Swiss Excellence.
Made in India.

INDIA GOLD CONFERENCE

Evaluation of various Hazards associated with Refining of Gold

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MMTC-PAMP India Pvt. Ltd. Introduction

solution

One-stop solution in Precious Metal Ecosystem

ONE-STOP SHOP FOR JEWELLERS

1 **Bullion**

Our products are tradable across the world and deliverable on global commodity exchanges

2 **Scrap Refining**

- 45 minute hassle free exchange of scrap metal
- Transparent process

3 **Minted Gold and Silver products**

Exquisite range of coins, bars, collectibles and customized products

4 **Master Alloys**

Developing a comprehensive range of master alloys to be used for the manufacture of jewellery.

PARTNERING WITH INDUSTRY

1 **Simplifying purchase of gold for consumers**

Gold accumulation plan

Enabling customers to purchase and accumulate gold for as low as Rs. 1. Anytime anywhere (365 days 24 x 7)

2 **Gold Monetisation scheme**

- Critical enabler of GMS ecosystem
- Refining and certifying purity for the customers
- Providing surety of quality as the only LBMA Good Delivery refinery in India

3 **Industrials**

- Separate business vertical
- Providing products and solutions for Industrial customers of precious metals

80 MN+
CUSTOMERS

16 TONNES
SCRAP

$12 Mn
INVESTMENT IN NEW PLANT

$1 Mn
PROFIT IN TRADING

12
RETAIL CENTRES

500+
EMPLOYEES

ANNUAL INSTALLED REFINING CAPACITY OF
300T
GOLD &
600T
SILVER

Evaluation of various Hazards associated with Refining of Gold

Introduction

- Primary Recovery and refining of gold from dore , jewelry scrap and other waste involves use of Pyrometallurgical processes.

- Chemical & electrochemical techniques such as Inquartation & Parting, Aqua regia, Electrolysis etc. are then mostly used to achieve a purity of 99.9% and more.

- The impurities which are usually associated with gold are varied namely Ag, Cu, Zn, Sn, Fe, Ni, Co, Bi, Al, Te, Se Cd, Pb , PGM (Ir, Ru, Os) which needs to be removed to arrive at required fineness. This can be estimated by proper analysis before we start the process

- The selection of the refining technique depends on various factors such as:

  - end product requirement
  - gold content and impurity content including Silver
  - physical and chemical characteristics of the material
  - Inventory holding capability
  - economic feasibility based on factors such as quantity , availability , location etc.
  - available expertise and skills
  - safety & environmental regulations .

Risks associated with refining of gold

Major Pyrometallurgical Techniques

The main processes used for Gold Recovery and Refining are as follows:

Incineration Burning of waste material having precious metal with an aim to remove moisture and organics

Volatilization Removing all metal including silver by applying vacuum and heat

Oxidation

(a) by air blowing or roasting - selective incineration and convert the chemistry to facilitate leaching
(b) by " bessemerizing" - selective removal of copper from the alloy by blowing air
(c) by sodium nitrate
(d) by metallic oxides
(e) by cupellation using lead to remove all base metal and leave gold and silver as alloy

Chlorination Purging of pure chlorine in molten metal and base metal as insoluble chloride (Miller process)

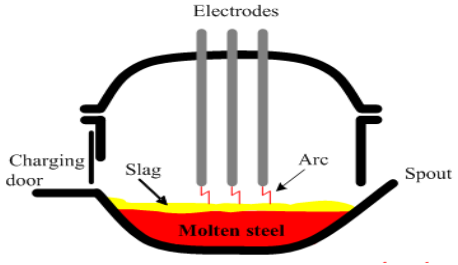
Equipment used in Pyrometallurgical process

Incineration

Induction furnace
(Induction heating)

