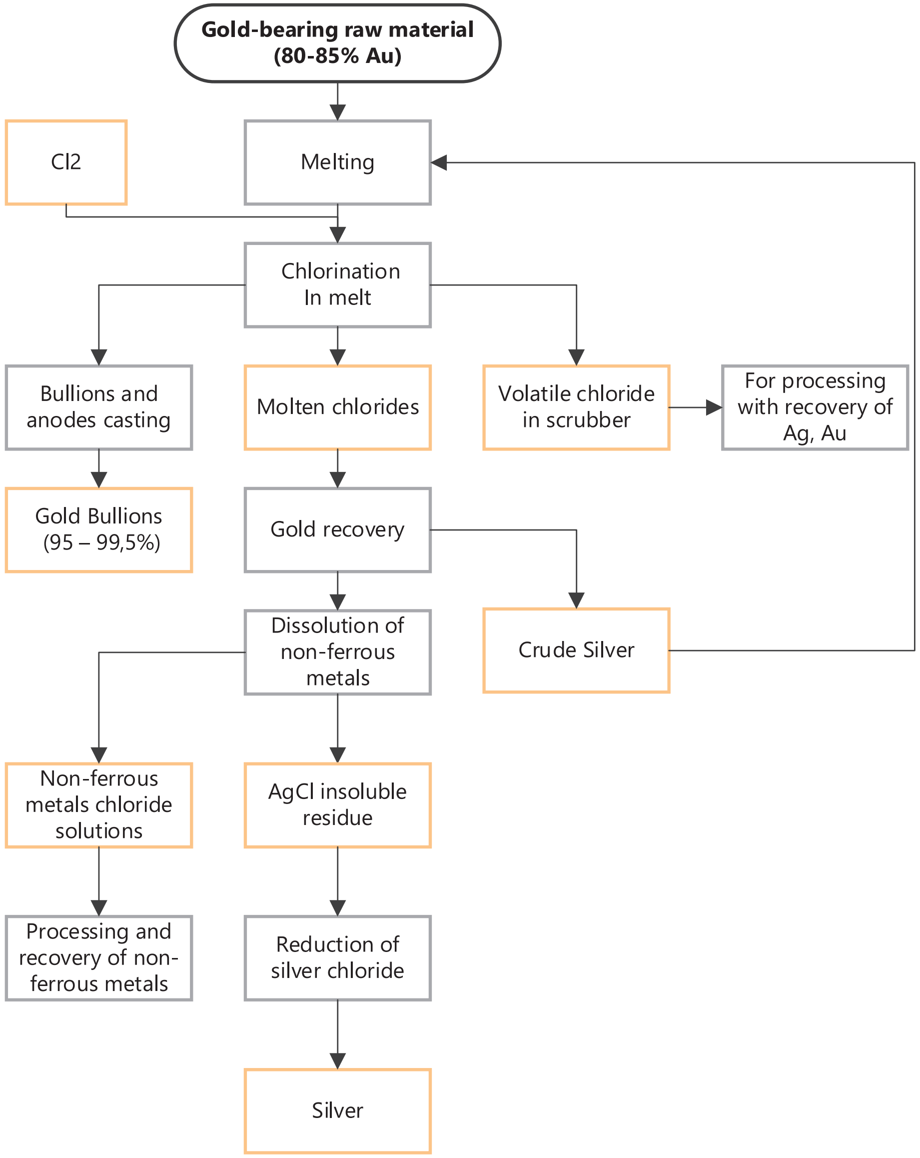


Fig.3 Complex flowchart of the Miller process.

Item	Advantages	Disadvantages
1	Possibility to remove with chlorination almost all base metals (BM) and silver in the melt to obtain gold with purity up to 99.5%.	Partial sublimation of gold into gas duct and scrubber at the end of the process at low concentrations of BM and silver in Dore alloys. **Solution:** stopping the chlorination at gold content 93 to 98% to avoid gold evaporation.
2	Quick turnaround times of refining, ease and suitability for refining gold of any purity.	Extended residence of gold in side products between recovery steps. Additional costs for utilisation of substantial amounts of middlings.

1.2 Smelting with fluxes

Smelting with fluxes is appropriate for processing zinc precipitates and lean gold-silver concentrates containing from 5% gold. As a rule, such materials have a high concentration of base elements (BE).

Either original concentrates or concentrates after hydrometallurgical enrichment are received at the smelting, which is determined by gold content and the type of impurity elements. Fig. 4 shows a complex flowchart of the process.

A preliminary hydrometallurgical enrichment is necessary to remove the bulk of zinc and other acid-soluble impurities complicating smelting with fluxes.

The smelting is required to remove additional impurities and obtain a gold-silver alloy suitable for refining. Soda, sodium borate, quartz sand and calcium fluoride are used as the fluxes. The precipitates always contain a certain amount of sulphur, therefore there is a risk of forming matte that effectively dissolves PM.

To exclude matte phase formation, in addition to fluxes an oxidiser, i.e., sodium nitrate $NaNO_3$ or manganese dioxide MnO_2, is introduced into the charging materials for smelting precipitates with high sulphur content. The addition of an oxidiser not only prevents matte formation, but also promotes oxidation of BM and their passage to slag, resulting in a higher purity of the gold-silver alloy.

This method is also used to enrich cathodic gold produced from thiourea and alkali eluates in the processing of gold ores by sorption cyanidation on resins or coals. The obtained cathode precipitates contain up to 10–20% iron, nickel, copper, and other metals. After smelting with fluxes and oxidiser, the total gold plus silver content in the alloy is 95–99%.

The slag produced by smelting contains entangled PM beads. It is therefore collected and remelted as accumulated. Upon pouring the remelted slag into molds, its lower part is found to be substantially enriched with precious metals. This part is separated, and gold and silver from the remaining part are recovered in a separate branch. The obtained gold-silver alloy is sent to refining.

Item	Advantages	Disadvantages
1	Possibility to process lean concentrates containing from 5% gold with a high content of impurity elements.	Implementation of the technology involves formation of a large number of middlings (et, slag, solutions and industrial waters) that require additional processing.
2	Smelting with fluxes produces a 95–98% alloy (total gold plus silver).	The forming middlings result in an incomplete production and a channel of PM waste; The mass of middlings increases due to using fluxes; The technology involves multiple steps.

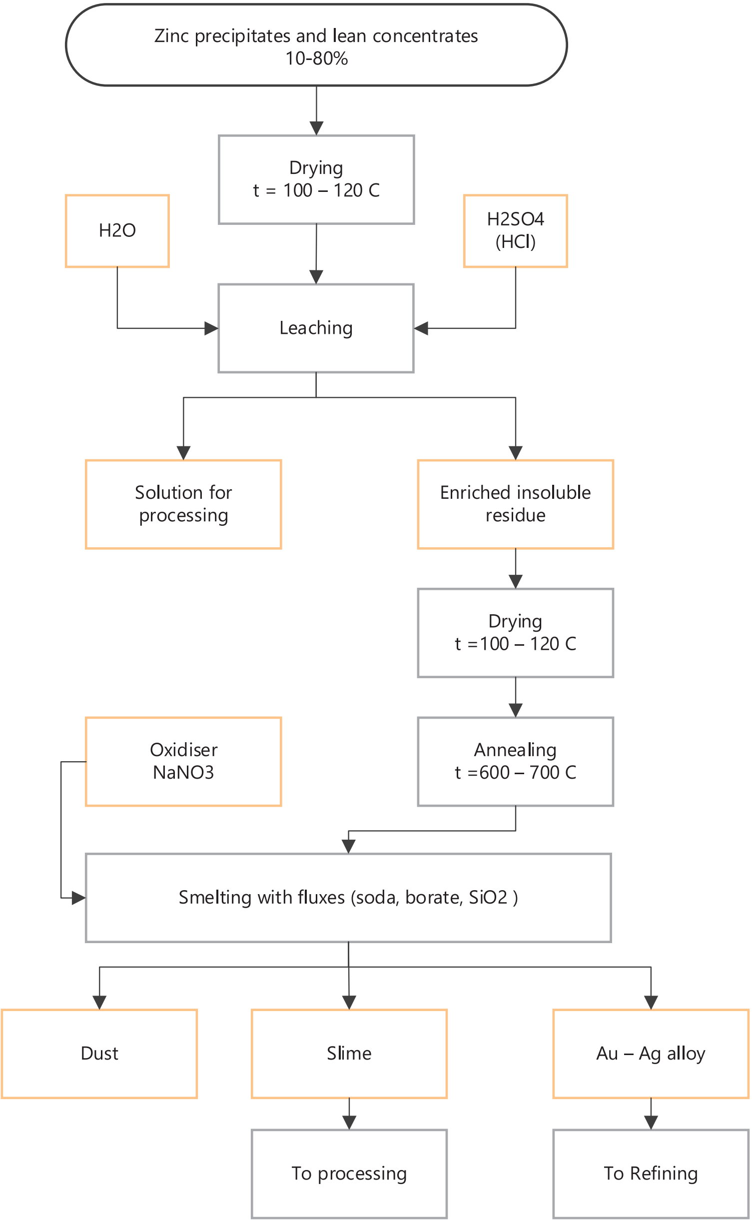


Fig. 4 Complex flowchart of the smelting with fluxes process.

1.3 Vacuum distillation

One of the most interesting modern methods is the process of “vacuum distillation”, developed in Russia. The method includes melting Dore alloy and then creating a vacuum to distill away volatile metals such as zinc, silver and lead. The evaporated metals are collected on a cooled condensation plate located before the vacuum pump.

A gold-silver alloy with silver content 1 to 90% is loaded into a graphite crucible. Then, rarefaction is created using a vacuum system. Following that, the graphite crucible is heated to 1220–1450°C, and the cone tip is heated to 900–1200°C, and the process of vacuum distillation is performed. In the process of distillation, the silver from the vapour phase condenses as solid metal particles on the cooled condenser.

By an appropriate choice of temperature and vacuum conditions, different metals can be distilled from the melt separately. The product is a bar containing mostly gold and copper, which can then be subjected to further refining by known methods.

Depending on the composition and mass of the charged material for processing, the complete cycle may take 40–90 min, after which it is repeated; recovery is more than 98%. The plant can be operated continuously given sufficiently large volumes of feedstock received for processing. Fig. 5 shows the principal process flowchart, and Fig. 9 illustrates the plant design.

This is essentially a process of preliminary purification and separation of gold and silver that can be considered as a potential substitute for the Miller process. The process has substantial advantages, as it eliminates chlorine usage and formation of a large number of side products containing low amounts of precious metals.

Item	Advantages	Disadvantages
1	Reduces expenses for recirculated metal, lowers operating expenses, and minimises hazardous emissions to working zone and environment.	High cost of equipment.
2	Significantly shortens the duration of refining gold-silver alloys with high silver content (above 10–15%).	Equipment requires qualified service and maintenance.
3	Process automation, reduction of waste, environmentally safe technology.	
4	Minimum amount of middlings in easily processable form.	

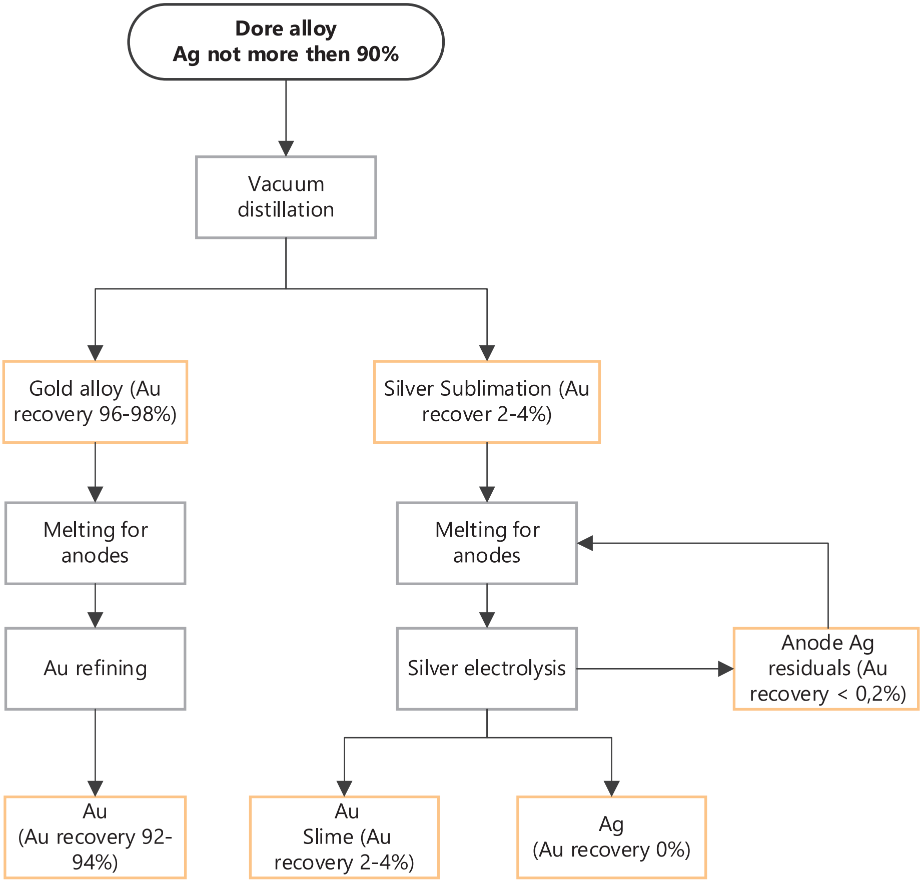


Fig. 5 Complex flowchart of the vacuum distillation process.

