Chapter 5

PRECIOUS METALS REFINING PRACTICE

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ABSTRACT

Anode mud, the residual material collected from the bottom of the electrolytic cells during the refining of copper is leached, roasted, fire-refined and cast into Dore' metal anodes. Dore' metal is a gold-silver-copper alloy containing 80 percent silver. The metal is processed electrolytically using the Moebius system to refine silver and separate gold, platinum and palladium. The Moebius cell cathodes receive a deposit of silver crystals which are melted and cast into 1000 ounce silver bars with 999 Fine minimum purity. Gold mud is collected in fabric bags and cast into gold anodes for further refining in the Wohlwill cells. Wohlwill cells are unique in that gold, the noble metal, can be put into solution electrolytically without the use of aqua regia. Gold is collected on high purity gold foil cathodes and cast into 400 ounce bullion with 999.7 Fine minimum purity. Platinum and palladium remain in the electrolyte progressively increasing in concentration and are finally separated and purified by precipitation.

INTRODUCTION

Anode mud, the residual material collected from the bottom of the electrolytic cells during the refining of copper, is pumped to the Silver Refinery plant to process for precious metals and selenium. Anode mud contains up to twelve percent selenium combined as copper and silver selenides. Gold exists in the uncombined state and in combination with tellurium. The color of anode mud is predominantly black with streaks of grey gypsum. Particle size range from minus 300 mesh down to micron range. Particle size characterizes it as a slime hence it is also known as anode slime.

General chemical and physical characteristics of slime vary with its constituents. From time to time change is noted in color, particle size, and free settling rate wich may adversely affect filtering. Gold and silver content also varies considerably depending upon the ore body. Typical anode mud composition is shown in Table 1.

Table 1. - Anode Mud Composition

Copper	30 %
Selenium	12 %
Tellurium	3 %
Lead	2 %
Arsenic	2 %
Antimony	0.5 %
Silver	2900 oz per ton
Gold	290 oz per ton
Palladium	2.3 oz per ton
Platinum	0.2 oz per ton

The objective in treating anode mud is to recover precious metals by the most direct and expeditious means available, but direct smelting of slime is not always desirable (1,2). Although a high initial gold fall is obtained by this method, excessive matte and slag formation causes heavy recirculation of precious metals, particularly silver. The general plan practiced by most silver refineries is to separate the slime components one by one. Separation should provide high recovery of each element separately to permit immediate withdrawal from the circuit. By this plan each product may be recovered in a reasonably pure state. It is essential that the recovery of each component is sufficiently high to preclude the necessity for reworking large volumes of residues. If separation is inefficient, run-around products will be generated which cannot be handled by the basic metallurgical flow sheet. Then in order to treat the low grade residues the flow sheet becomes further complicated by additional treatment steps. This in turn increases operating and maintenance costs. Consequently most plant prefer to treat anode mud by hydrometallurgical methods prior to smelting (3). The Utah Refinery also prefers this method.

TREATMENT OF ANODE SLIME

Dry slime from the Kennecott Refining Corporation at Baltimore, is blended with leached Utah slime and charged to two 6 ft x 14 ft rotary kilns where a fusion with sodium bisulfate is effected. The slime is decomposed at 1000 to

1200 °F in a strong acid environment. Selenium compounds are decomposed and the selenium is volatilized off as elemental selenium and selenium dioxide. The fusion brings about complete oxidation or sulfatization of remaining elements except gold and the platinum metals group. The following chemical reactions take place:

$$Cu + 2\,H_2SO_4 \longrightarrow CuSO_4 + SO_2 + 2\,H_2O \qquad (1)$$

$$Ag_2Se + 2\,H_2SO_4 + O_2 \longrightarrow Ag_2SO_4 + SeO_2 + SO_2 + 2\,H_2O \qquad (2)$$

$$CuSe + 2\,H_2SO_4 + O_2 \longrightarrow CuSO_4 + SeO_2 + SO_2 + 2\,H_2O \qquad (3)$$

$$AuTe + 2\,H_2SO_4 \longrightarrow Au + TeO.SO_3 + SO_2 + 2\,H_2O \qquad (4)$$

Further detail showing side reactions encountered during fusion and treatment of product gases are given in a previous paper "Separation and Purification of Selenium from Anode Slimes" (4).

Elemental selenium is collected by passing the fume through a train of water-spray scrubbers and an electrostatic precipitator. The amorphous selenium produced is in turn collected from the scrubber solutions by flotation using methyl amyl alcohol and liquid colloid glue.

