

# Technical Aspects of Platinum Refining

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The combination of high value and widespread application of platinum to new designs and jewelry articles brings the inevitable requirement for recovery through refining procedures. The methods for recovering fine gold from process scraps and discarded jewelry articles have been known and practiced for centuries. Platinum has unique characteristics and inherent chemical properties that make it more difficult to recover than gold.

Technical aspects of platinum refining are considered to include melting, sampling, assaying, high

grade treatments and complex separations of multiple elements. Financial subjects such as charges, percentage returns, metal markets and settlement periods are not discussed.

## CONTAMINATION LEADING TO REFINING:

Platinum has a propensity for becoming contaminated in the common jewelry working environment. Contamination can result in a loss of desirable physical properties such as ductility and malleability. It also includes such aesthetic issues as alteration of color, reflectivity, unpleasant surface blotching or an excessive increase in hardness. From a legal and ethical standpoint, contamination can also mean a dilution of platinum content below an acceptable marking standard. When this happens, refining to recover the platinum content in purified form may be the only alternative. The metal can then be alloyed again and shaped into product form. A detailed description of the factors contributing to platinum contamination was provided at New York Platinum Day (I) in 1996

Six main sources were noted as follows:

- *silicon* and *phosphorous* from crucibles and/or investment
- *iron* from forming mill surfaces, bench tools or annealing equipment
- *gold* or *silver* from other alloys used in fabrication or assembly
- *abrasive particles* can be reduced to Al or Si when an embedded particle is reduced during high temperature annealing or melting.

The very process of manufacturing and finishing jewelry articles can produce scrap in the form of an inseparable mix of materials that can only be recovered through complete chemical refining. Inadvertent contamination of clean ductile metal by mixing other metals or converting processing materials into damaging forms cannot always be avoided. See Figures 1 and 2 as illustrative proof. When accidents, mistakes or lessons learned create damaged metal, refining restores order.



Figure 1. Overview of embrittled platinum with trace contamination that has destroyed physical properties for further working.



Figure 2. An embrittled cast article. Grain boundary fracture indicates loss of ductility.

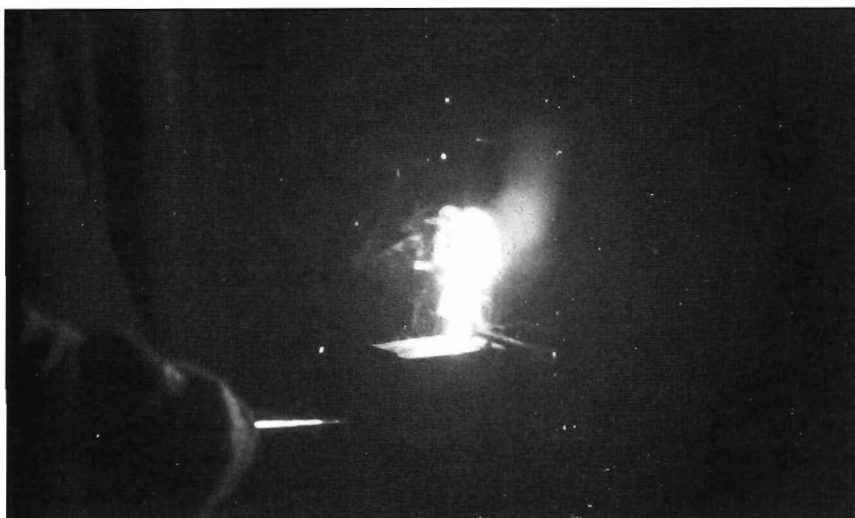
## MELTING PLATINUM MATERIALS:

A random mix of process scraps or pre-melted ingot of platinum alloy for refining is always subject to a melting operation to ensure homogeneity for sampling purposes. Some of the fundamentals of platinum melting summarized in 1996 apply to refining operations as well.