2. Breaking down gold-silver materials

2.1 Aqua regia dissolution

Breaking down with aqua regia is applicable only to alloys containing not more than 10% silver. Research staff members at Krastsvetmet have developed a method to perform aqua regia dissolution capable of processing feedstock with silver content of up to 20% silver in the starting alloy.

The alloy to be purified (in the form of chips, powder, granules, etc.) is treated with aqua regia upon heating. Gold passes into solution, forming chloroauric acid, and silver, in the form of chloride, remains in the insoluble residue, from which metal silver is obtained.

Dissolution in aqua regia occurs according to one of the following two reactions:

$$\mathrm{Au + 3HNO_3 + 4HCl \rightarrow HAuCl_4 + 3NO_2 + 3H_2O} \qquad (1)$$

$$\mathrm{Au + HNO_3 + 4HCl \rightarrow HAuCl_4 + NO_2 + 2H_2O} \qquad (2)$$

Silver content in the feedstock above 10% results in the risk of incomplete dissolution of gold by forming a passivating layer of silver chloride at the surface of metal. Melting and dispersing the material enhances the process of dissolution in aqua regia, ensuring a sufficient surface area for acceptable reaction kinetics. To accelerate the reaction, the solution is heated in the course of dissolution.

Silver is one the most common sources of contamination in refined gold, therefore dilution and cooling of aqua regia leaching solutions are employed to minimise AgCl solubility prior to filtering. The technology of aqua regia dissolution demands higher standards of filtration quality to avoid contamination with silver chloride.

Item	Advantages	Disadvantages
1	Allows dissolution of much larger particles due to its reaction mechanism, with NOx evolution at dissolution border.	Formation of large volumes of off-gases containing NOx that increase the cost of gas cleaning. Process solutions after refining contain nitrate and nitrite ions that have to be neutralised.
2	Aqua regia dissolution is a simple, rapid and efficient method to obtain a gold-containing solution of high concentration.	The method consumes high amounts of expensive nitric acid, which reduces its operating efficiency in comparison with hydrochlorination.
3		Processing feedstock with silver content above 10% using a conventional approach is problematic.

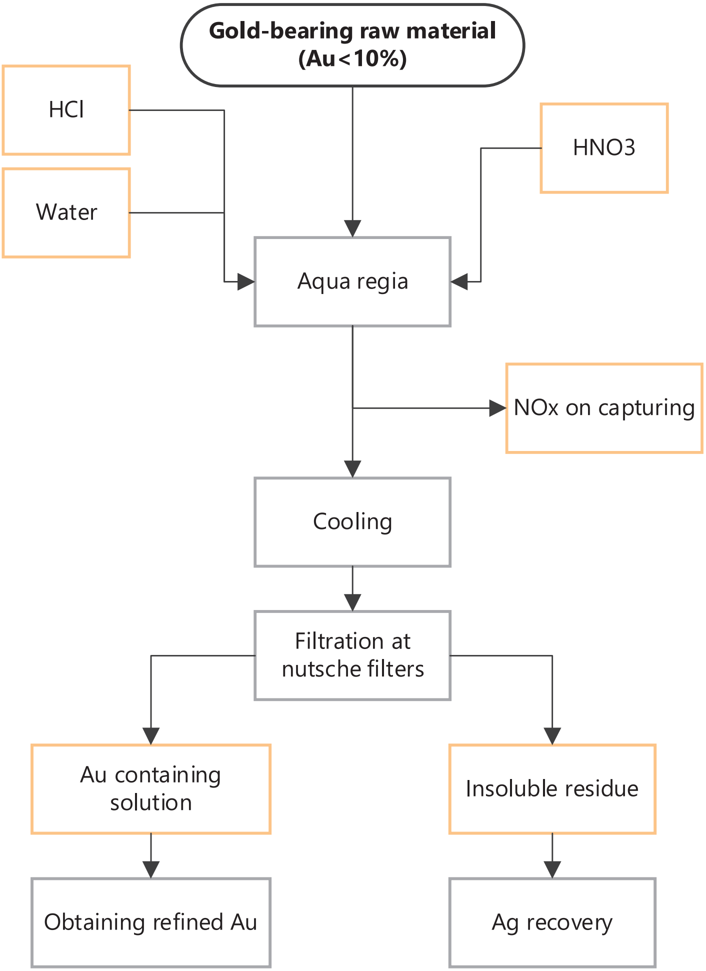


Fig. 6 Complex flowchart of the Aqua regia dissolution process.

2.2 Hydrochlorination

The use of chlorine gas in combination with hydrochloric acid is an alternative to dissolution in aqua regia. In this process, chlorine gas is passed through a vigorously agitated suspension of gold powder (chips) and hydrochloric acid. Gold dissolution occurs according to the following reaction:

$$2Au + 2HCl + 3Cl_2 \rightarrow 2HAuCl_4 \quad (3)$$

As in the aqua regia dissolution process, the silver content in the feedstock should not exceed 10% to avoid passivation by silver chloride. In practice, the silver content should not exceed 8% to achieve higher recovery.

The dissolution rate of gold in aqua regia is reported to be higher than in hydrochlorination. Comparable dissolution kinetics can be achieved for hydrochlorination if gold is fed in the form of fine powder (flakes) before breaking down the material.

The rate of gold dissolution depends on the solubility of chlorine gas in the solution. Improved dissolution kinetics are achieved by conducting dissolution in a pressurised reactor. The partial pressure created by the unabsorbed chlorine in the space above the solution in the reactor is a reaction control parameter.

As in the case of dissolution in aqua regia, excess oxidiser should be removed from the solution to minimise the negative effect of chlorine on the subsequent reduction process. The residual dissolved chlorine is easily removed by displacement with air while the solution is still hot.

This operation requires much less time and energy than the repeated and lengthy operation of adding HCl and boiling the solutions required to remove nitrates from the aqua regia solution.

Item	Advantages	Disadvantages
1	The method is efficient because its cost is 30–40% lower than that of aqua regia dissolution.	Necessary infrastructure is required to handle liquefied chlorine.
2	The unused chlorine in the gas phase is much easier to scrub than NOx gases produced by dissolution in aqua regia.	More stringent standards for storage, handling, and control of chlorine gas than for nitric acid.
3	Technology allows for process automation and ease of control.	

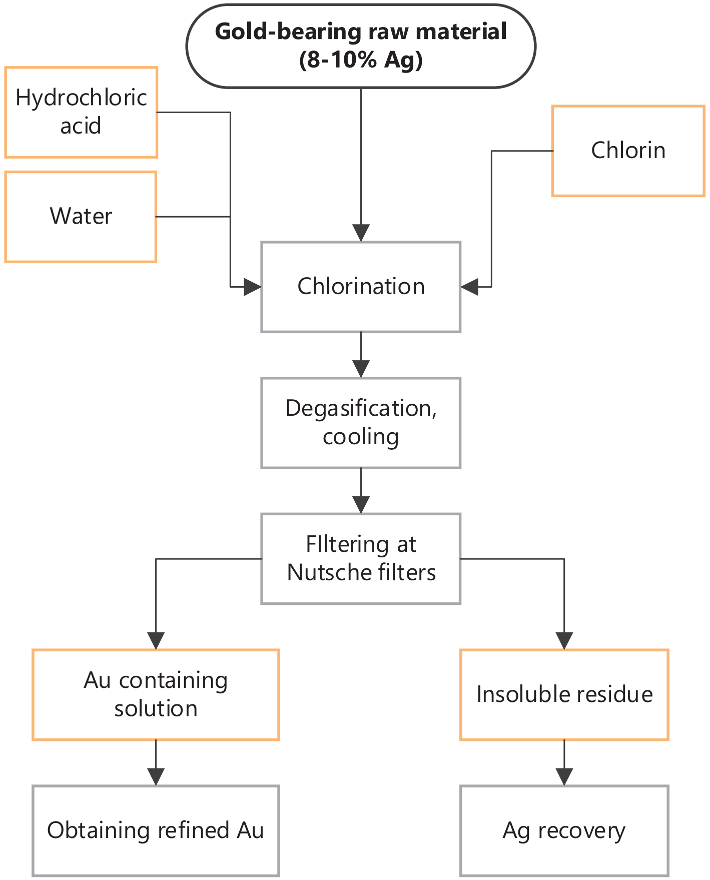


Fig. 7 Complex flowchart of the Hydrochlorination process.

3. Gold reduction

3.1 Electrolytic method

3.1.1 Chloride electrolysis technology (Wohlwill Process)

Gold anodes obtained as a result of breaking down and smelting are refined in concentrated hydrochloric acid electrolytes. Contaminated anodes are electrolytically dissolved, while pure gold is plated onto the cathode. The basic electrorefining configuration shown in Figure 10 has little changed since its invention in 1878 by Emil Wohlwill in Norddeutsche Affinerie (Germany).

The processes of anodic dissolution and cathodic reduction are simple, but the process is complicated by the formation of Au+ and AuCl2 particles in the solution that disproportionate into metallic gold and Au3+, creating a substantial amount of gold slime at the bottom of the electrolysis cell. A periodic collection of slime is necessary to process the stagnant gold reserves at the bottom of the cell.

Anodic dissolution $Au + 4Cl^- \rightarrow AuCl_4^- + 3e$

Cathodic reduction $AuCl_4^- + 3e \rightarrow Au^0 + 4Cl^-$

$3AuCl_2^- \rightarrow 2Au^0\downarrow + AuCl_4^- + 2Cl^-$

Gold is reduced at cathodes and collected mechanically using various methods, most of which are based on manual labour. Some refineries avoid manual separation of the deposited gold from cathodes by depositing a plating of pure gold. This decreases the demand for manual labour, but manufacturing and additional gold stock introduce new operating expenses.

Similar operations limit anodes in bags to separate anodic slime from bulk electrolyte and capture insoluble materials, in particular AgCl that forms at the anode.

One of the main problems related to electrolytic refining is maintaining the level of gold concentration in electrolyte. Electrolyte requires gold concentration higher than 100 g/l. Control and reduction of concentration of BM and PGM (platinum group metals) that continuously build up in the solution is also required to avoid exceeding the allowable limits.

To limit the continuous depletion of gold from electrolyte, some processers add nitric acid. Nitric acid performs two functions: the first is to oxidise Au+ to Au3+ and thus reduce the amount of slime; the second is to dissolve gold from slime and anode by reaction of aqua regia dissolution.

Anodic slime is unloaded from cells and washed from electrolyte with water. The washing waters are used to tip the cells. The slime is loaded into a silver sieve drum immersed into a bath filled with water. As the drum is rotated, silver chloride is washed into the bath through sieve openings, while larger particles of golden anode scrap and cathodic gold dendrites remain in the drum.

The gold residue is dried and returned to melting for anodes. Silver chloride is reduced with iron scrap or powder in hydrochloric acid medium, washed with water, and melted for anodes for silver electrolysis.

In the process of electrolysis, the electrolyte is enriched with impurities and depleted in gold. When operating with contaminated electrolyte, contamination of cathode deposits due to deposition of impurities is possible. Furthermore, with electrolyte contamination at the cathode, dendrite growth begins, which leads to shortening of the electrodes, while at the anode, salt crystallisation occurs, resulting in anode passivation.

The electrolyte is not suitable for further use if the concentration of gold in it is below 100 g/l, and the concentration of impurities exceeds the following limits, g/l: 90 Cu, 50 Pt, 15 Pd, 1.5 Pb, 4 Te, 2 Fe. To process the spent electrolyte, it is poured into special cells, where most of the gold is recovered using electrolysis with insoluble anodes.

Gold reduction from spent electrolytes and repeated dissolution of the deposited gold sponge, together with repeated dissolution of gold slime from the cell, are cyclic operations that increase production reserves.

3.1.2 Technology of aqua regia electrolysis

For finishing purification of Dore alloy from impurities, a process of electrochemical refining using aqua regia electrolyte is available.

The process of electrochemical gold refining using aqua regia electrolyte can successfully recycle jewellery waste with gold content 55–60%, Dore alloys having relatively high (above 15%) contents of silver and platinum group metals, with straightforward recovery of silver, platinum and palladium from solutions and slimes.

The amount of impurities in cathodic gold does not exceed 40 g/t for any quality of the anodic metal. To process anodic metal with high silver content (18–22%), an aqua regia electrolyte with varying concentration of nitric acid (floating concentration method) is used.

The method takes advantage of the tendency of any electrochemical system to reach an equilibrium state. At the first step, a concentration of nitric acid exceeding the usual process norm by a factor of 1.5–2 is maintained in the electrolyte. At such parameters, the process shifts to anodic dissolution, with practically no metal being deposited at the cathodes.

As the anodes dissolve, the concentration of acid decreases, and the process of cathodic deposition gradually takes over. To intensify the process of anodic dissolution, a reversed current supply to electrodes is employed at the first step, with the ratio of the durations of direct and reversed current being 40:1.

At the second step of the process (after reaching 60–70% dissolution of anodic metal), the reverse is switched off, and the process of cathodic gold deposition proceeds in normal mode. The obtained cathodic gold (the content of the main component is above 99.99%) is melted into final product bars or is partially (in case of production need) used as immobilised (recycle) material to reduce silver concentration in the anodic metal.

After separation and reduction smelting or after electrochemical silver reduction, the obtained silver chloride is sent to refining. Platinum group metals are accumulated in the electrolyte and are recovered using existing technologies.

To eliminate the passivating effect of slimes on anode dissolution, a regular mechanical cleaning of anodes is required; it is necessary to periodically (once daily) remove silver chloride from anode surface to ensure the required rate of the anode dissolution process.