When the fusion is complete, the molten material is granulated by pouring the melt into a fast moving stream of cold water. The granulated fusion cake is then leached with hot water. At this point all the copper sulfate, silver sulfate and most of the sodium bisulfate have been solubilized. During the leaching operation copper powder is added in stoichiometric proportions to cement out soluble silver completely but without leaving unreacted copper in the slurry. The leach is then settled, the supernatant liquid removed by decantation, the settled solids filtered, washed and dried in a 42 in. Shriver pressure filter. A simplified flow sheet is shown in Figure 1.

The partially dry filter cake, about 18 % moisture, is charged manually to a 75 sq ft natural gas fired reverberatory furnace. The first slag taken is a slime oxide slag. The second slag is a soda slag containing many of the amphoteric impurities, e. g. , arsenates, selenates, antimonates, tellurates and a small amount of copper oxides. These impurities are removed from the metal bath by oxidizing with air and fluxing with sodium carbonate. The third and final slag is a niter slag resulting from oxidation with air and sodium nitrate. The third slag contains copper oxides together with remaining impurities (5).

All slags are returned to the copper smelter since these contain varying amounts of precious metals. When the copper content in the dore' metal has

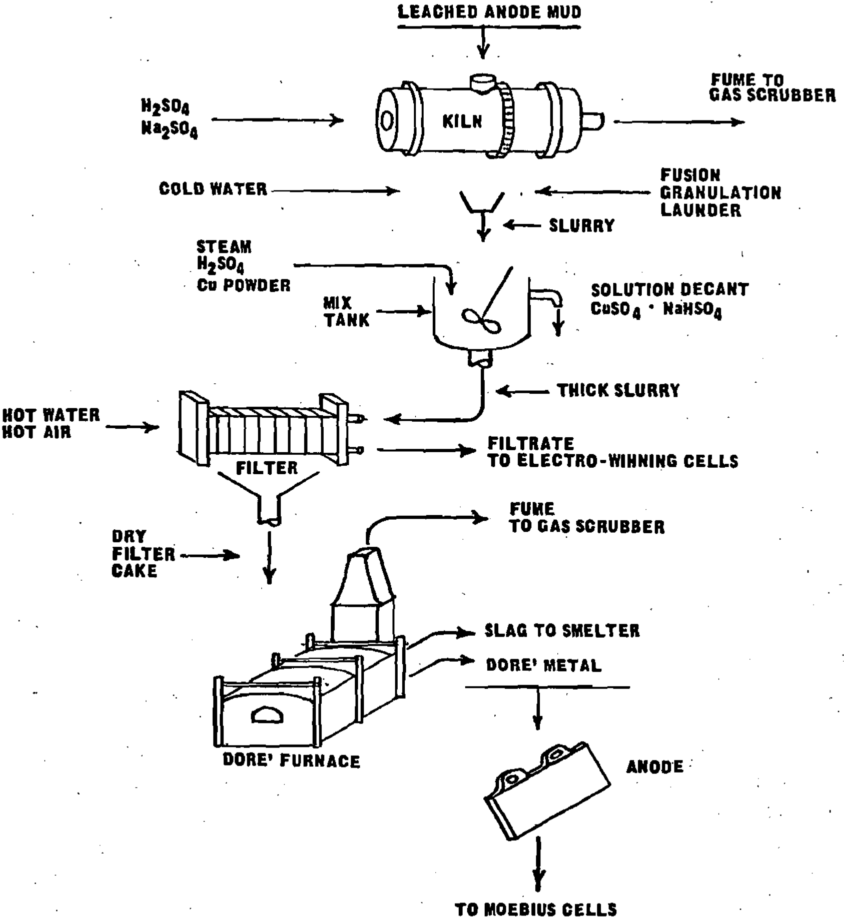


Figure 1. - Simplified Flow Sheet for the Treatment of Anode Slime

been reduced to less than one percent by fire refining, the metal is ready to cast. Copper content is a good indicator to judge the purity of dore' metal. As the impurities oxidize they leave the metal bath and enter the slag. Copper is the most difficult to oxidize and the last impurity that is removed from the molten bath.

Prior to casting, the metal bath is cleaned by skimming off all slag. Furnace heat is reduced and Portland cement is scattered uniformly on the bath to collect slag. Slag and cement is then carefully skimmed off leaving clean metal. The material skimmed is rich in metal and it is returned to the furnace at the start of the next charge.

During the casting of anodes, the hot metal is transferred from furnace to mold with a hand ladle supported by a crawl and beam. The finished anodes are 8.5 in.x 17 in.x 1 in.thick and weigh about 48 lbs. Two eyes are cast in the top side of the anode for suspension in the cells with copper hooks.

