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Foreword

It is with great pleasure that we announce the availability of this third issue of the IPMI Journal, a publication of the International Precious Metals Educational and Scientific Foundation. This digital peer reviewed publication has been created as a vehicle for the sharing of technical information related to the science and technology of precious metals.

Since 1976, the International Precious Metals Institute has championed the exchange of information of critical importance to the precious metals scientific and commercial communities through its various communications vehicles. This has included instructional videos, annual conference symposia, special topic committee meetings, regional seminars, and professional and student achievement awards. Due to the breadth of important topics related to all aspects of precious metals, it has been the vision of the IPMI to provide a publication available to the general public that would become a key source of pertinent topics containing high quality publications by experts in their fields of study.

Historically, the IPMI has attracted world renowned experts in many fields (including Nobel Laureates Henry Taube, Ei-ishi Negishi, Robert Grubs, Professor Ben Feringa, and David MacMillan) in the dissemination of discoveries, inventions, and industry proven practices. Such information has a total value greater than the sum of its parts as seemingly unrelated innovations from distinct focus areas can be adapted to solve problems. Because of this important characteristic of information exchange, we have decided to create a digital journal, available to the general public, that will not only communicate state of the art discoveries and sound practices, but will also review historical communications from the IPMI's archives that have value and use even in today's environment.

On behalf of the members and leaders of the IPMI, we hope you will find value in this new publication.

Dr. Corby G. Anderson, co-editor

Dr. Robert M. Ianniello, co-editor

Mark Caffarey, co-editor

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In 1976, the International Precious Metals Institute, Inc. (“IPMI”) was founded to promote the development of precious metal science and technology. Over the past 45 years, the IPMI has provided its members with an extraordinary body of technical and educational work and an exceptional series of technical videos. The IPMI has also recognized leaders in the industry and academia and students through its long standing Awards Program. This recognition and financial support for continued dedication and research in the field of precious metals is a cornerstone of the IPMI and owes its support to generous sponsorships and endowments.

In 2019, the IPMI made a fundamental structural change by reorganizing IPMI into a trade association to focus on its membership and the needs of the precious metal industry. At the same time, IPMI preserved its scientific and educational roots by renaming its original organization the International Precious Metals Educational and Scientific Foundation (the Foundation).

The Foundation will continue IPMI’s charitable activities by focusing on its long-standing Student and Industry Awards Program and by continuing to promote the science and technology of precious metals as its primary mission. This Journal of the International Precious Metals Institute is a cornerstone project of the Foundation.

Another of the Foundation’s primary goals will be to expand its fundraising activities to ensure the long term sustainability of its educational and scientific work, including new and expanded initiatives, such as the student internship program, designed to attract a new generation of trained professionals to the precious metals industry.

On behalf of both the IPMI and the Foundation, I want to personally thank our Board of Directors, Awards Committee, corporate sponsors, donors, and the benefactors of our endowments for their continued hard work, support, and dedication to our mission.

I would also like to thank Dr. Corby Andersen, Dr. Bob Ianniello and Mark Caffarey, who are the co-editors of our Journal. Their research through our historical treasure trove of technical papers has produced an extremely important and relevant body of work. Special thanks to all the authors of the papers in this third issue. It is through work like yours that the industry has continued to grow and improve technologically. And lastly, thank you to the sponsors of this publication. Because of your generosity, the net proceeds of the Journal will go directly to the Foundation and help provide continued support for our programs.

Larry Drummond
Executive Director

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June 10-13

IPMI 10th Annual

Platinum Dinner

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New York, NY

September 14

LONG RUN DEPENDENCY: A STUDY OF GOLD PRICES

(This paper was originally presented at the 2008 IPMI Conference)

Rohnn Sanderson
University of New Mexico

ABSTRACT

Historically price changes of commodities over time have been modeled with random walk methodology. However, there is evidence that randomness alone is not a sufficient explanation for the behavior of prices. This paper investigates an alternative approach of analysis using the concept of non-linear dynamic systems.

I. INTRODUCTION:

Many business are concerned about how price changes will affect both their business and their industry. In the precious metals industry the underlying price of the commodity is very important to a firm's profitability, due to the relatively few number of participants in the various precious metals markets and costs that can remain relatively fixed in comparison to the change in revenue from market price changes.

Additional complexity to the problem exists because many economic variables are time dependent and operate under a framework that is best described as a dynamic system. Prices of precious metals certainly fall into this category. This fact necessitates the need for an understanding of the underlying dynamic system that the precious metals price is operating in to correctly identify its characteristics in order to make reasonable conclusions about the behavior of the prices.

