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Manuel Boscato graduated in Product Innovation Engineering in 2012, from the Department of Industrial Management and Technology of the University of Padua, with a degree thesis supervised by Prof. Franco Bonollo, on the subject: “Optimisation of special cast iron use in centrifugal pumps”.
After professional experience in various areas of metallurgy, since 2013, Manuel Boscato has been working in Research and Development at IKOI S.r.l., a company specialising in the construction of machines, systems and technology for casting, refining and the heat, chemical and physical treatment of precious metals.

The cutting-edge refinement technology, known as ACIDLESS SEPARATION® (ALS®) comes from close collaboration between IKOI and Ekaterinburg Non Ferrous Metals Processing Plant (EZ-OCM)[1].
This technology makes it possible to pre-refine doré and jewellery alloys with the prerogative that the process is extremely efficient, even with a high silver content, which is normally a problem for existing chemical pre-refinement processes.
ALS® does not require the use of acids or toxic substances, which is a practically unique feature compared to current refining systems. It is to all intents and purposes a green technology.
Compared to the panorama of traditional refining methods, it can be seen that the technology being presented guarantees a high degree of flexibility as it is not bound to the chemical composition of the alloy being treated.
After intense research and development, the process, which is based on the vacuum distillation principle, has made it possible to achieve excellent results in terms of selectivity and productivity, while at the same time guaranteeing a practically zero drop in precious metal mass .
The process, which stands out for its excellent scalability, is flexible when it comes to meeting different production capacities, ranging from the refineries in a medium gold industry, through to the large-scale precious metal refineries treating doré alloys downstream of mines or industrial precious metal waste.

“Presentation of a new acid-free refinement process for gold and silver”

Manuel Boscato (R&S IKOI Srl)
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INTRODUCTION

We are hearing more and more about green technology, even in the metallurgy sector; suffice to mention the continued innovations in powder metallurgy, bioleaching in extractive metallurgy and the recent “ecoMetals” initiative presented at the last edition of “The Bright World of Metals”, the world trade fair for foundry technology.
When we look at precious metal refining, the innovations are few and far between, especially when it comes to green technology. All too often, traditional processes use gas, acid or toxic solutions, or substances that emit pollutants into the environment.
In these terms, ALS® technology is a breakaway from conventional refining techniques since, based on the physical principle of vacuum distillation, it does not use toxic substances.

Although vacuum distillation is a well-known process in other areas of metallurgy, this new technology has been patented at international level specifically for the treatment of precious metals.

A LOOK AT TRADITIONAL REFINING METHODS

Looking briefly at secondary refining, we can identify the following incoming crude materials: ingots of “crude” metals from mines, known also as doré bars, alloys from jewellery and the gold and silver industries, alloys from minting waste, and alloys from electronic and industrial production waste.
The secondary refining process can be divided into two stages. The first stage, known as pre-refining, usually aims to reduce the base metal and silver content in order to make the alloy suitable for treatment in the subsequent final refining stage. This latter gives the gold a purity of 99.9% or higher.
The traditional refining processes are [2,3]:

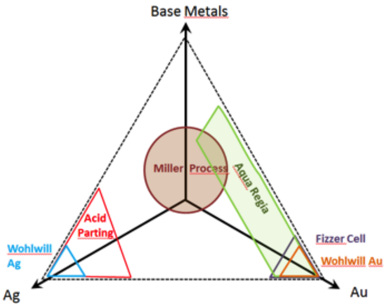
PRE-REFINING METHODS:

- Pyrometallurgical chlorination (Miller Process)
- Pyrometallurgical oxidation
- Acid parting

FINAL REFINING METHODS:

- Wet chlorination (Aqua regia, Chlorine in hydrochloric acid)
- Electrolytic methods (Wohlwill process, Fizzer cell)
- Solvent extraction.

If we place the above refining techniques on a ternary graph (see graph 1) considering the base metal content, and the gold and silver in the alloy being refined, it can be seen that with high base metal and silver content, pyrometallurgical separation methods with oxidation or chlorination of the alloy in order to separate the most reactive elements, making them volatile or form slag on the top of the bath, are the most traditionally used. top of the bath, are the most traditionally used.