Item	Advantages	Disadvantages
1	The process of aqua regia electrolysis guarantees the quality of cathodic gold with purity of at least 99.99% at any quality of the anodic metal.	If low-grade Dore alloys (having gold content 60–80% and silver content 12–15%) are used as anodic metal, a substantial amount (up to 30% of the weighted anodic metal) of anodic slime is formed that consists mostly of silver chloride.
2	Dore alloys with gold content 65–70% can be used as anodic metal, while in the Wohlwill Process the gold content in anodic metal cannot be lower than 85%.	Given equal quality of anodic metal and other conditions being equal, a chloride electrolysis cell has a higher (by 8–10%) throughput.
3	The process of aqua regia electrolyte preparation is simplified, i.e., the electrolyte is prepared directly in the electrolysis cell from anodic metal and acid solution by electrochemical dissolution. In chloride electrolysis the electrolyte is prepared using cathodic gold and a separate electrolysis cell with a thorough filtration of the obtained electrolyte.	The main disadvantage is a high degree of incomplete production and the duration of the electrochemical process, both conventional and aqua regia ones; Nitric oxides are formed in the process of aqua regia electrolysis.

The electrochemical method using aqua regia electrolyte is more efficient for processing Dore alloys with gold content below 85% than the Miller method (melt chlorination with gaseous chlorine) and the method of aqua regia dissolution with subsequent selective precipitation of gold and silver.

3.2 Liquid extraction

In the operations of liquid extraction the hydrochloric breakdown solutions containing gold are subjected to the step of solvent extraction for selective removal of gold from a heavily contaminated solution.

Many known solvents are used to recover gold from solution by extraction: methyl isobutyl ketone (MIBK), dibutylcarbitol (DBC), tributylphosphate (TBP), chlorex, extragents based on dialkylsulphides and petroleum sulphides.

An example is the implementation of the extraction technology, in which gold is extracted from hydrochloric (2-5 M HCI) solution with tributylphosphate (or its solution in kerosene), and gold re-extraction from the organic phase is performed with a solution of a reducing agent, such as sodium sulphite. Thus, obtained metallic gold powder (by purity) corresponds to high grade gold.

Vale Acton refinery (Great Britain) uses dibutylcarbitol for selective extraction of gold from PGM-rich chloride breakdown solution, after which gold is precipitated from the organic phase using oxalic acid. Johnson Matthey (Great Britain) and Anglo American Platinum (South Africa) also use methyl isobutyl ketone to extract gold from PGM-containing solutions with subsequent direct reduction of gold from the organic phase with oxalic acid.

Item	Advantages	Disadvantages
1	Allows gold extraction from solutions with low gold content and high impurity content.	Allows gold extraction from solutions with low gold content and high impurity content. Process fire hazard, more stringent requirements to rooms.
2	Possibility to obtain rich concentrates with above 98% Au content from solutions with high BE content.	Solubility in water and residual content of the organic phase in solutions after extraction.
3	Possibility to obtain refined gold from solutions with low impurity content.	Substantial amounts of WIP in solutions for most devices (less in centrifugal ones).

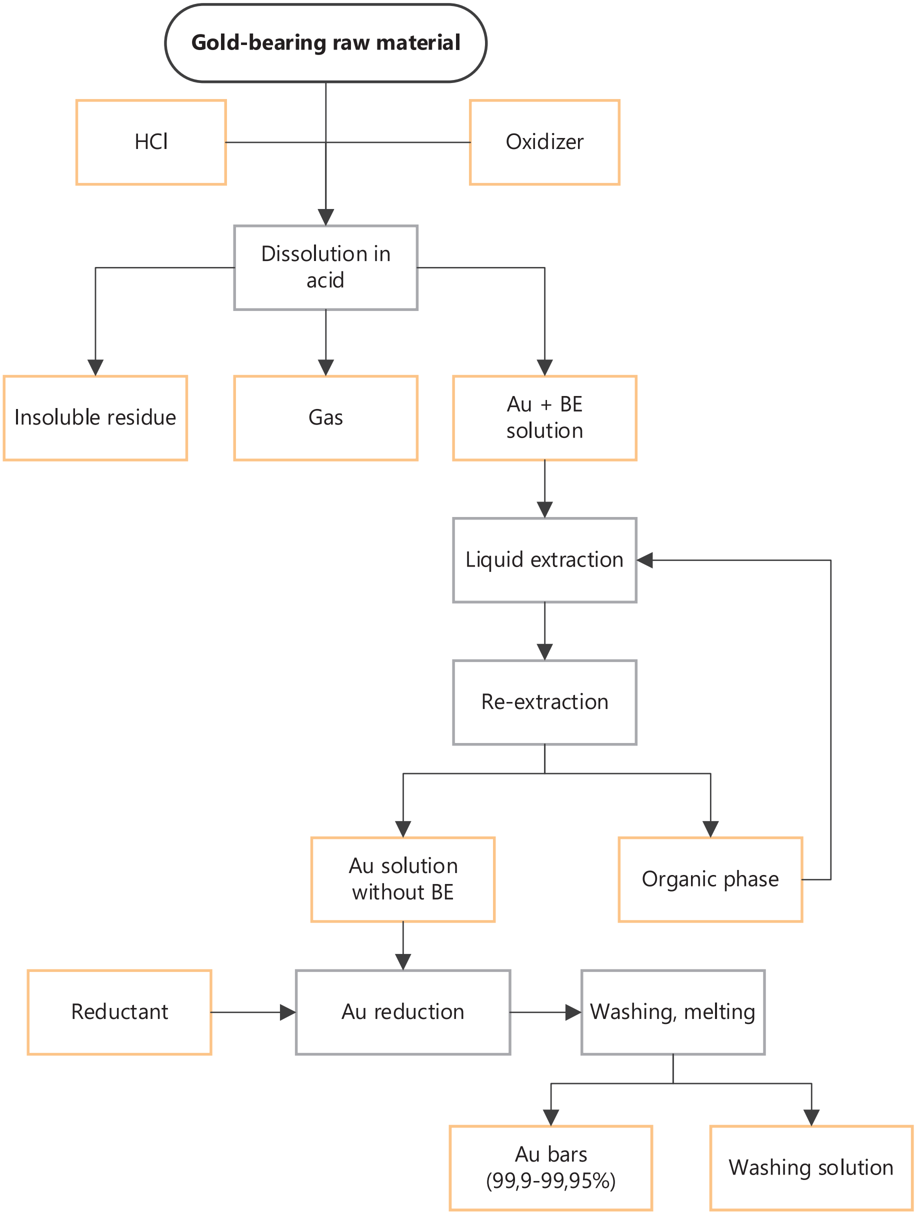


Fig. 8 Complex flowchart of the liquid extraction process.

3.3 Precipitation by reagents

Precipitation by reagents is typically the final stage in Au refining process, after the stages of purification, separation of gold from silver and basic impurities, and breakdown of gold-containing materials.

A great number of various reagents can be used to reduce gold from solutions, including base metals, their compounds, in which metals are in their lowest oxidation states, organic compounds, inorganic reducing agents. The following are most commonly used for this purpose: sulphur dioxide (SO2), sodium metabisulphite (Na2S2O5), ferrous sulphate (FeSO4) and formic acid (HCOOH), sodium nitrite (NaNO2), hydrazine hydrate (N2H4*H2O). The respective reduction reactions are shown in equations 7 to 12.

$$2HAuCl_4 + 3SO_2 + 6H_2O \rightarrow 2Au + 8HCl + 3H_2SO_4 \quad (7)$$

$$2HAuCl_4 + 3Na_2S_2O_5 + 9H_2O \rightarrow 4Au + 10HCl + 6NaCl + 6H_2SO_4 \quad (8)$$

$$HAuCl_4 + 3FeSO_4 \rightarrow Au + HCl + FeCl_3 + Fe_2(SO_4)_3 \quad (9)$$

$$HAuCl_4 + 3NaNO_2 = Au + 3NaCl + 3NO_2 + HCl \quad (10)$$

$$4HAuCl_4 + 3N_2H_4 = 4Au + 3N_2 + 16HCl \quad (11)$$

$$2HAuCl_4 + 3HCOOH \rightarrow 2Au + 8HCl + 3CO_2 \quad (12)$$

The most common method for recovering dissolved gold is to purge the rich solution with gaseous SO2 in the presence of approximately 6 g/l of sodium ions added to the solution in the form of sodium chloride. Sodium ions promote the formation of easily filterable and dried gold sponge.

Although precipitation can be performed in one step, care should be taken to avoid oversaturation with SO2, especially if the concentrations of selenium, tellurium and PGM are high. Once all the gold is completely reduced from the solution, any subsequent reduction of these metals will contaminate the gold sponge product.

There is a two-step approach, in which up to 95% of gold is precipitated at the first step by controlling oxidation-reduction potential (ORP) to about 650 mV (relative to saturated calomel electrode): after reaching 650 mV, the deposited gold is filtered from the solution and washed with dilute hydrochloric acid and hot water.

This produces a > 99.99% pure gold sponge, which is then dried and melted in preparation for the production of bullions or added-value products. The depleted solution and wash waters are reheated and purged with SO2 until the ORP drops below 350 mV (compared to the standard hydrogen electrode) to precipitate the remaining gold from the solution.

The reduction of gold with sodium sulphite (bisulphite) occurs in a similar manner. The difference is the absence of difficulties associated with feeding a solid reagent into the solution and its availability.

Iron chloride is also an inexpensive and accessible reagent, the use of which does not cause any difficulties. But the main disadvantage of its use is lower purity of the resulting product. This reagent is often used for the recovery of gold from solutions resulting from the breakdown of PGM concentrates containing platinum and palladium in prevailing amounts.

Sodium nitrite selectively reduces gold without affecting platinum and base elements, in relation to which it is an oxidising agent. It can reduce gold from solutions deeply enough, to residual concentrations of several milligrams per dm3. It recovers gold from neutral or weakly alkaline solutions best. The main disadvantage of its use is the formation of nitrogen oxides, which should be disposed of.

Formic acid and hydrazine hydrate do not act selectively on gold. They can also reduce platinum, palladium, silver and, when in excessive amounts, also base elements (selenium, tellurium, copper). In addition, hydrazine hydrate is a Hazard Class 1 substance. It is necessary to take special precautions and use special protective equipment during its handling. The relatively high cost of these reagents also limits their use. They are normally used to recover gold from impurity-free solutions, or to concentrate gold from barren solutions.

Item	Advantages	Disadvantages
Sulphur dioxide, sodium bisulphite		
1	High reduction rate.	Chemical composition requirements to solutions received for reduction.
2	Low operating expenses.	The biggest disadvantage of the two-step precipitation is unfinished gold reserves: depending on the size of refinery, the cost of storage can be substantial.
3	High purity of the produced precipitate.	In case of sulphur dioxide, the absence of manufacturers in the Customs Union countries.
Ferrous sulphate		
1	High reduction rate.	Non-selective to gold.
2	Low operating expenses.	Insufficient purity of the produced precipitate.
Sodium nitrite		
1	Selective to gold. High purity of the produced precipitate.	NO_2 disposal required.
2	High reduction rate.	
3	Low operating expenses.	
Formic acid		
1	High reduction rate.	Relatively high cost.
2		CO2 emission, foam formation is possible.
3		Non-selectivity.
4		Formation of finely dispersed (colloidal) precipitates, which are difficult to separate from the stock solution.
Hydrazine hydrate		
1	High reduction rate.	Relatively high cost.
2		Non-selectivity.
3		High gas emissions, foam formation is possible.
4		High toxicity, special safety measures are required during its handling.
5		Formation of finely dispersed (colloidal) precipitates, which are difficult to separate from the stock solution.

PROCESS EQUIPMENT FEATURES

1. Miller method

A specific feature of the Miller process is utilisation of gaseous chlorine and the formation of metal chlorides, whose corrosive nature requires continuous maintenance of the equipment. Furnace hoods and air ducts are made from inert materials, such as titanium or high-chromium alloys. Glass fibre or polyvinyl chloride (PVC) are used as necessary.

The starting material is melted in a tilting furnace powered from the induction unit. The employed crucible is made from annealed coal-graphite mixture, and is rigidly secured at the place of installation using stuffed refractory material and cement filler. Gaseous chlorine is supplied to the melting location via steel tubes lined with ebonite, and is bubbled under the surface of the molten charge through fixed graphite bubbling tubes having height adjustable openings.

Chloride slags forming during the process are removed using manual scooping equipment and are transferred to a transportable stainless steel container with water for subsequent processing.

For example, in South Africa, at a refinery of Rand Refinery Limited, alloys are chlorinated using high-induction crucible furnaces. Gaseous chlorine is fed to the melt through graphite tubes, and chlorides of impurity metals are caught in electrostatic condensers.

Swiss Prior Engineering has developed an advanced system of providing chlorine to the melt that eliminates losses of gold due to its carryover to the gas cleaning system in the form of volatile chloride at the end of the process. The chlorine injection tube used in the process is positioned below the melt surface and rotates at a constant speed.

Such technique ensures rapid and complete dispersion of gaseous chlorine, which in turn results in a fuller interaction of melt components with gas and significantly increases the process rate. The reaction is controlled by measuring melt temperature in situ with a thermocouple attached to the chlorine supply tube.

2. Smelting with fluxes

Smelting for gold-silver alloys can be performed in furnaces of varying designs. For a long time gold recovery factories used crucible and small reverberatory furnaces heated with liquid or solid fuel (petrol, fuel oil, coal). The smelting is usually performed at 1100—1200°C. Oxides, including lead oxide forming upon dissociation of lead sulphate, transfer to slag.

