

THE ASSAYING AND REFINING OF GOLD

A Guide for the Gold Jewellery Producer

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Fire Assay: Loading a cupel tray into the furnace

1 INTRODUCTION

Gold is a precious metal, as are silver and the platinum group metals (platinum, palladium, rhodium, iridium, ruthenium and the extremely rare osmium). They are called precious metals because of their great resistance to chemical (and environmental) attack, because of their scarcity and, particularly in the case of gold and silver, because of their universal use in jewellery. They frequently occur in nature as “native” metals, that is in the metallic state and not as compounds, though often they are in combination with other metals in mineral form, and frequently in combination with each other. Because of their strong resistance to chemical attack, techniques for separating the individual precious metals are often complex, particularly those for the platinum group metals (pgm’s).

In 1996 some 2300 tonnes of newly mined gold was produced around the world, with an additional 600 tonnes produced from scrap jewellery, dental gold, bullion coins, electronic products and a whole range of waste materials containing very small amounts of gold - sludges, solutions, slags, filings, refractory investment from jewellery castings, even residues from old mines. For all these materials, whether available in tonnage quantities or a few grammes, refining is necessary to extract and separate out the gold. At the same time, analysis is a significant part of the refining exercise, both to determine the gold content in the refinable material and also the gold purity after completion of refining.

This booklet is designed to help gold jewellery producers by providing information on currently available analytical and refining techniques for gold. It initially looks at the types of materials that are available to the refiner (large- and small- scale), covering the whole range of materials including jewellery and other products. The fire assaying technique for the analysis of gold is discussed together with its limitations. Instrumental techniques which are now available are referred to while the touchstone and density measurement methods for determining gold are also outlined. Finally, a review is made of gold refining processes and the extent to which they are capable of producing pure gold.

2 REFINABLE MATERIALS

2.1 MINED GOLD

Deep mined gold (shafts already reach a depth of 3000m in South Africa) or surface mined gold will initially be crushed and the heavy gold-containing fraction separated out. Further concentration will take place at the mines usually culminating in a smelting operation to produce gold doré, an alloy containing 50-90% gold. Most of the other constituents will be silver and copper, with smaller quantities of other base metals and perhaps traces of platinum group metals (pgm's).

For example, the average composition of doré produced in the South African mines is 89% gold, 9% silver, with small amounts of copper, lead, zinc and iron, and traces of nickel and pgm's.

Doré is sent to a gold refinery for specialised treatment to produce pure gold.

2.2 ALLUVIAL GOLD

Alluvial deposits are found in stream or river beds, usually as native metal, and may contain in excess of 90% gold. These deposits are widespread in Africa and South America, often collected in relatively small quantities by individual 'miners'.

2.3 SCRAP JEWELLERY

The universal appeal of gold as a decorative material is based on its outstanding resistance to corrosion, its attractive appearance, its malleability and, despite its relative scarcity, its widespread distribution throughout the world, often in metallic form. These characteristics have been recognised for many thousands of years, with gold artefacts currently in existence dating from as far back as 7000 BC.

Gold, however, is inherently soft in its pure form and it has long been recognised that additions of other elements are needed to increase the strength and to modify other properties. The usual alloying elements are silver and copper which can be added in quantities up to 60-65% and which impart considerable strength benefits. Copper also has a marked reddening effect on the gold. Zinc, cadmium and nickel are other alloying elements which have found widespread use. Zinc improves the flow characteristics of casting alloys, cadmium markedly reduces the melting point of gold alloys and has been used in the formulation of gold soldering alloys, while nickel is renowned for the whitening effect it has on gold. Recent concerns over possible health hazards associated with the use of cadmium and nickel have led to efforts to find alternatives and, as far as whiteness is concerned, palladium has now largely superseded nickel, despite its relatively high price. Gold alloys containing up to 15% palladium are currently produced. Platinum could also perform a similar role but has found little use in gold jewellery as it is about three times more costly than palladium. Rhodium will often be used to plate white gold jewellery which contains soldered joints so as to ensure a consistent white colour.

One of the microstructural characteristics of significance when producing gold alloys for jewellery use is grain size. For casting small items of jewellery where shrinkage stresses may induce cracking of small sections, and for forming or bending of strip or wire in the manufacture of chain or bracelets, a fine grain size is desirable. In these cases it is common practice to add small quantities of a grain refiner to the molten gold alloy before casting so as to encourage the formation of a fine grained microstructure. Frequently the grain refiner is a platinum group metal, with iridium being the most common, but rhodium and ruthenium are also used. The quantities used are unlikely to exceed 0.05%, but may, of course, build up if scrap is recycled and further additions of grain refiner are made.

2.4 SCRAP DENTAL ALLOYS

Gold also has a long history in the field of dental applications, with evidence that it was being used 4000 years ago. Today it is recognised as the basis for casting and bonding alloys, and for wires and solders.

As in the case of jewellery alloys, it has proved necessary to alloy gold with silver and copper to improve the strength of a dental restoration. Up to 20% of alloying elements has been used allowing the alloy to retain its biocompatibility and corrosion and tarnish resistance. Platinum and palladium also found application some years ago when they were less expensive than gold and could be used as a substitute for some of the gold.

The development of bonding alloys, where dental ceramics are required to be fused to the gold alloys at temperatures of up to 1000°C rendered the standard gold-copper-silver alloys unsuitable because of their relatively low melting points. Hence, platinum and palladium became standard alloying element additions to the gold in order to raise the melting point of the bonding alloy to 1100°-1200°C while still retaining the other desirable properties. The whitening effect of palladium particularly means that some bonding alloys, though gold based, are white in colour, although there are now alloys available which are predominantly palladium with only minor quantities of gold (less than 20%) or no gold at all. However, typical gold-based alloys might contain 70-90% gold and up to 15% platinum and palladium.

In parallel with jewellery alloys, small quantities of iridium, ruthenium or rhodium are added to most gold-based dental alloys as grain refiners, with beneficial effects on both mechanical properties and corrosion resistance. Typical amounts might be 0.1-0.2%.

2.5 OTHER GOLD MATERIALS

Gold can become available as a by-product from other metal refining processes. In particular, the anode slimes which form during the electrolytic refining of copper will frequently contain small quantities of precious metal which will be sent to a refinery for recovery.

From time to time scrap bullion will become available for refining. Often coinage is made from high carat gold alloys, typically 91.6% gold (22 carat), with the alloying elements being silver and copper, the

proportions depending on whether a yellow (mainly silver) colour or red (mainly copper) colour is required.

Electronic equipment will often contain gold plated components for electrical integrity, and this can be a significant source of gold.

Finally, all manufacturers who handle gold will generate scrap or waste in some form or other. Much will be directly recycled. Some will be “cleaned up” prior to re-use and some will be fully refined for recovery of pure gold. However, it should be emphasised that all too frequently recycling of allegedly clean scrap leads to subsequent problems. Full refining is the only sure way to avoid contamination.

