THE CLASSICAL FIRE ASSAY

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INTRODUCTION

The status of precious,metals in taday's society becomes more significant, due to various technological, advances and the world's monetary problems. The price structure and supply of these metals have consequently been drastically altered in recent years. We find ourselves mining lower grade ores, and reclaiming scrap with a lower noble metal content. This has led to a critical assessment of the methods used to sample and analyze these materials.

Yesterday, we were presented with an excellent selection of papers on the theory and practical aspects of sampling various materials. Today, the subject of discussian will be the analysis of that sample by variety of methods, the first of which will be the classical fire assay.

DEFINITION AND HISTORY

Fire assaying is defined as a branch of quantitative chemical ana1ysis, which is applied in determining the precious metal, content of ores, metallurgical products, and scrap material. The method is a pyro-metallurgical technique which separates the metal to be determined from the impurities and gangue present in the sample. This is accomplished by employing dry reagents and heat in a selective fusion process.

The subject of fire assaying has created a prodigious history since its inception. A search of the available literature would show that the method has been used for many centuries. The process seems to have evolved from the techniques used in the extraction and refining of the precious metals.

The literature states that cupellation was being used in 12th century England, and that parting was introduced in France in the 13th century. During the 16th century, the basic fire assay procedure was essentially the same as that in use today. Although the use of the fire assay is now confined to the analysis of precious metals, it was used in previous times for the assay of base metals, such as lead, bismuth, tin, and copper.

Fire assaying has always been considered more of a backroom art than a science. The reason for this is partially due to the high degree of practical knowledge and manipulative skills needed to complete a successful fire assay. The theoretical chemistry pertaining to the fire assay has never been completely investigated. This has left us with a process based upon some fundamental principles, which depends upon experience and observation alone, without due regard for theory. The fire assay remaina as a prolific subject for basic research.

In his classical text De Re Metallica,1 written in 1556. Agricola offered this ageless advice on the fire assay:

“It is necessary that the assayer who is testing ore or metals should be prepared and instructed in all things necessary in aasaying, and that he should close the doors of the room in which the aasay furnace stands, lest anyone coming at an inopportune moment might disturb his thoughts when they are intent on work.”

OBJECTIVES OF FIRE ASSAYING

As in all other tasks we perform, fire assaying has an objective. This is to provide a number which represents the true value of a precious metal in a given amount of material. Some of the more important uses of an assay result are:

(1) The valuation of a mining property,
(2) The basis for buying and selling varioua materals,
(3) In plant quality control,
(4) Accounting and inventory requirements,
(5) Environmental considerations.

The degree of accuracy required is governed by how the assay result is utilized. There are permissible limits of error for each of the above uses.

CRUCIBLE FUSION

The classical fire assay of precious metals involves three basic operations. The first is the collection of the metals, usually by a crusible and/or a scorification step. Secondly, the saparation of the metals by various methods. Then the mass of each metal is measured by weighing, or by some other means.

A crucible fusion is employed to separate the precious metals fromany impurities by collecting them in a metallic phase, while absorbing the impurities into a slag phase. This is accomplished by melting a suitable portion of the sample with the proper flux, in a crucible at approximately 1100°C.

A flux is used which will convert infusible matter into fusible compounds at a certain temperature. This flux usually consists of the following four reagents: litthargo (PbO), sodium carbonate (NaCO3), borax glass (Na2B407), and silica (Si02).

In the fire assay these four reagents provide a medium, which will lower the melting point of the fusion. They also dissolve and absorb the metal oxides present forming complex borates and ailicates. The first two of the above mentioned reagents are basic in nature, while the other two are acidic.

A fire assay fusion is a typical example of a controlled oxidation- reduction reaction. As the fusion progresses, the impurities are converted to their oxide stete and absorbed by the slag, preventing them from entering the metal phase. In general, metallic oxides are quite soluble in the slag phase, but not the metallic phase.

This principle forms the basis of the separations made in a fireassay. The key to these separations by oxidation or reduction is the electromotive series. The metals low in the series, which happen to be the precious metals, are difficult to oxidize, while the base metals and other metals higher in the series combine more readily with oxygen.