Traditional time series methodology has been employed as one solution to the problem ie. ARIMA (Auto Regressive Integrated Moving Average). The ARIMA model is a general class of statistical models that involve using historical periods and moving averages to explain the movement of the causal variable. In other words the ARIMA model using factors from the data you are trying to explain in order to explain its behavior. These models are good at prediction but are lacking in providing a causal description of the underlying behavior of the variable one is considering. To compound problems further most time series analysis assumes that a dynamic system follows Brownian motion, meaning that events in the future happen at random and are independent and identically distributed from one another. Of course this assumption is a fairly strong one. Consider the prices of stock market derivatives as an example, most have some sort of persistence. That is to say that most derivative contracts will have some underlying up or down persistence that is not random and not independent from one period to the next. Of course there are many more examples of this as will be discussed further on.

If this is the case then there is the possibility that a different estimation methodology can provide a superior analysis of a dynamic system. The true hallmark of a dynamic system is its path. Take for example a butterfly flapping its wings, when plotted out it will look random and if one didn't know what they were looking at they might confuse it for a random process, but it is far from it. On the contrary the system is completely deterministic. The same is true for the classic double pendulum experiment in physics. Dynamic systems can attenuate, grow or persist depending on the environment and the physical characteristics of the phenomena in question.

II. DIFFERENCES BETWEEN ARIMA MODELS AND DYNAMIC SYSTEMS:

To understand the difference between the more traditional approach and a dynamic model let us look at some of the differences in assumptions as well as develop a traditional model as a means of comparison. The differences in the two methodologies are summarized in Table 1 [1].

Table 1: Comparison of ARIMA vs Dynamic Models

ARIMA	Dynamic
Constant Mean	May or May Not Have Constant Mean
Invertible	Not Invertible
Variable is Independent and Identically Distributed	Variable is Not Independent and Identically Distributed
Series has Infinite Dimension	Series Lies in Restricted Space
Series is Additively Separable	Series is not Additively Separable

Let us look at each of these differences one at a time. The first assumption of a traditional ARIMA model is that of the series in question having a constant mean. What this says is that the fluctuations that are seen are purely random and due to the randomness being a 50/50 equally likely event in the future the mean will stay constant. This is not necessarily the case for a dynamic series. It may be the case for a dynamic series if the cycles over time have the same strength in up and down movements, if not then the mean would not stay constant. The second assumption of ARIMA models is that the series is invertible, this means that the series is the same forwards and backwards. This is not true of a dynamic system since its motion is always in equilibrium and on a specific path that is not random and cannot be the same when reversed. The third assumption made by ARIMA models is that the variables are Independent and Identically Distributed (IID). This means that at each point in time the probability of occurrence is the same for all and that each period in the data series is mutually exclusive of one another. In a dynamic system this is not true the previous period does determine where the next periods value will be. ARIMA models make the assumption that the range or domain of the phase space of the series in infinite, this is due to the fact of the previous assumptions. A dynamic system however lies in a finite space due to the dependent nature of the series. Finally ARIMA models assume that series are additively separable that is to say we can divide the series up into components that added together forecast the series. In a dynamic model the series is not able to be separated into components that are additive due to the non-linear nature of the dynamic series.

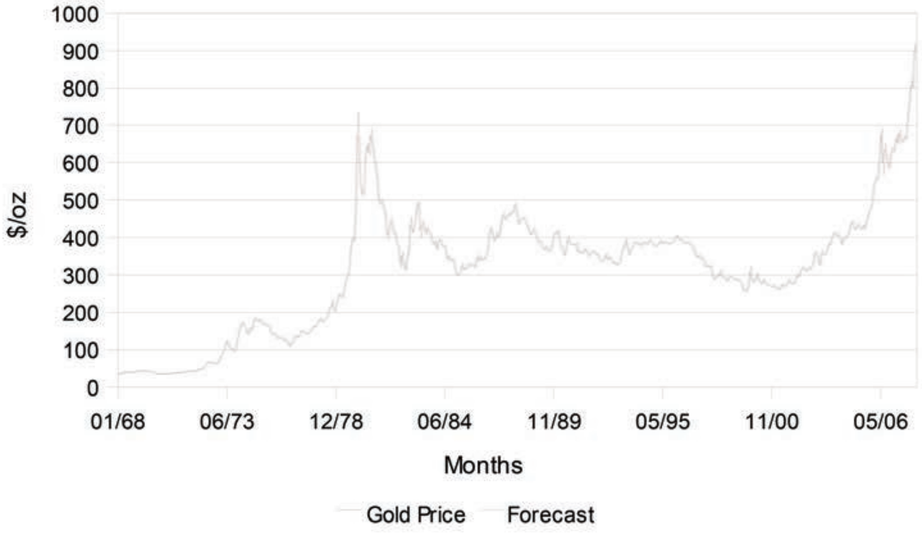
To illustrate these differences first we develop a standard ARIMA forecast based on the historical average monthly gold price from January 1968 to February 2008. For the sake of simplicity only one auto regressive (one period lag) and one moving average (average of two months together) term are used and they will produce a very good forecast. The results can be seen in Table 2.