The process continues until the slag is completely free-running. After finishing the melting, the contents of the furnace are dumped into molds. After melt solidification, the molds are tipped over and the slag is separated from the alloy. If the purity of the smelted metal is not sufficient, it is granulated by slowly quenching in water, and then subjected to repeated smelting together with fluxes.

Today, the smelting of precipitates is performed in electric furnaces. Thus, major refineries in South Africa use tilting three-electrode arc furnaces with graphite electrodes and a 750 kg capacity by metal. Such furnaces require less service personnel, have much higher throughput, their operation is completely mechanised and partially automated.

Slags produced in such furnaces are much leaner in PM in comparison to slags from crucible and reverberatory furnaces. This allows sending them to the main process cycle of the factory rather than having to process them in a separate branch. The smelting of precipitates in such furnaces is less expensive than in reverberatory and crucible furnaces.

3. Vacuum distillation

An apparatus for separation of gold-silver alloys by vacuum distillation comprises a vacuum chamber with a melting crucible and a turning arrangement configured to tumble the crucible located therein, a heating element in the form of an inductor positioned around the crucible, at least one cooled condenser with traps, and a mold.

The cooled condenser has a semispherical shape. The cone tip is made of graphite. The apparatus additionally comprises a bounding screen made of a refractory metal which, in this case, is titanium. The semispherical shape of the condenser simplifies servicing when removing condensed silver.

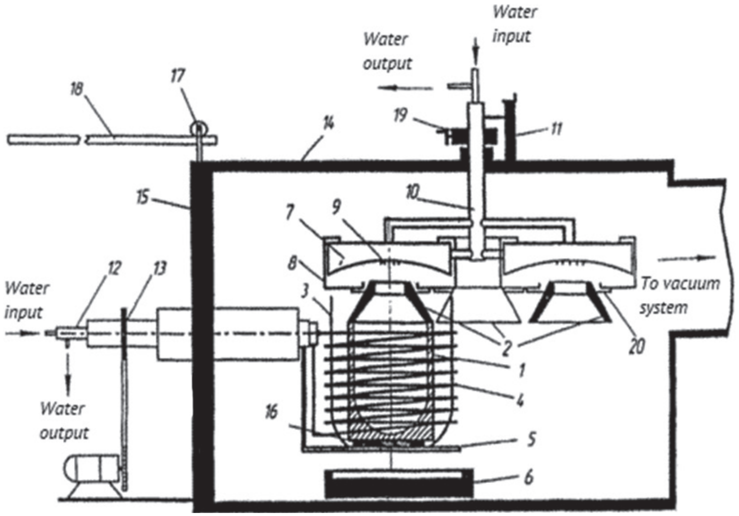
The bounding screen is configured as a lid with an opening for the graphite cone tip, snugly fits the condenser, and is secured thereupon. Inside the semispherical condenser, from its middle to its edges, are welded rods positioned in a staggered order to retain the condensed silver.

The melting crucible is made of graphite and has s spherical bottom. The thermal shield is mounted on a ceramic support. The bounding screen is made of titanium.

The thermal shield is made of ceramics. It is positioned between the inductor winding and the crucible, and the cone tip, which substantially reduces thermal losses on the graphite crucible, otherwise the process of silver condensation on the condenser is significantly impeded or impossible.

The graphite cone tip prevents overheating upon induction heating and does not interfere with operation of the apparatus.

The bounding titanium screen that is placed over the condenser from its bottom serves to keep the vapour stream within the closed space (graphite crucible, graphite cone tip and condenser) and to reduce to minimum vapour stream spraying into the chamber, which reduces the operating efficiency of the apparatus.



1 – melting crucible (evaporator), 2 – graphite cone tip, 3 – ceramic thermal shield, 4 – heating element (inductor), 5 – support for shield (3), 6 – graphite mold, 7 – semispherical condenser, 8 – bounding factor, 9 – retaining rods, 10 – water-cooled shaft, 11 – shaft (10) raising/lowering device, 12 – coaxial current feed, 13 – tumbling turning arrangement, 14 – vacuum chamber with high vacuum pumps, 15 – vacuum chamber (14) door, 16 – ceramic support, 17 – bearing roller, 18 – guide arm, 19 – arrangement to move shaft (10) about its axis, 20 – pressure clamp.

Fig. 9 - Vacuum distillation apparatus to separate gold-silver alloys.

4. Aqua regia dissolution

Aqua regia dissolution uses conventional hydrometallurgical reaction equipment operating in the system reactor (performing aqua regia dissolution) absorber (capturing nitric oxides):

- Reactors;
- Nutsche filters;
- Containers to collect solutions;
- Filter presses.

The equipment directly in contact with the solution can be made both from titanium and from polypropylene.

The general layout of equipment is similar to the layout for hydrochlorination (Fig. 10).

5. Hydrochlorination

To perform hydrochlorination, a system of process apparatuses, consisting of a chlorinator and an absorber, as well as auxiliary equipment for separating solutions from the insoluble residue (nutsche filter) and measuring tanks for storing solutions and reagents, is used. Recycled water, hydrochloric acid, and chlorine gas will be required to dissolve the material. Processing is performed while stirring and heating and then, after cooling, the pulps are filtered.

The feedstock material is loaded into the reactor, which can be made of titanium, and recycled water and hydrochloric acid are then poured over the material. Hydrochloric acid is fed from the measuring tank into the water pulp via a pipeline connecting the reactor and the measuring tank. The measuring tank and the pipeline are made of acid-resistant materials. Chlorine is fed into the vessel via a chlorine ramp made of acid-resistant materials. Upon completion of the chlorination process, the pulp is cooled and filtered in vacuum with a nutsche filter made of acid-resistant materials. The pulp is discharged from the reactor using a bottom unloading valve.

The absorber effectively removes the excessive chlorine. During the process, the steam-gas mixture containing chlorine gas, hydrogen chloride, and water steam is drawn from the chlorinator into the absorber, where it is also used to break down the feedstock.

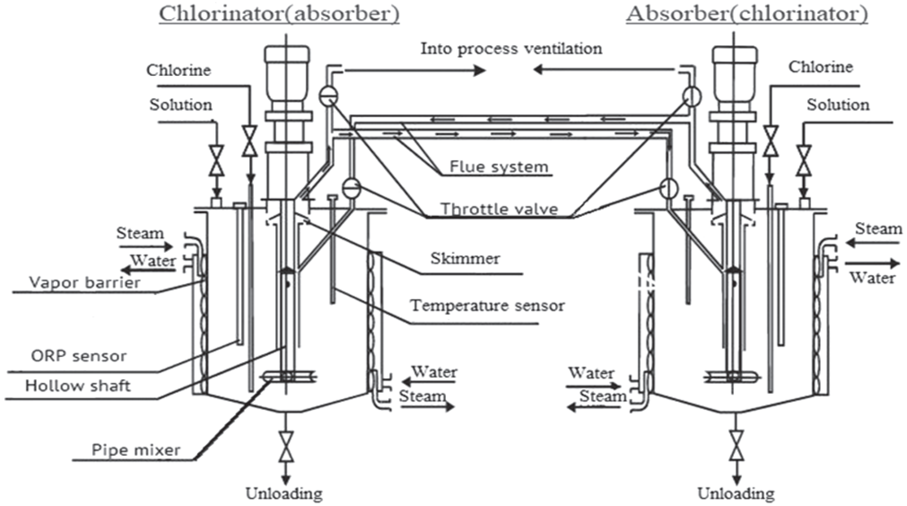


Fig. 10 - Equipment for chlorination, chlorinator (left) и absorber (right).

6. Electrolytic method

Electrolysis of gold is performed in small porcelain or vinyplast cells with 20–65 l capacity. Porcelain cells with a capacity of 25 l are used in Russian practice. Gold sheeting with a thickness of 0.1–0.25 mm, obtained by rolling pure electrolytic gold, is used as cathodes.

To impart rigidity to cathodes, they are subjected to corrugation on a special press. Anodes are suspended to poles using golden bands alloyed into the metal when casting the anodes. To maintain the required temperature of the electrolyte, the cells are placed into water baths.

Electrolyte is agitated with compressed air supplied to the cells through glass tubes. As chlorine evolves during electrolysis, the cells are in a special fume hood. Outside the hood the current is supplied via copper busses, and inside the hood silver busses are used as more resistant to chlorine atmosphere. The poles to suspend electrodes are also made from silver.

Cathodes are thin gold plates, anodes are made from graphite. The process is performed using direct current with a density of 200–500 A/m2. From the obtained solution platinum and palladium are precipitated with ammonium chloride, and then the remaining gold is precipitated using iron chloride solution. Copper is cemented with iron.

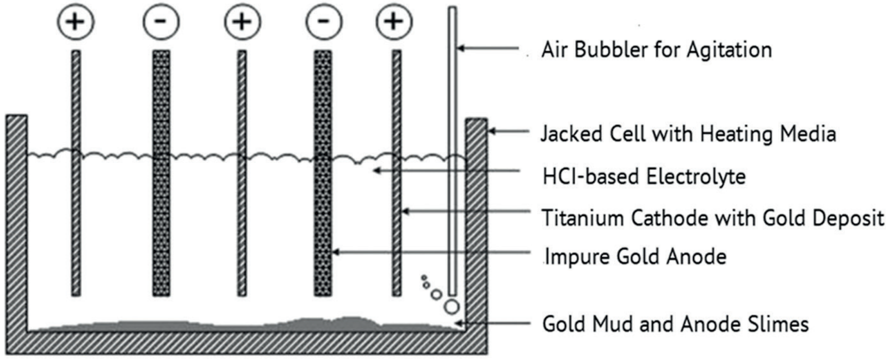


Fig. 11 – Basic configuration of electrolysis of gold.

7. Precipitation by reagents

Gold refining with precipitation methods is performed using hydrometallurgical reaction equipment:

- Reactors;
- Nutsche filters;
- Containers to collect solutions;
- Filter presses.

Considering the specifics of chemical processes, the equipment directly in contact with the precipitation solution is made of titanium or polypropylene.

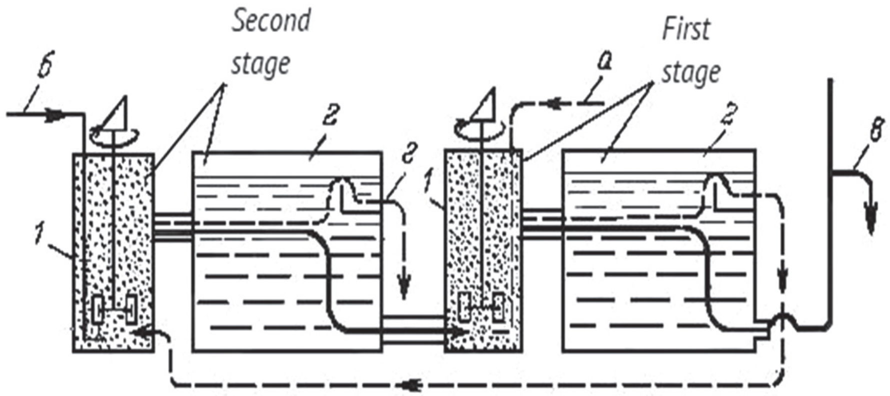
Fig. 12 – Polypropylene reactor (left) and titanium reactor (right).

8. Liquid extraction

Gold is obtained with liquid extraction using extraction devices of different forms.

8.1 Conventional mixer-settler extractor

Each stage of a mixer-settler extractor consists of a mixer, in which the liquids are mixed to attain a state as close to equilibrium as possible, and a settler, where separation of extract from raffinate occurs. Within a stage the phases move concurrently, but the device as a whole, comprising any number of stages connected in series, operates with counterflow of phases. Device stages are positioned in one horizontal plane (Fig. 13) or are arranged as a cascade.



1 – mixer; 2 – settler; a – light phase; b – heavy phase; c – final product (heavy phase); d – final product (light phase).

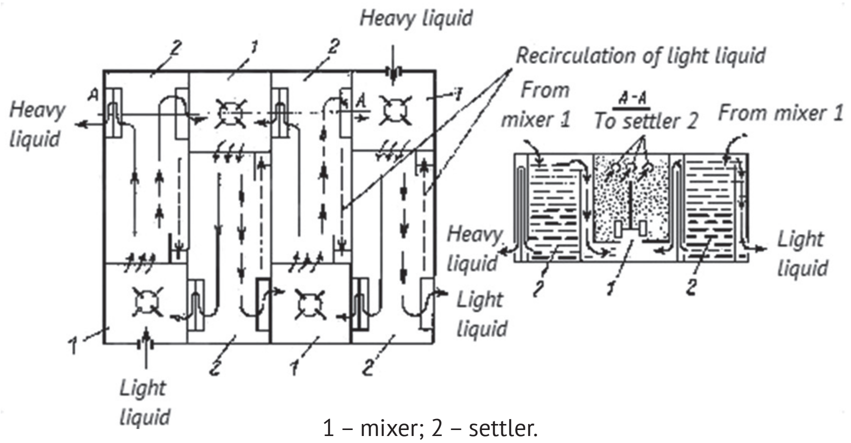
Fig. 13 – Diagram of mixer-settler extractor.

The operating principle of the mixer-settler extractor can be seen in Fig. 13, in which only two stages of the device are shown for simplicity. The light phase (a) is fed to the mixer (1) of the first stage, to which, in a parallel flow, the heavy phase from the settler (2) of the next (second) stage, is supplied. After mixing, the phases separate into layers in the settler of the first stage, from which the heavy phase is taken as the final product (c), and the light phase is fed to the second stage. Here it mixes with fresh heavy phase (b) and is separated from it in the settler (2) of the second stage. From this settler the light phase (the final product (d)) is removed at the top, while the heavy phase is taken from the bottom and is fed for mixing to the first stage.