Graph 1 Diagram of traditional refining processes

The fastest pre-refining process, but also most critical in terms of operator health and safety and the most expensive in terms of precious metal loss, is certainly pyrometallurgical chlorination, which blows chlorine gas into the molten metal so as to gradually transform the base metals and silver into chlorides, which are then vaporised or mechanically separated in the form of slag.
Nitric acid separation, also known as "acid parting", need the alloy being refined to have a gold content of less than 25%[4]. For this purpose, it is normally necessary to add silver or copper alloy (quartation) to correct the chemical composition.
On the other hand, final refining methods often feature strong limitations to the chemical composition of the alloys being treated. Suffice to think of the electrolytic systems where gold purity should be in excess of 98.5%[2], otherwise there would be a high level of bath pollution and a slowing in the process.
Aqua regia also has a limit regarding the silver content of the alloy being refined. Usually this limit is 10%[3], otherwise the dissolution process is halted by the intense formation of silver chloride.

To avoid using pre-refining methods, such as in the case of quartation as a preliminary treatment for acid parting, the chemical composition of the alloy is corrected by adding fine silver or gold in alloy form. These systems are burdensome as they increase the volumes of the metal being refined and also require superior production capacities for processes downstream. As well as this, we should also consider the high cost of immobilising precious metals to be alloyed.

3. ACIDLESS SEPARATION® TECHNOLOGY

3.1 DESCRIPTION

The system substantially consists of:

- Water-cooled vacuum chamber in stainless steel
- Vacuum pump unit
- Load moving system
- Foundry head for induction heating
- Cooled condensers
- Electrical control panel
- Frequency generator
- Continuous weighing system for the metal.

The image below shows a finished system, equipped with a melting pot with a 30 kg capacity.

Fig.1 Acidless Separation® system

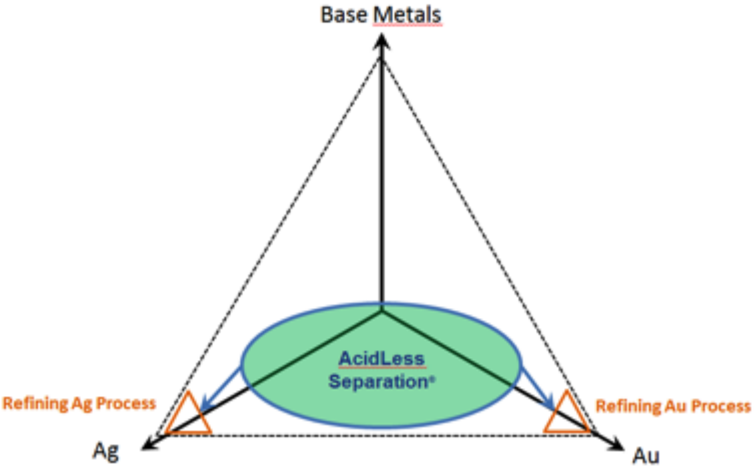
The metal to be refined is placed inside a melting pot, which melts it down via induction heating, with successive overheating of the liquid metal.
To increase the performance of this system in terms of evaporation speed, making energy use more efficient, this is carried out in an ultra-vacuum atmosphere.
During the process, the alloy mass is measured continuously to understand the evaporation process and to adjust the process parameters automatically. The system is managed by software which defines the process parameters to optimize the process in terms of evaporation speed and selectivity according to the chemical composition of the mass of the alloy being refined.
The most volatile elements, such as zinc, lead, etc., are evaporated in the initial stage and are deposited on a specific condenser. The less volatile elements such as silver are left to deposit on a second condenser.
At the end of the separation process, the melting pot will contain an alloy essentially consisting of gold and other not very volatile elements, while the condensers will collect the volatile elements evaporated from the initial alloys.

The main advantages of ALS® technology are:

- Absence of the use of acids, gas, or toxic or harmful solutions.
- Reduction in refining operating costs
- Cancellation of lock-up costs for precious metals due to quartation or addition
- Easy-to-use process on account of its highly automatic nature
- Negligible loss of precious metal
- Much faster process times

3.2 PROCESS POSITIONING

ACIDLESS SEPARATION® technology needs to be placed with pre-refining technology since it makes it possible to achieve an alloy with a maximum gold purity of 98%. Positioning technology in the diagram shown previously, the graph is as follows:



Graph 2 Placement of ACIDLESS SEPARATION® technology

As it is possible to note, the ALS® process is specifically suited to the primary refining of:

- doré alloys with a high silver or volatile base metal content

- alloys from jewellery and the gold and silver industries, alloys from electronic and industrial production waste.