3 ASSAYING OF GOLD

A vital part of working with precious metals has to be the ability to determine accurately the composition of materials at all times. In the manufacture of gold jewellery products it is essential to know the exact composition to ensure conformity with carat gold standards and to avoid “giving away” precious metal for which a customer is not paying. In-house quality control demands a knowledge of the composition of all new or recycled material that goes into a product at the make-up stage. In addition, it is important to be able to monitor the composition of work-in-progress both to control and minimise metal losses and to be able to effect regular inventory checks. Finally, refiners, large and small, have to have the ability to determine precisely the precious metal composition of materials sent in for treatment.

Accurate analysis of gold has been conducted for centuries by the use of the fire assay technique. It is universally used and has been the basis for gold analysis as long as analytical techniques have been practised and is specified by the International Standards Organisation as the referee method for the determination of the fineness of carat gold jewellery alloys. However, there are other techniques available which are also discussed, while Table 1 compares the major features of all the techniques.

It is stressed that assaying and analysis involves the use of strong acids, high temperatures and the production of toxic fume. Thus, **safety** is important and appropriate equipment should be used and approved safety procedures followed.

Table 1. Comparison of Assaying Techniques

Technique	Versatility	Sample Size	Accuracy	Limitations	Equipment Cost
Fire Assay	Only determines gold	About 250 mg	0.2 parts per thousand	Modifications needed when nickel and pgm's present	Low
ICP Spectrometry	Can determine other elements	20 mg	1 part per thousand	None	High (150k US\$)
X-Ray Fluorescence	Can determine other elements	Non-destructive	2-5 parts per thousand in best conditions	Restricted largely to flat specimens	Moderate (up to 50k US\$)
Touchstone	Only determines gold	Non-destructive	Largely a sorting test, 15 parts per thousand	Unsuitable for high carat and hard white golds	Low
Density measurement	Only determines gold	Non-destructive	Poor		Low

3.1 FIRE ASSAYING TECHNIQUE

The basic technique is suitable for determining accurately the gold content of alloys containing 30 to 99.9% gold, with certain limitations which are dealt with in Section 3.2. It is important to remove non-metallic impurities before sampling - in other words the technique can be applied directly to samples from ingots, cast products, semi-finished or finished articles of jewellery and metallic scrap pieces.



Figure 1. Sampling a gold ring by scraping



Figure 2. Weighing sample on an analytical balance



Figure 3. Wrapping gold sample and silver addition in lead foil



Figure 4. Samples in refractory cupels placed in furnace



Figure 5. Cupels after removal from furnace showing residual bead of gold-silver



Figure 6. Flattening gold-silver bead after cupellation

The principle on which fire assaying is based is that, unlike base metals, the noble (precious) metals essentially do not oxidise at high temperatures. A carefully taken, representative sample (Figure 1) of the gold alloy which is to be analysed is weighed (Figure 2) and melted at 1150°C in a porous refractory crucible, with an addition of lead (the sample is wrapped in lead foil) (Figure 3) to assist in the melting and oxidation of the base metals, and their absorption into the crucible or cupel and with an addition of silver. This stage in the process is called cupellation (Figure 4). A metallic bead is left behind in the cupel which comprises the noble metals - gold, silver and any pgm's (Figure 5). The silver (and any platinum and palladium) is removed from the flattened (Figure 6) and rolled (Figure 7) bead by dissolution in nitric acid, this stage being called parting (Figure 8), leaving behind the gold and any insoluble pgm's (rhodium, iridium, ruthenium and osmium). In the absence of these pgm's, comparison of the weight of the remaining gold (Figure 9) with the original sample weight gives a direct measure of the gold content of the alloy. A preliminary assay is often useful to determine the approximate gold content to help establish the quantities of lead and silver which need to be added. A fuller description of the technique is given in the Appendix while its use as a referee method is described in International Standard ISO 11426: 1993.

3.2 LIMITATIONS OF FIRE ASSAYING TECHNIQUES

3.2.1 GOLD ALLOYS CONTAINING NICKEL

Nickel is often used to produce white golds and its presence requires a modification to the fire assaying technique. Nickel does not readily dissolve in molten lead and may remain in the cupel as a black scale which can trap some of the gold. An increased quantity of lead or a pre-cupellation stage involving the addition of lead, silver and anhydrous borax can be used to ensure nickel does not interfere with the gold assay. Both modifications are detailed in the ISO standard 11426.

3.2.2 GOLD ALLOYS CONTAINING PALLADIUM BUT WITH NICKEL ABSENT

Palladium is an alternative, and increasingly used, alloying addition in the manufacture of white gold. It is possible that some palladium will remain in the gold bead after cupellation and parting. In order to ensure its complete removal, it is good practice to carry out a second cupellation and parting, details of which are again given in the ISO Standard 11426.

Platinum behaves in exactly the same way as palladium and so its presence, though extremely unlikely, can be treated in the same way.

3.2.3 GOLD ALLOYS CONTAINING INSOLUBLE PLATINUM GROUP METALS (PGM'S): RHODIUM, IRIIDIUM, RUTHENIUM OR OSMIUM

It is possible for gold alloys to contain insoluble pgm's either as residual elements from mined gold (for example traces of osmium and iridium) or as additions to the alloy (for example iridium and ruthenium as grain refiners, rhodium as a plating for white golds). In this context they would

typically be present in very small quantities (say 0.1%) but, in the fire assaying procedure, their resistance to oxidation and acids means they will be carried over with the gold and so affect the accuracy of the final assay result.

Their very insolubility in gold means that obtaining a representative sample is, in itself, a difficult exercise. Carrying out a normal fire assaying procedure in the presence of any of these metals will give a cupelled bead which is likely to exhibit grey/black particles which persist after the parting operation.

When this occurs, the final gold sample should be dissolved in 25 ml of freshly made 50% aqua regia (3 parts hydrochloric acid, 1 part nitric acid, diluted with an equal volume of de-ionised water) in a beaker under gentle heating, leaving a grey/black powder collected at the bottom of the beaker, this being a clear indication of the presence of insoluble pgm's. The solution should be diluted to 50 ml, and the powder collected by filtering through a pre-weighed, dried sintered Gooch crucible, maximum pore diameter of 10 to 16 microns. The crucible and contents should be dried to a constant weight at 80°C, the net increase being the weight of insoluble pgm's which has to be subtracted from the weight of the original parted gold sample to enable the true gold assay to be calculated.

3.2.4 GOLD ALLOYS CONTAINING 40% OR MORE SILVER

The fire assaying procedure normally requires the addition of pure silver equivalent to 2-3 times the weight of gold present. When the sample itself contains 40% silver, allowance for this has to be made when determining the weight of silver that should be added. The purpose of adding silver in the first place is to avoid a situation where very small initial quantities of silver in the sample could be masked by gold during the parting operation.

3.3 DETECTION OF NICKEL AND PGM'S IN GOLD ALLOYS PRIOR TO FIRE ASSAYING

Although there are established modifications to the fire assaying procedure to enable the effects of nickel and pgm's to be allowed for in determining the gold content of materials, these modifications presuppose a knowledge of the presence of these metals. This is relatively straightforward for nickel (e.g. Dimethyl Glyoxime test) and palladium as one or other of them will be present in white golds as the whitening agent but far less so for the insoluble pgm's, rhodium, iridium, ruthenium and osmium. It is unusual for these elements to be present and there has been very little reported on ways to detect their presence. In Section 3.2.3, the presence of grey/black particles on the cupelled bead, persisting after parting, is noted as a strong indication of the presence of insoluble pgm's. Rhodium, if present in quantities above about 0.3%, will cause the molten bead to split during cupellation. The resultant cooled bead takes on a bluish-grey coloured surface which deepens to a blue-black colour with increasing rhodium content.

