Silver is a reflective white metal that holds a shine a long time and is used for jewelry, coinage, flatware, photography, x-ray, many chemical and electronic applications. This article will explore the techniques used to refine silver and take it to a pure state. There are four generic refining techniques: Pyrometallurgical (fire refining), chemical, electrolytic, and electro winning.

OVERVIEW

Silver refining has been used from ancient times to change the characteristics of the metal. Early metallurgists refined silver by heating it a couple hundred degrees above its melting point and holding the metal at an elevated temperature for a period of time. This was a good way to remove impurities that tended to make the metal brittle. The purpose of heating the metal was to oxidize many of the impurities so that they could be dissolved in the flux. Pyrometallurgical refining will be discussed later in a section.

Chemical refining is a technique in which the metal is dissolved in nitric or sulfuric acid to make a silver salt which can be then precipitated as a chloride and washed to remove impurities adhering to the chloride particles. The silver metal is recovered from the chloride by a chemical reduction process.

Chemical refining consumes a lot of acid. Refining large quantities of metal is normally accomplished electrolytically in a cell in which the impure silver serves as the anode and silver is transported by the electrolyte to a cathode that is inert to the chemistry of the cell. In this process the acid is consumed, but in smaller quantities than in the chemical technique. Because the product is silver crystal, it can be melted directly and the silver chloride reduction step is not needed.

The three techniques defined above assume that the silver is in metallic form either as a chunk of metal or as an alloy. If the metal is in the form of a dilute solution rather than in metallic form, it can be recovered by electro winning or selective precipitation or by ion exchange. This is the process that is used to sequester metal from heap leaching, from photographic fixer, or other processes that have silver dissolved in an aqueous solution.

Other processes are touted in the literature, but they are generally adaptations or combinations of the above methods. Regardless of the process, the objective is to make metal that can be poured into a bar or stamped into a coin as shown in Photo # 1.
Pyro metallurgy or fire refining is used to recover metals from ores, concentrates, placer sands or other sources that may contain metals or metallic salts in combination with silica or other rock like constituents that come along with the valuable metal in the concentrating process. Pyro metallurgy involves heating the concentrate with fluxes that are chosen to dissolve the unwanted constituents of the melt. Fire refining may be selected to remove a combustible component of the concentrate or to heat the melt to a point at which the impurity would form an oxide that dissolves in the flux or burns off in the atmosphere of the furnace. In the case of ore concentrates, the unwanted metal may be removed by fluxing the high temperature melt.

Soda ash is used in the flux to remove and complex low melting impurities like lead and zinc and other metallic oxides. Borax is used as a diluent in the flux to reduce the activity of the soda ash and cause the fluxes to melt at a lower temperature. Niter or sodium nitrate is sometimes used to oxidize sulfur and tellurium and to remove them from the melt or heat. If the primary impurity in the silver is sulfur, it can be removed by extended heating of the melt at high temperature or by adding metallic iron to the melt. The iron will react with the sulfur making pyrite or iron sulfide. This will free the silver to fall in the melt and combine with the metal at the bottom of the crucible. The furnace man must keep an eye on this process to insure that the flux on top of the metal does not become too viscous or the little beads of silver formed from the reduced silver sulfide will not be able to fall through the flux into the pool of...
silver at the bottom of the crucible. If the flux ceases to be the consistency of water, extra borax is added to dilute the flux and increase its fluidity, or the furnace temperature is increased to make the flux more fluid. A typical pot furnace that can hold a crucible with a one gallon capacity of molten material is shown in Photo 2.