Table 2: Basic ARIMA Forecast

Coefficient	Estimate	Std. Error	T value	Pr(>|t|)
AR	0.9997	0.0071	141.1640	2e-016***
MA	0.2923	0.0528	5.5410	3e-08***
Intercept	1.9443	2.4940	0.7800	0.463

Signif. Codes: 0 '***' 0.001 '**' 0.01 '*' 0.05 '.' 0.1 "

The t statistic indicates that both of the coefficients are significant at 1%. The accuracy of the model can be seen in Figure 1.



Forecast vs Gold Price

Figure 1

While this modeling provides accuracy, there is no causality that can be determined. That is to say we don't know what is effecting the change in the price of gold. If we don't understand the causation there is no ability to forecast the impact of events. Considering gold prices as a dynamic system allow us insights into the cause and effect. We begin with the long run dependency.

III. SEEING DEPENDENCY AND CHAOS:

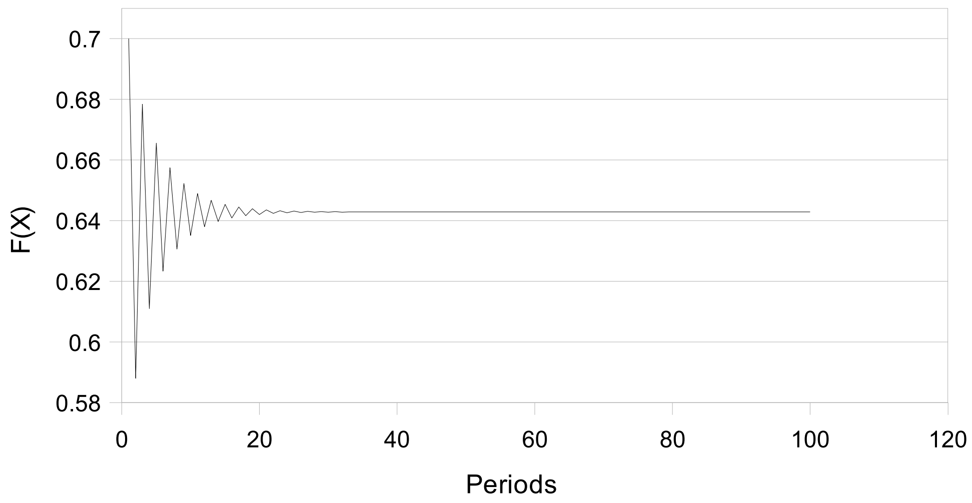
In order to analyze causation we begin with determining the long run dependency in gold prices. To get an in depth idea of what is occurring lets look in depth at the logistic function, which is frequently used by economists to model renewable resources as well as populations and other phenomena [2]. In discrete time the logistic function takes the form:

(1) $XT+1 = \alpha XT (1 - XT)$

This is a non-linear dynamic system that describes the behavior of one variable in the present and the future dependent on the coefficient of sensitivity alpha, which can theoretically take on any value from 0 to 4. In this case it is the variable alpha that causes the motion of the variable X. Since this is a non-linear dynamic equation we can see that the value of X in the future is dependent on its past by definition. Let's study some of its behavior when the value of the alpha changes and see how that affects the results of the equation. In Figure 2 alpha is equal to 2.8 and the starting value for X at time zero is .5.