3.3 OPERATING PRINCIPLES

As mentioned previously ACIDLESS SEPARATION® technology uses a physical principle historically well known, vacuum distillation, which is currently used in different areas such as oil & gas and in the chemical and pharmaceutical sectors.
The process uses the properties of each chemical element possessing a specific saturated vapour pressure at a specific temperature, which is expressed by the Clausius-Clapeyron equation. (1)

$$p=A^{((-\Delta Hvap)/RT))} \qquad (1)$$

In a ratio: A is a specific constant for each element, -ΔHvap is the vaporisation enthalpy, R is the universal gas constant and T is the temperature of the element.
The graph underneath shows a saturated vapour pressure according to temperature for the chemical elements mostly affecting the precious metal refining industry.

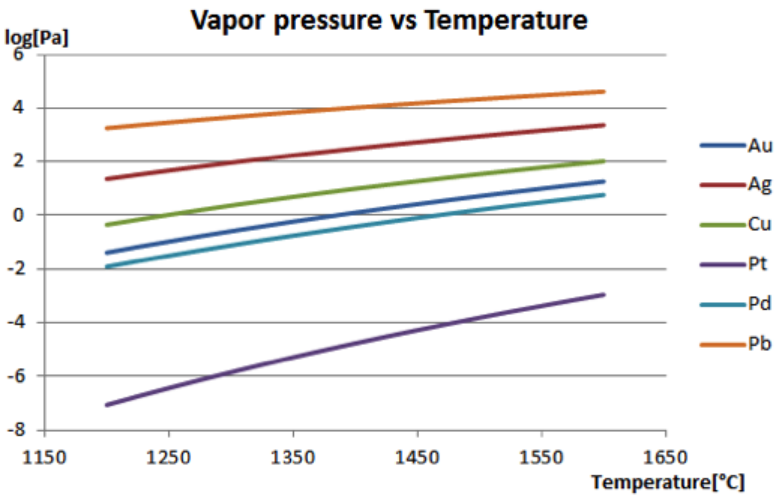


Grafico 3. Tensione di vapore degli elementi in funzione della temperatura

According to the theory of thermodynamic equilibrium [5], the separation coefficientβ can be used to decide whether two components can be separated using vacuum distillation and quantifies the selectivity of this separation of different elements into binary or multicomponent alloys.

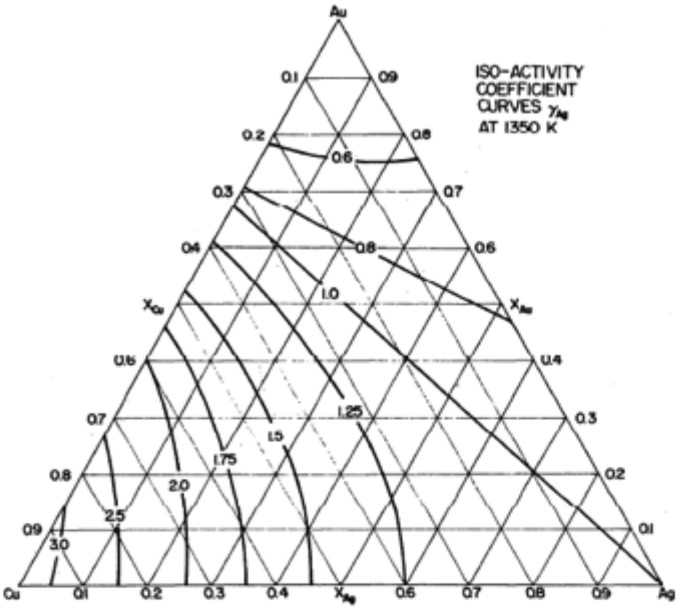
The separation coefficient is represented by the equation below (2)

$$\beta=(\gamma_i/\gamma_j)(p_i/p_j) \qquad (2)$$

Where γ_i, γ_j are the activity coefficient, while pi and pj are the saturated vapour pressures of the elements i and j.
Separation is possible if ββ is higher or lower than 1, while it is not possible if it is equal to 1.
The activity coefficient γ takes into account the total of the chemical and physical relations created between the element considered and the different alloys.