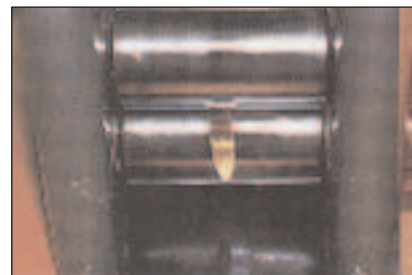


Figure 7. Rolling the flattened gold-silver bead



Figure 8. Gold-silver rolled sample heated in nitric acid to remove silver



Figure 9. Final Weighing operation of pure gold sample after parting

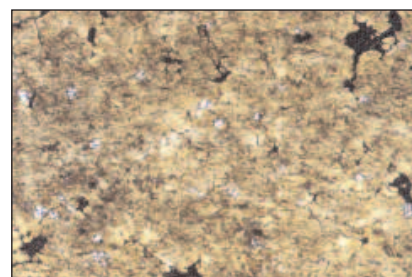


Figure 10. Metallographic section of 18 ct gold alloy, containing 0.5% iridium. Clusters of Iridium on the surface



Figure 11. Centrifuge tube with cyanide solution (top) and ceramic boat after sample dissolution showing residual iridium (bottom)



Figure 12. Rubbing from test piece (left) and touch needle



Figure 13. Applying touch acid to rubbings



Figure 14. Soaking up excess acid with filter paper

It may also be possible to detect insoluble pgm's in jewellery items because their very insolubility makes polishing difficult and gives rise to "comet tails". Figure 10 is the surface of a metallographic section of an 18 ct gold alloy to which 0.5% iridium has been added. The insoluble iridium particles can be clearly seen and highlight the difficulty of obtaining a representative sample as their distribution may vary throughout the alloy.

It is also possible to devise tests for individual pgm's but, again, the use of such tests would normally be triggered by a knowledge of the possible presence of the pgm. For example, a test which is suitable for detecting the presence of iridium makes use of a centrifuge tube with a conical-shaped bottom (15 ml) and polyethylene stopper, and a testing solution made as follows:-

5g gold stripper 'Entgoldung 645' (Degussa AG) is dissolved in 200 ml de-ionised water, heating to 40°C if necessary. Cool, add 2.5g potassium cyanide and make up to 250 ml with de-ionised water.

Fine filings are taken from the test piece (minimum 30 mg) and placed in the tube which is half-filled with testing solution and stoppered. The tube is placed horizontally and left for three hours. The presence of iridium is revealed by a fine dispersed residue, best viewed with the tube upright against a white background. Detection limit can be as low as 0.1% iridium depending on sample size. Some experience of the test is required, particularly to avoid confusing iridium with undissolved sample.

Figure 11 depicts the centrifuge tube with cyanide solution (top) and a ceramic boat after sample dissolution showing residual iridium.

3.4 OTHER TECHNIQUES FOR THE DETERMINATION OF GOLD

3.4.1 ICP SPECTROMETRY

The fire assay technique, in the hands of an experienced analyst, is well capable of giving results which are accurate to 0.2 parts per thousand. This has led to its adoption as the internationally-recognised referee method for gold analysis. However, there have been developments in the field of ICP (inductively coupled plasma) spectrometry which have led to the technique finding application in some laboratories for analysis of gold with an accuracy of close to 1 part per thousand. The technique consists of dissolving a small test sample of say 10 - 20 mg in a hydrochloric/nitric acid mixture and buffering it with a solution of copper chloride and sodium nitrate. A precision weighed amount of the solution is analysed in the instrument together with reference solutions for calibration and standardisation. The instrument measures the atomic emission lines for every element present in the sample. The intensity of emission is related to the amount of the element present in the sample.

The disadvantage of this technique compared to fire assaying is the relatively high cost of the equipment. This apart, however, it offers interesting prospects for determining other elements simultaneously with the gold and is free from the limitations of fire assaying caused by nickel and pgm's. It may well be that future developments will lead to

comparable levels of accuracy as fire assay and significantly reduced equipment cost, in which case it is likely to find much wider use.

3.4.2 TOUCHSTONE TESTING

This is another very old established method with evidence of its use over 2500 years ago.

The test consists of taking a rubbing onto the touchstone from the article to be tested. A similar rubbing is taken from a touch needle of known caratage and colour so that a direct comparison can be made between the two (Figure 12). Various touch acids, usually nitric acid of increasing strengths for the different caratage ranges with perhaps other additives, are applied in turn to the rubbings by a dropper (Figure 13). After a suitable time has elapsed, a filter paper is used to soak up the excess acid (Figure 14) and a visual examination of the rubbings is made (Figure 15). If the test rubbing is a darker colour than that of the touch needle, or has even completely dissolved, it can be assumed that the test sample is of lower caratage than that of the touch needle. With care, it is possible to distinguish between alloys of slightly differing gold contents. Figure 16 shows rubbings from left to right of alloys containing 700, 720 and 750 parts per thousand of gold. In skilled hands, the differences of 10 to 20 parts per thousand are detectable. Figure 17 shows a central rubbing of an unknown alloy with rubbings on either side from a 750 gold touch needle. They are identical in colour and the unknown alloy is assumed to be an 18 ct gold.

The equipment is simple (Figure 18). It is important that good quality touchstones of uniform colour and sufficient hardness are used. The best stones are the natural stones, lydite and radiolarite, and black agate. Touch needles must be of known composition with gold content confirmed by fire assay. Touch acids do not deteriorate as such but their strengths may change due to evaporation of water and it may be necessary to restore them to their original strengths by addition of drops of distilled water.

It should be stressed that the test is not in itself an accurate assaying method for gold. However, it can be used as a quick sorting test and, in skilled hands, it can indicate the approximate caratage. Accuracy is dependent on:-

- the composition and colour of the alloy
- the quality of the touchstone
- the strength of the touch acid
- lighting conditions
- operator skill

The test is not suitable for very high carat golds or hard white golds.