Logistic Function Over 100 Periods (Alpha = 2.8)

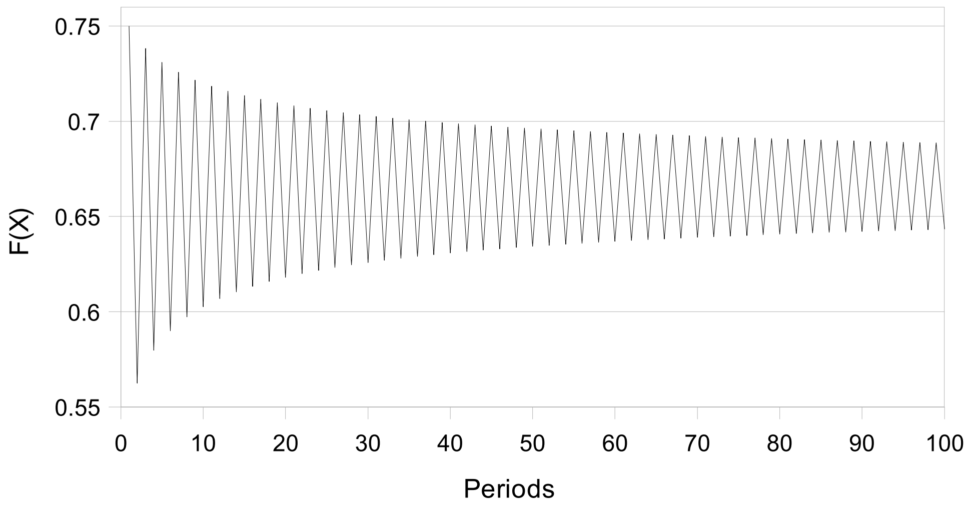
Figure 2



This is an example of a dynamic system that is attenuating to a constant level. Note that it oscillates for the first 20 periods or so before it dies down to a constant level. The alpha is critical in how this logistic function behaves. As the alpha gets beyond 3.57 [1] the system becomes “chaotic” that is to say the pattern of oscillations in the system looks completely random but of course with this logistic function we know that is not the case, it is in fact completely deterministic. Lets look at another example this time with the alpha value at 3 in Figure 3.

Logistic Function Over 100 Periods (Alpha = 3.0)

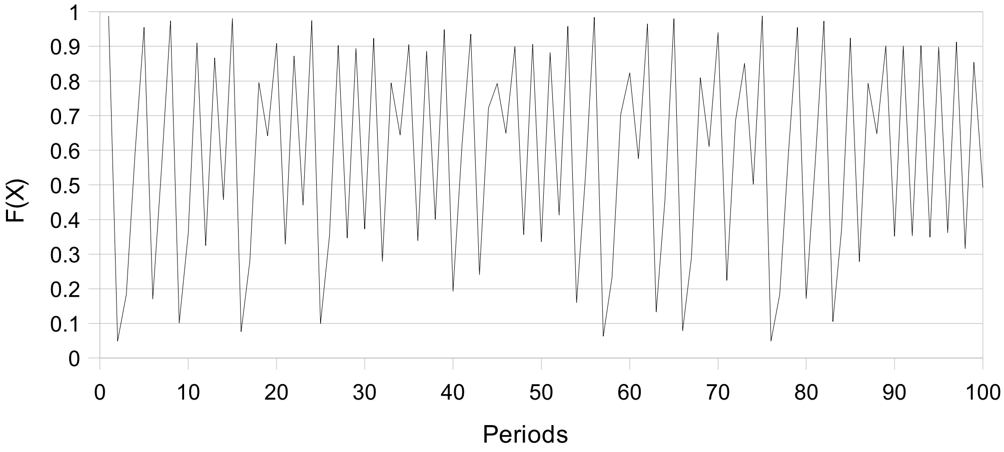
Figure 3



Notice this time that the series is starting to converge this time, but does not fully attenuate instead its final pattern oscillates between two points. Now let’s look at one final example where the alpha is 3.95 in Figure 4 which results in a chaotic series.

Logistic Function Over 100 Periods (Alpha = 3.95)