Flue gases leave the dore' furnace at 2500 °F, pass through a brick flue, brick-lined primary scrubber, Heil 14,000 cfm venturi scrubber, and two 10,000 cfm electrostatic precipitators before being discharged to the atmosphere. Water circulates through the scrubbers at a rate of 600 gpm to cool and scrub the gases. Particulate matter scrubbed out of the gas stream is settled in a 1180 cu ft collection tank. Scrubber mud collected is continuously pumped from the bottom of the tank and dewatered by filtering through a Sperry 36 in.pressure filter. Scrubber mud re-enters the process for the recovery of gold and silver.

A good quality dore' anode is a prerequisite for fine silver bullion. Since silver bullion cannot tolerate impurities greater than one part per thousand, very careful fire refining of dore' metal is necessary to eliminate impurities including selenium, tellurium, antimony, lead and arsenic. Copper, up to one percent, can be tolerated. But since copper fouls the silver nitrate electrolyte in the Moebius operation, it is good practice to keep the electrolyte concentration in copper at about 45 gpl. Heavy discard of electrolyte must also be held to a minimum since all discarded electrolyte must be reprocessed to recover silver content. A typical analysis of dore' metal is shown in Table 2.

Table 2. - Dore' Metal Analysis

Gold	8 to 9 %
Silver	86 to 92 %
Copper	0.5 to 1.0 %
Palladium	0.16 to 0.18 %
Platinum	0.005 to 0.009 %
Lead	0.02 %
Tellurium	0.003 %
Selenium	0.00002 %

ELECTROLYTIC PARTING OF DORE' METAL

The dore' anodes are processed electrolytically to refine silver and separate gold. Four anodes are suspended from four separate buss bars in each Moebius cell. Each anode is encased in a polypropylene woven bag which collects gold mud as the anode dissolves. Cathodes are titanium plates 20 in.x 15 in.x 1/16 in. thick. Anodes and cathodes are both suspended in a stainless steel basket having a filter cloth bottom supported with stainless screen. Oscillating scrapers continuously brush the silver crystals from the cathode plate into the collection baskets. During the period that the cell is energized, the whole assembly , including the baskets, is submerged in a 26 in.x 26 in.x 22 in.deep polyester fiberglass tank filled with silver nitrate electrolyte. The Parting room contains a total of 36 cells in 6 banks. Each bank contains 6 cells. Each bank is equipped with a hydraulic hoist to lift the baskets.

The anodes are depleted 60 hours after charging. The collection baskets are then hoisted out of the tanks and the electrolyte is allowed to drain free of the silver crystals. The bottom of the baskets are then dropped and the crystals are collected in stainless steel filter carts where the crystals are washed several times with distilled water. Vacuum is applied to the filter carts to remove wash water. The crystals are then dried in the same manner by pulling air through the crystal bed. The dry crystals are then transferred to a melting furnace and cast into silver bullion bars.

The furnace is a natural gas fired, 25,000 oz capacity graphite retort equipped with a tilting control for pouring. The molds are cast iron with a pin hinge at one end and a lifting eye at the other end to allow the mold to be inverted and the bar to drop out. The silver is cast into 1000 troy ounce bullion bars assaying 999.7 parts per thousand silver, 0.2 parts per thousand copper and less than 2 parts per million gold. Each cast is sampled by pouring a shot sample into distilled water contained in a stainless steel beaker. Each cast is identified by cast number and each bar by bar number. Each bar is weighed and check weighed to 1/100 of a troy ounce and stamped accordingly.

Parting plant data is shown in Table 3 (6). The electrolyte is silver nitrate. New electrolyte is made by dissolving scrap anodes in hot nitric acid. For this purpose a stainless steel vessel is used which is carefully hooded to collect toxic nitric oxide fume that is released during the process. As mentioned previously, copper content in the electrolyte is an impurity picked up from the anode. When the content exceeds 45 gpl the electrolyte is removed, desilverized and discarded. Free acid content varies between a range which corresponds to a pH of 1 to 1.5. Fresh electrolyte and distilled water is added to replace the foul electrolyte discarded. Electrolyte mixing is necessary to provide uniform silver ion concentration at the cathode. This is accomplished by the oscillating