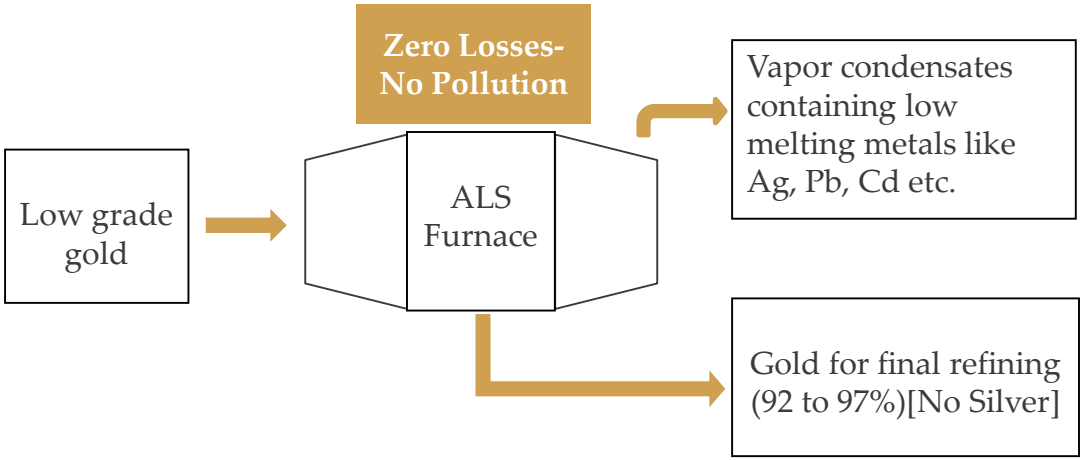
Small Resistance Furnace
(resistance heating)

Top Blown Rotary Furnace (fuel fired)



Electric Arc Furnace (high voltage heating)

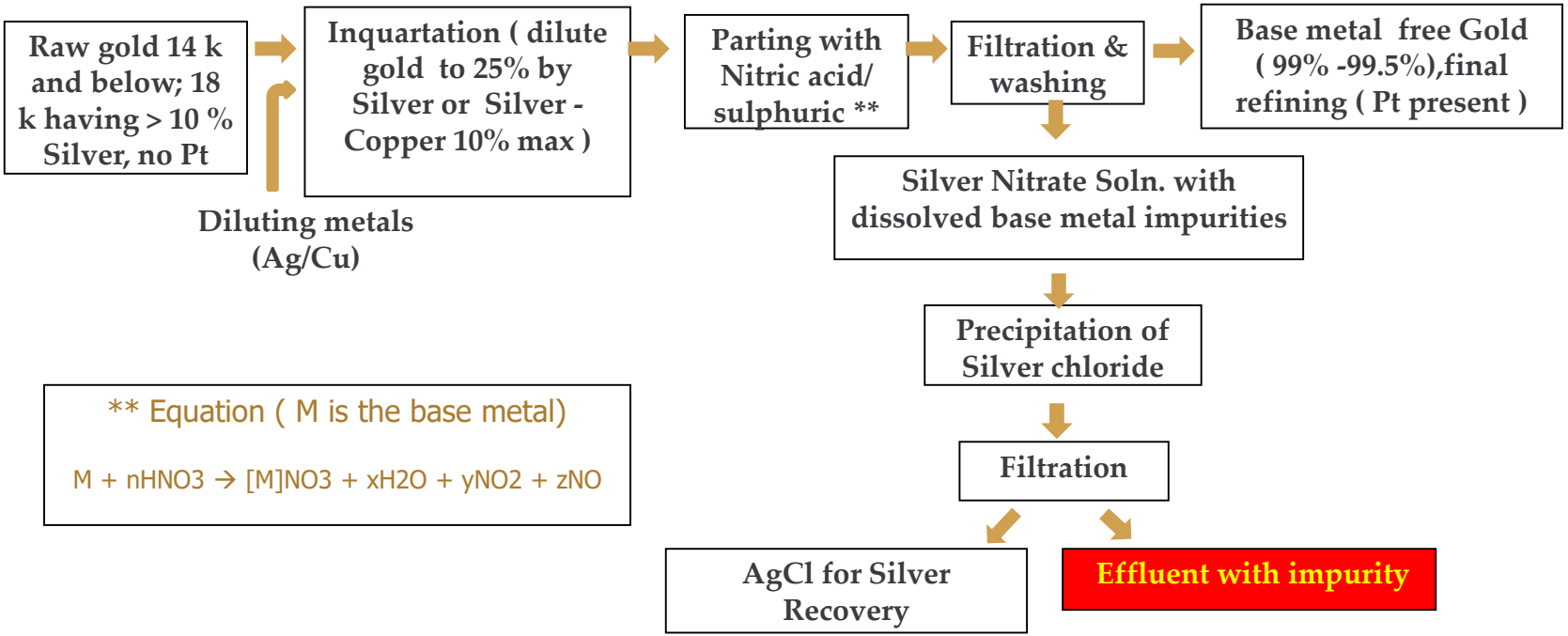
Acid less Separation (ALS) - the latest technology