3.4.3 X-RAY FLUORESCENCE

An increasingly popular technique is x-ray fluorescence spectroscopy (XRF). A sample to be tested is placed in an x-ray chamber and irradiated under appropriate conditions, with automatic display of analysis results via a computer terminal. The surface of the jewellery is bombarded with radiation and this causes the emission of x-rays, which are collected and

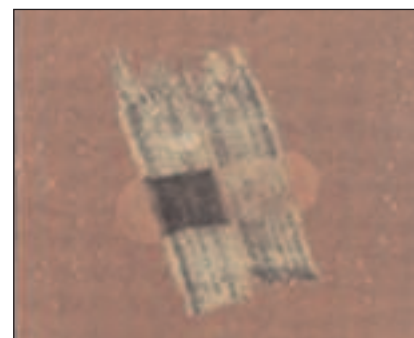


Figure 15. Visual observation of rubbings



Figure 16. Rubbings of alloys containing 700 (left), 720 and 750 (right) parts per thousand gold

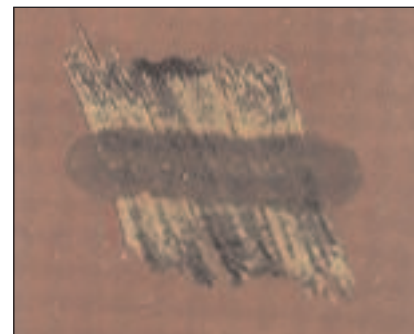


Figure 17. Rubbing of unknown alloy (centre) compared with rubbings from 750 parts per thousand gold

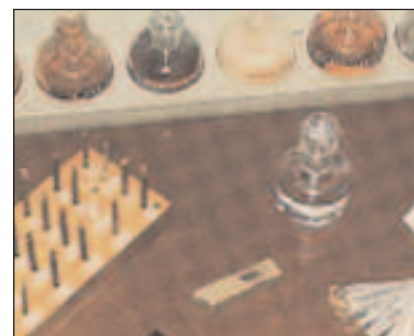
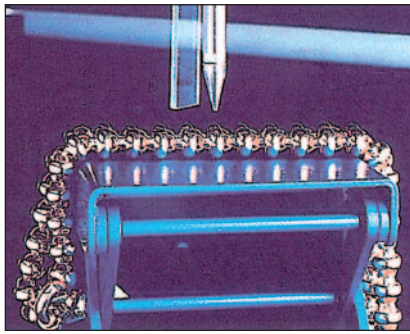


Figure 18. Equipment for touchstone testing



XRF analysis of ball chain links



Typical XRF machine

measured in a spectrometer. The different metals of the alloy emit x-rays of different wavelengths and the amount emitted will depend on the relative number of atoms of that metal present.

The sample should have a clean, flat surface of at least 3 mm diameter, with the x-rays only penetrating 10-50 micrometres during exposure. Accuracy can be as good as 1-2 parts per thousand, but this reduces rapidly on curved surfaces, typical of jewellery. Measurements take about 2-3 mins with the instrument computing the results automatically. Ensuring the sample is typical of the bulk alloy is critical. Electroplating or chemical treatments, such as bombing and acid pickling which change the surface composition, will distort the analysis.

These restrictions limit the use XRF. It is not quite accurate enough for hallmarking purposes, where its use is limited to preliminary testing and scanning of items prior to fire assay. In this role, it is finding increasing use in assay offices, replacing the touchstone. For quality control during production of precious metal alloys and jewellery, it is well suited and finding increasing use. XRF spectrometry is useful as a means of detecting the presence of other metals in the alloy and may be used prior to Fire Assay to detect nickel and the PGM's, for example, although the random distribution of the insoluble PGM's may make them difficult to detect. In this case, use of XRF on the final gold after fire assay testing should reveal their presence.

There are many manufacturers of XRF instruments with models tailored for assaying of gold alloys and jewellery. An example is shown in the figure. The price and performance of these varies, depending on the type of counter fitted. Typical cost of suitable instruments is US\$ 20,00 - \$35,000, depending on performance and additional features fitted.

3.4.4 DENSITY MEASUREMENT

Use has been made of the high density of gold (19.3 g/cc) and the fact that the density of gold alloys will decrease with decreasing caratage. For example, 14 ct golds have densities ranging from about 13.3 g/cc for a red gold to about 14.6 g/cc for white gold; 18 ct golds have densities in the range 15.15 - 16.0 g/cc. However, density is dependent not only on gold content but also on the actual content of every other constituent in the alloy. Even if one measures in a production alloy an identical density to that of a reference alloy of supposedly the same nominal composition, minor variations in any constituent will give erroneous results in terms of gold content. This is, therefore, **not** a method to be generally recommended. From a theoretical viewpoint it would best be applied to binary alloys only, ie gold-copper and gold-silver.

4 REFINING OF GOLD

It has been seen that the various gold-containing materials available to the gold refiner, whether primary material from mines or natural sources or scrap gold products, have a high probability of containing silver and copper, and frequently may contain other base metals and platinum group metals. For the purposes of discussing the refining techniques, it is therefore assumed that the refinable gold material also contains silver, pgm's and base metals and their behaviour in the processes will be addressed in turn. A comparison of the refining techniques is given in Table 2.

It should also be stressed that **safety** is of paramount importance during refining as the processes can involve, for instance:

- use of strong acids, including aqua regia
 - use of chlorine gas
 - generation of significant fume, including lead and cadmium oxide
 - handling of molten metal,
- and full use of appropriate safety equipment and adoption of approved safety procedures must be practised.

Table 2. Summary of Gold Refining Techniques in Current Use

Refining Technique	Removes Base Metals	Removes Silver	Removes PGMs	Suitable for Large Scale Refiners	Suitable for Small Scale Refiners
Cupellation	✓	×	×	✓	✓
Inquartation and Parting	✓	✓	×	×	✓
Miller Process	✓	✓	×	✓	×
Wohlwill Electrolytic Process ¹	✓	✓	✓	✓	×
Fizzer Cell	✓	✓	✓	×	✓
Aqua Regia Process ²	✓	✓	✓	✓	✓
Pyrometallurgical Process	✓ ³	×	×	✓	×

¹ Can only be used when initial gold content is about 98%

² Only suitable when initial silver content is less than 10%

³ Copper remains in gold

4.1 CUPELLATION

Cupellation is one of the stages in the fire assaying analytical technique and involves the addition of lead to the unrefined gold followed by heating in air to melt the metals, dissolve the metals in the lead, and then form base metal oxides which, in the case of fire assaying, are removed by absorption into porous bone-ash crucibles or cupels in which the heating takes place. Any precious metals - gold, silver and platinum group metals - are left behind as a metallic bead.

The purpose of adding lead in cupellation is that the molten lead will initially dissolve the precious metals, forming lead bullion, but during the oxidation stage, lead oxide will act as a solvent to the other base metal oxides which form, rendering them sufficiently fluid to be absorbed into the cupels.

In fact the process is not really a refining process but is a means of separating precious metals from base metals. It finds application on a large scale in heating low grade scrap where initial incineration is followed by smelting with a flux (carefully chosen composition), iron sulphide (to recover copper as a metal), and lead oxide which releases lead droplets to dissolve the precious metals. Subsequently the “lead bullion” is oxidised in a cupellation furnace to leave behind an alloy of gold, silver and platinum group metals, which requires further refining to separate out the gold.

On a small scale the process can be much simplified to parallel the fire assaying technique, with the cupellation stage being carried out in a crucible, followed by pouring into a mould where a metallic bead of the precious metals separates out from a slag of the base metal oxides.

The procedures for the two versions of the process are illustrated in Figures 19a and 19b.