Table 3. - Moebius Cell Data

Anodes:	Size - 17in. x 8 1/2 in. x 1 in.
	Weight - 48 lbs
	Anodes per cell - 4
	Anode life - 60 hours
	Scrap - 15 % of anode
	Anode bag size - 20 in. x 14 in. x 1 3/4 in.
Cathodes:	Titanium plate - 20 in. x 15 in. x 1/16 in.
	Cathodes per cell - 5
Electrolyte:	Silver nitrate
	Ag - 150 gpl
	Cu - 50 gpl
	pH - 1.0 to 1.5
	Temperature - 90°F
Current:	Cathode current density - 28 amps/sq ft
	Amps per circuit - 400 amps
	Voltage per cell - 2.7 volts
	Circuit system - multiple
Cells:	Number of cells in parting plant - 36
	Number of cells per circuit - 18
	Number of cells per bank - 6

cathode scraper which also brushes the silver crystals off the cathode plates. Without mixing, catholyte will be formed. Depletion of silver ions at the cathode face will result in codeposition of impurities, which in turn will contaminate the silver crystals. The electrolyte is heated by electrical resistance of the current passing through the electrolyte. Normally, another means of heating the electrolyte is not required.

Foul silver nitrate electrolyte and silver sulfate, decanted from the gold boiling operation are de-silverized separately by cementing the soluble silver out of solution with copper powder. The reaction is simple metal replacement from each of the two solutions:

$$Ag_2SO_4 + Cu \rightarrow 2\,\underline{Ag} + CuSO_4 \qquad (5)$$

$$2\,AgNO_3 + Cu \rightarrow 2\,\underline{Ag} + Cu(NO_3)_2 \qquad (6)$$

The silver precipitate is collected, joined with the dore' anode scrap, remeltec and cast into dore' anodes. Another method that may be used to recover silver from foul electrolyte is precipitation as the chloride (7).

Figure 2 is a graphic summary of the Moebius operation showing the dore' anode entering the Moebius cells, intermediate products and the resultant product, silver bullion.

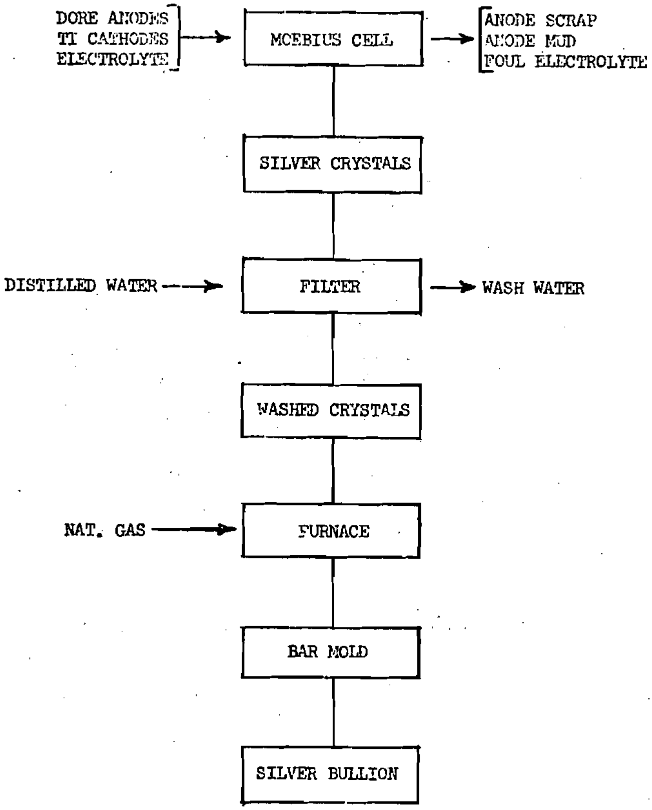


Figure 2. - Summary Flow Sheet for the Parting of Dore' Metal

Electrical power is supplied to eighteen cells by a 40 kw, direct current motor-generator unit. The other eighteen cells are supplied by a 45 kw, direct current silicon rectifier. Each unit is rated at 500 amps. The system uses the multiple circuit configuration as shown on figure 3. Each cell is in series