“While pure platinum melts at 1773°C (3223°F), most commercial jewelry alloys melt in the range of 1700-1800°C. This range exceeds the 1400-1500°C commonly employed for iron and steel production. A sufficiently intense heat source for melting cannot be obtained by mixing ambient air with a fuel source or employing common electrical resistance. Oxy-fuel melting, preferably with hydrogen to avoid detrimental reactions with carbon is required to render platinum molten. Platinum sponge and high velocity torch gasses do not interact well. Electric induction heating is the preferred melting method for any significant amount of platinum. A

typical setup is shown in *Figure 3*. Ceramic melting crucibles and implements are required because graphite and silicon carbide react with platinum to cause embrittlement. This inherent limitation comes with the high melting point required to withstand molten platinum.”

Most oxy-fuel melting equipment is limited to rendering about 250g molten for a few seconds. If larger equipment is deployed the risk of the torch gas velocity blowing fine particles of material out of the melting vessel is very real. Induction can melt large volumes, but struggle with small melts in the range of 250 to 750g. This problem can be overcome by inquartation with copper. A known weight of clean copper shot is added to the material to be melted. This increases the metal volume to assist inductive coupling while simultaneously lowering the melting range into a region more easily attained (1300-1500°C). Inductive and mechanical stirring are required to ensure the liquid metal becomes homogenous prior to solidification.



*Figure 3. The extreme temperatures encountered with platinum melting challenge advanced ceramics and are well beyond graphite or clay-graphite capabilities.*

The specifics must be noted to provide an understanding of mass balance. If 555g of 90% platinum scrap contain 500g of pure platinum, adding 445g of copper will allow induction melting equipment to melt and homogenize the resulting 1000g lot. The anticipated 90% platinum assay cannot be applied to total weight of 1000g. The assay will be diluted to 50% reflecting the addition of copper. Many times it is best to report the actual assay and provide correction for the necessary in-quartation step.

This method works when melting high grade scrap of known approximate composition. When handling complex scraps that contain considerable gold and other metals melting to a homogeneous mix can be more difficult. The relationship between gold and platinum at high temperatures is summarized in *Figure 4*. The melting range becomes very broad and slushy when the two metals are mixed. This makes it difficult to mix and pour the materials. They also separate into two phases of different chemistry when solidified. This creates very hard and brittle ingots. The situation is further compounded by the relationship between copper and platinum noted in *Figure 5*. Solid state hardening reactions contribute to ingot hardness.

## OBTAINING A REPRESENTATIVE SAMPLE FOR ASSAY:

A representative sample is supposed to be composed of the same amount of each of the elements contained within the entire melted bar. For a few grams to be representative of a few hundred to several thousand grams, the molten metal must be completely homogenous up to the point of so-

lidification. After solidification, the bar should not segregate on a macroscopic level. The sample taken must be a size or shape easily weighed to a high level of accuracy. It may be necessary to roll a ductile sample into thin foil for further cutting into small pieces that ease digestion for assay purposes.

If the inherent properties of a material make it difficult to obtain a homogenous solidified ingot, sampling in the molten state can be attempted. This is usually done with a glass vacuum pin tube that melts when immersed in the molten pool, allowing metal to be drawn upwards to form a 2-3mm round shape about 3 inches long. The method is commonly de-

ployed with gold alloys that are ductile and can be rolled afterwards to provide a thin strip for careful sampling and assay. With the extreme temperatures involved with platinum alloys, the glass tube usually melts, exposing the vacuum section to the air above the melt rather than the molten metal. The tube falls into the melt providing no rod of metal for further sampling. The technique is particularly difficult when a torch is used to keep a small pool of metal molten. Even if a quick hand can obtain a pin sample from the liquid pool, it often can't be worked or shaped thinner to facilitate dissolving in aqua regia required for liquid instrumentation analysis.

Sampling in the solid state is more common with platinum alloys. They are inherently resistant to the type shear common to drilling. Platinum can easily wear out a tool steel drill in just a few holes. If an ingot contains considerable gold, silver and copper it may simply be too hard to drill sample. The risk of contaminating a sample with broken fragments of hard steel or carbide drill is very real. Sampling routines for dealing with a segregated bar usually involve drilling the top, middle and bottom of both sides. Only a quality sharpened drill will complete five to six holes without failure. In an extreme case, a few drills may be required to get a 2-3g sample for determination of the contents. A steel band saw offers a chance to