As far as concerns the vacuum distillation process, the vapour pressure of the elements being separated needs to be sufficiently different for the purpose of guaranteeing a good degree of selectivity to the process.
An empirical rule suggests that the coefficient βis at least 100 to guarantee a good level of selectivity.

The ternary graph [6] below illustrates the activity coefficient of silver γ_{Ag} given by a ternary alloy Au-Ag-Cu

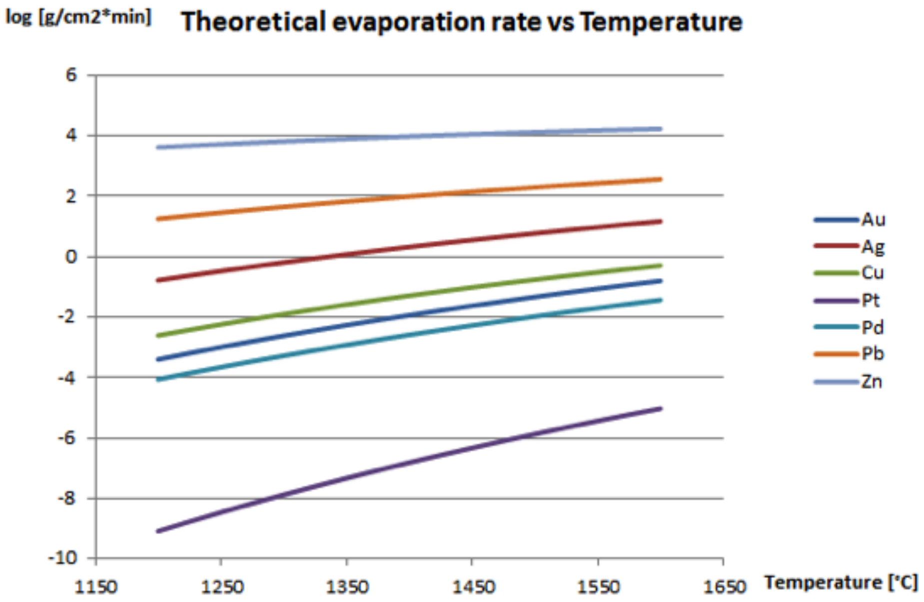


Graph 4 The ratio of silver activity in a ternary alloy Au-Cu-Ag

The evaporation speed of an element according to vapour pressure is expressed by the Langmuir equation (3):

$$dM/dt=\gamma(p_v-p_p)\sqrt{(m/2\pi RT)} \qquad (3)$$

In the relation, γ is the activity ratio, pv represents the vapour pressure of the element, pp the pressure of the condensation zone, m the atomic mass, K the universal constant of the gas and T the temperature of the element.
Specifically, since the chamber pressure is clearly lower compared to the vapour pressure, the contribution of pp can be considered negligible.
The graph underneath shows the theoretical evaporation speed (considering for the sake of simplicity α=1) for the chemical elements mostly affecting the precious metal refining industry.



Graph 5 Specific evaporation speed for different elements

3.4 PERFORMANCE OF ACIDLESS SEPARATION® TECHNOLOGY

Now we can look at the performance of an ACIDLESS SEPARATION® system refining 2 real doré alloys tested in a refinery during a normal production cycle. The system taken in consideration has a production capacity of 30 kg/batch and is equipped with 2 condensers: one destined to condense more volatile base metals, the other to condense silver.

3.4.1 LEGA DORE' #1

The alloy being refined is a doré alloy substantially containing gold and silver in similar proportions, the process includes a single evaporation stage for silver, with the amount of alloy impurities as being practically null.