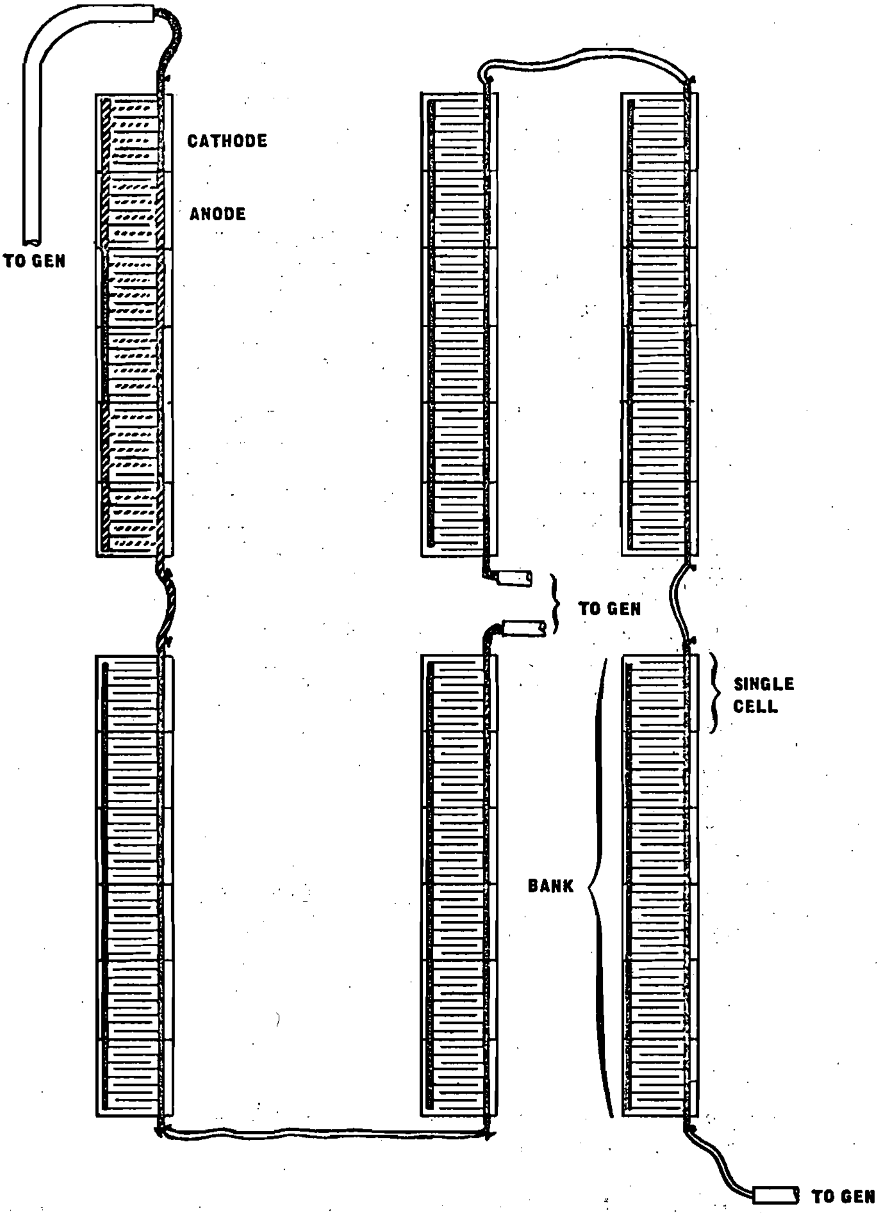
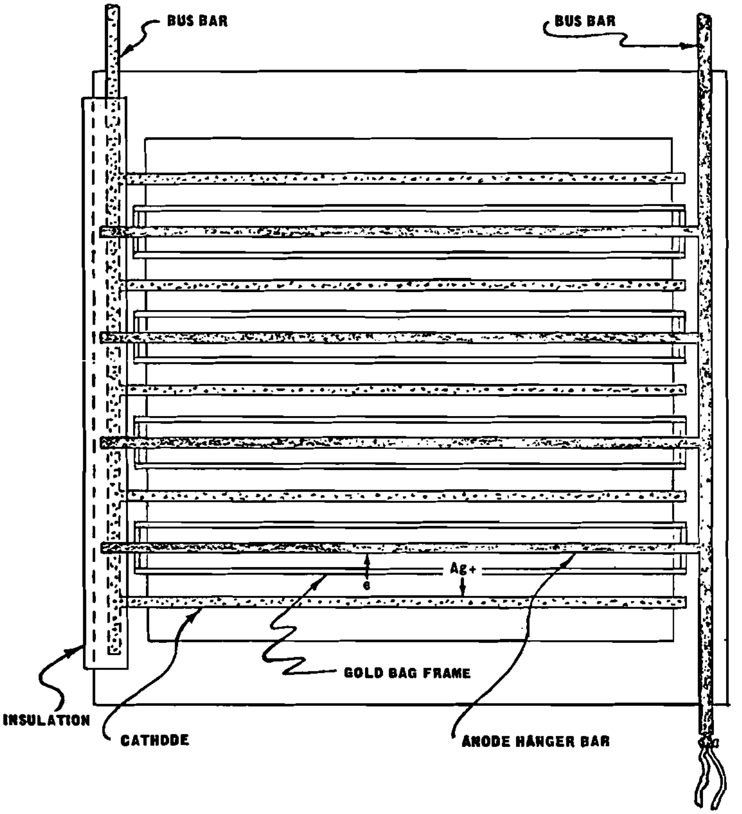