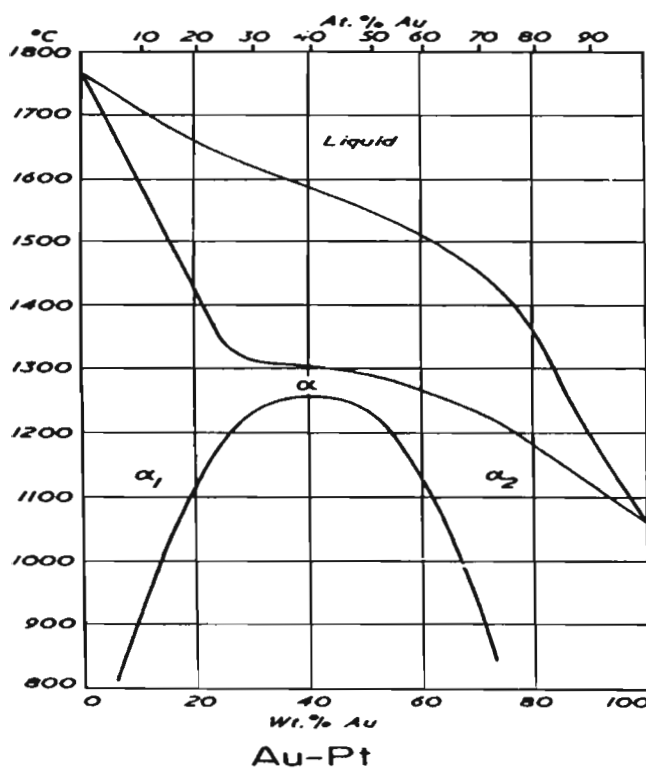


Figure 4. The platinum-gold phase diagram depicting a broad melting range at 50% Au to 50% Pt. A strong phase separation leading to segregation and sampling issues is shown during cooling from solidification.

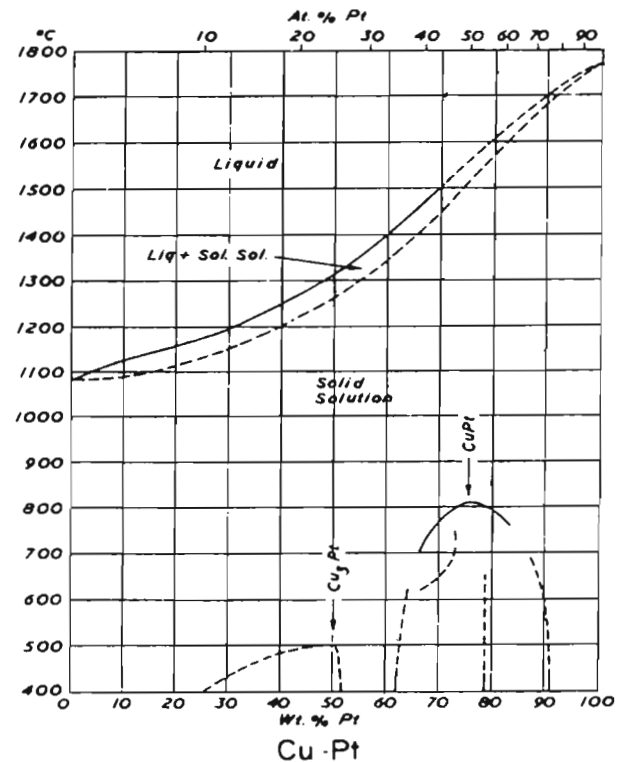


Figure 5. The platinum copper phase diagram showing solid state hardening that affects a solid bar during cooling.

cut slices through a bar that run completely through the thickness at several locations top to bottom. The tiny chips generated by the band saw do not need any further manipulation prior to weighing and dissolving for assay.

Regardless of the method chosen, sampling platinum ingots can be difficult. Extremely hard and brittle materials are often the result of melting complex scraps that contain mixtures of 18k gold with silver and platinum alloys.

Bars so brittle they break like glass when dropped are difficult to cut with any equipment that does not contaminate the sample. This is an area of considerable difficulty with platinum materials for refining.