DORE' ALLOY #1

Chemical composition

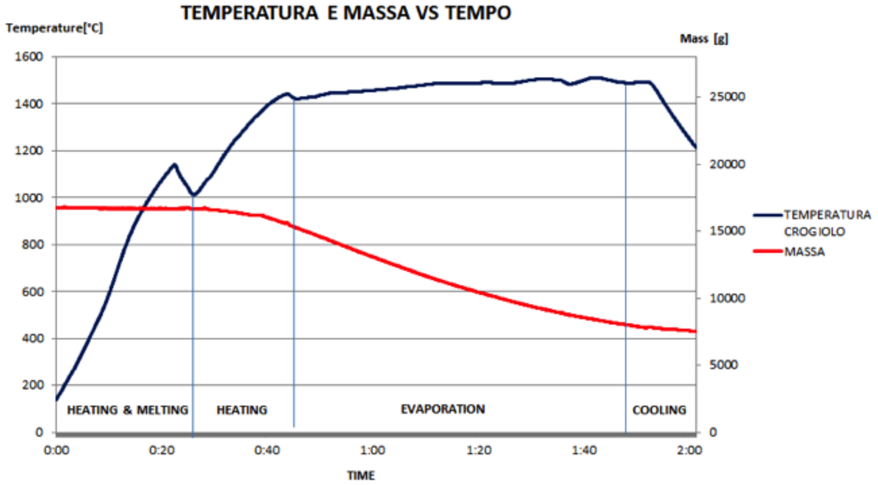
%Au	%Ag	%Cu
49	50.8	0.2

Initial mass = 16749g

PROCESS DATA

T max= 1480 °C
Pressure=0.01mbar
t evaporation=70 min
average evaporation speed=118g/min
The graph below shows the temperature trend for metal and mass according to time.

Figure 2 Image and technical data for doré alloy #1 before refining



Graph 6 Temperature and mass of metal during the doré alloy #1 refining process

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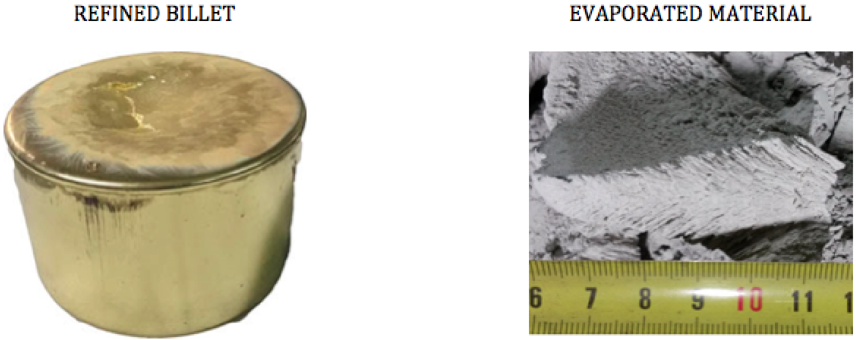


Chemical composition

%Au	%Ag	%Cu
96.6	3.1	0.3

Mass=8365g

Chemical composition

%Au	%Ag	%Cu
2	97.9	0.1

Mass=8374g

Figure 3a. 3b.Respectively, the refined alloy and condensed material at the end of the process

The evaporated material recovered by the condenser is like a dry, crumbly mud, which can be directly placed into a melting pot to produce anodes for the process of electrolytic refinement.

The selectivity of silver separation is 96.3% while for gold it is 98.4%.

3.4.2 DORE' ALLOY #2

The doré alloy to be refined contains a high amount of base metals such as zinc, lead, copper and selenium. In this case, the distillation process occurs in two stages to separate the silver from the volatile base metals and to guarantee the successive final refining stage without intermediate treatment.