Liquid transfer and mixing can be effected not only with mechanical stirrers (as shown in Fig. 13), but also using pumps, injectors, and other means. In a similar way, phase separation can be achieved not only in gravity settlers (Fig. 13), but also in centrifugal type separators, such as hydrocyclones or centrifuges. Therefore the number of possible designs of mixer-settler extractors is rather large.

To reduce the area occupied by the device, compact box extractors are used. In a box extractor (Fig. 14) all stages are contained in a common box of rectangular cross-section. The heavy phase is supplied to the mixer located in the upper right corner of the box, and is taken away from the outermost settler at the left side of the box.

As can be seen in the figure, the light phase moves in counterflow to the heavy phase in the device. The heavy phase (see section A—A) is taken via liquid seal from the bottom part of the settler to the next mixer, and the light phase overflows the barriers and is taken from the top part of the settler.



1 – mixer; 2 – settler.

Fig. 14 – Diagram of box extractor.

The mixer-settler extractors achieve an intense interaction between phases, with the efficiency of each stage approaching one theoretical separation stage. Such devices are well adapted to treat liquids at significantly different phase volume flow rates, e.g., at the ratio of flow rates 10:1 and higher. To reduce the phase volume ratio, a partial recycling of the phase with a lower volume flow rate from the settler to the mixer of each stage is sometimes employed, as shown with dotted lines in Fig. 14.

An important advantage of mixers-settlers is the possibility of their efficient application for extraction processes requiring numerous stages.

The mixer-settler extractors occupy a larger area than column devices, but require less height in the production rooms (for horizontal arrangement of the stages).

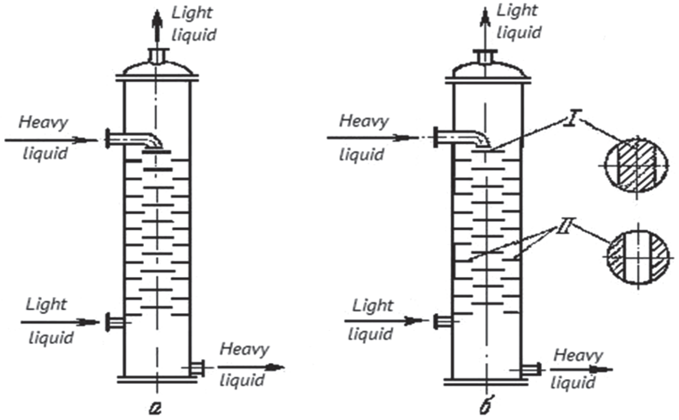
A disadvantage of many variants of mixers-settlers is slow settling of liquids, which influences the throughput and size of the devices, as well as phase carry away with the flow of solution, which is undesirable in the treatment of expensive, explosive or flammable substances. To this corresponds a disadvantage of a large load of the device, which is alleviated by using centrifugal extractors.

In addition, the presence of stirrers with drives in each stage complicates the structure of the device and results in increased capital costs and operating expenses.

8.2 Tray column extractors

Tray extractors are columns with baffles-trays of various designs. The baffles are configured as either alternating disks and rings, or dead trays with flanges and segmental cutouts that are installed as in barometric condensers (see Fig. 15, a), or as disks with cutouts shown in Fig. 15, b. The distance between adjacent trays is usually 50–150 mm.

Droplets flow around the trays as a thin film washed by the continuous phase. The intensity of mass transfer in tray columns is somewhat higher than in spray columns, mostly due to their sectioning with trays, which results in reduced back mixing.



a –with disks and rings; 6 – with adjacent trays type I and II.

Fig. 15 – Tray column extractors.

8.3 Sieve column extractors

In a sieve extractor, the dispersed phase, for example, the light phase, as shown in Fig. 16, passing through the openings of sieve trays, repeatedly breaks down into droplets and jets, which in turn break down into droplets in the inter-tray space. After interacting with the continuous phase, the droplets coalesce and form a layer of the light phase under each of the next upper tray. In case the heavy phase is being dispersed, the layer of liquid is formed over the trays.

When the hydrostatic pressure of the liquid layer becomes sufficient to overcome resistance of tray openings, the liquid, passing through the tray openings, is once again dispersed. The continuous phase (in this case, the heavy liquid) flows from tray to tray through overflow pipes.

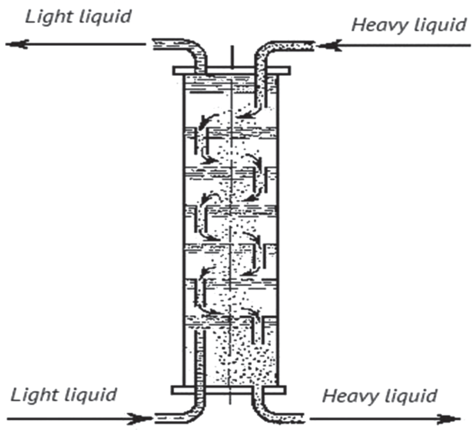


Fig.16 – Sieve column extractors.

All gravity extractors are characterised by simple structure due to absence of any moving parts. Correspondingly, the cost of these devices and expenses related to their operation are relatively low.

However, in most cases the intensity of mass transfer in gravity extractors is low. Column type extractors are usually flooded with phase ratio 1:1. They are intended only for continuous processes, and a stop requires a stabilisation period. Gravity extractors are hardly suitable for operation with high phase flow rate ratio. Such devices are better used as separators for finishing purification of aqueous stream from traces of the organic phase.

8.4 Centrifugal extractors

Centrifugal forces are an efficient means to improve not only mixing, but also phase separation upon extraction.

The operating principle of a centrifugal extractor is clear from Fig. 17. The liquids are supplied under pressure from the opposite ends into the channels of a rapidly rotating shaft 1, onto which a rotor (drum) 2 is fixed. The tightness of connection between the tubes supplying the liquids and the rotating shaft is ensured by seals at shaft ends. A spiral baffle 3 made of perforated band is positioned inside the rotor over its entire width. The light and heavy phases move in counterflow fashion in the channels between its turns. The heavy phase moves from the axis towards the periphery of the rotor, and the light phase moves from the periphery towards its axis.

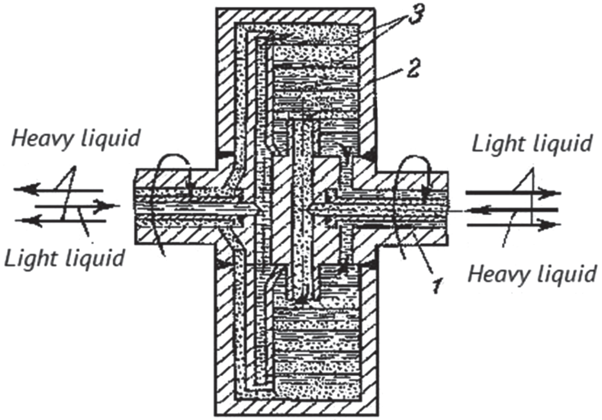
The two phases intermix by passing through openings in the spiral, and are separated in the channels by centrifugal forces. Thus, liquid mixing and separation occur simultaneously and are multiply repeated. The light phase is taken away at the outer rotor surface, while the heavy phase is taken near its axis. Both phases are removed via separate take-out channels of the shaft, as shown in Fig. 17.

Centrifugal extractors have significant advantages. These devices are rather compact and combine high throughput with high mass transfer intensity. They can efficiently treat liquids with low density differences.

On the other hand, centrifugal extractors have low retaining capacity and short residence time of liquids in the device, which is an advantage in that it allows to use expensive (and unstable) extracting agents in small amounts.

This feature of centrifugal extractors promotes their successful application for extraction of easily degradable substances, such as antibiotics (penicillin and the like), sensitive not only to heating, but also to extended residence in solution at normal temperature.

On the other hand, these devices are not suitable for extraction accompanied by a chemical reaction, when an extended time of interphase contact is required, and in the case of presence or formation of precipitates in the system.



1 – shaft; 2 – rotor (drum); 3 – spiral baffles made of perforated band.

Fig. 17 – Diagram of Centrifugal extractors.

Centrifugal extractor throughput is determined by the width of its rotor, and the number of attained theoretical stages – by its diameter. In industrial centrifugal extractors the rotor speed varies in the range 1200–5000 rpm, which limits the dimensions of the rotor (drum), whose diameter does not exceed 1.2–1.5 m.

In the extractor illustrated in Fig. 17 the heavy phase is taken away via a channel located at the revolution axis of the rotor.

SUMMARY OF GOLD REFINING TECHNOLOGIES

Technologies	**Advantages**	**Disadvantages**
Removal of impurities		
1. Miller method	Possibility to remove with chlorination almost all base metals (BM) and silver in the melt to obtain gold with purity up to 99.5%.	Partial sublimation of gold into gas duct and scrubber at the end of the process at low concentrations of BM and silver in Dore alloys. Solution: stopping the chlorination at gold content 93 to 98% to avoid gold evaporation.
	Quick turnaround times of refining, ease and suitability for refining gold of any purity.	Extended residence of gold in side products between recovery steps. Additional costs for utilisation of substantial amounts of middlings.
2. Smelting with fluxes	Possibility to process lean concentrates containing from 5% of gold with a high content of impurity elements.	Implementation of the technology involves formation of a large number of middlings (dust, slag, solutions and industrial waters) that require additional processing.
	Smelting with fluxes produces a 95–98% alloy (total gold plus silver).	The forming middlings result in an incomplete production and a channel of PM waste; The mass of middlings increases due to using fluxes; The technology involves multiple steps.

3. Vacuum distillation	Reduces expenses for recirculated metal, lowers operating expenses, and minimises hazardous emissions to working zone and environment.	High cost of equipment.
	Significantly shortens the duration of refining gold-silver alloys with high silver content (above 10–15%).	Equipment requires qualified service and maintenance.
	Process automation, reduction of waste, environmentally safe technology.	
	Minimum amount of middlings in easily processable form.	
Breaking down gold-silver materials		
1. Aqua regia dissolution	Allows dissolution of much larger particles due to its reaction mechanism, with NOx evolution at dissolution border.	Formation of large volumes of off-gases containing NOx that increase the cost of gas cleaning. Process solutions after refining contain nitrate and nitrite ions that have to be neutralised.
	Aqua regia dissolution is a simple, rapid and efficient method to obtain a gold-containing solution of high concentration.	The method consumes high amounts of expensive nitric acid, which reduces its operating efficiency in comparison with hydrochlorination.
		Processing feedstock with silver content above 10% using a conventional approach is problematic.

2. Hydrochlorination	The method is efficient because its cost is 30–40% lower than that of aqua regia dissolution.	Necessary infrastructure is required to handle liquefied chlorine.
	The unused chlorine in the gas phase is much easier to scrub than NOx gases produced by dissolution in aqua regia.	More stringent standards for storage, handling, and control of chlorine gas than for nitric acid.
	Technology allows for process automation and ease of control.	
Gold reduction		
1. Electrolytic method 1.1 Chloride electrolysis technology (Wohlwill Process) 1.2 Technology of aqua regia electrolysis	The process of aqua regia electrolysis guarantees the quality of cathodic gold with purity of at least 99.99% at any quality of the anodic metal.	If low-grade Dore alloys (having gold content 60–80% and silver content 12–15%) are used as anodic metal, a substantial amount (up to 30% of the weighted anodic metal) of anodic slime is formed that consists mostly of silver chloride.
	Dore alloys with gold content 65–70% can be used as anodic metal, while in Wohlwill Process the gold content in anodic metal cannot be lower than 85%.	Given equal quality of anodic metal and other conditions being equal, a chloride electrolysis cell has a higher (by 8–10%) throughput.
	The process of aqua regia electrolyte preparation is simplified, i.e., the electrolyte is prepared directly in the electrolysis cell from anodic metal and acid solution by electrochemical dissolution. In chloride electrolysis the electrolyte is prepared using cathodic gold and a separate electrolysis cell with a thorough filtration of the obtained electrolyte.	**The main disadvantage** is a high degree of **incomplete production and the duration** of the electrochemical process, both conventional and aqua regia ones; Nitric oxides are formed in the process of aqua regia electrolysis.

2. Liquid extraction	Allows gold extraction from solutions with low gold content and high impurity content.	Process fire hazard, more stringent requirements to rooms.
	Possibility to obtain rich concentrates with above 98% Au content from solutions with high BE content.	Solubility in water and residual content of the organic phase in solutions after extraction.
	Possibility to obtain refined gold from solutions with low impurity content.	Substantial amounts of WIP in solutions for most devices (less in centrifugal ones).
3. Precipitation by reagents	Shorter process duration in comparison to electrochemical reduction.	Requirements to chemical composition of solutions received for reduction.
	Can provide 99.99% gold.	Is an integral finishing part of most methods (aqua regia dissolution, liquid extraction, hydrochlorination, etc.).
	Low operating expenses.	The biggest disadvantage of the two-step precipitation is unfinished gold production: depending on the size of refinery, the cost of storage can be substantial.

AVAILABLE GLOBAL TECHNOLOGIES FOR SILVER REFINING

1. Breaking down silver-containing materials

1.1 Dissolution in nitric acid

An alternative approach to silver refining includes a complete dissolution of silver-containing feedstock in nitric acid with its subsequent recovery from solution by known methods (electroextraction, reduction from solution, precipitation in the form of low-solubility compounds with subsequent reduction). The silver-containing feedstock is chemically dissolved, and the solution is filtered to remove any insoluble substances, such as gold or PGM.

A specific feature of this technology is its ability to shorten the duration of silver refining in comparison with the conventional electrorefining process, in which silver is bound in anodes.