#### ASSAYING PLATINUM SCRAPS:

An assay is a determination of the precious metal content of a sample. If the sample is representative, it's also the determination of the contents of a melted ingot. The accuracy of an assay process is limited by the accuracy of the sample provided. A poor quality sample will not provide an accurate reflection of the metal content of a bar. Consideration of assaying methods can be subdivided into solid state and liquid phase with further division into instrumentation or complex gravimetric methods.

#### SOLID SAMPLE X-RAY FLUORESCENCE ANALYSIS:

If the quantity of major elements in a sample are known within a narrow range and an accurately prepared standard exists, it is possible to determine the platinum content on a sample to an accuracy of 0.10%. This eliminates the

difficulties associated with dissolving a specimen in aqua regia for liquid phase analysis. Standards are most easily prepared for commercial binary alloys of iridium, ruthenium or cobalt. In situations where trace element contamination with silicon, phosphorous or silver destroys the *ductility* of a batch of melted metal, XRF can confirm the platinum content accurately. The method is based upon statistical counting of the secondary x-rays emitted by the solid sample after irradiation with a controlled and filtered x-ray beam of known makeup. The method does not apply with a high level of accuracy to complex mixes of gold and platinum scrap unless a broad range of good standards exists. In many cases, solid state XRF analysis can provide a spectral scan that identifies what elements are present in approximate compositions to clarify methods for more detailed liquid sample or gravimetric analysis.

#### ANALYSIS BY A.A OR I.C.P INSTRUMENTATION:

Liquid phase analysis is limited by the time required to dissolve a thinly rolled or high surface area specimen in the 3:1 mixture of hydrochloric and nitric acid known as aqua regia. If sufficient surface area is present, heat, full strength acid and time are required to complete the dissolution. If too large a sample is used, it may not dissolve at all. Undissolved elements must be filtered to avoid clogging the nebulizer of the unit. Figure 6 depicts a typical instrument. Both an atomic absorption unit and an inductively couple plasma analyzer are based on the principle that an element will absorb light of a characteristic wavelength when excited to an atomic state by vaporization in a high temperature fuel source. The characteristic light is produced by a special lamp that has a filament composed of the element being analyzed. The amount of absorbance is measured and compared

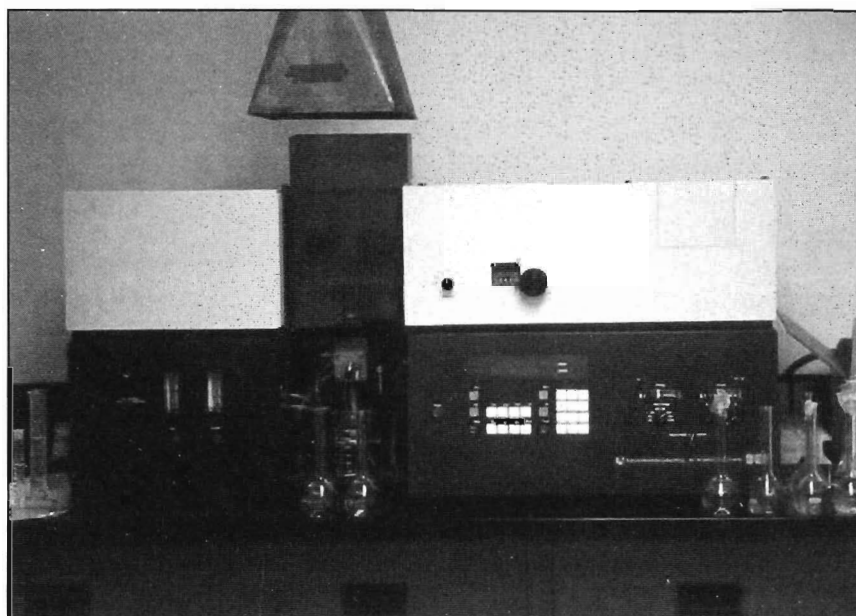


Figure 6. Typical Atomic Absorption Spectrograph for platinum determination.