PHOTO 2. McENGELEVAN NUMBER 16 POT FURNACE MELTING SILVER

Old timers often referred to iron as the mother of silver and gold because it was used to oxidize the sulfur to pyrite and to reduce the silver to metallic form so that it could fall through the fluxes and coalesce with the molten silver at the bottom of the melt. This high temperature replacement technique comes with a problem because silver sulfide is soluble in pyrite and pyrite has the ability to hold more than one atom of sulfur in its molecule. (Yes, this iron sulfur compound may have other chemical names, but for the simplicity of this discussion we will refer to it as pyrite.) By using a stainless steel tube or pipe held below the liquid level of the silver to inject compressed air into the melt, the excess sulfur can be oxidized out of the melt. Blowing with compressed air also oxidizes some of the pyrite to iron oxide that will not dissolve silver sulfide, but the iron oxide will dissolve in the remaining pyrite and fluxes. Conversion of some of the pyrite to iron oxide eliminates this loss of silver in the flux. Blowing with compressed air also eliminates the zinc and lead that may remain in the heat. In addition, the compressed air oxidizes some of the copper, removing it from the silver. The oxides made by compressed air blowing are soluble in the soda ash and borax in the flux, and are removed with the flux. The final step in the fire refining step is to pour the melt or heat into a conical mold. Metals sink to the point of the cone and slag components rise to the surface. Slag can be separated from the cooled mass by striking the metal-slag interface with a hammer after it has cooled and solidified. The metallic
component is taken to the next step of the refining process. Often this metal cone or “king” as the old timers would call it, was remelted and poured into an anode mold and used as the starting material for the electro refining cells. This is shown in Photo 5. Slags generated by this process can be used as the starting material for other procedures if there is enough value present to justify further work.
PHOTO 4. CRACKING THE SILVER FROM THE KING

PHOTO 5. POURING SILVER INTO AN ANODE MOLD
Years ago before oxidizing the melt with compressed air became popular, a green log or branch was thrust into the molten silver in the final refining stages and used to stir the melt. The burning sap and wood would oxidize impurities and bring them to the surface so they could combine with the fluxes or skimmed off. The old timers referred to this process as poling the melt.

CHEMICAL REFINING

Small quantities of silver can be refined by dissolving them in nitric acid. The acid will solubilize the silver and copper and other base metals leaving any gold or platinum as a sludge on the bottom of the dissolving vessel. If the nitrate solution is filtered, these more valuable precious metals can be separated and remain on the filter paper for later treatment or melting. The nitrate solution can be treated with sodium or another soluble chloride to precipitate the silver in the form of silver chloride according to the equation. An alternative to the silver chloride oxidation would be direct replacement of the silver with scrap copper. This makes a silver metal fluff that can be melted directly, but it also adds copper to the liquid.

\[
\text{AgNO}_3 + \text{NaCl} = \text{AgCl} + \text{NaNO}_3 \quad \text{OR} \quad \text{AgNO}_3 + \text{Cu} = \text{Ag} + \text{Cu(NO}_3)_2
\]

The silver chloride can be filtered and separated from the nitrate solution and washed with a number of batches of distilled water to free it from the base metals and copper contained in the nitrate solution. Silver chloride can be dried and smelted directly. But the direct smelting of silver chloride often results in a loss of up to 5 percent of the silver through the sublimation of silver chloride at the high temperatures in the furnace. Sublimation is the process of a solid passing directly into a gas without first becoming a liquid. Those of us who remember clothes washing day during freezing weather can recall that when the damp clothes were first hung on the clothes line they flapped in the breeze. As the water froze they became stiff as boards, but with extended time on the line they became supple and soft again. The final stage of the drying from the stiff board to the flexible cloth is an example of sublimation. The ice in the clothing sublimed into the air leaving the clothes ready to be taken inside and warn.

Chemical refining is often the first step of refining small batches of gold. The gold containing material is mixed with 4 times its weight of silver and melted. This process is referred to inquartation. The inquarted metal is poured into water to make small chunks or pellets or shot that are more easily dissolved in acid than a bar. The pellets are dissolved in nitric acid. Solution from the dissolution is permitted to settle and gold sludge is separated for later processing. The silver nitrate generated in the above step is often precipitated with chloride, reacted with a reducing agent to make silver metal which is then melted to produce the shapes needed for sale to others.