In the crucible fusion the oxidation is accomplished by the oxygen present in the flux, or if needed, by adding an oxidizing agent such as potassium nitrate (KNO3).Excess litharge is added for its ability to keep the base metals present oxidized, and prevent them from being reduced and entering the metal phase.

The reduction part of the process consists of the reducting constituent converting a portion of the litharge to lead metal. The reducting agent generally used is ordinary household flour. This lead which appears as a fine mist of small droplets settles through the slag phase, forming a pool at the bottom of the crucible. The molten droplets act as an excellent collector, since most precious metals exhibit an affinity for lead and alloy readily with it. Noble metals which do not alloy with lead will sink through the slag phase, due to their high density. They then enter the metallic phase at the bottom of the crucible, forming a mechanical mixture.

It is essential to conduct a fusion which, by the proper selection of flux, temperature, and time, produces a metallic phase with the following characteristics:

(1) a minimum amount of impurities,

(2) a bright, soft, malleable buton,
(3) a buton close to the desired weight,
(4) a complete recovery of the noble metals.

On the other hand, the slag phase, which consists of various forms of silicates and borates, should have completely decomposed the sample and absorbed all the impurities and ganguc material.

E. Bugbee,2 one of the more well known authorities on the subject of fire assaying, states that a suitable slag phase should possess the following properties:

(1) It should have a comparatively low formatian temperature, readily attainable in an assay furnace.

(2) It should be pasty at its formation temperature in order to hold up the particles of reduced lead until the precious metals are liberated from their mechanical or chemical bonds, and are free to alloy with the lead.

(3) It should be thin and fluid when heated to somewhat above its melting point, so that shots of lead may settle through it readily.

(4) It should have a low capacity for noble metals, and should allow a complete decomposition of the sample by the fluxes.

(5) It should not attack the metarial of the crucible to any great extent.

(6) Its specific gravity should be low, to allow for a good separation of lead and slag.

(7) When cold, it should separate readily from the lead, and be homogeneous, thus indicating complete decomposition of the sample.

(8) It should contain practically al the impurities of the sample.

If irregularities appear in a crucible fusion, the person conductingthe assay must be concerned that the proper corrective measures are taken in the repeat determination. The source of the problem must be identified and remedial action taken.

Frequently, the cause of the difficulty may be detected from some peculiarity exhibited by the first fusion. This could include the color and viscosity of the slag, or the presence of unfused sample material and lead shot appearing in the slag.

The button also could show characteristics which would indicate an unacceptable fusion, such as hardness or brittleness caused by the presence of base metal sor sulfur. The size of the button could indicate whether the sample was fluxed-properly. Buttons which hava a detectable layer of matte or speiss are also undesirable.

When the fusion is complete, the crucible is removed from the furnace and its contents are poured into a mould. After the lead has solidified, it is separated from the slag. The lead button is then usually shaped into a cube to complete the removal of the slag, and to facilitate the bandling of it. Now the button is ready for the next step which 1a cupellation.

SCORIFICATION ASSAS

The scorification assay is an oxidizing fusion carried out in a shallow fire-clay dish called a scorifier. A relatively small sample portion is usad; it is placed in the scorifier with test lead, borax, and sometimes, silica. This is then placed in the furnace under appropriate conditions for scorification to take place.

Direct application of the scorification method to the assaying of any material is severely limited. These limitations restrict its use to materials which are free of oxides, decrepitating compounds, and are sufficiently rich in precious metals to obtain a weighable bead from a small sample aliquot.

Today, the more useful applications of the scorification process are:

(1) The retreatment of a crucible fusion button to remove impuritiesi or to decrease its size.

(2) To combine a series of crucible fusion buttons from the same sample, thereby upgrading the precious metal content.

(3) It is also useful for fusing residues from samples, which were first subjected to a preliminary acid treatment.

The scorification metnod does not have any essential chemical advantage over the crucible method.

