

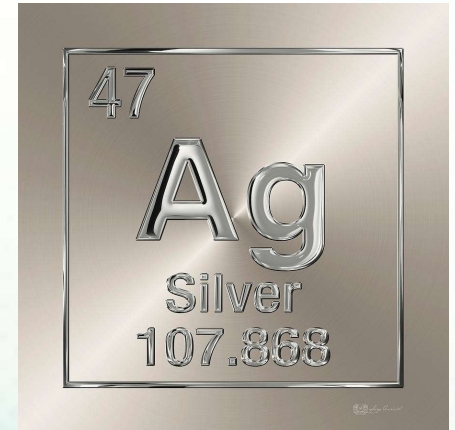
# *Chapter 8*

# *The Silver Extraction Process*

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## Introduction

- Silver is a chemical element with the chemical symbol Ag, it is soft, white, lustrous transition metal.
- It possesses the highest electrical conductivity of any element and the highest thermal conductivity of any metal.
- The metal occurs naturally in its pure, free form, as an alloy with gold and other metals, and in minerals such as argentite and chlorargyrite.
- Most silver is produced as a byproduct of copper, gold, lead, and zinc refining.



## History

- Silver occurs both uncombined and in ores such as galena and argentite.
- Silver sometimes occurs in native form (found as an element in its natural state) and so, along with gold and copper.
- Was one of the first metals known to humans. For thousands of years, it has been valued for its beauty, and silver ornaments and jewelry dating from 4,000 BC have been found in Egyptian tombs.
- By about 800 BC it was in use as currency over the whole of the Middle East; silver coins were being minted in Greece about 700 BC.
- Although silver occurs free in nature, it is much more often found as silver sulfide, mixed with lead sulfide, in the ore galena.



- *As early as 2,500 BC galena was mined and smelted; the silver was separated from the lead by cupellation.*
- *In this process the lead is oxidized in a furnace and removed as a scum from the surface of the molten silver which remains behind.*
- *The galena which was mined in Greece about 600 BC probably contained about 60 ounces of silver per ton of ore.*
- *Silver was mined in Europe, mainly in Bavaria and Spain, in medieval times.*
- *The discovery of the New World, and particularly Mexico and Peru, led to an enormous increase in the world supply of silver during the 16th and 17th centuries.*
- *Mexico and Peru continue to be major suppliers.*

## Physical Properties

- Silver is harder than gold but softer than copper.
- Apart from gold, it is the most malleable (bendable) and ductile (it can be stretchable) of all metals.
- One gram of silver can be drawn out into a thin wire  $1\frac{1}{2}$  km long, and it can be beaten out into sheets only 0.00025 mm thick.
- It is an excellent conductor of heat - better even than copper - and is also a slightly better conductor of electricity than copper.



## Chemical Properties

- Silver, with few exceptions, is monovalent in its compounds.
- It is very resistant to attack by oxygen and tarnishes in air only if sulfur compounds are present, when a thin film of sulfide forms on its surface.
- The film which appears on silver egg spoons is caused by the action between organic sulfur compounds and the silver.
- It is attacked by the halogens chlorine, bromine, and iodine.
- Silver is resistant to attack by most alkalis and acids, except nitric acid and hot concentrated sulfuric acid.
- Silver chloride, bromide, and iodide are all sensitive to light, and for this reason are used in the manufacture of photographic films and papers.
- It forms alloys, which are used in jewelry and coinage, with copper and gold.



## Compounds of Silver

- Silver halides ( $\text{AgX}$ ) are crystalline salts used in photography.
- The chloride is white (and occurs naturally as the mineral horn silver), the bromide pale yellow, and the iodide yellow.
- On exposure to light, a crystal of silver halide becomes activated, and is preferentially reduced to silver by a mild reducing agent.
- Silver nitrate ( $\text{AgNO}_3$ ) is a transparent crystalline solid, the most soluble of the silver salts.
- It is used in chemical analysis, silver-plating, and dyes.



## Uses

- Silver has long been valued as a precious metal, used in currency coins, to make jewelry, high-value tableware and utensils.
- Silver metal is used industrially in electrical contacts and conductors, in mirrors and in catalysis of chemical reactions.
- Its compounds are used in photographic film and dilute silver nitrate solutions and other silver compounds are used as disinfectants and microbicides.
- While many medical antimicrobial uses of silver have been supplanted by antibiotics.