Silver chloride can be reduced to silver metal in a number of ways to minimize the sublimation losses incurred by direct smelting. In actuality we are reducing the silver chloride to silver oxide, which then is a direct smelt to silver metal. Technique one uses an aqueous reduction with iron. The iron is placed in a bucket and the slurry of silver chloride is pored over it. Because the reaction takes place in an acid environment one or 2 drops of sulfuric acid are added to the mix. After a few hours one will be able to
see the formation of dark silver oxide growing in the bulk of the chloride away from the individual pieces of iron. Normally the reaction will be complete in one to two days. This reaction follows the following equation.

\[ 2\text{AgCl} + \text{Fe} \rightarrow 2\text{Ag} + \text{FeCl}_2 \]

Technique 2 uses caustic soda and sugar. The pad of moist chloride is weighed and added to a bucket or container with enough tap water to cover the chloride about an inch or two. Forty grams of sodium hydroxide are added to the bucket for every 120 grams of moist chloride, and the bucket is stirred to insure that all of the caustic dissolves. A gallon of water in a separate container is saturated with glucose (common sugar), and a quarter liter or less of this solution is poured into the bucket containing the silver chloride and caustic. WARNING: This reaction is delayed by as much as 5 minutes and generates much heat and foam that may rise and overflow the bucket when it reacts. For this reason the bucket should never be more than half full to provide enough free board for the reaction to expand. As the reaction progresses the silver chloride will turn black. Sugar solution can be added in increments to keep the reaction under control until it is completed. One can tell that this reaction is done when the addition of 250 milliliters sugar water does not create extra heat or foam. An excess of sugar is not a liability because sugar is so economical. Technique number 3 involves the use of caustic soda and sodium borohydride. Like the sugar reaction this reaction can get very hot. The sodium borohydride comes as a 50% solution of caustic soda and is diluted to twice its volume before addition. The dilute borohydride is injected at the bottom of the vessel containing the silver chloride and the reaction mixed gently. The reactants for this reduction are expensive and for this reason sodium borohydride reduction is seldom used except for special industrial applications.

Environmental concerns of today like to trace the progress of each element in the equation. Impurities in the chemical refining step end up in the acid solution from which the silver chloride is precipitated. If these impurities contain enough metal to make recovery profitable they are recovered. If the value is below the economic threshold, the liquids are disposed of as a hazardous waste. Insoluble impurities including gold and platinum along with silica report to the sludge that is later melted and returned to the gold processing area of the refinery. The sweet caustic solution from the silver chloride reduction can be used to neutralize acids generated in other stages of the process.

**ELECTROLYTIC REFINING**

Chemical refining consumes a lot of acid that is discarded once the silver is removed as silver chloride. Chemical refining also requires an extra step to reduce the silver chloride to silver metal. If this acid could be used to make the electrolyte used in electrolytic silver refining, acid use could be decreased by at least half. Electrolytic refining is an electrochemical procedure where by impure silver is electrically dissolved or corroded at an anode into a solution composed of silver nitrate, copper nitrate and free nitric acid and deposited in pure form at a cathode. This solution is referred to as electrolyte. The purity of the silver crystals that grow on the cathode (negative electrode) is controlled by the voltage used to dissolve the silver, the purity of the silver anode, and the composition of the electrolyte. At a direct current voltage of 2.0 volts, only pure silver is deposited. At voltages above 2 volts copper will co-deposit with the silver. Copper deposition on the silver crystals is dependent on the purity of the anode,
the amount of copper in the electrolyte and the cell voltage. Refinery operators adjust the cell voltage to obtain the optimum silver quality for the specific cell in use. For this reason the voltage on each cell is carefully controlled. The current across the cell defines the amount of silver that will be deposited on the cathode. Under ideal conditions a current of one ampere per hour will deposit 4.025 grams of silver on the cathode. This is the theoretical criteria of operation. This implies that a cell operating at 50 amperes for 12 hours at 90% efficiency will produce 69.88 Troy ounces of silver. Weekly production from the Moebius cell described later in this discussion will be 69.88 ounces per cell times the 4 anode boxes times 5 days per week or 1397 Troy Ounces per week. In actual practice a small operation would probably reduce the voltage and current during the evening hours so the operator could take a break. Because it easier to produce direct current voltages greater than 2 volts using a generator or rotary inverter, it is common for large industrial refineries normally have a number of cells in series like a battery so that the voltage across the entire bank of cells is greater than 2 volts. If fresh silver is added to the cells on a regular basis and pure silver crystals are removed at the same rate, cell operation can be controlled. But if one cell in the battery is permitted to deplete its silver, the voltage on that cell will increase. For this reason an electrolytic refining operation smaller than 2000 ounces per day normally keeps the cells in parallel so that voltage and silver produced can be controlled. And they use a transformer and rectifier that has a voltage regulator to convert line voltage and make the potential needed to operate the cell. A typical power supply is shown in Photo 6.