Figure 19a. Outline of operations during large-scale smelting and cupellation

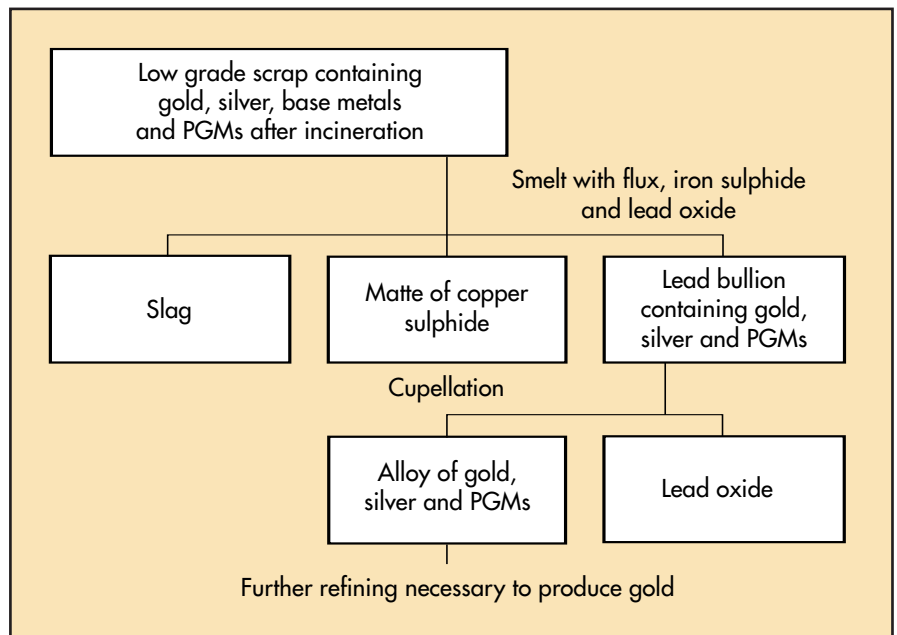
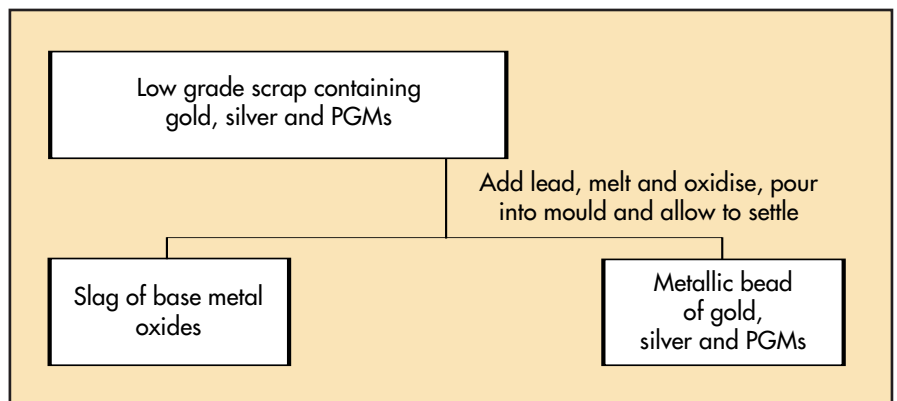


Figure 19b. Outline of operations during small-scale cupellation



4.2 INQUARTATION AND PARTING

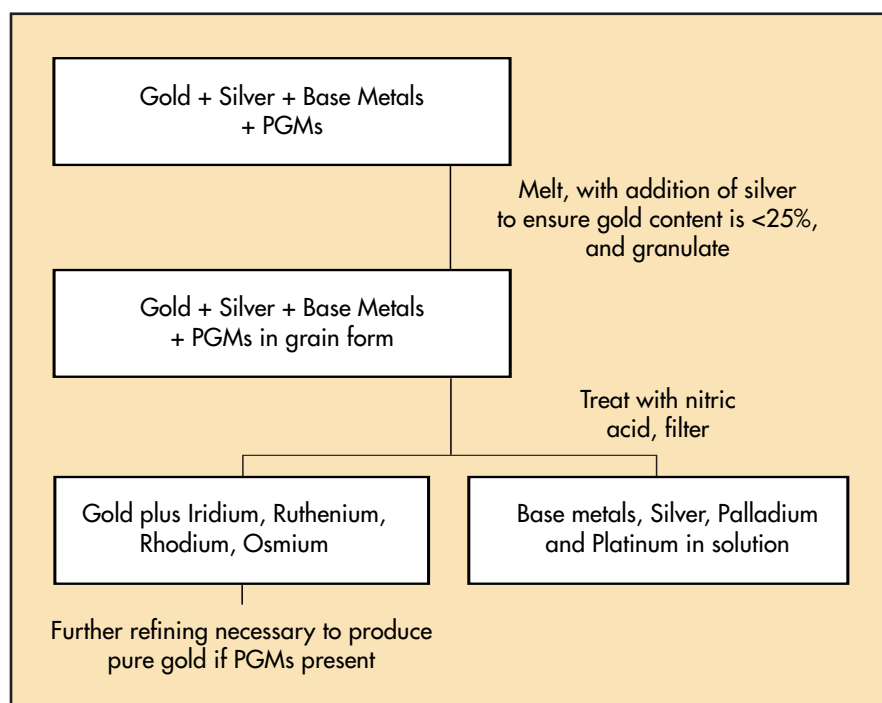
Inquartation involves initially diluting the gold of the refinable material to less than 25% (if necessary) by melting with the appropriate addition of silver (or copper), granulating the melt so as to generate a high surface area, and then treating with nitric acid. The nitric acid will dissolve base metals and silver and leave behind gold. The acid treatment is known as parting as it 'parts' the gold from silver and base metals.

Dilution of the gold content is necessary to ensure that the nitric acid can readily attack and dissolve base metals and silver, some of which may otherwise be masked by the gold.

With regard to platinum group metals that may be contained in the gold, inquartation and parting will remove palladium and platinum, although in the fire assay technique it is usual to carry out two inquartation and parting operations to ensure complete removal of palladium. The other metals, iridium, ruthenium, rhodium and osmium will remain unattacked with the gold.

The technique does find commercial application, both as a refining technique in its own right capable of producing 99.99% pure gold in the absence of pgm's, and by using the nitric acid treatment as a preliminary procedure for reducing the silver content of silver-rich refinable material from 40-50% to below 10% prior to full refining by the aqua regia route (Section 4.6). The procedure is shown diagrammatically in Figure 20.

Figure 20. Outline of operations during inquartation and parting



4.3 MILLER PROCESS

This is one of the oldest and most widely used techniques in large-scale refining, Figure 21. The process involves bubbling chlorine gas through molten metal, converting base metals and silver to chlorides which either volatilise and are fed through fume treatment facilities or form a liquid

Figure 21. The Miller Process



Chlorine gas injection into furnace of molten bullion.



Sampling of molten bullion, to determine degree of fineness.



Removal of chlorides, formed during the Miller process, from the molten bullion.