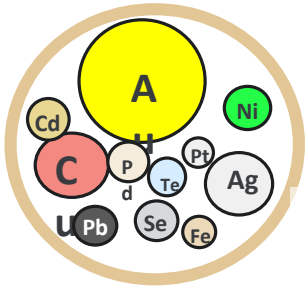
Major Chemical and electrochemical Techniques

1. Inquartation and Parting
2. Aqua Regia digestion and precipitation
3. Wohlwill Electrolysis process

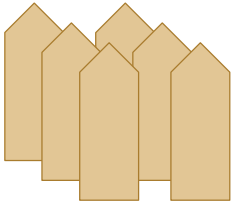
Inquartation and Parting



ELECTRO REFINING

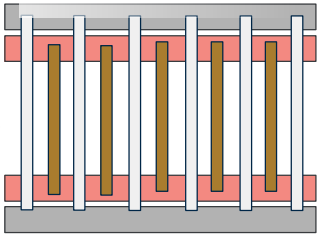


DORE



ANODES

ELECTROLYSIS

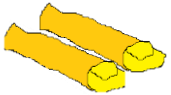


RECYCLING

GRAINS

Melting

SPONGE

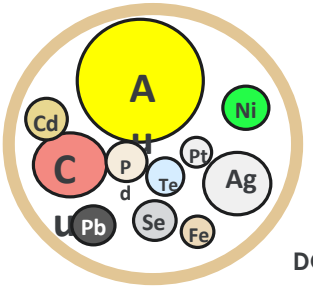


Melting in Tunnel Furnace

24K Bullion Product

CONSUMED ANODES

CHEMICAL REFINING



DORE

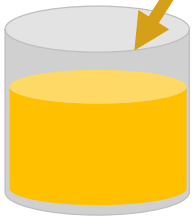
DISSOLVED IN AQUA REGIA

24K GOLD

CEMENTED GOLD

SMBS

PRECIPITATION



Capabilities of various techniques

REFINING TECHNIQUE	REMOVES BASE METALS	REMOVES SILVER	REMOVES PGMS	LARGE SCALE REFINERS	SMALL SCALE REFINERS
PYROMETALLURGICAL PROCESS					**N**
CUPELLATION	**Y**	**N**	**N**	**Y**	**Y**
CHLORINATION PROCESS	**Y**	**Y**	**N**	**Y**	**N**
ACIDLESS REFINING	**Y (w/out Cu)**	**Y**	**N**	**Y**	**N**
CHEMICAL PROCESS					
INQUARTATION AND PARTING	**Y**	**Y**	**N**	**N**	**Y**
AQUA REGIA PROCESS	**Y**	**Y**	**Y**	**N**	**Y**
WOHLWILL ELECTROLYTIC PROCESS	**Y**	**Y**	**Y**	**Y**	**N**

Identifying the various hazards

Pyrometallurgical process	Chemical process
• Fumes having dust , untreated carbon compounds , metal oxides , heavy metal particles - their treatment • Slags having toxic material as waste - its disposal	• Fumes having untreated acids , Nox, Sulphur dioxide , Chlorine – treatment • Effluents high acidic, chemical salts of dissolved base metal - treatment • Sludges and salts waste - disposal

Specific causes for fumes

Fumes from Pyrometallurgical processes Generated during heating and melting and may contain untreated carbon compounds, dust particles , metal oxides , heavy metal vapours etc. ; fuel fired furnaces cause more fumes

Fumes from Chemical Refining Generated during acid digestion , gold precipitation , neutralisation and may consist of Nox, Sox , Chlorine , ammonia vapours etc. formed during reactions :

1. $Au + 3\ HNO_3 + 4\ HCl \rightarrow [AuCl_4]^- + 3\ [NO_2] + [H_3O]^+ + 2\ H_2O$