to accurately prepared standards. Both the unknown and standards must be prepared by diluting a strong solution of high concentration to a lower level that can be measured on the specific unit. The accuracy of measuring standard concentration samples and diluting them to a known volume to produce a specific concentration is a limit of the process. The same limitation is faced when diluting unknown samples to a specific large volume to reduce the signal intensity to within the measurable range. Also, certain elements behave similarly and absorb the characteristic light of other elements. This effect is known as interference. It can be overcome by close matching of the matrix to have the standards contain very similar quantities of all the elements found with the unknown. This can be a complex problem when 8-12 elements are combined with platinum. Deploying solid state XRF semi-quantitative analysis with liquid phase accurate determination can be useful. Quantifying the actual concentration of a specific element is done by a process of linear interpolation where the unknown must fall within the range of absorbance versus concentration established with the standards. The requirement to maintain a broad catalogue of standards for a wide variety of unknowns can be a burden.

#### GRAVIMETRIC ANALYSIS:

A classical wet chemistry method of separating the various elements in a sample can be combined with instrumentation methods to yield accurate results. A 14 step process can be summarized as follows:

- Accurately weigh the unknown sample.
- Dissolve in aqua regia over sev-

eral hours.

- Filter the undissolved elements such as iridium, ruthenium, Silver etc.
- Precipitate the gold fraction.
- Wash the residue acid free, dry and burn off the ashless paper.
- Weigh the gold fraction and calculate the percent of the original sample.
- Boil all of the wash solutions and liquors to reduce their volume.
- Precipitate most of the platinum as a salt with ammonium chloride.
- Filter the salt from the solution and dry.
- Thermally convert the salt to metallic platinum.
- Accurately weigh the metal
- Dissolve again in aqua regia and use instrumentation to quantify the impurities of Ir, Ru, Pd etc. against standards.
- Calculate the contamination and make corrections to the platinum metal weight found previously.
- Check all liquid fractions for platinum content and add this amount back to the metal weighed.

The method produces accurate results when executed properly. The problem of matrix matching that plagues instrumentation is minimized by stripping out the bulk of the metal for weighing before impurity analysis. The method is not limited by the scrap complexity. Overall, the process is slow and requires detailed record keeping to make corrections for the platinum content of the various fractions.

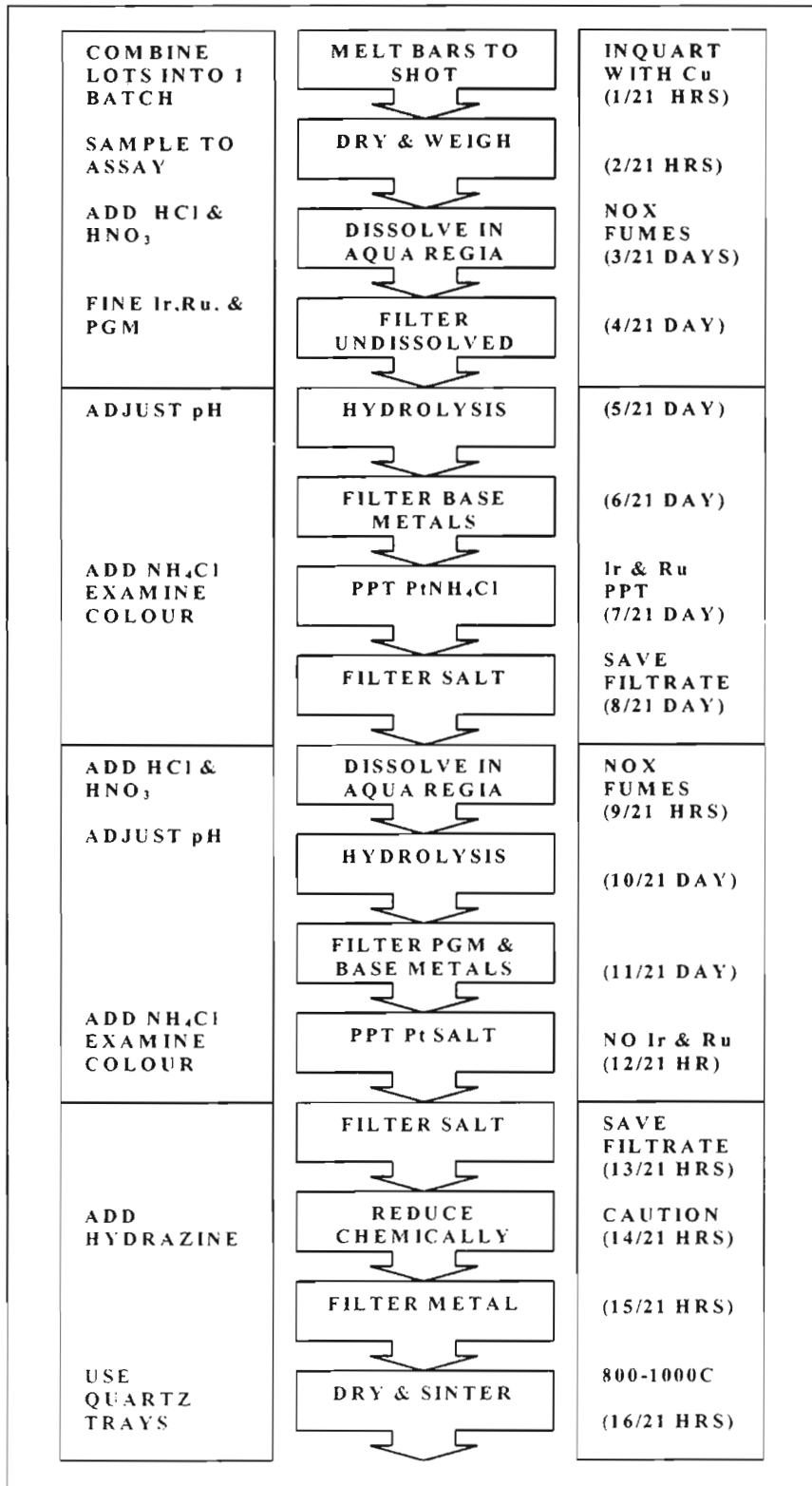
Regardless of the method used, platinum determinations are more complex than gold assaying. The clean reliable oxidation separation of base metals from gold and silver