DORE' ALLOY #2

Chemical composition

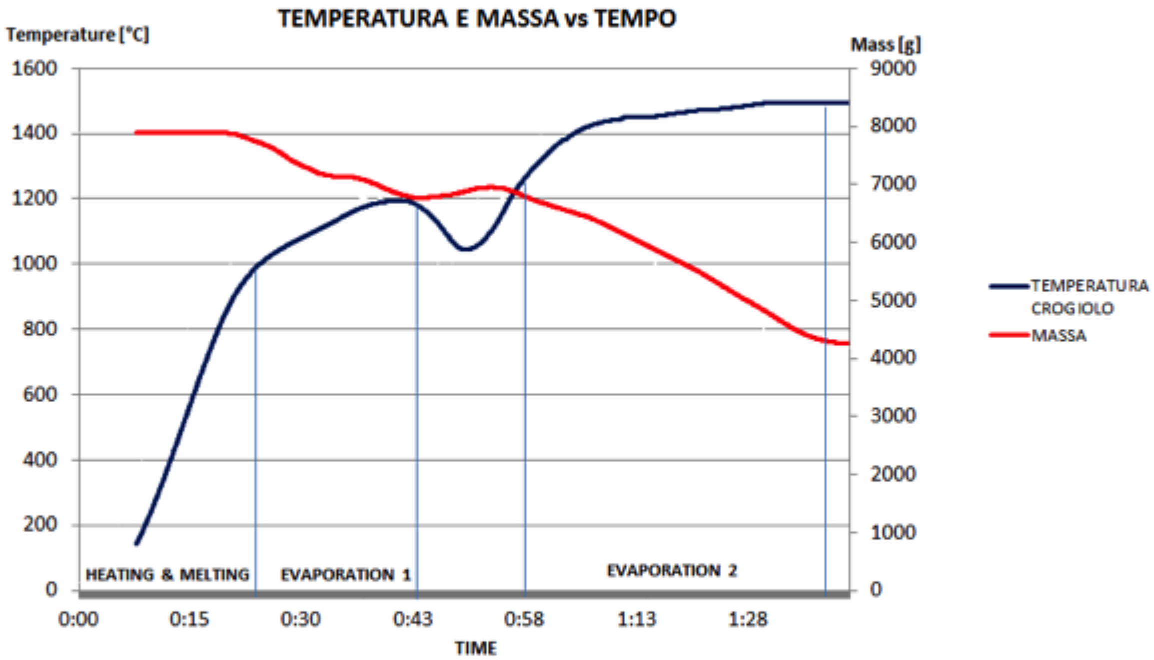
%Au	%Ag	%Cu	%Zn	%Se	%Pb
49	35	3	6	4	3

Initial mass = 7800g

PROCESS DATA

1ST EVAPORATION STAGE
T max= 1200 °C
Pressure=10 mbar
t evaporation=20 min
average evaporation speed=58g/min
2ND EVAPORATION STAGE
T max= 1500 °C
Pressure=0.01mbar
t evaporation=35 min
average evaporation speed=70g/min

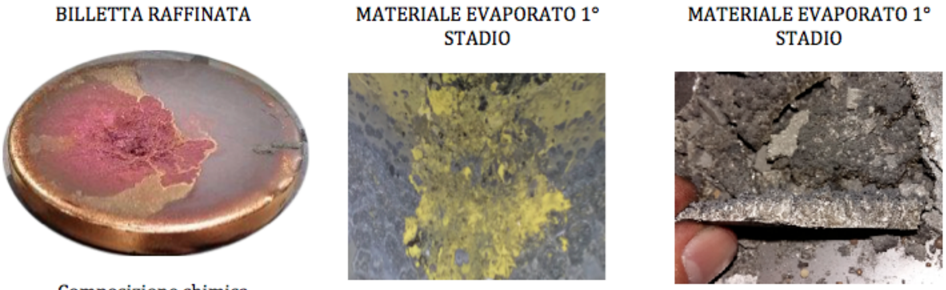
Figure 4 Image and technical data for doré alloy #2 before refining



Graph 7 Temperature and mass of metal during the doré alloy #2 refining process

RESULTS

After the process, the system produces a refined metal billet and evaporated material in two condensers.



BILLETTA RAFFINATA

Composizione chimica

Au	Ag	Cu	Zn	Se	Pb
89,8	5,3	4,9	/	/	/

Massa=4230g

MATERIALE EVAPORATO 1° STADIO

Composizione chimica

Au	Ag	Cu	Zn	Se	Pb
0,1	10,5	0,3	39,3	23,9	25,9

Massa=1150g

MATERIALE EVAPORATO 1° STADIO

Composizione chimica

Au	Ag	Cu	Zn	Se	Pb
0,8	96,4	2,8	/	/	/

Massa=2420g

Figure 3a. 3b. 3c Respectively, the refined alloy, stage 1 condensed material and stage 2 condensed material.

The process selectivity is close to 100% for more volatile elements such as zinc, lead and selenium.
As far as silver and gold are concerned, the value is 85% and 99.3% respectively.

4. FUTURE AIMS AND CONCLUSIONS

ALS® technology, thanks to its strong points, is turning out to be a very interesting proposal for the refining method panorama.

Since 1883 no secondary refining methods using non-chemical processes have been introduced for precious metals [7], and for this reason, we can state that the new process presented, being a physical and non-chemical separation process, is, since 1883, the first real totally GREEN innovation process available to secondary refineries.

The excellent performance of systems made and installed to date encourage a deeper look at further aims such as:

- Increasing the efficiency and productivity of the system
- Making the system completely automatic
- Optimising the integration of the process with the refining processes downstream.

Given the flexibility of the technology, now released from the limitations set by the chemical composition of the alloy being refined, we are convinced that it has the potential to become a common denominator in metal refineries over the coming years.

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