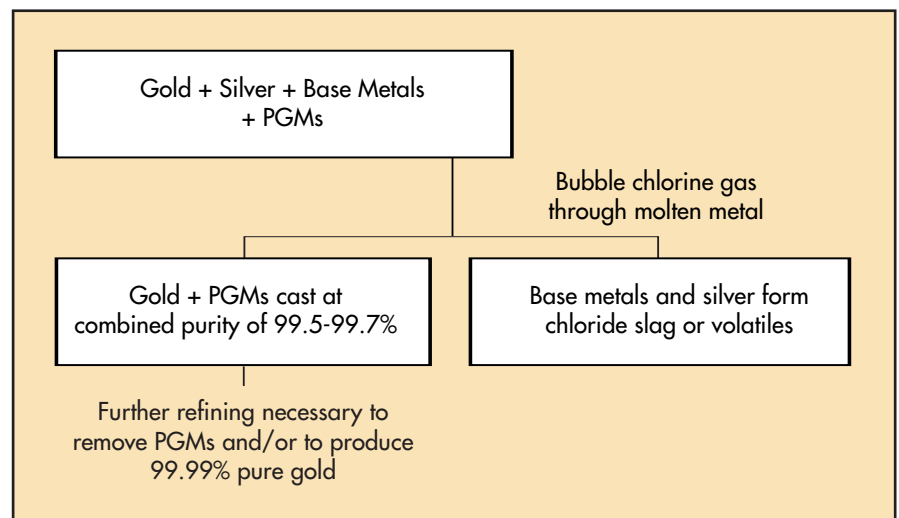
slag on top of the molten metal. Typical batch sizes are from a few kilograms up to 150 kilograms at a time.

The process will gradually remove all base metals and silver, leaving behind gold and any platinum group metals. The end of the process can be recognised by the start of the formation of purple fumes of gold chloride, which will become apparent when the gold content reaches 99.6 to 99.7%.

The process can consistently produce gold with a purity in excess of 99.5%, suitable for trading in the international gold markets. However, to produce gold of 99.9% or higher purity requires an additional refining operation as does the removal of any platinum group metals, and the Miller process is frequently used in combination with electrolytic refining (Section 4.4) in major refineries around the world. It has the attraction of producing refined gold very quickly (within 24 hours) and there is very little “lock-up” of gold in the process. For a charge of 150kg, a typical refining time might be 6 hours for a starting composition of 70% gold.

However, an efficient fume extraction and treatment facility is an important part of the process and leads to the recovery of significant amounts of gold. The slag which forms on top of the melt is largely silver and copper chlorides and is removed regularly during refining by baling. Small quantities of gold can be trapped in the slag (up to 0.25% typically), and it is customary to treat the molten slag with sodium carbonate to reduce some of the silver chloride to silver when, as the droplets of silver percolate through the molten slag, any gold dissolves to form a silver-gold alloy button at the bottom of the crucible. Most of the gold can be recovered in this way. Finally, handling of chlorine gas needs to be treated with great care and awareness, with warning systems and established evacuation procedures high on the list of priorities. For all these reasons, the process is most suited to a major industrial refinery and not a small-scale operation. Figure 22 outlines the procedure.

Figure 22. Outline of Miller Refining Process



4.4 WOHLWILL ELECTROLYTIC REFINING PROCESS

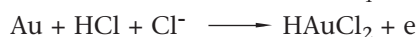
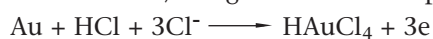
This technique is also old, well established and in widespread use in major gold refineries around the world, usually in conjunction with the Miller process.

The essential steps are to prepare anodes of impure gold (minimum gold content ideally 98.5-99.0%, but in certain circumstances it can be lower), and to deposit pure gold onto cathodes which may be of pure gold sheet or titanium, and which are suspended in an electrolytic cell containing gold chloride/hydrochloric acid at about 60°C as the electrolyte.

Typical material for anodes is gold from the Miller refining process which is required to be upgraded from 99.6% to 99.99% purity, or which contains platinum group metals as the process will allow the separation of pgm's and gold. The operation is frequently run in 24 hour cycles to avoid gold being "locked up" in the process for too long.

As it is, financing gold used for the cathode and gold in the electrolyte is a major cost of running the operation. A cycle could start at the end of a working day (say 16.00 hours), run through the night and the following morning (08.00 hours), after 16 hours' electrolysis, the cathodes would be "pulled". The working day would then comprise washing and recovery of the cathode gold deposits, preparation of new anodes and cathodes and setting up ready for recommencing the cycle at 16.00 hours. A single cell might contain typically 9 x 5 kg anodes, of which 20 - 25 kg might be deposited on cathodes during a daily cycle. A large refinery would operate many such cells.

At the anode, the gold dissolution process reactions are:



Base metals in the anode will form chlorides, some of which are soluble in the electrolyte (copper, zinc) and others of which are insoluble (silver, lead) and sink to the bottom of the cell as anode slimes. HAuCl_2 is unstable and disproportionates in the electrolyte forming HAuCl_4 and fine gold particles which also sink to the cell bottom and accumulate in the anode slimes.

Of the platinum group metals that may be present in the cathode, platinum and palladium will dissolve in the electrolyte, while iridium, ruthenium, rhodium and osmium are insoluble and will be collected in the anode slimes.

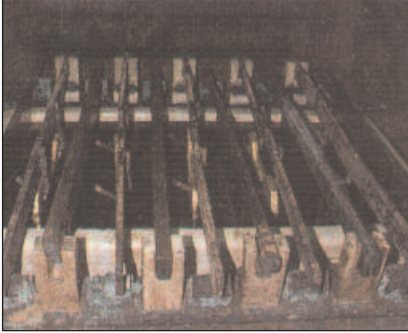
At the cathode, gold is deposited out of solution according to the reaction:



The process can regularly produce gold of a purity in excess of 99.99% and also eliminate all pgm's. In fact failure to achieve this purity is most likely to be because of physical entrapment of silver chloride in the gold cathode deposit. However, to achieve high purities does require constant attention to controlling the process, in particular:

- Anode quality (purity levels should exceed 98.5%)
- Gold content of electrolyte (daily check)
- Acid content of electrolyte (daily check)
- Avoid build-up of copper, zinc, platinum and palladium in electrolyte (change solution at predetermined impurity levels)

Figure 23. The Wohlwill electrolytic Process



The cell arrangement



Gold collected on cathode, 99.99% purity

- Operating temperature (60°C, continual monitoring)
- Voltage and current density (continual monitoring)
- Agitation of electrolyte (air bubbling to equalise gold concentration in electrolyte and avoid silver chloride precipitates building up on anodes)
- Gold cathode washing (removal of any trapped silver chloride and electrolyte).