PHOTO 6. RECTIFIER

In practice the silver used to make the anodes (positive electrodes) has been pyrolitically refined so that it does not contain sulfides or any metals below copper in the electromotive series. The anode may contain silver, copper and platinum group metals. As the anodes corrode silver and copper are removed. The silver is deposited on the cathode, but the copper builds up in the electrolyte.
Periodically electrolyte is removed from the cells, silver reclaimed either by replacement with copper or by chloriding. Fresh electrolyte is made by dissolving silver scrap and adding the amount of nitric acid called for by the electrolyte formula. Bags between the anodes and cathodes (septa) collect the slimes and sludge which contain gold, platinum and other precious metals, for processing by other parts of the refinery. A quality control laboratory tests the electrolyte periodically and adjusts the acid content to insure that there is sufficient acid to dissolve the copper. If the cell is operated to exhaustion the excess acid will be consumed and silver nitrate in the electrolyte will deplete and be replaced by copper nitrate. When this happens the cell voltage will rise if the cell is in a battery. If the cell is on a fixed power supply the current across the cell will drop and silver will cease being deposited on the cathode. As the electrolyte becomes depleted of silver nitrate the deposited silver on the cathode becomes less dense and fluffier, making it hard to harvest. This cathode silver will retain more copper salts than normal and require extra washing to guarantee that the silver melted from the crystal is pure.

There are two generic types of silver refining cells; The Moebius cell works with vertical electrodes and the Thum cell that uses horizontal electrodes. The Moebius cell uses vertical anodes encased in polypropylene bags and stainless steel cathodes. The Thum cell uses a larger stainless steel cathode and operates with each anode in a polypropylene basket that collects the sludge generated by the corrosion of the anodes. In this way the Thum cell consumes anodes completely. Both types of cells use electrolyte of the same composition. Electrolyte composition will be discussed later. Sketch A shows the two different types of refining cells.

**SKETCH A. MOEBIUS and THUM CELLS**

The Moebius cell requires that the cathodes be removed about every 24 hours of operation and crystals of silver harvested. Under some conditions silver crystals will grow from the cathode to the anode that short out the cell. For this reason the cathodes in cells designed by one vendor were raised and lowered 8 times per minute by a cam system. This cathode motion kept large crystals and trees to a minimum. As the anodes corroded they reduce the surface area of the anode. This decreases the deposition of silver on the cathode. For this reason a volt meter was placed across each cell in the battery. Rising voltage in one cell was the clue that the cell needs attention. Anodes corrode unevenly. Frequently
anodes corrode off at the solution level. Because each anode is in a separate bag, this open circuit is not visually obvious except that the deposition of crystals on the cathode next to the open anode is less than normal. The Moebius cell produces a greater mass or silver crystals per unit of time than the Thum refining cell, but requires that anodes be remelted frequently.

The Thum cell uses more floor space and a greater volume of electrolyte than the Moebius cell, but it is easier to operate and it takes less operator labor. Thus the set up costs are greater, but operating costs are less than the Moebius cell because of reduced labor requirements. Because the anodes are in a basket that holds them parallel to the cathodes and have a polypropylene septum under them to catch the anode material that does not dissolve, the anodes do not have to be remelted and can corrode evenly. This saves remelting time and money.

Photo 7 shows a commercial Thum cell that consists of 2 cathodes, one on either side of an electrolyte well. The electrolyte well contains a box that is designed to hold silver crystals which are periodically scraped from each cathode and pushed to the center. Each cathode is serviced by 2 anodes, each in a basket or box that is lined with polypropylene cloth to retain material that does not corrode in the electrolyte. This style of cell is operated by placing a nominal 150 ounce anode in each anode basket. The 4 anodes are connected together and the two cathodes are electrically connected together. Two volts D.C. is between the anodes and cathodes. This discussion assumes that the electrolyte level is set about an inch above the tops of the anodes.