Figure 4

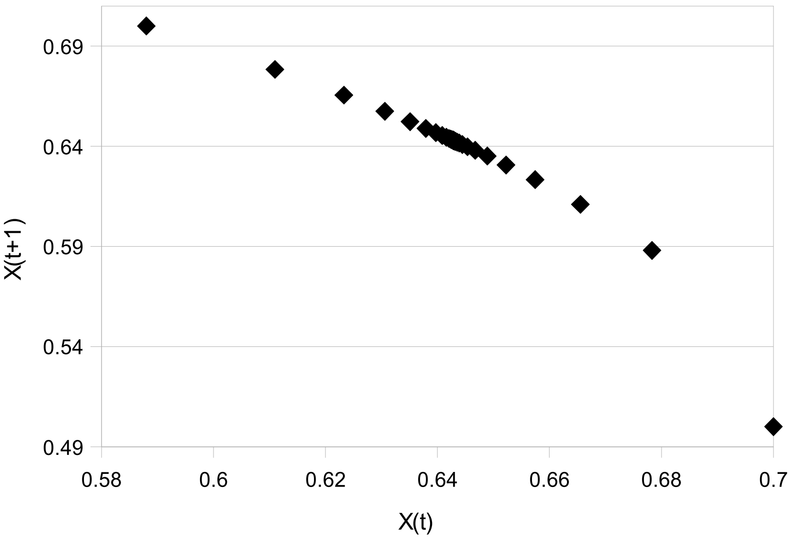


Notice that to the eye the series in Figure 4 looks random, but is in fact completely deterministic as it is produced by a logistic function. This can occur in many data series and without proper investigation a series can be misclassified as random when it is not.

So now that we have seen that series that look random can be deterministic let's discuss how to show that. One of the most common graphical methods is through the use of attractor plots [3]. This is simply plotting the variable X against itself for different time periods. This is used to see if the value converges to a particular value or not. Let us look at the first series produced when the alpha is equal to 2.8 as seen in Figure 2. Figures 5 and 6 are attractor plots for (X(t),X(t+1)) and (X(t),X(t+2)) respectively. Notice that in Figures 5 and 6 the observations converge toward .64 which is the value the logistic function attenuates to.