2. $Au + HNO_3 + 4\ HCl \rightarrow [AuCl_4]^- + [NO] + [H_3O]^{++} H_2O$

3. $HNO_3 + 3HCl \rightarrow NOCl + Cl_2 + 2H_2O$

4. $2\ HAuCl_4 + 2\ NaHSO_3 \rightarrow 2\ Au + 8\ HCl + Na_2SO_4 + SO_2$

5. $3\ SO_2 + 2\ AuCl_3 + 4\ H_2O \rightarrow 3\ H_2SO_4 + 6\ HCl + 2\ Au$

6. $2\ AuCl_3 + 6\ FeSO_4 \dashrightarrow 2\ Au + 2\ Fe_2(SO_4)_3 + Fe_2Cl_4$

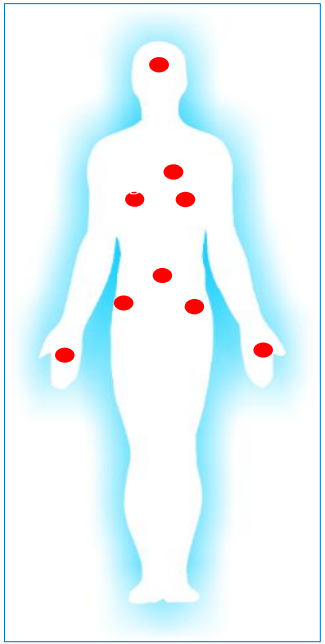
ENVIRONMENTAL IMPACTS

ENVIRONMENTAL IMPACT CATEGORY	MEASUREMENT UNIT & DESCRIPTION
Global Warming	**Carbon dioxide equivalence (CO_2 equivalence)** Measuring the impact of green house gases on global warming over 100 yr time period
Eutrophication	**Nitrogen equivalence (N equivalence)** Measuring the impact of nitrogen on the aquatic life
Respiratory Effects	**Particulate matter 2.5 equivalence (PM2.5 equivalence)** Measuring the impact of dust on human respiratory system due to inhalation
Ecotoxicity	**Comparative toxic unit for environment (CTUe)** Measures eco impact where 50% of a species displays an adverse effect; it is measured as the potentially affected fraction of species (per kilogram of chemical emitted)
Carcinogenics	**Comparative toxic unit for human (CTUh)** Estimated increase in human morbidity related to carcinogenic illnesses (no of cases per kilogram of emission)
Non-Carcinogenics	**Comparative toxic unit for human (CTUh)** Estimated increase in morbidity of the total human population related to non-carcinogenic illnesses (expressed in cases per kilogram of emission)
Fossil Fuel Depletion	**Mega-joules of surplus (MJ)** This measures the depletion of fossil fuel resources
Acidification	**Sulphur dioxide equivalence (SO_2 equivalence)** Measures impact of increasing concentrations of hydrogen ions that can cause damage to ecosystem
Photochemical Smog Formation	**Ozone equivalence (O_3 equivalence)** Measures the impact on human respiratory system caused by the formation of ground level ozone and also crop damage

Effects of heavy metals on human health

When the gold containing impurities is melted, metals may get carried off as particulate matter and volatile oxides along with the fumes and add to the particulate matter (PM) of the environment.

Element	Behavior in molten condition	Effect on human health	
Cadmium	Forms volatile oxide	Possible Carcinogens	Affects the respiratory and cardiovascular system.
Lead			Lead has severe effect on renal functions over long exposure; impair body's ability to produce haemoglobin; affect the nervous system too
			High exposure may lead to collection of fluid in the lungs and bronchitis.
Selenium & Tellurium			Arsenic trioxide may induce, vomiting, diarrhea, gastrointestinal hemorrhage, cerebral edema and hypovolemic shock.
Arsenic			
Iron, Nickel, Cobalt and Copper	Are removed as slags; may also be carried as metallic particles in fume.	Metallic fumes if inhaled, may lead to asthma, rhino-conjunctivitis, and dermatitis.	
Mercury	Vaporizes as metal at a temperature of 357 ºC	Vapors can produce harmful effects on the nervous, digestive and immune systems, lungs and kidneys, and may turn fatal.	
Zinc	Produces bright flashes of light and dust cloud .	Over-exposure to zinc oxide fume may cause metal fume fever.	