## Ores

### *1- Silver Sulphide ( $\text{Ag}_2\text{S}$ ), [Argentite]:*

- *Occurs as a soft, malleable greyish-black substance, which is readily fusible.*
- *It contains 87 % of silver.*
- *Deposits containing it in a state of purity occur in Norway, Hungary, Saxony, Bohemia, Mexico, and the United States.*
- *It is the principal ore of silver.*



### *2- Silver Chloride ( $\text{AgCl}$ ), [Horn Silver]:*

- *It is found in South America.*
- *The bromide and iodide also occur.*



### 3- Pyrargyrite

- Dark-red silver ore is a sulphantimonide of silver ( $3\text{Ag}_2\text{S} \cdot \text{Sb}_2\text{S}_3$ ).
- Found in Mexico, South America, Transylvania, and elsewhere.
- Proustite is light-red silver ore--is a sulpharsenide ( $3\text{Ag}_2\text{S} \cdot \text{As}_2\text{S}_3$ ).
- Stephanite is another mineral of the same class.

### 4- Polybasite and Argentiferous Fahlore

- Are compounds of copper, silver, arsenic, and antimony Sulphide.
- The latter often contains other metals also.





5. Galena (a lead ore containing significant amounts of silver).

- Silver occurs in the ores of many other metals, probably as Sulphide.
- Lead, zinc, and copper ores often contain it, and small quantities occur in iron pyrites and mispickel (arsenical iron pyrites).
- The production of silver from these sources is nearly one-half of the total extracted.
- As silver is often found in conjunction with these or alloyed with other metals such as gold, it usually must be further extracted out through amalgamation or electrolysis.





## Silver Prices



## Extraction Processes

- Silver is obtained principally as a by-product when lead, zinc, and copper ores are refined.
- However, it is also obtained from ores mined for their silver content, the commonest of which is argentite, a sulfide of silver.
- The high price of silver permits of poor ores being treated and the adoption of more costly methods.
- Hence chemical methods, preceded by careful mechanical preparation, are often followed.
- The treatment of silver ores may be divided into amalgamation processes, wet processes, smelting with lead or lead ores, and smelting with copper.

## Extraction of Ag from PbS

- This is very old process of extraction.
- The ore used to extract silver was not a silver ore but Lead Sulphide ( $\text{PbS}$ ), known as Galena or Galenite which contains 87% lead.
- The local variety of Galenite is silver-bearing and is known as Argentiferous Galenite  $[(\text{PbAg})\text{S}]$  and the lead obtained from this ore contains just a small percentage of silver from 0.8% up to 5% (other sources Laurion galena contains typically only 0.13 to 0.30% Ag).





## Procedure

- The ore as mined was not pure as it was mostly encased in rock, combined with earth, and also contained traces of iron ore and other minerals.
- Firstly, it had to be pounded into small fragments on stone tables with rock hammers, then ground to a fine powder of 1-mm grain size in a stone mill (very hard work!).
- Then it had to be washed in a "washery" to remove as many of the impurities as possible.
- The washed ore was then dried and formed into bricks.



- Next, the bricks of washed ore were heated in a furnace where the lead/silver mixture was released from its Sulphide and separated from iron oxide impurities and run-off into "pigs" or blocks.
- Since lead was also valuable, it was recovered by placing the litharge (lead oxide) remaining from the cupellation process into yet a third furnace and heated to 250 °C and air was blown through it.

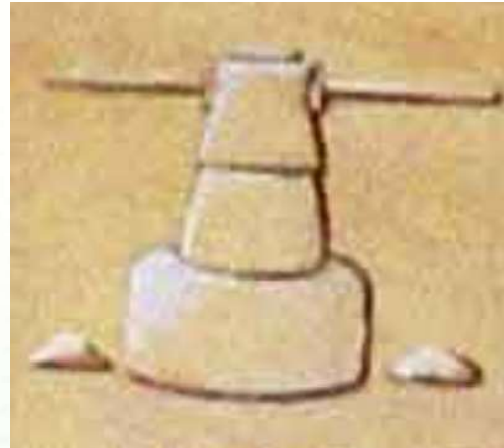


*Transporting the ore to the pounding area*



*Crushing the ore by pounding with a special hammer*

- The lead was run-off and formed into rods.
- Since lead is a cumulative poison, many slaves must have died from its effects; not to mention from the toxic Sulphur dioxide fumes from the original lead Sulphide processing furnaces - & the arsenic contained in small quantities in the lead.