CUPELLATION

Cupellation is an oxidizing fusion of an alloy of lead and precious metals. The process of cupellation is accomplished in an absorbent vessel made of bone-ash or magnesia, called a cupel.

During cupellation, the lead is oxidized to litharge (PbO), most of which is absorbed by the cupel. The bead resulting from the cupellation will contain silver, gold, and same of the platinum group metals.

The sequential steps involved in completing a successful cupellation are first, the preheating of the cupels to drive off any water, organic matter, and carbon dioxide.

After the cupels have reached cupellation temperature, the lead buttons are placed in them and the furnace door closed. As the temperature of the button rises, it will melt and be covered with a dark scum composed mostly of litharge. In a moment the scum will fuse, exposing the melted alloy. This phenomenon is known as the “opening” or “uncovering”.

After the button has “opened” and the lead is being oxidized, one can actually observe the molten litharge sliding off the surface of the lead and being absorbed by the cupel.

The control of temperature is of the utmost importance in all phases of a cupellation. Although the actual temperature of the button cannot be measured, an accurate estimate can be made by the interpolation of known melting-point data with temperature measurements from a thermocouple pyrometer.

Heat and air supplied to the cupellation should be regulated so that both the air and temperature and uniform and constant throughout the muffle. Remember the most significant errors made during a fire assay are those made due to improper temperature control. A satisfactory oxidation rate of the lead would be in the order of one gram per minute.

The cupellation is reaching completion when a rainbow effect appears on the surface of the lead. This play of colors is caused by the last drops of molten litharge moving rapidly over the surface of the bead. It is followed in a few seconds by a dullness in the bead, and then a flash of light, or what is known as a “blick”. This is caused by the sudden release of the latent heat of fusion, which occurs when the bead cools to its solidification temperature.

When the cupellation has been completed, the cupel is removed from the furnace and allowed to cool. If any of the beads are pure silver, they must be cooled slowly to prevent sprouting. This is caused by silver's ability to dissolve large yolumes of oxygen, while in a molten state. Upon solidification, which starts at the surface, the oxygen could be trapped inside. As the rest of the bead solidifies, the oxygen is sometimes expelled violently causing some of the interior silver to be ejected.

When the beads have cooled, they are removed from the cupel. The bottom surface of the bead is cleaned to remove any adhering cupel material. The cupel and bead should be examined at this time for any evidence of impurities or platinum group metals.

PARTING

In the determination of gold and silver the doré beads derived from cupellation are weighed. Then the silver-gold alloy is separated by dissolving the silver in an acid media. The gold res1due is then washed, dried, and finally annealed by heating the parting cup in a muffle or over an open flame until it is bright red. The gold is now weighed, and the weight of the silver is determined by subtracting the weight of the gold from the doré weight.

The operation known as parting is governed by several factors. The ratio of silver to gold must be at least three, otherwise the silver will not dissolve. This problem can be overcome by adding silver to the fusion, if the approximate silver-gold ratio is known, or by recupeling the doré bead with three times its weight in silver. A third solution to the problem is to run a preliminary assay. The addition of this silver during the assay is known as inquartation.

Before the bead is subjected to the acid treatment, it must be flattened to facilitate a rapid and complete parting of the silver-gold alloy. This is accomplished by flattening small beads with a hammer and anvil. Larger beads are rolled thin in successive stages, using a set of bullion rolls.

Nitric acid is almost universally used to dissolve the silver, although in a few special methods sulfuric acid is used. Particular care must be taken to ensure that the-acid and wash water used are free from any form of chlorides. They would tend to precipitate the diasolved silver, or even combine with the nitric acid to dissolve gold. Either of these reactions would adversely affect the outcome of the assay. The most frequent strength of acid used ranges from a ratio of 1:4 to 1:8 parts acid to water. In many determinations a secondary parting using a stronger acid is needed to ensure a complete separation of the silver-gold alloy.

The completion of a normal parting process is usually indicated when the evolution of nitrogen oxide gas bubbles has ceased. At this time, the presence of platinum and/or palladium is indicated by the distinctive color they impart to the acid solution.