Breaking down of silver-gold materials with nitric acid is based on the difference in the chemical properties of gold and silver: while dilute nitric acid has no effect on gold, silver dissolves even in nitric acid solutions of low concentration. Concentrated nitric acid dissolves silver according to reaction (13), forming nitric oxide, and dilute nitric acid interacts with silver according to reaction (14), with evolution of nitrogen monoxide:

$$Ag + 2HNO_3 = AgNO_3 + NO_2\uparrow + H_2O$$

$$3Ag + 4HNO_3 = 3AgNO_3 + NO\uparrow + 2H_2O$$

Besides acid concentration, the mechanism and result of interaction are also influenced by process temperature, feedstock composition, the presence of impurities in the leaching solution, and other factors. Nitric acid is simultaneously a strong oxidiser and a good solvent. Of all metals only gold, platinum, rhodium, and iridium are resistant to its action. Certain metals, such as aluminium, iron, and chromium, are passivated by it. Practically all salts of nitric acid are soluble. Aqueous solutions of nitric acid are complex systems comprising the molecules of nitric acid, the products of its dissociation, as well as dissolved nitric oxides.

When dissolving a silver-gold alloy in nitric acid to transfer silver into solution, the complete dissolution of silver is impeded by the formation of golden “film”. A complete separation of silver and gold requires that the ratio of gold and silver contents in the alloy be not higher than 1:2, better still 1:3. In these conditions silver can be entirely dissolved, while gold remains undissolved.

If the alloy contains copper, lead, zinc, palladium, they readily pass to nitric oxide solution; in case tin, antimony or arsenic are present in the alloy, a preliminary smelting with ammonium nitrate or cupellation are required to separate these elements.

Silver chlorides have low solubility in aqueous nitric acid solutions. Silver chlorides accumulating in insoluble precipitate can be reduced to metallic state and then again subjected to nitric acid treatment. To achieve a fuller recovery of silver from the insoluble precipitate, selenium that is present in the precipitate should first be removed.

The peculiarities of formation and the morphology of the “golden” layer (crust) upon chemical and electrochemical dissolution of silver-gold alloys are considered in the review of technologies for gold.

Both conventional and improved methods of nitric acid dissolution can be applied in industrial practice. A method of nitric acid dissolution of silver materials in nitric acid with oxygen is known. This technology can reduce nitric acid consumption by as much as 40% and eliminate emissions of nitric oxides. The process is implemented in hermetically sealed devices with low oxygen gauge pressure.

For example, at Uralelectromed factory, metal bars are dissolved in nitric acid solutions in the presence of ammonium nitrate to reduce the formation of nitric oxides. The process is implemented in hermetically sealed devices with low gauge pressure. Gold is recovered from the residue by dissolving in aqua regia.

Item	Advantages	Disadvantages
1	Shorter duration of refining.	Evolution of nitric oxides that either have to be trapped or need additional methods for neutralisation.
2		Generation of solutions containing nitrates and nitrites, which incurs additional expenses for their utilisation.
3		Obtaining refined silver requires several additional process steps to remove BE. As a rule, feedstock with gold content less than 5–10% is not recommended for processing using this technology.

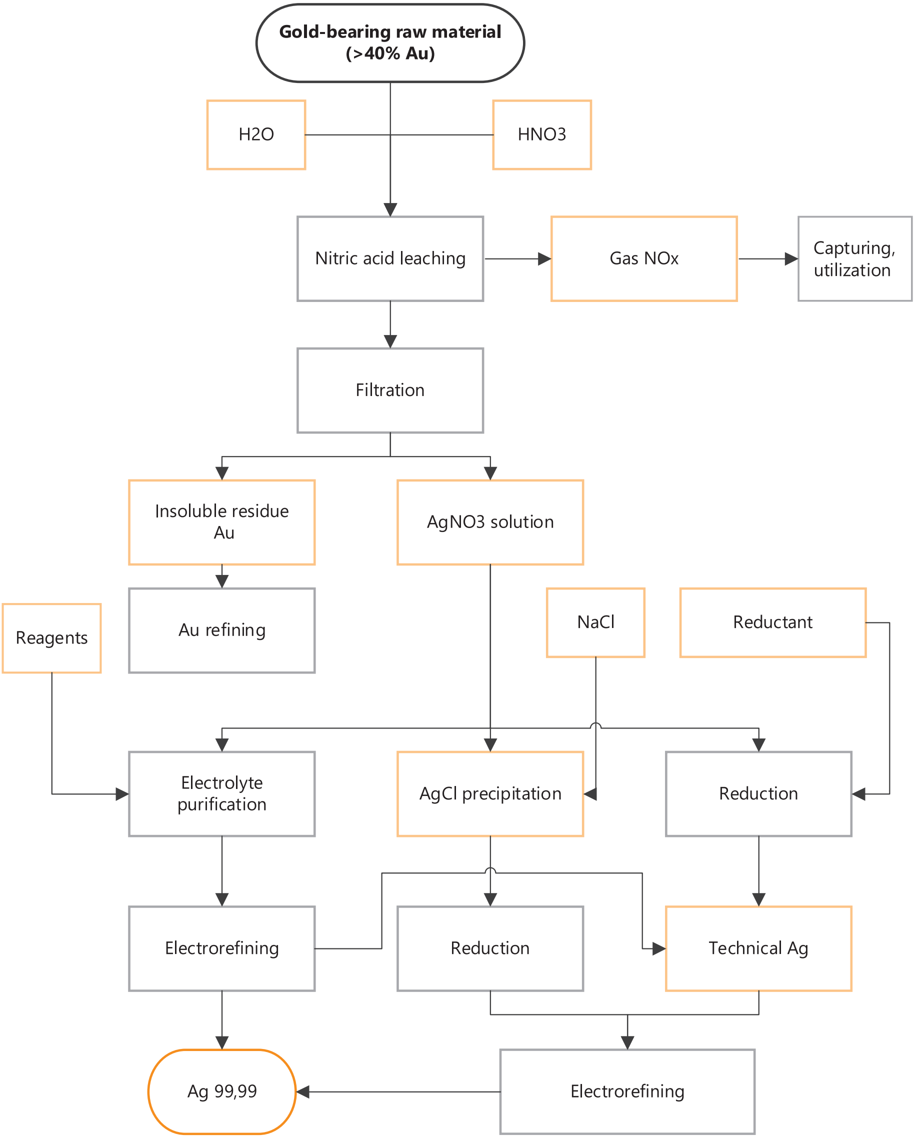


Fig. 18 Complex flowchart of dissolution in nitric acid.

1.2 Dissolution in sulphuric acid

The practice of silver refining includes a broad range of methods for its leaching by solutions of certain mineral acids. The most common are oxidising acids, i.e., nitric or sulphuric acids, of varying concentrations. The forming simple silver compounds of these strong mineral acids differ vastly in their solubility.

The solubility of silver nitrate (AgNO3) at 25°C is 253.9 g per 100 g of H_2O, while the solubility of silver sulphate (Ag_2SO_4) is just 0.86 g. Nevertheless, this makes it possible to perform the primary operation of refining — the transfer of metallic silver into dissolved state. The subsequent stages of purification use the known precipitation or electrolytic methods.

Despite a wide range of nitric acid concentrations (HNO_3) at which rapid silver dissolution occurs (often without heating the solutions), this step has a serious disadvantage related to the formation of ecologically hazardous and difficult to trap nitric oxides (NO and NO_2). Furthermore, due to its strong oxidising properties, HNO_3 dissolves a large number of other chemical elements, including platinum group elements, which noticeably contaminate the target silver and require additional steps for its purification.

A common operation to transfer Ag into solution is sulphatisation, performed by solutions of sulphuric acid (H_2SO_4) of varying concentrations, also leading to the formation of simple binary silver sulphate. Since silver-containing electrolysis slimes always contain platinoids, the main prerequisite for using it should be complete absence of platinum group metals (PGM) in the solution. In most cases this requirement is not met, as for many platinum metals, especially in finely dispersed state, H_2SO_4 functions as a good oxidiser.

Thus, widely available in patent literature methods for silver recovery by primary treatment of various silver-containing materials with solutions of oxidising acids, nitric or sulphuric acids, result in the formation of simple silver salts with the corresponding acid residue as the anion.

As a rule, this method is used for processing silver-containing electronic scrap or copper-electrolyte slimes.

Silver-containing feedstock, containing a large amount of BM, is leached in the presence of an oxidiser, usually oxygen or hydrogen peroxide, for selective dissolution of BM in sulphuric acid.

However, silver has a significant solubility in sulphuric acid, and therefore it is important to create such breaking down conditions that would promote selective dissolution of BM before silver, with subsequent solution treatment to remove any soluble silver.

Silver recovery is performed by cementing with BM, such as copper, zinc and iron, or even copper-containing silver feedstock. The dissolved silver can also be recovered by precipitating in the form of silver chloride.

The result of dissolution in sulphuric acid depends on the surface area of the starting material (granulation or grinding may be required), breakdown conditions (temperature, acid concentration, oxidiser and stirring), and the efficiency of recovery of any dissolved silver. The advantage of this technique is that BM, in particular copper, eventually pass into sulphate solution that can then be sent for electrochemical recovery of metallic copper.

Item	Advantages	Disadvantages
1	Possibility to process lean concentrates containing more than 70% of BE.	Limited silver solubility in sulphuric acid solutions leads to multistep processing and requires more rigid conditions (temperature and acid concentration).
2		The required water consumption is several times higher than conventional electrolysis or electroextraction.
3		As a rule, the technology is applied for processing and preliminary enrichment of lean silver-containing scraps with high BE content and is to a significant extent an auxiliary operation for refining.

2. Silver reduction

2.1 Electrolytic method

Silver electrorefining includes anodic dissolution of silver and BM from the anode and simultaneous silver reduction at the cathode:

Anodic dissolution $Ag^0 \rightarrow Ag^+ + e$

Cathode reduction $Ag^+ + e \rightarrow Ag^0$

Silver is formed as thin needle-like crystals at the cathode that are constantly scraped away to avoid short circuit between the anode and cathode. Silver crystals fall to the bottom of the electrolysis cell and are collected manually or automatically, on a continuous or periodic basis.

The morphology of silver particles can be controlled by introducing certain additives, such as tartaric acid. In ideal conditions the cathodic process selectively reduces silver, but in practice the degree of selectivity depends on the composition of the solution, applied voltage and current density.

Anodic dissolution of contaminated silver is not selective, and any easily oxidisable metallic impurity in the anode will dissolve. The dominant impurity in the anode is copper with a low amount of lead, cadmium and zinc. Metals that do not dissolve in nitric acid, such as gold and platinum, end up in anodic slime.

The gold-containing slime, which can cause passivation of silver anodes, has to be periodically removed to avoid refining problems. The anode compartment should be isolated from the cathode compartment with a membrane to avoid contamination of silver crystals with anodic slime.

Since the anodes are not fouled, and cathodic reduction is selective for silver, the dissolved copper and other BM constantly accumulate in the solution, as silver content in the electrolyte is depleted. A part of contaminated electrolyte should be periodically removed and replenished with fresh electrolyte containing high concentrations of dissolved silver.

Silver in the spent electrolyte is recovered and returned to the refining branch, where together with incompletely dissolved anodes it passes the cycle of recycling in the process of electrorefining.

At an increased concentration of insoluble elements in the anode material, the internal core of the silver material becomes blocked by these materials and inaccessible to anodic dissolution. This causes anode passivation, which results in the formation of free acid and oxygen upon anodic oxidation of water:

$$\text{Anodic oxidation of water} \quad 2H_2O \rightarrow O_2 + 4H^+ + 4e \quad (17)$$

The presence of an excess of free acid in the electrolyte causes problems, as it re-dissolves the purified silver and thus decreases overall current efficiency and silver yield. A further problem is the evolution of NOx to the atmosphere, which creates exposure hazards for the operator.

A high content of free acid also promotes hydrogen formation at the cathode, which additionally decreases the efficiency of silver electrorefining:

$$\text{Cathode oxidation of water} \quad 2H^+ + 2e \rightarrow H_{2(g)} \quad (18)$$

Some operators let accumulate an excess of free nitric acid (or even add fresh nitric acid) to promote repeated dissolution of silver crystals. This decreases the amount of silver that has to be dissolved in standalone mode to replenish silver concentration in the cells, however, it also decreases current efficiency.

Figure 3 shows a process flowchart for a typical silver electrorefining operation. The two key blocks are production of freshly prepared electrolyte and silver processing in the spent electrolyte. The fresh electrolyte containing up to 400 g/l of silver is typically obtained by dissolving a purified but non-standard crystal of silver in nitric acid. Silver is reduced from the spent electrolyte by precipitating silver chloride that is then filtered, reduced to metal, and turned into silver anodes.

In comparison to electrorefining of gold, the operation of silver electrorefining is more labour-intensive, and many refineries have implemented various degrees of its automation. The automated operations may include simple scraping of sliver crystals from anodes, dumping silver from cell bottom using screw conveyors or bottom discharge ports, as well as using particulate anodes with continuous removal of anodic slime.

Item	Advantages	Disadvantages
1	Well-established technology, wide selection of equipment, simplicity and reliability.	Extended duration of gold refining if using anodes with high Au content.
2	The method ensures stable production of refined silver that is more than 99.99% pure.	Limitation on gold content, less than 10%.
3	The method can be combined with vacuum distillation, resulting in providing silver to electrolysis containing less than 3–5% Au.	Silver retention in electrolyte and anode residuals.
4		Limited throughput in the presence of Pd, Te as impurities.