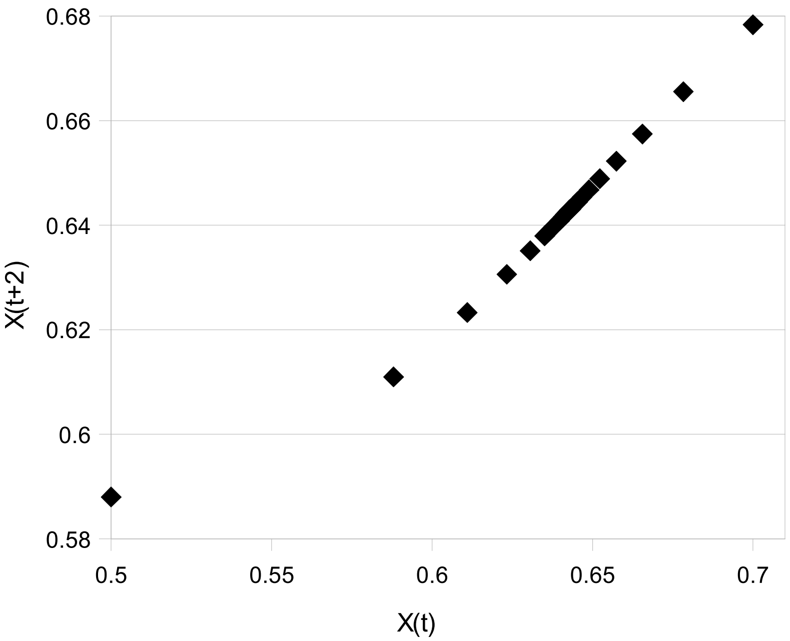
Attractor Plot

Figure 5



Attractor Plot

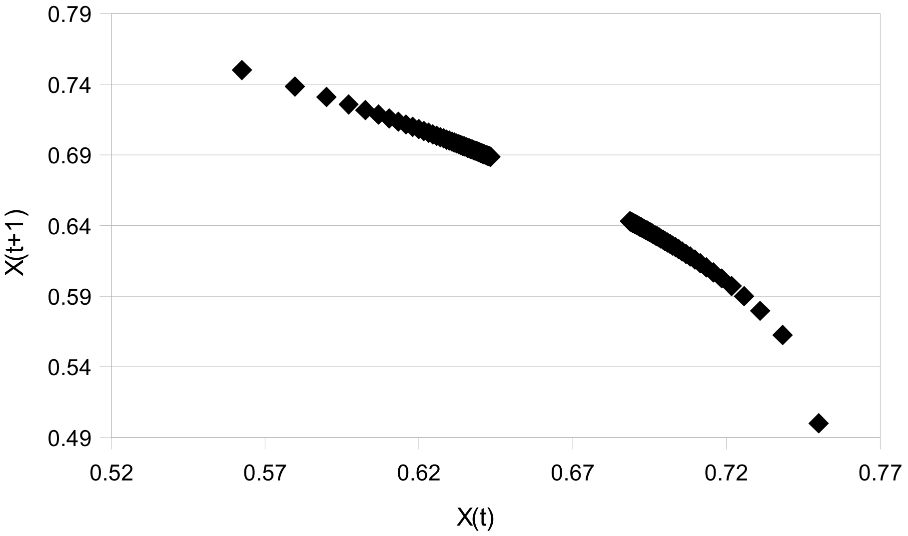
Figure 6

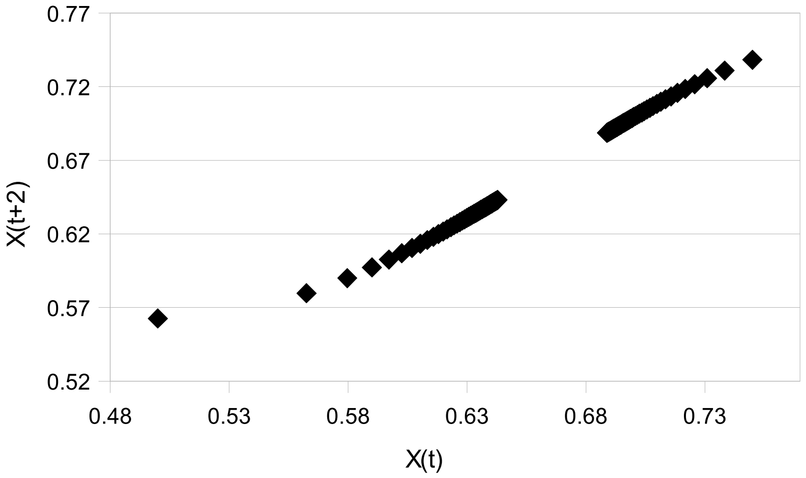


Compare this to our results from Figure 3 where alpha is 3. Figures 7 and 8 are the attractor plots for (X(t),X(t+1)) and (X(t),X(t+2)), respectively, now the series does not converge to one point, but instead oscillates between two different values.

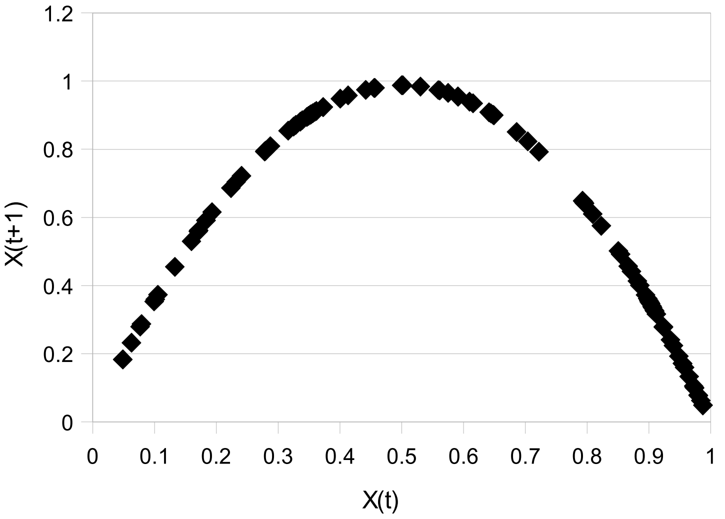
Attractor Plot

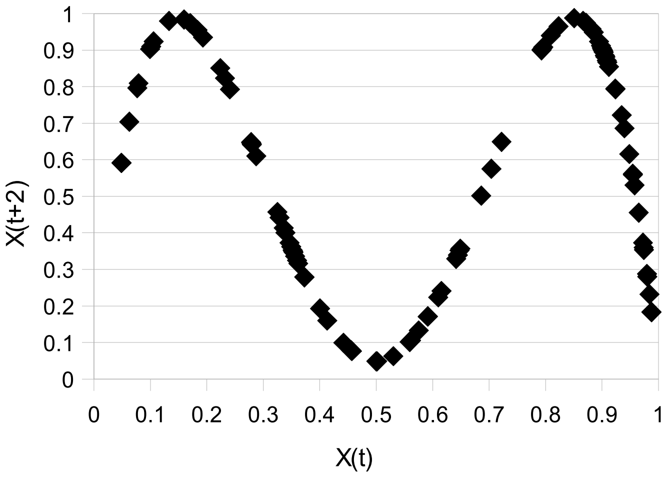
Figure 7




Attractor Plot
Figure 8

Again when the alpha is 3 the series is driving toward convergence, but in this case the series does not converge which is what we saw in the series plot of this function as well. Finally consider the attractor plots for the chaotic series in Figure 4, where alpha was 3.95. Figures 9 and 10 show that in this case not only does the series not converge to one point but, instead the values oscillate among a multitude of equilibria.