*Grinding the ore to a fine powder with a stone mill*

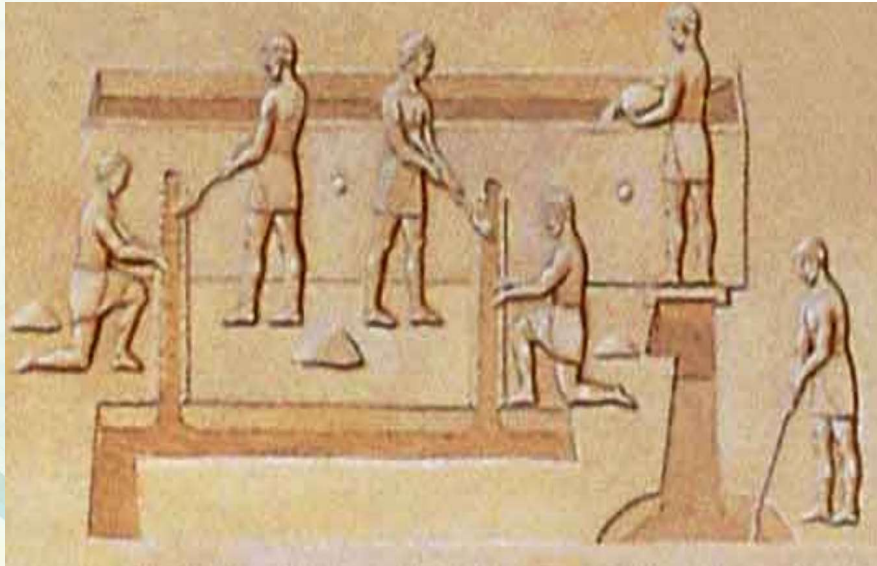


*Further grinding of the ore by hand*

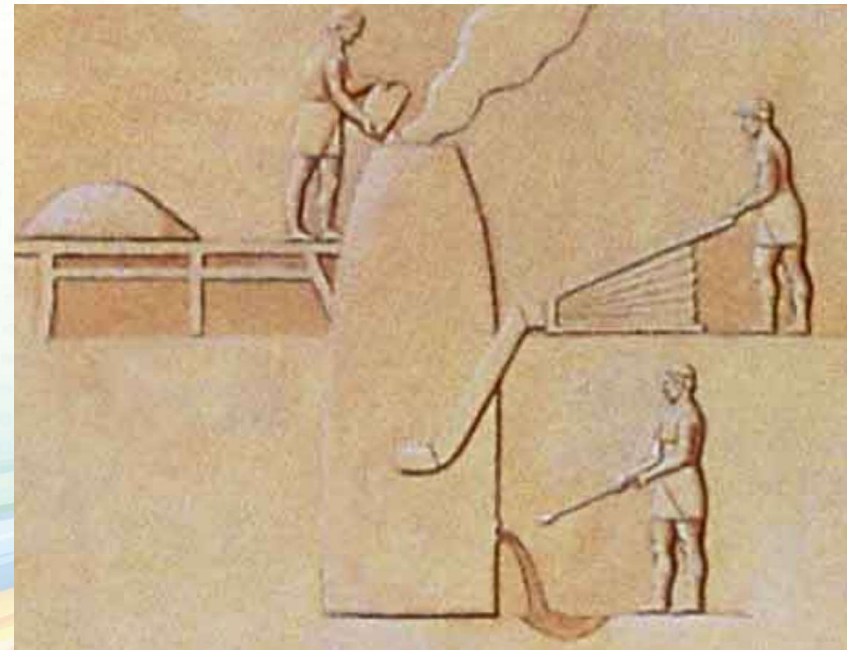


*Drawing water from the cistern*





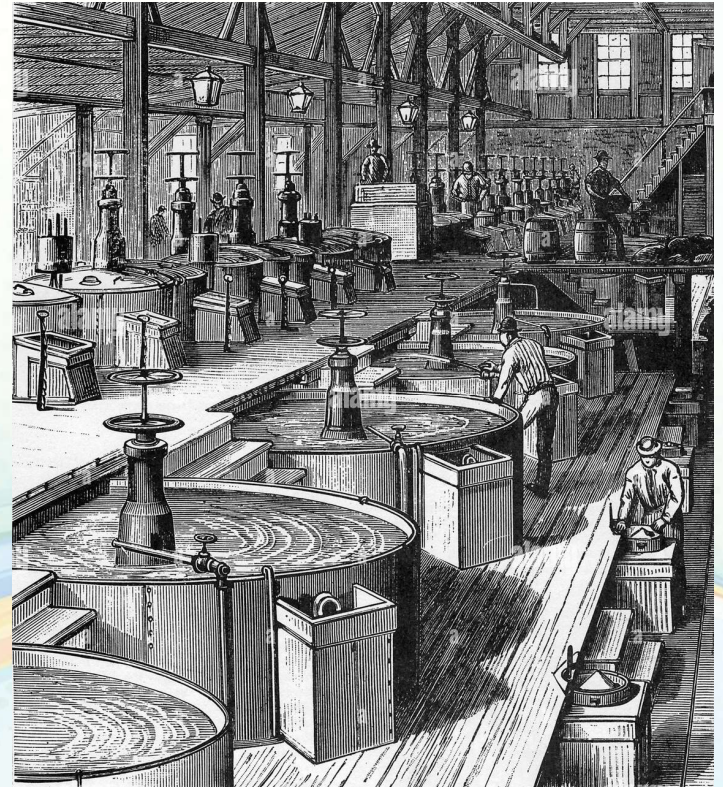
*Removing the impurities at the ore washery*



*Creating silver-bearing lead pigs by processing in a furnace*

## Amalgamation Processes

- Amalgamation Processes include those in which the silver is obtained as an amalgam with mercury, from which it is recovered by distillation and volatilizing the mercury.
- They may be divided into “floor” “barrel” and “pan” amalgamation processes.
- If not present as free silver or as chloride the first step of the process is to convert the metal into chloride.





## Floor Amalgamation

- *This process is still followed in Mexico and South America.*
- *The ores are hand-picked; the ore contains some 80 ozs. of silver per ton, as native silver, chloride, and sulphide.*
- *Base ores containing large amounts of foreign sulphide are unsuitable for treatment by this process.*
- *The ore is first reduced to a fine state of division by stamping or grinding.*
- *Water is added, and, if much free silver or gold is present, a little mercury, to amalgamate them. The ore is thus reduced to mud.*



- *The mud is taken to the amalgamating floor (a paved court) and spread out in a layer 6 inches to a foot thick.*
- *Some 3 to 5 % of salt is added and well trodden in by mules for several hours, after which the heap is allowed to rest.*