After the completion of the parting process, the gold that remains is black in color, or if a large mass, brassy.

By annealing the gold we change its allotropic form back to the one with which we are more familiar. This also avoide the possible effect of absorbed gases, weighing matter other than gold, and gives us the opportunity to examine the gold bead for impurities.

WEIGHING

The balance used to weigh both the gold and the doré beads is an extremely delicate micro baiance. Its sensitivity is on the order of 1/500 of a milligram, and the maximum load capacity is about one or two grams. The balance is installed in a location free from dust, vibration, and rapid temperature changes.

After the gold and silver are weighed, their weights are usually expressed in a unit which shows their proportion in the material sampled. The unit used varies with the material assayed, and in which part of the world the assay is performed.

APPLICATIONS OF FI.RE ASSAY TECHNIQUES

In the preccius metal industry, fire assay techniques are usually applied to ores, sweeps, metal alloys, and solutions.

Ores and Sweeps

The efficiency of the fire assay in recovering precious metals from ores has been well documented. Variations in precision depend upon homogeneity, physical nature of the precious metal, ore particle size, and the size of sample portion taken for analysis.

A general principle to remember is that a siliceous ore requires a basic flux, and a basic ore needs an acid flux. There is no substitute for experience; the trained intuition of the assayer may suggests suitable flux composition by just a visual examination of the ore, but he should also possess the knowledge of selecting a suitable flux through some scientific approach.

As the sulfide and base metal content of an ore increases, it becomes more difficult to adjust the flux composition to fit the ore. The possibility of incomplete decomposition, accompanied by the formation of a matte or spiess, becomes a most important consideration. To perform an intelligent assay, some estimate of the metal impurities must be made and special measures taken to eliminate them.

It is frequently claimed that the precious metals in some material occur in a colloidal or volatile form, and are unrecoverable in a fire assay. There may be a small amount of truth in this statement, but tests have shown that samples which have been spiked with noble metals in their chloride or colloid form have invariably been recovered in an ordinary fusion. Noble metals are referred to as being coloidal in nature when their particle size is less than .024 microns in diameter.

A fine example3 of this occurrence is the ore body of Carlin Gold Mines; the gold occurs as submicron particles encapsulated in a quartz and sulfide matrix. Without the assistance of fire assay, an effective evaluation of this ore body would not have been possible.

The analysis of sweeps for precious metals by fire assay is fairly consistent with the guidelines outlined for ores.

Bullion

The determination of precious metals in metallic alloys is genereally referred to as bullion assaying. This includes all alloys in which the noble metal content is of economic significance. The various types of bullion are usually named fort he major metal present.

Bullion samples are generally received in the form of shot, borings, or mechanically prepared granules.

Base metal bullions, if rich in precious metals. are. subjected to a crucible fusion. The assay portion is mixed with powdered sulfur, and then placed in the bottom of a crucible. A flux with a high litharge content is added, and the charge fused.

The sulfur reacts with the base metal. forming a sulfide matte. Then the flux reacts with the matte, oxidizing it and absorbing the sulfur and base metal into the slag. The fusion then proceeds, following the principles outlined previously in discussing the crucible fusion. Placing the base metal--sulfur mixture in the bottom of the crucible avoids the reduction of lead before the base metal is oxidized.

In some situation, the bullion to be analyzed has a high base metal content, but only a small amount of precious metals. Due to the large sample portion needed for a reliable assay, a direct fusion would be impossible. The recommended procedure for the removal of the base metal is a preliminary acid treatment.

By dissolving the interfering metal, the precious metals can be separated from it using a filtration step. The residue is then fused by scorification.

The methods employed for the analysis of gold and silver bullion are quite different from the standard fire assay. Due to the monetary value of these bullions, they are more complex and time consuming. Extreme diligence must be exercised in every step of the assay.

Although silver bullion is usually assayed by a volumetric method such as the Gay-Lussac wet chemical procedure, it is possible to obtain reasonable results using a direct cupellation method similar to the one used for gold.