Figure 3. - Moebius Cell Banks Multiple Circuit



OHM'S LAW

E = IR
I = CONSTANT
R VARIES
E VARIES

FARADAY'S LAW

26.8 AMP/HR DEPOSITS 107.88 grams Ag

$$\text{CURRENT EFFICIENCY} = \frac{\text{ACTUAL DEPOSIT}}{\text{THEORITICAL DEPOSIT}} \text{ X } 100 = \qquad \%$$

Figure 4. - Moebius Cell Detail

hook-up with the generator and each cell is in parallel hook-up in reference to anode and cathode as illustrated on figure 4.

Optimum current density is 28 amps per sq ft of cathode area. Higher cathode current densities may be obtained but higher densities also increase the frequency of burning gold mud bags. When bags burn, silver is contaminated with gold, and the entire crystal harvest from the cell must be reprocessed.

ELECTROLYTIC REFINING OF GOLD

As the silver dissolves from the anode in the parting cell, and is transferred by ion migration to the cathode, insoluble gold falls from the anode and is collected in mud bags. When the bags are full they are removed from the cells and the black gold mud is harvested by dumping the bags in a filter cart where the gold is combined with gold collected from cleaning the anode scrap. The material is thoroughly washed on the filter to remove nitrates, boiled with concentrated sulfuric acid several times to dissolve silver and finally washed repeatedly in a filter cart with distilled water to remove soluble silver. The resulting yellow gold sand is dried, melted in a 5,000 troy ounce capacity Ajax-Northrup electrical induction furnace and cast into gold anodes. Average weight of the anode is 225 troy ounces, and it measures 7 1/2 in. x 7 in. x 1/2 in. thick. Each anode is cast with two eyes for suspension in the Wohlwill cells with silver hooks. Typical analysis of the gold anode is given in Table 4. Process flow of anode mud to the gold anode is shown on Figure 5.

Table 4. - Gold Anode Analysis

Gold	991.8 Fine, parts per 1000
Palladium	5.0
Silver	1.0 or less
Platinum	0.8 or less

Anode casting equipment is a simple table type mold carrier with leveling screws on the legs. Mold chills are set on a roller plate and moved into position under the pouring spout of the furnace. Core plugs are set in the chills to provide eyes in the gold anode for attaching suspension hooks.

In the Wohlwill process, the gold anodes are electrolyzed in a hot solution of gold chloride ($AuCl_3$). The solution is kept hot (140°F) primarily by the resistance of current passing through the electrolyte. However, the solution is also heated during cold weather when room temperature is below 70 °F. Anode current density is 115 amps per sq ft.

Two gold anodes are suspended with silver hooks in each cell. The cell tanks are porcelain-ceramic, 11 in. x 11 in. x 12 in. deep. Solution level is carefully adjusted to prevent submersion of the silver hooks in the gold electrolyte.

There are three cathodes in each cell. Each cathode consists of three sheets of gold foil strips, 2 in. wide by 0.015 in. thick attached to a copper hanger