Attractor Plot
Figure 9



Attractor Plot

Figure 10

When the series is chaotic it does not converge to one value, but instead to a "set" of multiple equilibria. This shows that the chaotic series is not random, but since it continually oscillates there is not one single equilibrium point in the system. Instead all points are in equilibrium and each movement from one point to another is a movement from one equilibrium to another.

This change of interpretation of a series of data changes how we measure and account for economic phenomena. If we look first at how economic data behaves physically and understand its motion, we can then arrive at a better analysis.

IV. TESTING FOR LONG RUN DEPENDENCY:

Now that we have seen how dynamic systems work let us investigate how to determine whether a series is dynamic or not and random or not. Let us investigate one such series; gold prices. For the purposes of this paper nominal monthly average gold prices from January 1968 to February of 2008 were used. A summary of the data is in Table 3 and Figure 1.

Table 3: Summary Statistics for Average Gold Price ($/oz)

Minimum	1st Quartile	Median	Mean	3rd Quartile	Maximum
$34.94	$178.50	$342.60	$314.40	$395.90	$922.30

In order to determine if a system is dynamic or not three tests on the data need to be performed: Hurst exponent, ACF and Lyapunov exponent. First we will use the Hurst exponent to determine whether or not the series is random and work at finding the underlying signal of the data by using the Autocorrelation Function (ACF) and the Lyapnuov exponent to separate the data into two different categories: endogenous(internal effects) and exogenous(external effects).

The Hurst exponent was originally used to measure water levels on the Nile river in the 1950's to determine how much previous years precipitation affected the current water level. The Hurst exponent shows the amount of dependency on the past and falls within the range of zero to one theoretically. A Hurst exponent of .5 would mean that series is random, that is to say that the previous period has no impact on the current period and that the assumption of IID in Table1 would hold for ARIMA modeling.

If the Hurst exponent is above .5 then the series has some level of dependency on the past and the dependency increases as the Hurst exponent increases towards 1. To derive the Hurst exponent for the gold prices I will use a Fractional Autoregressive Integrated Moving Average (FARIMA) model to estimate the Hurst exponent. This model is similar to that shown in Figure 1 and Table 2 with one change. The differencing parameter or exponent on the autoregressive and moving average terms is allowed to vary and is not fixed at one as it was before. In Table 4 are the results of an FARIMA(1,d,1) model that is to say 1 Auto Regressive and 1 Moving Average component allowing the fractional differencing (d) component to be estimated to determine the level of dependency. It turns out that Hurst exponent is 1-d.

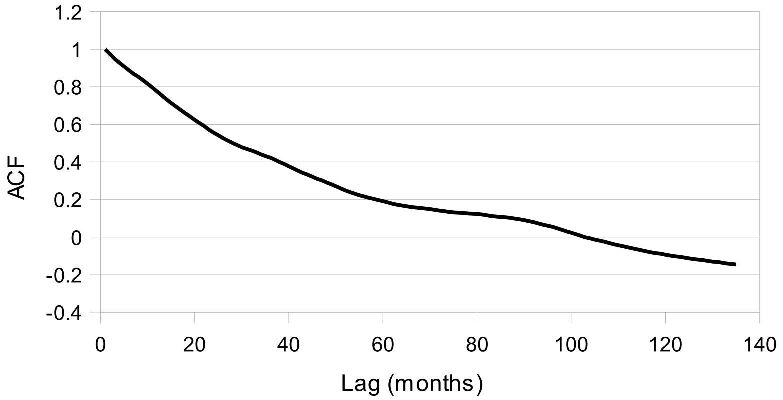
Table 4: FARIMA Results (1,d,1)

Coefficient	Estimate	Std. Error	T value	Pr(>|t|)
d	4.58E-005	0	Inf	2E-016***
,-	0.9995	0.0000	Inf	2E-016***
MA	-0.2980	0.0071	-42.1200	2E-016***

Signif. Codes: 0 '***' 0.001 '**' 0.01 '*' 0.05 '.' 0.1 "
Log likelihood: -2115 ==> AIC = 4231.933 [1 deg.freedom]

In this case the Hurst Exponent = 0.999. Showing that the dependency on the past is rather large. The derived Hurst exponent suggests that there is definitely some dependence between prices over very long intervals.