The general method of assaying gold bullion is by cupellation and parting. First, a preliminary analysis to determine the approximate composition of the bullion is required. Then sample portions are weighed, and wrapped in a predetermined amount of lead foil, which is governed by the gold content. The proper inquartation of the sample with silver is important to ensure a satisfactory parting. A small amount of copper is also added to aid in the removal of lead during cupellation and minimize cracking of the bead while it is being flattened.

The errors in the assay are corrected by assaying a synthetic sample of approximately the same weight and composition as the unknown. Any loss or gain in the proof sample is applied to the unknown.

Assay of Solutions

The monitoring of processes which use solutions of precious metals necessitates the assay of these aqueous solutions. Most industrial applications use a solution containing either the cyanide or chloride complex of the metal.

Although today, the assay of these solutions are generally performed using some form of instrumentation analysis, the fire assay can provide an excellent check on the reliability of these other methods.

There are two principal techniques employed to recover precious metals from solution. The first employs an evaporation step from which the salts are then assayed. A reduction/precipitation step is used to isolate the noble metals in the second method. The type of fire assay utilized will depend on which method is used.

THE FIRE ASSAY OF THE PLATINUM GROUP METALS

Platinum, iridium, osmium, palladium, rhodium, and ruthenium comprise what is known as the platinum group of metals. The first three are known as the heavy platinoids, while the last three are referred to as the light platinoids. Platinüm occurs in the greatest quantities, and the other metals are usually produced as by-products of its production.

The assay of any of the above group of metals is considered amongst the most difficult in analytical chemistry. Under the best of conditions, their determination requires a considerable degree of skill and knowledge.

The fire assay of the metals is generally used as a concentration step. Not only are the metals concertrated, but they are presented in a matrix which is more conducive to obtaining satisfactory results.

The matrix may be a gold and/or silver bead, a lead buton or a buton of some other base metal. By employing a series of wet determinations or some form of instrumental technique, such as atomic absorption or emision spectrophotometry, the precious metal content of the concentrated sample can be measured.

The group as a whole present many difficulties in completing a successful fire assay. Strict attention must be paid to the composition of the flux, the rate of fusion, viscosity of the slag, matrix of the sample, and noble metal content. All of the above greatly influence one’s ability in conducting an ideal fire assay for this group of metals.

In recent years a considerable amount of literature has been published dealing with the analytical methods used in determining the platinum group metals. The fire assay procedures have also been extensively reviewed.

Researchers have developed new fire assay procedures using metals other than lead as the collector. These have included the use of copper, nickel, and tin.

The National Institute for Metallurgy in South Africa4 has developed a procedure where nickel sulfide is used as a collector. They report that the efficiency of nickel sulfide as a collector of the platinum group metals was quantitative.

They have also developed a high temperature cupellation techniqueS to eliminate silver from precious metal beads.

In the opinion of some of the leading authorities in the field, such as F. E. Beamish,6 we will profit from these new procedures in specific instances, but they do not surpass the ability of the classical fire assay. Due to its manipulative simplicity, lead remains the best collector for platinum, palladium and possibly, rhodium.

They also felt that the recovery of osmium and ruthenium from a lead button was at least as efficient as any other assay procedure.

It is likely that the fire assay will remain as a useful tool in the analysis of material for the platinum group metals. It is one of the fertile areas available to the researcher investigating new separation techniques for these metals.

THE ACCURACY OF THE FIRE ASSAY

When considering the reliability of the fire assay, or any assay for that matter, we must constantly ponder the comparison between the theoretically attainable and the actual accuracy of a reported value.

Whether accuracy and precision is obtained in a fire assay depends upon what errors are introduced during the following steps. (SLIDE)

Errors introduced during sample preparation include contamination from other samples, dilution by impurities, loss of fine particles, drying, and the degree of comminution employed.

Errors introduced in the fusion process are due to improper flux composition, temperature, and the size of the lead button obtained. These errors cause the incomplete recovery of the precious metals in the lead button. The metal lost is usually in the slag or crucible, and can be recovered by reasssaying the slag in the original crucible.