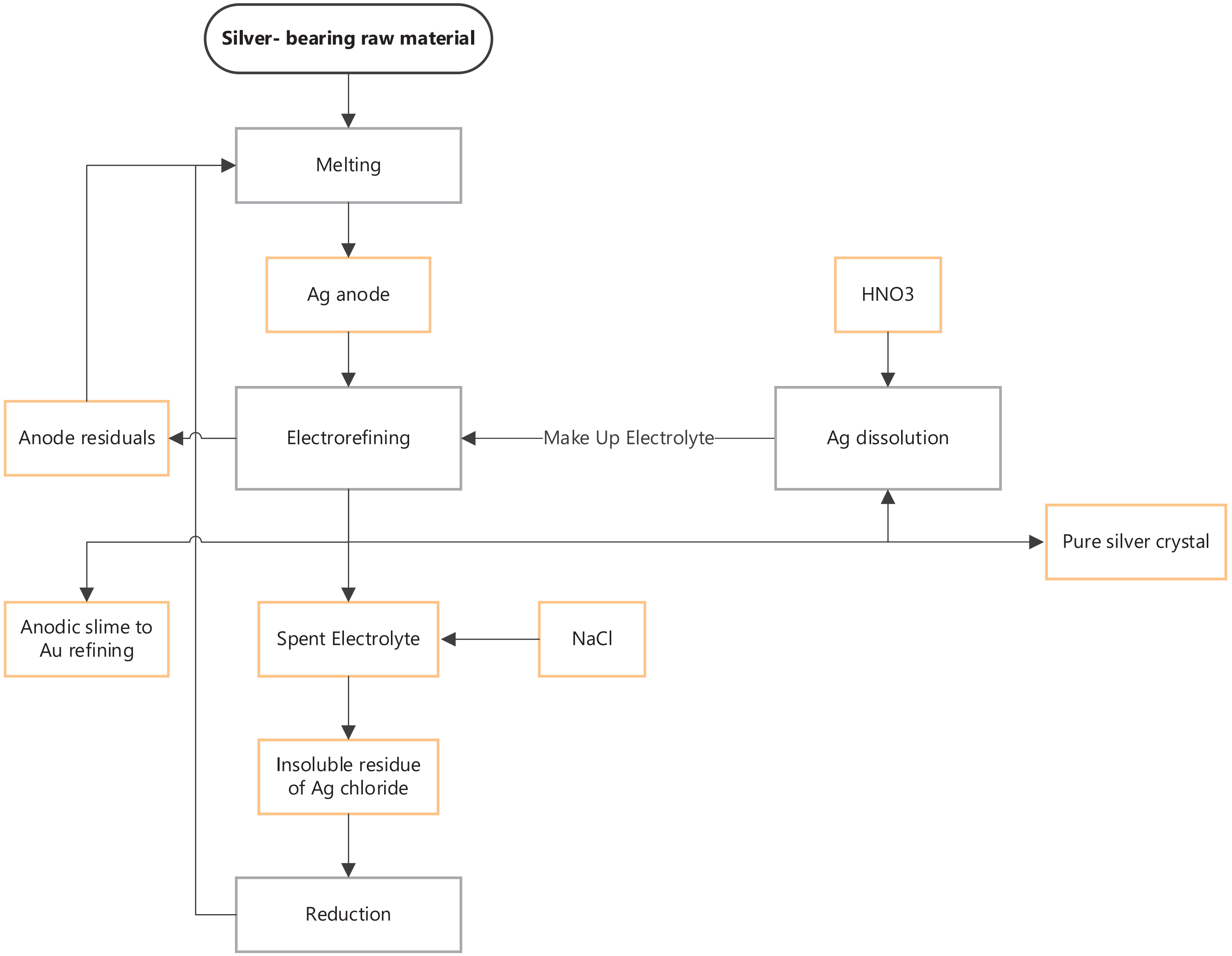


Fig. 19 – Complex flowchart of silver Electrorefining process.

2.2 Electroextraction

Electroextraction is direct electrochemical recovery of silver from solution. Instead of a dissolvable anode, an inert anode is used, usually made of platinised titanium or niobium. The anodic reaction is evolution of oxygen and formation of acid. The interest to silver electroextraction has currently re-emerged due to development of a cylindrical electrolysis cell by Electrometals Corporation, the so-called EMEW cell. Reports indicate that 70–80% of silver can be extracted directly in the form of 99.99% Ag in a single pass.

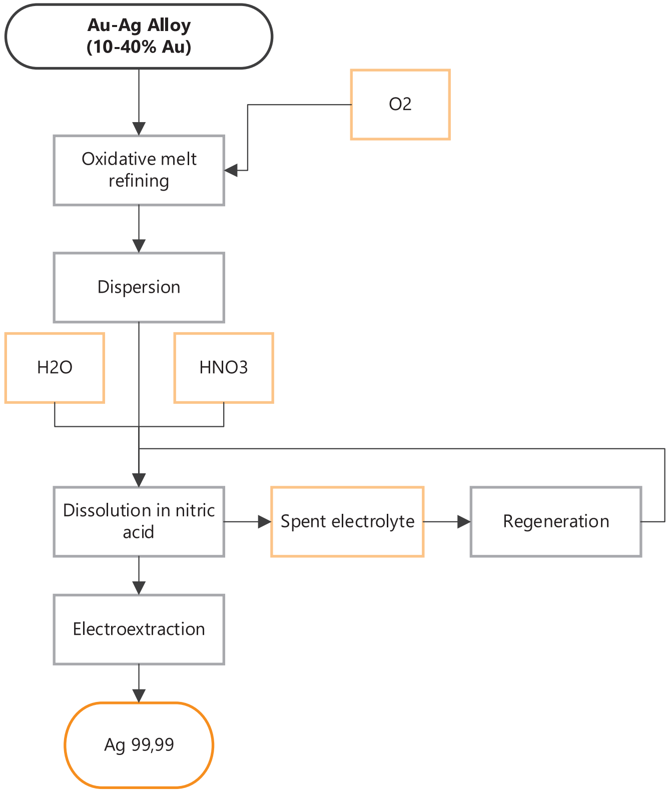


Fig. 20 – Complex flowchart of silver electroextraction.

Item	Advantages	Disadvantages
1	Shorter duration of silver refining.	Stringent requirements to electrolyte (by Pb, Se, Te); the need to adapt electrolyte and use feedstock with minimal content of impurity elements.
2		The need to utilise nitric oxides at the step of nitric acid dissolution, the need to perform oxidative melt refining.
3		Low current yields and high operating expenses, in particular, it is not recommended if the gold content in feedstock is less than 5−10%. Expensive equipment.

2.3 Precipitation by reagents

In conventional processes of breaking down gold-silver alloys with aqua regia leaching and hydrochlorination silver remains in the insoluble residue (IR) in the form of chloride. Then, silver is leached from the IR, re-precipitated and sent for the reduction step with subsequent smelting for anodes and electrolytic refining, with the number of steps and the set of processes possibly varying depending on the chemical composition of the material.

Today, alternative technologies to process products containing silver chloride have been developed and are being improved upon. For example, a technology of sulphite-ammonium production of refined silver is known.

The technology to obtain refined silver was developed on the basis of cake from aqua regia leaching (ARL) of a gold-silver alloy. This product is the purest of all middlings containing silver chloride.

To obtain refined silver, purified silver chloride rather than silver was precipitated from the solution obtained by leaching ARL cake, which was then washed with hydrochloric acid solution that was subsequently leached again with sulphite-ammonium solution (second dissolution step), and then precipitated the refined silver, i.e., silver obtained with repurification (Fig. 21).

A high degree of precipitation of the purified silver chloride is provided by using a dilute solution of hydrochloric acid. Using sodium chloride to precipitate the solution is accompanied by high consumption of the reagent and a high residual mass concentration of silver in the filtrate (up to 1.4 g/l).

Insoluble residues from the first and second dissolution steps with mass fraction: Au 1–20% and Ag 30–70%, respectively, are sent for incoming smelting of the initial feedstock.

Further technological studies of the hydrometallurgical scheme of obtaining refined silver allowed advancing the technology to include not only ARL cakes but also chloride slags in processing.

A characteristic feature of the advanced technology is

- washing the precipitated silver chloride with aqua regia solution;
- silver reduction from silver chloride is achieved either with formaldehyde or with hydrazine.

Inclusion of the step of washing with aqua regia solution ensures a deeper and guaranteed purification of silver chloride from impurities.

Utilisation of formaldehyde to reduce silver from purified chloride substantially decreases the volume of process solutions, furthermore:

- Formaldehyde consumption is close to the theoretical one;
- The products of the reduction reaction are carbon dioxide, hydrogen, water, and sodium chloride, which do not contaminate the obtained refined silver and are easily removed upon washing;
- The cost of formaldehyde in comparison to hydroxylamine sulphate is almost 1.5 times lower.

Item	Advantages	Disadvantages
1	Possibility to process not only hydrochlorination and ARL cakes, but also chloride slags.	High operating expenses for the reagents.
2	Separation of gold from silver already at the first process step.	Higher demands with respect to impurity profile in the initial feedstock; as a rule, the precipitation methods work in combination with electrolysis or electroextraction.
3	Reduced recirculated gold in subsequent electrolytic technology of silver refining.	Additional expenses for neutralising formaldehyde-containing solutions.
4	Possibility to obtain refined silver without electrolysis.	

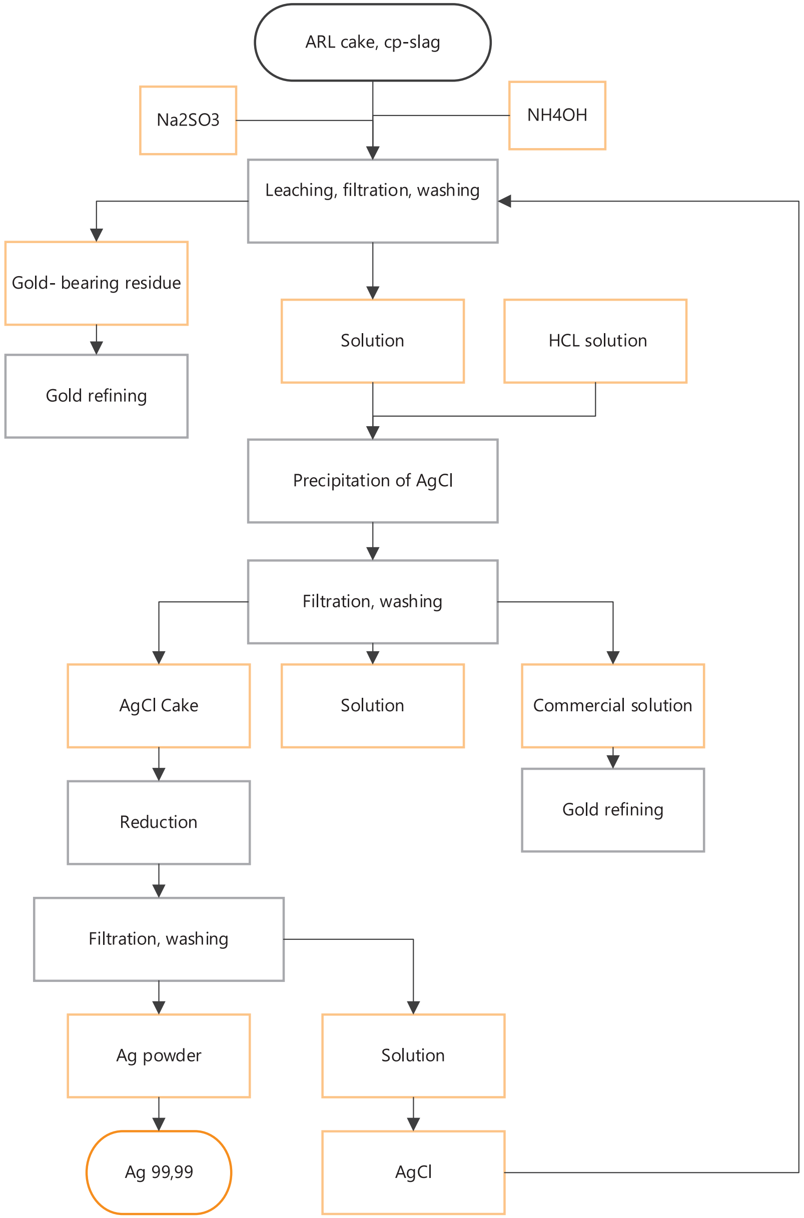


Fig. 21 – Complex flowchart of precipitation by reagents.

PROCESS EQUIPMENT FEATURES

1. Dissolution in nitric acid

Dissolution of silver-containing materials in nitric acid is performed in titanium or Hastelloy alloy reaction equipment. This equipment is used in combination with nitric oxide utilisation complex.

Fig. 22– Reactor for dissolution in nitric acid (left), Scrubber for the utilization of nitrogen oxides (middle) and reactor for dissolution in sulphuric acid with oxygen (right).

2. Dissolution in sulphuric acid

Dissolution of silver-containing materials in sulphuric acid is performed in reaction equipment lined with acid-resistant tile. The guidelines outlined below should be taken into consideration when selecting the material for building reaction equipment.

At sulphuric acid concentration of about 50–55% iron surface passes into a passive state. As temperature and sulphuric acid concentration are further increased, the surface of iron becomes active (iron corrosion in sulphuric acid is observed).

In solutions of sulphuric acid, as in other acids, the rate of iron corrosion is significantly affected by the nature of the anions. This is related to slowing down of the cathodic and anodic processes and their adsorption at the metal surface.

In 95–98% sulphuric acid, at normal temperature, good resistance is demonstrated by chromium steels (with chromium content about 17%) with a small addition of molybdenum or without it. At Krastsvetmet refining facilities, measuring containers and tubes made of ST20 steel are used for concentrated sulphuric acid.