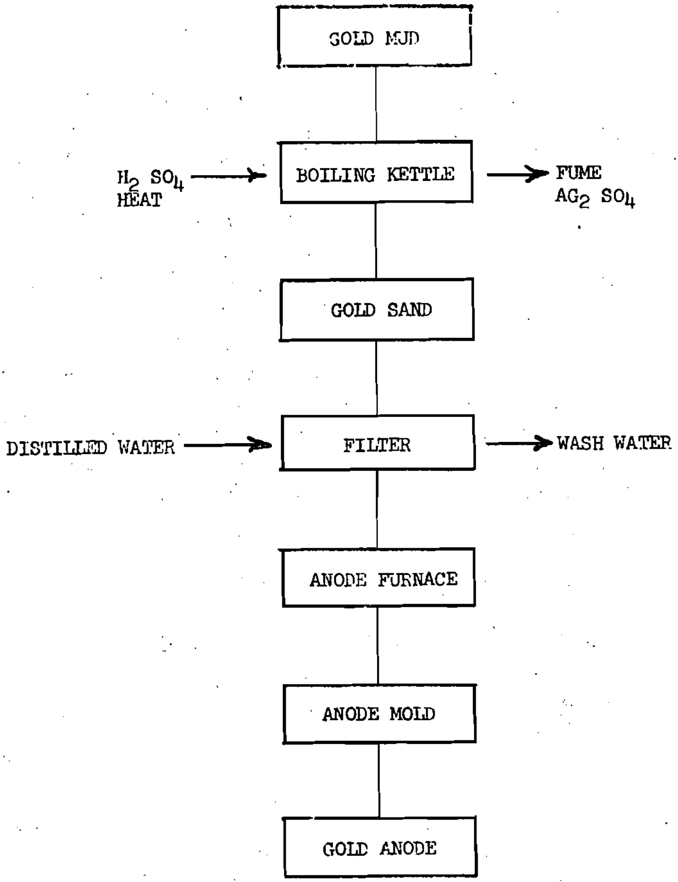


Figure 5. - Process Flow of Anode Mud to Gold Anode

bar and suspended in the electrolyte 1/2 in. from the anode. The electrolyte is stirred by means of a small air lift bubbling constantly at low rate. Anode life is about 18 hours. Gold plates rapidly on the cathode producing rough nodular deposits. The nodular deposits will bridge to the anode if allowed to do so. To prevent shorting between anode and cathode, the cathodes are lifted out of the solution periodically, nodules removed and the cathode returned to the cell. Cell efficiency drops rapidly when shorting occurs. Co-deposition of impurities also begins to occur if shorts are not immediately corrected.

As the gold anode dissolves electrolytically, impurities in the anode also dissolve. Platinum and palladium dissolve and remain in solution. Silver dissolves but is immediately converted to insoluble silver chloride, which will normally settle to the bottom of the cell as sludge unless the air lift agitation is excessive. Other metals that will dissolve anodically if present are copper, lead and other platinum group metals (Iridium, Rhodium, Ruthenium). Copper and lead are soluble in the electrolyte but iridium, rhodium and ruthenium will settle to slime.

Control of electrolyte composition, temperature, current density and other variables in the cell is critical to the production of high quality gold cathodes. Electrolyte is replaced periodically when the combined concentration of platinum and palladium salts exceed 75 gpl.

Table 5. - Gold Electrolyte

Au	150 - 200 gpl
Free HCl	140 gpl
Pt and Pd	75 gpl
Temperature	140 °F

The most common cathodic impurities that will co-deposit with gold is silver, palladium and platinum. As mentioned previously, excessive agitation of electrolyte will stir up insoluble slime material from the bottom of the cell which will migrate to the cathode along with the gold ion. When this condition occurs, the gold bullion bar may contain silver as well as metals of the platinum group. The practice of maintaining strong concentrations of gold in the electrolyte overcomes to a great degree the adverse influence of impurities to co-deposit on the cathode.

New electrolyte is made by dissolving gold in hydrochloric acid electrolytically. Gold anodes are suspended in an electrolytic tank containing hydrochloric acid. The cathode (gold foil) is placed in an unglazed, porous ceramic cup which prevents gold from plating on the cathode. Aurous chloride ($AuCl_2$) therefore becomes concentrated in the electrolyte. New electrolyte is pale-yellow due to aurous chloride salt. This salt is unstable and will either decompose to metallic gold and hydrochloric acid, or in an oxidizing environment will go to auric chloride ($AuCl_3$). The air lift provides oxygen for this conversion. With continued use in the production cell, the electrolyte is entirely converted to the stable, red-brown $AuCl_3$. Auric chloride is very soluble at cell operating temperatures. The best deposits, and best current efficiencies, are obtained in the range of 180 °F, but volatilization of HCl increases. This in turn increases the concentration of gold salts in the electrolyte causing metallic gold to precipitate in cell mud and increasing acid consumption.