(Table 3) Behavior of elements during melting and casting and their effects on Human being

Effects of heavy metals on environment

Element	Behavior in molten condition	Effect on Environment
Cadmium	Forms volatile oxide	When absorbed by soil and water sources, may cause growth and functional defects in living organisms.
Lead		When accumulated in organisms, can cause damage to aquatic and terrestrial life forms.
Selenium & Tellurium		Extremely high concentrations can cause reproductive failure and birth defects in animals
Arsenic		Inhibits photosynthesis in plants affecting their growth and survival.
Iron, Nickel, Cobalt and Copper	Are removed as slags; may also be carried as metallic particles in fume.	No specifically mentioned effects.
Mercury	Vaporizes as metal at a temperature of 357 ºC	Equally potent towards aquatic and aerial life forms.
Zinc	Produces bright flashes of light and dust cloud.	Compounds of zinc metal can be toxic to the eco system.

(Table 4) Behavior of elements during melting and casting and their effects on environment

Government regulations for discharged air quality(CPCP norms)

Pollutant	Time Weighted Average	Concentration in Ambient Air	
		Industrial, Residential, Rural and Other Areas	Ecologically Sensitive Area (notified by Central Government)
Sulphur Dioxide (SO2), µg/m3	Annual* 24 hours**	50 - 80	20 - 80
Nitrogen Dioxide (NO2), µg/m3	Annual* 24 hours**	40 -80	30 - 80
Particulate Matter (size less than 10 µm) or PM10 µg/m3	Annual* 24 hours**	60- 100	60 - 100
Particulate Matter (size less than 2.5 µm) or PM2.5 µg/m3	Annual* 24 hours**	40- 60	40 - 60
Lead (Pb) µg/m3	Annual* 24 hours**	0.50 - 1.0	0.50 - 1.0
Arsenic (As), ng/m3	Annual*	6	60
Nickel (Ni), ng/m3	Annual*	20	20

*** Annual arithmetic means of minimum 104 measurements in a year at a particular site taken twice a week 24 hourly at uniform intervals.**
**** 24 hourly or 8 hourly or 1 hourly monitored value, as applicable, shall be complied with 98% of the time, they may exceed the limits but not on two consecutive days of monitoring.**
Source: National Ambient Air Quality Standards, Central Pollution Control Board Notification in the Gazette of India, Extraordinary, New Delhi, 18th November, 2009

Control measures to mitigate hazards from Pyro process fumes

Measures for mitigating risks due to hazards from Fumes from incineration , smelting and melting

- The suction hoods should be adequately cover the furnace mouth and ensure that all fumes are trapped.
- The cooled emissions then pass through series of filters which trap the air -borne particulates before going to scrubber
- The scrubber units spray alkaline solution and neutralize acidity if any in the fumes. The air gets washed as it flows through a column of strainers, becomes almost free from dust particles and exit through its stack.
- Monitoring the quality of the scrub solution as well as avoiding accumulation of sludge in the scrubber tanks is a necessity to ensure efficient functioning of the scrubbing operation.
- Stack emission sampling at frequency defined by CPCB (by authorized lab only) is a mandatory exercise ; it will ensure that processes are well controlled and avoid non-compliances during online monitoring by CPCB (CEMS).

Control measures to mitigate hazard from Chemical Fumes

- The suction hoods placed close to the furnace mouth and adequately covering the mouth to ensure that all fumes are trapped.
- The cooled emissions are then passed through series of filters to trap the air -borne particulates before they are processed in the scrubber.
- The scrubber units spray alkaline solution and neutralize acidity if any in the fumes. The air gets washed as it flows through a column of strainers, becomes free from dust particles and exit through the stack.
- Monitoring the quality of the scrub solution as well as avoiding accumulation of sludge in the scrubber tanks to ensure efficient functioning of the scrubbing operation.
- **Use expert vendor who understands suction calculation and are savvy with pollution norms to design the scrubber for you .**

Liquid Effluents from refining process

The chemical refining processes generates liquid effluents which contain impurities removed while processing the gold. The details of the solid and liquid residues/effluents generated from the chemical and electrochemical processes are summarized in the table 6 below:

Process	Liquid effluents
Parting	Acidic solutions containing bulk of metal nitrates only
Aqua Regia	Acidic solutions containing bulk of base metal nitrates, chlorides and sulphates.
Wohlwill's process	

(Table 6) Details of liquid effluent generated from various process

- The effluent generated from above processes are highly acidic (ph. 1 or less) and also contain large quantity of deleterious metals in form of their soluble salts e.g. chlorides, nitrates, sulphates etc.
- All effluent generated need to be treated before they can be finally discharged as per CPCB norms.
- Any solid sludge generated from the treatment of the above effluents is categorized under hazardous waste and requires proper authorizations before attempting its recovery and refining.