- *Next morning a quantity of roasted copper pyrites is scattered over the heap, and some mercury.*



- *This, after mixing with shovels, is well trampled in; the turning over and trampling are repeated every other day for some days.*
- *Mercury to the extent of some 5 or 6 times the weight of silver present is sprinkled over the heap from canvas bags, and trampled in.*
- *If much antimony and arsenic, or other foreign Sulphide are present, a hot solution of copper sulphate is added, together with copper precipitate (finely divided copper), and thoroughly incorporated.*
- *After a further rest with repeated trampling, a final addition of mercury is made to collect the amalgam, and after mixing, the stuff is conveyed to tanks where it is stirred up with water, and the heavy amalgam settles out.*

- The earthy matters are carried away by the water current.
- In this process a series of complicated reactions occurs.
- Copper chloride is formed by the reaction of the salt and copper sulphate.



- This attacks the metallic silver, thus:



- This cuprous chloride, which is soluble in the excess of salt employed, reacts on the sulphide of silver and converts it into chloride.



- Some free sulphur is also , separated, probably thus:





- Or 
$$2\text{Ag}_2\text{S} + 4\text{Cu}_2\text{Cl}_2 + 6\text{O} \longrightarrow 2(\text{CuCl}_2 \cdot 3\text{CuO}) + 2\text{S}$$
- The above reactions in some degree represent the chlorination, but the changes are very obscure. The silver chloride is decomposed by mercury, thus:



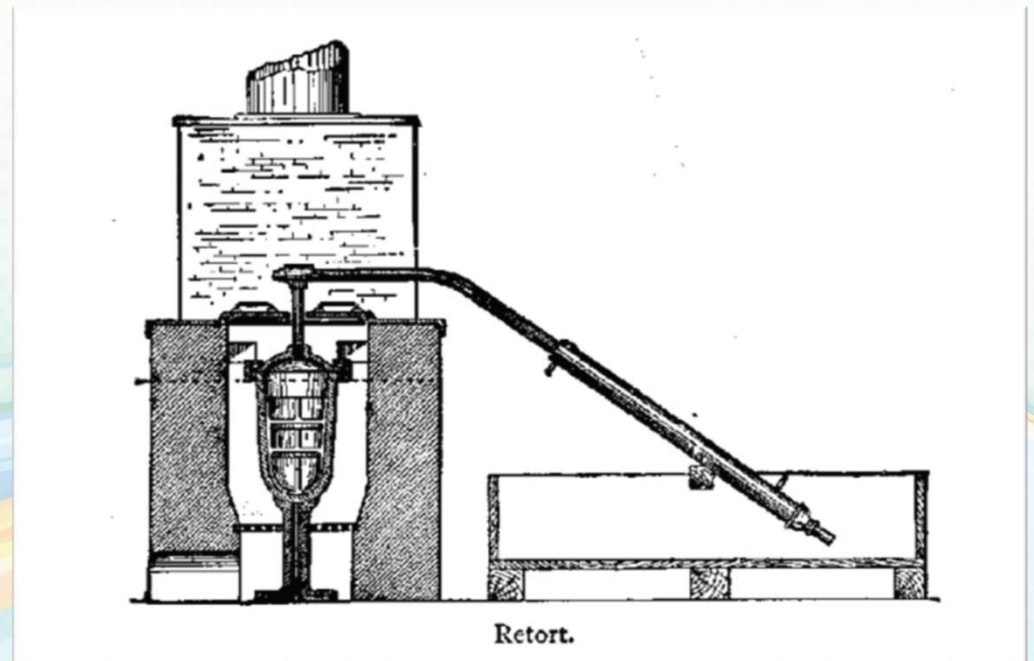
- The metal (Ag) being dissolved by the excess of mercury.
- The operation occupies from 2 to 7 weeks.
- The addition of copper precipitate is to ensure the reduction of the cupric salt to the cuprous state, or it will attack the mercury, forming calomel, and will thus increase the consumption of mercury.

## Treatment of Amalgam

- The amalgam from the settlers and agitator is often transferred to a smaller "clean-up" pan and stirred with water to free it from heavy particles.
- It is then strained through canvas bags, or squeezed through wash-leather, or in cylinders, the ends of which are made of wood cut across the grain, by hydraulic pressure.
- The excess of mercury which is thus removed is used again. It contains silver, but this is recovered in the subsequent working.
- The pasty amalgam which remains is then "retorted" to expel the mercury.

- *The amalgam is put into the crucible, which is of iron, the head adapted, and the mercury as it distils off is condensed by the water-cooled tube.*
- *The crucible is coated with limewash.*
- *The porous mass obtained is subsequently melted down in crucibles and cast into bars weighing about 1,000 ozs.*
- *The crude bullion contains bismuth, antimony, copper, zinc, arsenic, etc.*
- *It is subsequently refined. This is partially affected by exposing the surface to the air while molten, and permitting the impurities to oxidize, the scum of oxides being scraped off.*
- *It is afterwards refined by cupellation.*





## Cyanide Processes

- *Of the many processes which have been developed over the years, the cyanide process is normally used now in extracting silver from argentite.*
- *After the ore has been crushed, it is ground to a fine powder in a ball mill which also contains weak sodium cyanide solution.*
- *The silver sulfide and also any free silver present reacts with the sodium cyanide to yield sodium argent cyanide,  $\text{Na}[\text{Ag}(\text{CN})_2]$ , which is soluble in water.*
- *The suspension is agitated with compressed air for several days.*
- *This serves to oxidize the sodium sulfide formed by the reaction between silver sulfide and sodium cyanide.*

- *The solution of sodium argent cyanide is then filtered, and the dissolved air removed by vacuum.*
- *The silver is finally displaced from solution by adding a suspension of finely powdered zinc dust.*
- *The precipitated silver is filtered off and dried.*
- *This product contains at least 75% silver, but will always contain impurities, particularly the excess of zinc dust.*
- *Further purification is, therefore, necessary.*
- *As about three-quarters of the world's output of lead is obtained from ores which also contain silver, it follows that the recovery of silver is a profitable stage in refining lead.*



- One way of doing this is by *the Parkes process*.
- After removing other impurities, namely copper, antimony, arsenic, and tin, from the molten lead-silver alloy, zinc is added to the bath.
- Silver is much more soluble in zinc than in lead, so that after mixing the contents of the bath most of the silver migrates to the layer of molten zinc which floats on top of the lead.
- When the temperature of the bath is allowed to fall, the zinc-silver alloy is skimmed off as it solidifies on the surface.
- The zinc can then be distilled off leaving behind the silver which has a higher melting point.

- *In the Parkes process for de-silvering lead, zinc (in which silver is much more soluble) is added to the molten lead-silver alloy. After thorough mixing, the zinc-silver layer floats to the top and is skimmed off.*