during the cupellation stage of fire assay simply does occur with platinum group metals. It is important for an experienced lab to know the makeup of their sample for assay and use quality standards to produce accurate results. Simply running a platinum sample on an expensive I.C.P unit with no matrix matching or corrections will produce inaccurate results because of the tendency of ruthenium, iridium and platinum to co-assay. This usually results in falsely inflated values for the platinum content. The use of an experienced lab, provided with as much information as possible about the presence of various PGM elements is important for quality results.

#### HIGH GRADE PLATINUM REFINING:

For discussion purposes, high grade materials are defined as containing greater than 89% platinum with no gold, silver or significant quantities of base metals. These materials are considered to be mixes of commercial binary alloys containing iridium, palladium, ruthenium and cobalt that may or may not be embrittled with trace impurities. A graphical format is used to show the stepwise progression of processing that a material must undergo for purification.

The left side box provides explanation to the center box which displays progression to the next step with downwards pointing arrows. A time line and process step count is noted on the right side. The step number of the total is displayed and a relative processing time of hours, one day or several days is noted to provide perspective. When material is cycled back through the process a horizontal



arrow and note to the step number are used

Comparisons between platinum and gold provide perspective from the viewpoint of complexity:

Process Issue	Platinum	Gold
Number of process steps	More steps (21)	Few steps (8)
Dissolving rate	Slower	Faster
Base Metal Separation	Hydrolysis	To waste liquor
Precipitation	Ammonium chloride is not selective to Pt	Gold can be removed easily
Separation	Pt remains in many fractions	Gold can easily be split
Contaminating elements	Ir, Ru, Os, Pd, Re, Au	Ag, Pd
Waste treatment	Complex with Pt content not easily recovered	Simple free of Gold

After taking longer to dissolve because of higher chemical nobility the other platinum group metals must be removed, before precipitation of the platinum content. Similarly, gold materials require filtration of silver chloride. Precipitation of the valuable gold fraction is selective and complete. Ammonium chloride is not selective to just platinum. Any iridium, ruthenium or palladium that is not precipitated and filtered during the hydrolysis stage will be reduced by the ammonium chloride and contaminate the platinum. The reduction of platinum is not complete, even with the addition of excess reagent. A significant fraction goes into the waste solutions increasing the urgency for treating them. Final purity is generally lower than gold at 99.90 to 99.98%. Principle contaminants are the other PGM group metals and any traces of gold in the scrap.