Government regulations for Effluents (CPCP norms)

Process steps at ETP comprises of equalization, treatment with bases, bacterial treatment, sand and carbon filtration which ensure that the effluent discharge meets norms set by CPCB as mentioned below :

Sr No	Parameter	Permissible limits for disposal into surface water
1	pH	5.5 to 9.0
2	Total suspended solids (TSS)	<100 ppm
3	Oil & Grease	<10 ppm
4	Biological/biochemical oxygen demand (BOD)	<30 ppm
5	Chemical oxygen demand (COD)	<250 ppm

(Table 7) CPCB requirements for effluents disposal

Live monitoring of data and its transmission to CPCB server under OEQMS has been made mandatory and needs to be complied in order to ensure zero non-compliance.

Control measures for mitigating hazard from Effluent

Measures for mitigating risk due to hazards from Effluent (Chemical processes)

- The quantity of effluent to be treated should be reduced in planned manner with stoichiometric use of chemicals.
- Recycling of process water with proper study of the water parameters at all stages.
- All effluent generated from the above processes are highly acidic and laden with impurity elements in form of their nitrates, chlorides, sulphates etc.
- A series of processes involving resin treatment, neutralization, flocculation, settling and filtration are adopted prior to sending to ETP which ensures that the impurities and their salt are completely removed, and compliances are duly complied.

Treating all effluent with due diligence is a necessity as the refining process is a hazardous activity .

Conclusion

Gold recovery and refining consists of set of complex steps involving application of high heat and hazardous chemicals

Each technique described in slides above deals with hazardous chemical and by-products during the entire cycle . The risks posed by those hazards have severe impact on human being and ecosystem if not mitigated with due diligence.

OSHAS guidelines of HIRA (hazard identification and risk assessment) are becoming increasingly stringent to ensure safety to our ecosystem. Hence, all refinery needs to adopt a strategy which aims to mitigate the risks fully and provide convincing evidence in a transparent manner during any audit.

Regular safety audits , proactive monitoring of specified parameters , use of correct PPE, health examination of working personnel are some of the key points to be monitored regularly.

For the sake of business continuity, refineries who have their inhouse facility may thus require a re-evaluation of their existing capabilities and upgrade them in order to comply with set norms.

Outsourcing the refining activity to refiners who have set the benchmark in all aspect should be considered as a part of the strategy. This can help to meet the need of green gold certification too.

THANK YOU

Technical comparison of prevalent processes

Parameters	Electro Refining	Chemical Refining	
		Aqua Regia	Inquartation & Parting
• **Scale of Operation**	Suitable for large scale having multiple range of impurities ; Silver input 10% max. Area for large production is very low	Suitable for small scale batches having all base metal, PGM; silver content should be 10% max ; Requires more area and tanks	Applicable for less than 18 K or 18 K having more than 10% Silver; not suitable for Pt & Pd , Sn, Zn containing gold alloy
• **Fineness of Refined Gold**	99.99% & above ; almost zero impurity in output gold	99.95% maximum	99.2-99.5% if properly digested
• **Impurities in Refined Gold**	Adhering to limits as specified in ASTM B 562 on individual as well as cumulative basis	Presence of deleterious elements like Pb, Fe , Ir is common ; Copper may be high is not precipitated properly; fails to meet ASTM	All base metals removed ; Pt is present will not get removed;
• **Operating cost**	Low labour and chemical cost per unit of production; electricity cost is higher	Higher operating unit ; electricity cost is lower compared to electrolysis	cost than Aqua Regia; with additional cost for silver recovery Large scrubber required
• **Inventory in Process**	Huge inventory carrying cost	Cost of inventory in WIP is much lower than electrolysis ; prone to more gold loss ; depends to process and reductant	Silver inventory is higher
• **Effluent Generation**	Per unit output generation is quiet low	Consumption of chemicals is more; generates big effluent load, final effluent per unit of production is higher	only nitrate based effluent ; more Nox generation
• **Quality of Jewellery produced**	Higher productivity and lower rejection rate due to absence of deleterious element	Manual intervention leads to presence of impurities to hard spots , oxidation , brittleness	Gold quality though of 99.5% in fineness , is quite good free from impurity