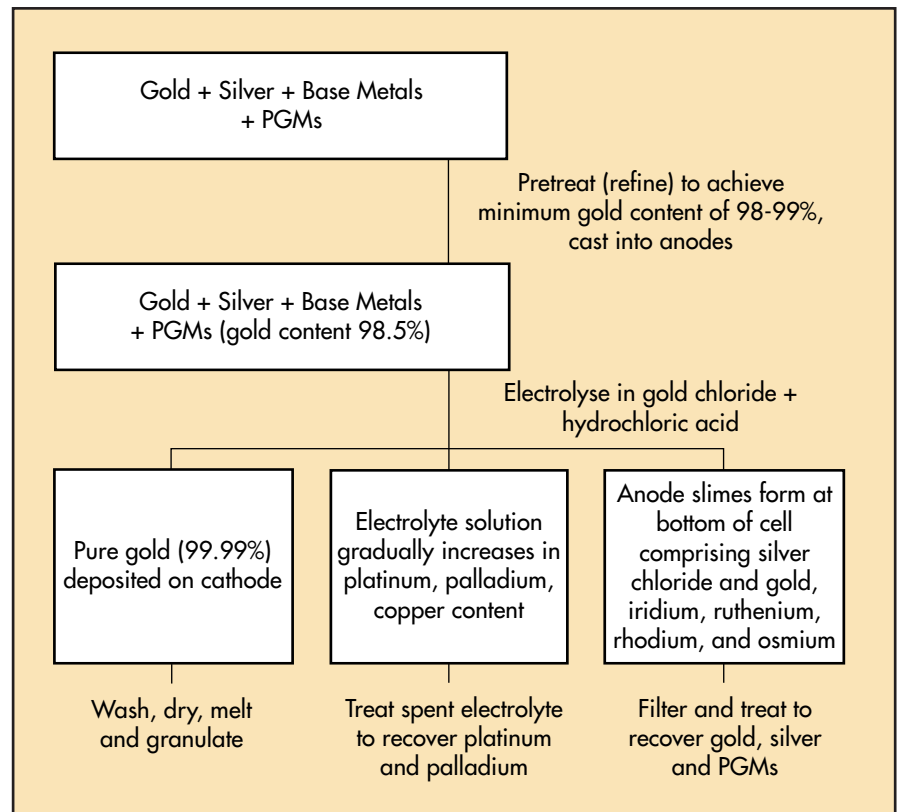
The reason why it is necessary to restrict the level of impurities in the anodes to 1-1.5% is that the major impurity is silver and significant levels of silver in the anode will result in silver chloride gradually building up on the surface of the anode and preventing gold going into solution. Should the impurities be other than silver then, again, if significant levels are present in the anode and they are taken into solution, frequent changing of the electrolyte would be necessary.

The process can readily be used to recover platinum and palladium from the gold by periodically treating the electrolyte, initially precipitating gold from solution, and then using standard platinum refining techniques on the residual solution.

The process is also used to produce specially high purity gold by double refining. For example, by using 99.99% purity gold for the anodes, it is quite straightforward to produce 99.995-99.998% gold at the cathode though, of course, great care is needed during washing and handling the deposit.

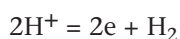
The process is shown in Figure 23 and illustrated schematically in Figure 24.

Figure 24. Outline of Wohlwill Electrolytic Refining Process



4.5 FIZZER CELL PROCESS

This process is a variant on the Wohlwill electrolytic refining process. The equipment comprises an electrolytic cell in which impure gold is the anode, the electrolyte is hydrochloric acid and the cathode is graphite. However, the cathode is contained in a porous pot, the walls of which form a semi-permeable membrane which do not allow gold to pass through. In contrast with the Wohlwill process, the reaction at the cathode is:



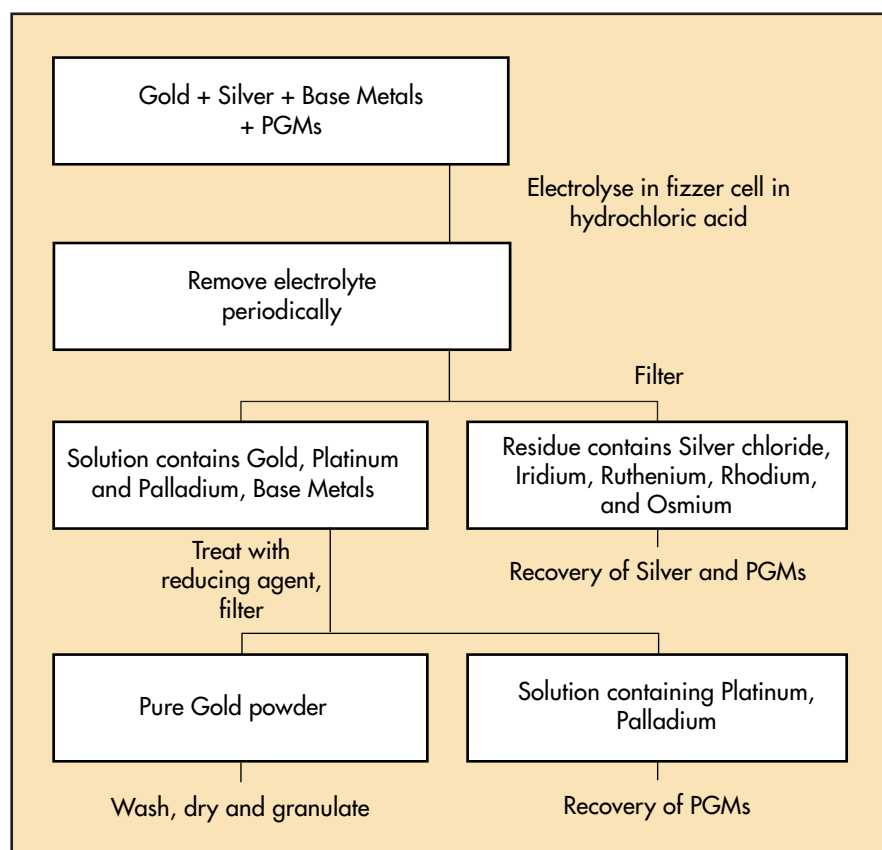
ie the evolution of hydrogen gas and it is this evolution of gas from which the process derives its name.

The electrolyte, therefore, will gradually build up in gold content and any other soluble chlorides (copper, zinc, platinum, palladium), while insoluble chlorides or metals will fall to the base of the cell (silver chloride, iridium, ruthenium, rhodium and osmium). Periodically the electrolyte is removed from the cell, filtered, and then gold is precipitated from solution. In this way pure gold (99.99%) can be produced and separation from any platinum group metals effected. As a reducing agent, ferrous sulphate, sulphur dioxide and sodium bisulphite are perhaps the best known, but several others are in use.



Figure 26. A Fizzer cell

Figure 25. Outline of Fizzer Cell Refining Process



Unlike the Wohlwill technique, the Fizzer cell lends itself to treating anodes containing up to 20% silver when used on a small scale, but the anode has to be scraped free of silver chloride at regular intervals.

Because of its simplicity, and the ability to dissolve gold without recourse to the more hazardous aqua regia, the process has found use in the jewellery industry for small scale recovery and refining of gold. A