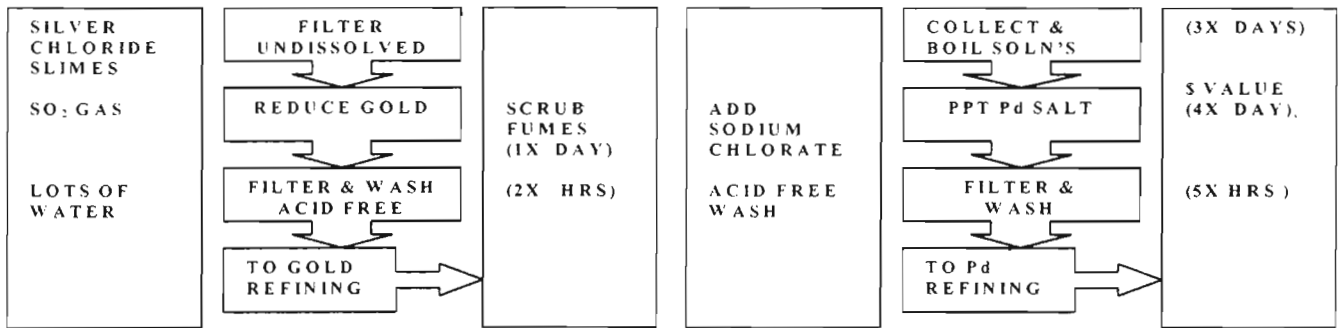
### COMPLEX SEPARATIONS OF PLATINUM:

Compared to high grade materials, the mixed materials formed when yellow gold, white gold and platinum alloys mix are more complex to treat. With gold content varying from 20-75%, platinum content between 20-75% and significant silver, copper, nickel and palla-

dium contamination several additional processing steps are required. These scraps are generated from two-tone rings assemblies or grinding and finishing scraps from shops that handle both gold and platinum in larger quantities. They may be further contaminated with the components of gold solders from assembly operations. They are difficult to melt and sample be-

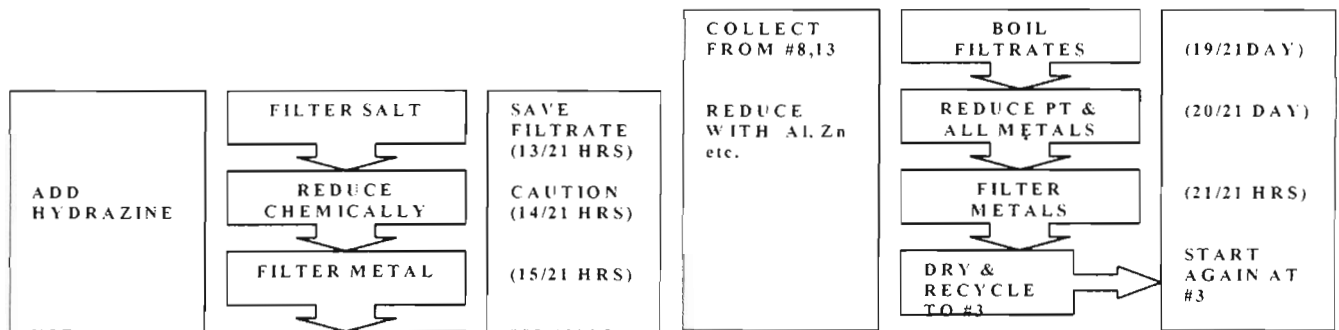
cause they are heavily segregated. The processing line shown for high grade platinum applies, with the additional steps noted with explanations.

After step number three in the high grade platinum processing procedure the silver content, in the form of silver chloride must be filtered and washed free of other precious metals.