Pure aluminium (99.5%) is more resistant to sulphuric acid than its alloys with copper excluded from their composition. Corrosion-resistant steels in 5% or 20% solution at the boiling point of sulphuric acid are stable only in the presence of corrosion inhibitors.

At regular temperature almost no copper corrosion in sulphuric acid is observed. When raising the temperature to 100°C, the degradation process intensifies. In 25% sulphuric acid solution, under increased pressure and a temperature close to 200°C, copper rapidly degrades.

Brass has no corrosion resistance in sulphuric acid solutions of any concentrations even at room temperature. Resistance of brasses to degradation in sulphuric acid can only be improved by introducing 30% $CuSO_4{\bullet}5H_2O$ salt into the solution.

3. Electrolytic method

Two main cell structures are used in silver electrorefining: Balbach - Thum cell (horizontal) and Moebius cell (vertical) (Figs. 23, 24). The common features of both cells include anodes, cathodes, electrolyte, and anode compartmentalisation in bags to trap any insoluble material (usually gold and PGM) appearing at the anode. Both configurations have advantages and disadvantages, but most refineries use Moebius cells due to their small footprint, a large number of anode-cathode pairs that can be fitted in one cell, and the operations of control and collection of silver crystals being less labour intensive.

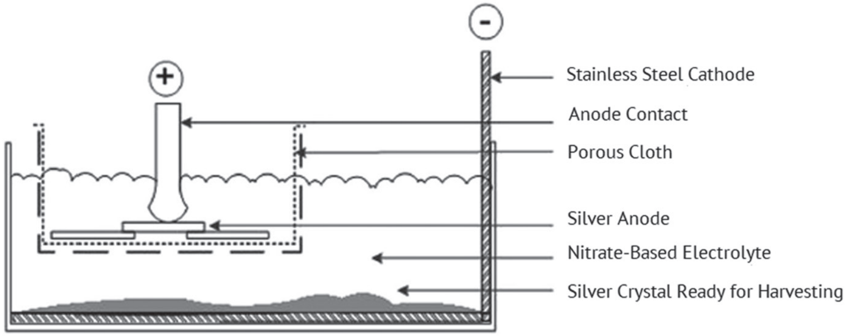


Fig. 23 – Configurations of Balbach–Thum silver electrorefining cells.

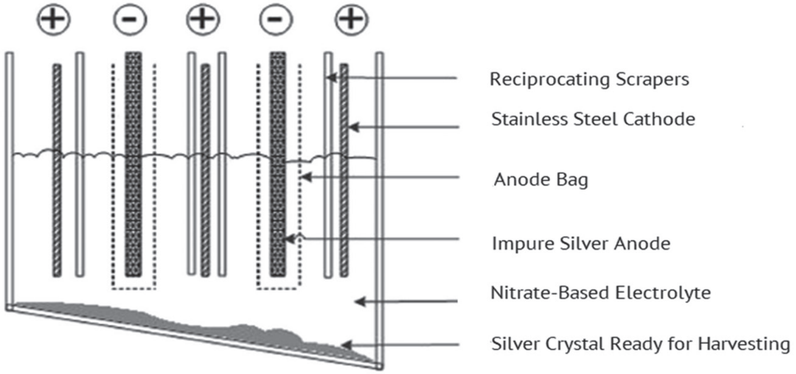


Fig. 24 – Configurations of Moebius silver electrorefining cells.

When implementing silver refining technology by electrolysis in vertical cells, anode residuals are formed. The forming residuals may reach up to 5–10% by weight of the starting anodes received for electrolytic refining. Conventional technology includes remelting of these middlings to produce starting anodes, which incurs additional expenses and increases metal retention time. The experts at Krastsvetmet have addressed this problem by developing a special anode basket that allows processing anode residuals without the need for the additional process step of remelting.

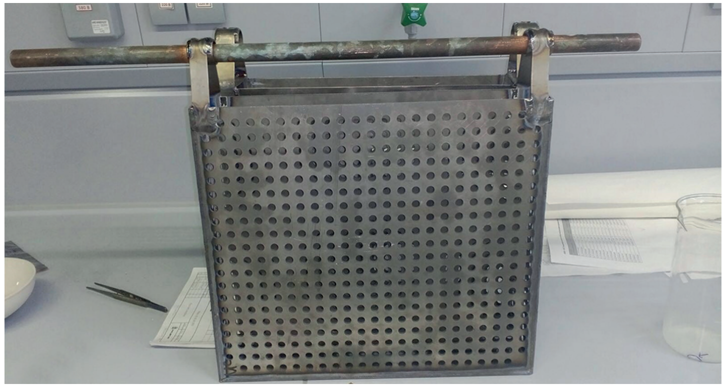
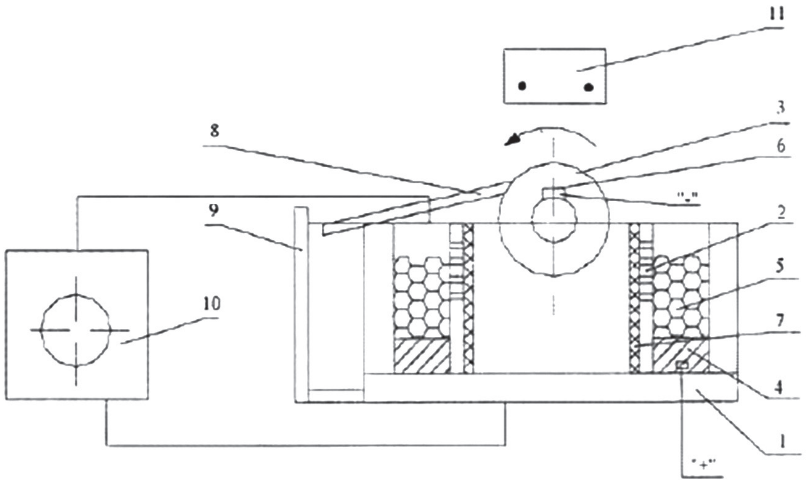


Fig. 25 – Anode basket, developed at Krastsvetmet.

Another way in which the technology of silver electrolytic refining can be improved is by developing the bulk anode technology.

At this moment, developed laboratory and pilot plants for electrolytic silver refining with bulk anode have been reported, and tests have been undertaken.

When conducting research, two models were studied – one with cylindrical and one with disk rotating cathodes. More stable results were obtained for the laboratory model with a rotating cylindrical cathode (Fig. 26), which was taken as the basis for designing the experimental device.



1 – electrolysis cell; 2 – cartridge; 3 – titanium cathode; 4 – graphite anode; 5 – pellets of crude silver; 6 – sliding contact; 7 – diaphragm; 8 – knife to scrape off refined silver; 9 – receiving container; 10 – pump; 11 – cathode rotation control unit.

Fig. 26 - Diagram of laboratory plant.

In the process of electrolytic refining, the dependence of refined silver yield on the following parameters was studied: mass concentration of silver, copper and nitric acid in electrolyte, and cathode density.

Spent electrolyte with correction for the composition in silver, copper and nitric acid was used as the electrolyte. After washing with one percent solution of nitric acid and distilled water, the cathode deposit was analysed for the following elements: arsenic, bismuth, platinum, palladium, lead, antimony, tellurium, cobalt, zinc, iron, gold, copper, manganese, rhodium, nickel.

In the course of laboratory studies, it was found that the structure of the electrolysis cell supports the electrolysis process in silver dissolution mode, with the process of silver accumulation in electrolyte proceeding effectively due to developed anodic surface of the pellets and the possibility of returning the first portions of silver crystals to the anodic chamber.

The dependence of nitric acid and silver content in electrolyte on the duration of the electrolysis process in silver dissolution mode was established. A working electrolyte with a mass concentration of silver of 200 g/l can be obtained within four-five hours.
This may allow for discarding the preparation of electrolyte in dedicated devices in the future.

The specific features of the developed electrolysis cell structure are:

- Utilisation of bulk anode, which increases anode surface for dissolution of crude silver pellets and decreases the amount of recirculated silver;
- Cathode revolution about a horizontal axis, which enables continuous recovery of refined silver crystals from electrolyte and improves product quality;
- Anodic slime and electrolyte from the anode chamber can be sent to the nutsche filter, and the obtained filtrate (electrolyte) is returned to the cell.

Tests of the built experimental device have confirmed its functioning, potential, and the need to develop a pilot plant.

As compared to electrolysis cell with vertical electrodes, the developed novel mechanised electrolysis cell with bulk anode and continuous discharge of the finished product allows to:

- Eliminate smelting of the entire metal for anodes, as the silver received at the factory after incoming smelting can be immediately granulated;
- Eliminate the operations of preparation, melting, and second refining of anode residuals;
- Improve the quality of refined metal;
- Decrease the amount of recirculated silver by 3–4 times;
- Reduce manual labour and improve labour productivity.

4. Electroextraction

The starting electrolyte containing the main components is loaded into a common circulation tank of the silver electroextraction plant. Electrolyte is circulated over the line of the circulation tank by a pump. Any excess of electrolyte from the electroextraction plant drains by gravity back to the circulation tank to avoid overflowing the electrolysis cell with electrolyte.

After starting electrolyte circulation, the scraping mechanism of the electroextraction plant is activated to separate the obtained cathodic silver from the cathode to the bottom of the electroextraction cell.

Current sources with preset (known) parameters of current and voltage are switched on.

The end of the process is determined by the threshold content of the main component Ag in the electrolyte, provided the content parameters for other elements in the electrolyte are met. Such electrolyte is considered spent, which in turn leads to the process being considered finished.

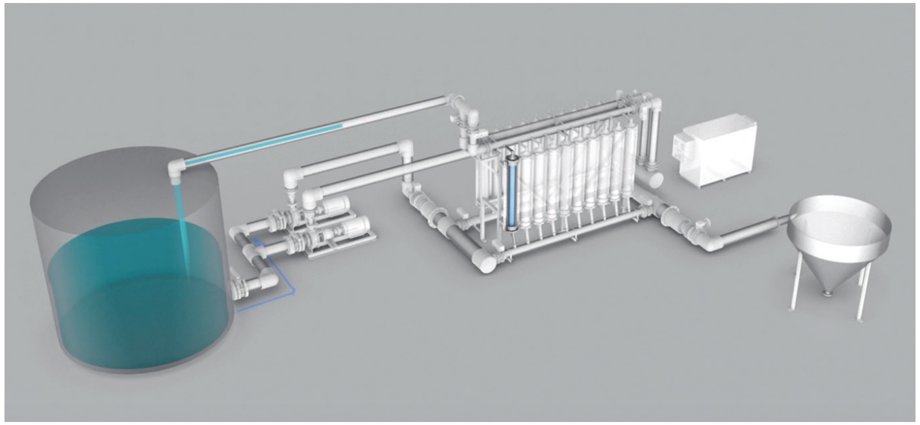


Fig. 27 – Equipment for electroextraction.

5. Precipitation by reagents

Silver refining with precipitation methods is performed using hydrometallurgical reaction equipment:

- Reactors;
- Nutsche filters;
- Containers to collect solutions;
- Filter presses.

Considering the specifics of chemical processes, the equipment directly in contact with the precipitation solution is made either ot itanium or of polypropylene.

Fig. 28 – Chemical reactor made of polypropylene (left) and titanium (right).

SUMMARY OF SILVER REFINING TECHNOLOGIES

Technologies	Advantages	Disadvantages
Breaking down silver-containing materials		
1. Dissolution in nitric acid	Shorter duration of refining.	Evolution of nitric oxides that either have to be trapped or need additional methods for neutralisation.
		Generation of solutions containing nitrates and nitrites, which incurs additional expenses for their utilisation.
		Obtaining refined silver requires several additional process steps to remove BE. Feedstock with gold content less than 5–10% is not recommended for processing using this technology.
2. Dissolution in sulphuric acid	Possibility to process lean concentrates containing more than 70% of BE.	Limited silver solubility in sulphuric acid solutions leads to multistep processing and requires more rigid conditions (temperature and acid concentration).
		The required water consumption is several times higher than conventional electrolysis or electroextraction.
		The technology is applied for processing and preliminary enrichment of lean silver-containing scraps with high BE content and is an auxiliary operation for refining.

Silver reduction		
1. Electrolytic method	Well-established technology, wide selection of equipment, simplicity and reliability.	Extended duration of gold refining.
	The method ensures stable production of refined silver that is more than 99.99% pure.	Limitation on gold content, less than 10%.
	The method can be combined with vacuum distillation, resulting in providing silver to electrolysis containing less than 3–5% Au.	Silver retention in electrolyte and anode residuals.
		Limited throughput in the presence of Pd, Te as impurities.
2. Electroextraction	Shorter duration of silver refining.	Stringent requirements to electrolyte (by Pb, Se, Te); the need to adapt electrolyte and use feedstock with minimal content of impurity elements.
		The need to utilise nitric oxides at the step of nitric acid dissolution, the need to perform oxidative melt refining.
		Low current yields and high operating expenses, in particular, it is not recommended if the gold content in feedstock is less than 5–10%. Expensive equipment.
3. Precipitation by reagents	Possibility to process not only hydrochlorination and ARL cakes, but also chloride slags.	High operating expenses for the reagents.
	Separation of gold from silver already at the first process step.	Higher demands with respect to impurity profile in the initial feedstock; as a rule, the precipitation methods work in combination with electrolysis or electroextraction.
	Reduced recirculated gold in subsequent electrolytic technology of silver refining.	Additional expenses for neutralising formaldehyde-containing solutions.
	Possibility to obtain refined silver without electrolysis.	