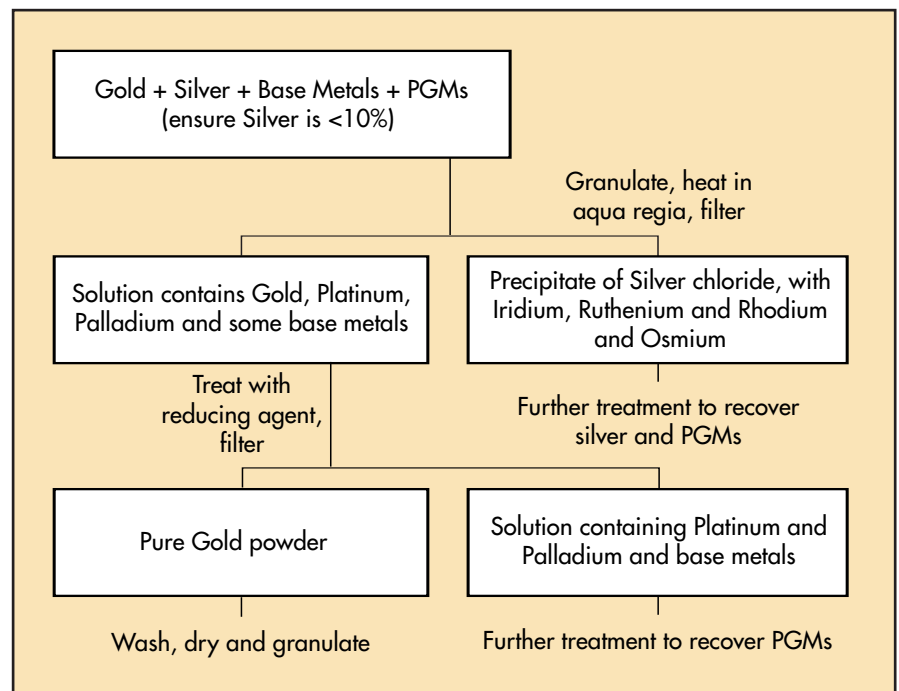
variation of the process uses sodium chloride as the electrolyte and has been marketed especially for the jewellery industry. The process avoids the “lock-up” of gold as cathode and electrolyte which is a feature of the Wohlwill electrolytic process and this also makes it attractive to the small-scale refiner.

The process is depicted schematically in Figure 25, while Figure 26 illustrates a Fizzer Cell.

4.6 AQUA REGIA PROCESS

This process is extensively used both by small scale refiners and major bullion refiners. It offers the opportunity to produce 99.99% pure gold in the one process, whereas the main alternative for large scale refineries is to combine the Miller process (Section 4.3) with the Wohlwill electrolytic process (Section 4.4).

Figure 27. Outline of Aqua Regia Refining Process



The essential steps in the process are to dissolve the gold material in aqua regia and precipitate gold from the resulting solution. Gold and most other metals will dissolve in aqua regia; silver, however, will form a silver chloride precipitate. Because of the reaction of silver, it is necessary to restrict the amount of silver in the start material to a maximum of 10%; any more than this will run the risk of the silver chloride preventing complete dissolution of the gold by masking it off. It is necessary, therefore, to blend batches of high silver content material with those with no, or low, silver content prior to dissolution or treat with nitric acid initially to remove silver if, for example, individual batches need to be kept separate during refining and cannot be blended.

To aid dissolution in aqua regia it is usual to melt and granulate the material first (essential when lots are blended) to provide as large a surface area as possible, and to heat the acid to speed up the dissolution

process. Filtration is then used to remove silver chloride and any other insoluble material. The solution is then treated with a reducing agent to precipitate pure gold. Of the reducing agents, ferrous sulphate, sulphur dioxide gas and sodium bisulphite are most widely used. In this way, extremely high purity (99.99%) gold powder is produced which needs to be filtered, washed, dried and usually melted and granulated ready for subsequent use.

If platinum group metals are in the original material, both platinum and palladium will dissolve in aqua regia while iridium, ruthenium, rhodium and osmium are insoluble and will therefore be separated out with silver chloride and any other insoluble material. When gold is precipitated from the solution, both platinum and palladium remain in the solution and can be recovered later. Hence the technique will effect a complete separation of platinum group metals from the gold.

The process is depicted in Figure 27.

4.7 PYROMETALLURGICAL REFINING

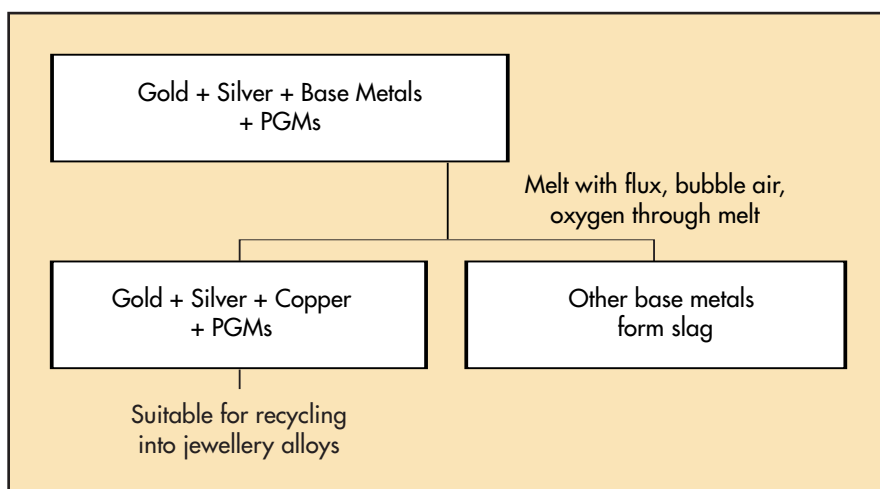
This process is not strictly a refining process but a means of converting scrap jewellery alloys into clean gold-silver-copper alloy suitable for re-alloying into new jewellery alloys.

The principle is to smelt scrap gold alloy under a flux and to bubble air or oxygen through the molten metal to selectively oxidise impurities such as zinc, cadmium, iron, tin, lead. The oxidised metal impurities combine with the flux to form a slag on the surface of the melt. Typically the reaction time can be about one hour and the end point is best determined by estimating the copper content of the slag. Detailed analysis of the metal is necessary before subsequent use.

The technique is, therefore, most suited to medium-or large-scale producers of jewellery alloys who have a constant requirement to recycle gold-silver-copper based scrap jewellery alloys both internally produced and externally purchased. Any platinum group metals present in the scrap alloys will remain in the gold-silver-copper as they are not, of course, oxidised during the process.

The process steps are shown schematically in Figure 28.

Figure 28. Outline of Pyrometallurgical Refining Process



A P P E N D I X

DETAIL OF FIRE ASSAY TECHNIQUE FOR DETERMINATION OF GOLD

Carefully taken representative samples of alloy, weighing about 250 mg, are weighed individually into 6g of lead foil with additions of fine silver equivalent to 2.3 - 3 times the expected gold contents. At the same time proof assay samples of gold and silver are prepared to be treated in the same way as the assay samples.

Each sample is placed in a magnesium oxide cupel which has been pre-heated to 1000°C. The cupels are then placed in a cupellation furnace at 1150°C under oxidising conditions for 25 minutes. The cupels are recovered from the furnace, cooled, and each button removed with pliers, brushed to remove any adhering cupel material, flattened on an anvil and annealed by heating to red heat. The beads are rolled to 0.15 mm thickness, annealed again and formed into cornets.

The cornets are placed in parting flasks with 20 ml of 33% nitric acid at a temperature just below boiling, and then boiled for 15 minutes or until evolution of fume has ceased, whichever is longer. Each sample is then removed and washed in warm water, re-boiled in 20 ml of 49% nitric acid for 15 minutes, and the operation repeated once more. Finally the gold is washed thoroughly in warm water and dried in small porcelain cups at 750°C for 5 minutes before weighing. Comparison of the final weight (of pure gold) of the sample adjusted for any possible systematic errors by the use of proof gold assays, with the original sample weight gives the gold content of the sample.

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