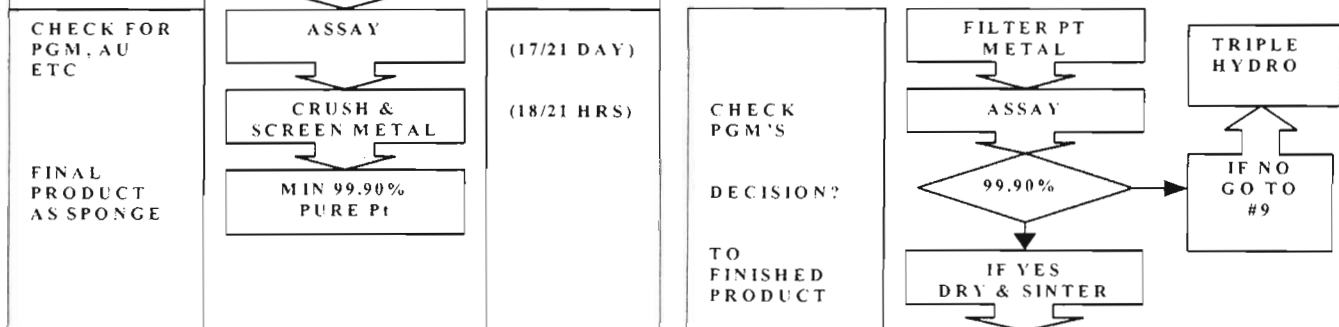


The gold content must be precipitated, filtered and washed to be free of platinum solution. This causes a significant increase in the volume of solution to be treated.

After gold recovery, but before platinum separation, the palladium content must be removed. If gold and palladium are not treated the platinum will not be 99.90% minimum purity.



Platinum removed from by-products is impure and must go through the complete refining process again.



Extra steps to strip platinum content from refining process byproducts.

At Step 17 of High Grade Treatment, the assay process may reveal an additional hydrolysis step is required to remove PGM residues.

Compared to high grade materials, these complex mixes require additional treatments noted, including extensive boiling and solution reduction steps and often an additional hydrolysis step to complete removal of the PGM content. Extra filtration is time consuming throughout the process for removal of elements that would otherwise contaminate the platinum. All of this additional handling takes time.

Comparison of the two distinct types of platinum processing to gold is summarized as follows:

COMPARISON OF PROCESSING STEPS AND TIME FOR VARIOUS MATERIALS			
	Regular Gold	High Grade Platinum	Complex Platinum
No. of Processing Steps	8	21	25-36
No. of Processing Days	5-6	15-20	25-30

The time shown for platinum treatment does not include complete treatment of all waste solutions. Cementation with zinc does not always return the platinum values. Sometimes the entire volume of solutions must be boiled down for reduction with hydrazine or run through a resin column for stripping. Gold reclamation to a

few ppm is complete with the initial precipitation. Platinum simply does not follow this pattern. This adds considerably to the cost and complexity of treating platinum materials.

#### SUMMARY:

Platinum refining procedures are required because the metal is more prone to contamination than other common jewelry materials. Gold, silver, silicon, phosphorous and iron can be incorporated into platinum from materials common to the fabrication process. The elevated temperatures required to melt and assemble platinum enhance the likelihood of melting and absorbing other elements. Process cleanliness contributes significantly to reducing contamination.

Unmixed high grade platinum can be treated in different processing circuit with fewer processing steps than complex mixes containing white and yellow golds. Melting and sampling of complex grades is impaired by the broad slushy solidification range with massive segregation from the inherent behavior of gold and platinum. Extremely hard and brittle materials often result from these complex scraps. This makes obtaining a

representative sample both important and difficult.

Platinum assaying procedures are more complex than gold fire assaying. Often a combination of solid state XRF examination must be mixed with instrumentation techniques and /or classical wet chemistry separations to minimize the effects of PGM interference. This can result in protracted assaying process times.

As noted in the previous tables, platinum refining has more processing steps, more incomplete separations, partial recovery, hydrolysis to strip base metals out before platinum recovery and waste streams that require more treatment compared to gold. Both high grade and complex mixes take considerably longer to treat than conventional gold materials. In the worst scenario, a complex mix of platinum and gold scraps can require 35 processing steps over a period of 25-30 working days for recovery compared to eight steps requiring six days for gold separation.

From a technical perspective, platinum is a more difficult metal to recover from jewelry process scraps than gold.