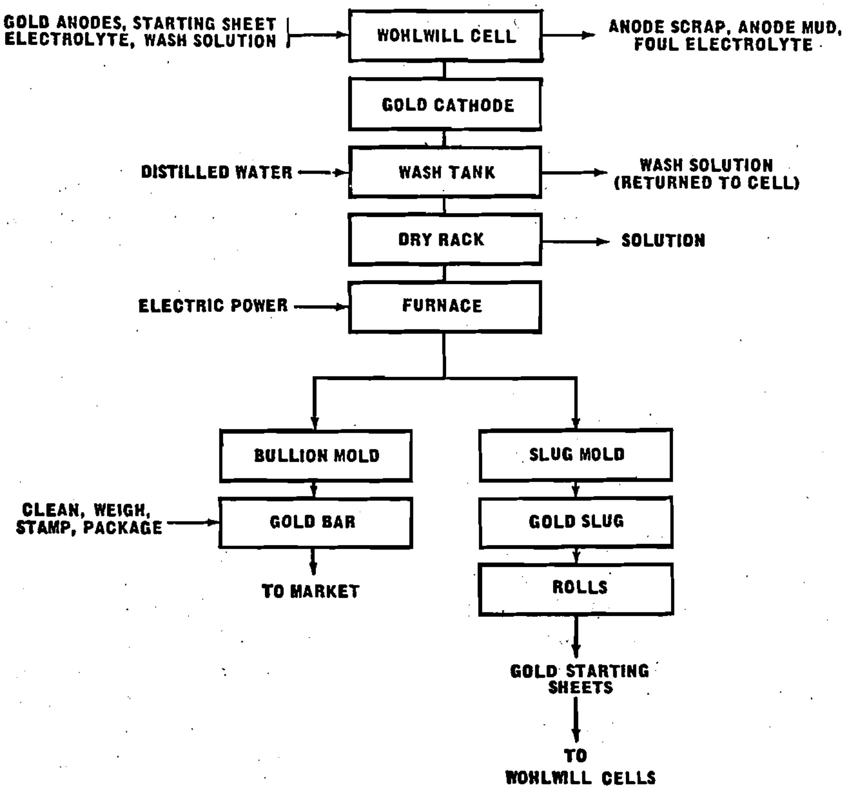


Figure 6. - Summary Flow Sheet for the Refining of Gold

With continued use of electrolyte, platinum and palladium increase in concentration in the electrolyte to a point that both can be removed by chemical processing (8). The processing of foul electrolyte to recover these precious metals and gold is detailed and time consuming. Each metal is removed separately as a metallic salt by chemical precipitation. Platinum is withdrawn from the solution as insoluble ammonium chloroplatinate, $(NH_4)_2PtCl_6$. Palladium is initially precipitated as ammonium chloropalladate, $(NH_4)_2PdCl_6$. Gold is precipitated as elemental Au by reduction with sulfur dioxide.

Initial precipitates have to be reworked since each precipitate contains occlusions of the other two metals. Ammonium chloroplatinate in particular requires considerable reworking. Reworking includes drying the precipitate, igniting in a furnace, reduction, redissolving the mixed metals in aqua regia, boiling to drive off nitric acid, redissolving in hydrochloric acid, dilution, gassing with sulfur dioxide to reduce gold, filtering to recover gold, boiling the filtrate to release SO_2, adjusting pH and finally reprecipitating as ammonium chloroplatinate. The precipitate is thoroughly washed to remove soluble palladium. The precipitate is then ignited in a furnace and reduced to elemental platinum. After two or more reworkings to remove other salts present, platinum is up-graded to a minimum 99.5 % purity, and it is marketed as sponge metal.

The filtrate from the initial precipitation carries the majority of the palladium. Gold is first removed by reduction with SO_2. After filtering off the elemental gold, the filtrate is processed in a similar manner as for the platinum and finally precipitated as a yellow palladium dichlorodiammine precipitate, ignited in a furnace and reduced to sponge palladium metal, 99.5 % palladium.

Savitskii is an interesting reference on the chemistry of palladium and platinum salts (9).

The gold precipitate is either returned to gold anodes or melted with cathodes and cast into gold bullion. Figure 6 illustrates the sequence of operations from the gold anodes entering the Wohlwill cell to the melting and casting of gold bullion.

REFERENCES

1. Benard, F., "Electrolytic Copper Refinery of Ontario Refining Co. Ltd.", Trans. AIME, 106, 1933, p. 369-397.

2. Mosher, M.A., "Recovery of Precious and Secondary Metals from Electrolytic Copper Refining", Trans. AIME, 106, 1933, p. 427-440.

3. Schloen, J.H., and Elkin, E.M., "Treatment of Electrolytic Copper Refinery Slimes", Trans. AIME, 188, 1950, p. 764-777.

4. Leigh, A.H., "Separation and Purification of Selenium from Anode Slimes", Master's Thesis, University of Utah, 1953, p. 38-41.

5. Schloen, J.H., and Elkin, E.M., "Canadian Copper Refiners Montreal East Plant", Trans. Can. Inst. Mng. Met., 49, 1946, p. 158-159.

6. Mantell, C.L., Electrochemical Engineering, Mc Graw Hill Book Co., New York, 4th Edition, 1960, p. 172-173.

7. Richards, A.E., "The Refining of Gold and Silver", The Refining of Non-Ferrous Metals, Symposium 1949, Salisbury House, London, 1950, p. 110.

8. Dale, H.G., "The Precious Metals", The Refining of Non-Ferrous Metals, Symposium 1949, Salisbury House, London, 1950, p. 128.

9. Savitskii, E.M., et al., Palladium Alloys, Translated from Russian by R.E. Hammond, Primary Sources Publishers, New York, 1969, p. 33-34.