Given the Hurst result we will check for linear dependency using the autocorrelation function (ACF). The ACF is a measure of the strength of the relationship of the prices to themselves over time. If the series exhibits a high degree of autocorrelation that means that the series is very dependent on its previous values over time. When the ACF is zero there is no relationship between the current price and the price that came before it. In the case of gold Figure 12 shows that the lag required to make the ACF = zero is 103 months.



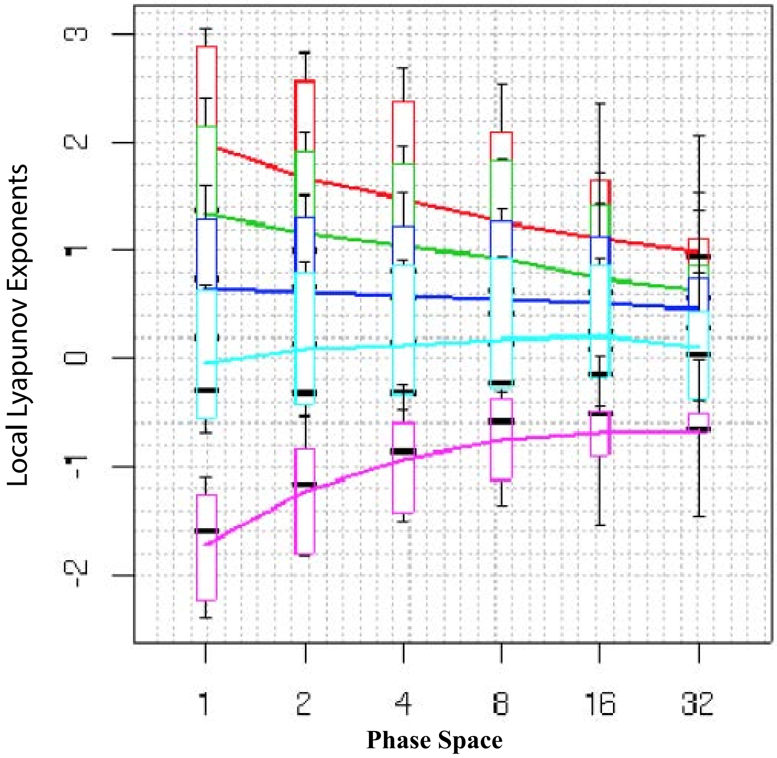
ACF Plot (Best Lag 103)

Figure 12

Finally to see whether or not gold prices are exhibit long run dependency or not is to check the dimensional space again from the assumptions listed in Table 1. If a series is random then it will exhibit infinite dimensional space whereas a deterministic function will have a finite set of dimensions.

To test for the dimensional space a Lypanunov Exponent was calculated as seen in Figure 13. The Lypanunov exponent characterizes the rate of separation between infinitesimally close trajectories of the dynamic system. Close trajectories indicate a dynamic system and positive Lypanunov exponents indicate chaos in the dynamic system. In the case of gold prices predominantly positive Lypanunov exponents were found and they were in finite quantity indicating that there is long run dependency and some chaotic behavior in the series. Also only five dimensions were calculated because the phase space is of finite dimensions and further dimensional analysis showed that there was no more significance to calculating more. Below is a chart of the Lypanunov Exponents for the five five dimensions that were calculated.

Figure 13



The Hurst, ACF and Lyapunov exponent indicate long run dependency in gold prices. We now turn to separating the data in order to isolate the component of the price that exhibits long run dependency versus the component that does not. To do this a Space-Time separation procedure was performed using the information gathered from the previous three tests. The results of this procedure produce a data series that does not have any long run dependency in it. To verify this a FARIMA(0,d,0) model was performed on the transformed data to test for long run dependency a Hurst exponent of .5 is measured indicating the transformed data is now random. The long run dependent data is formed by subtracting the actual data from the random data. The descriptive statistics are in Table 5. We have now separated the long run dependent portion on the price (endogenous) and the random portion (exogenous), as shown in Figure 14 and 15.

Table 5: Descriptive Statistics

Endogenous Descriptive Statistics for Gold

Min.	1st Qu.	Median	Mean	3rd Qu.	Max.
-27.040	0.041	1.745	2.643	3.071	55.920

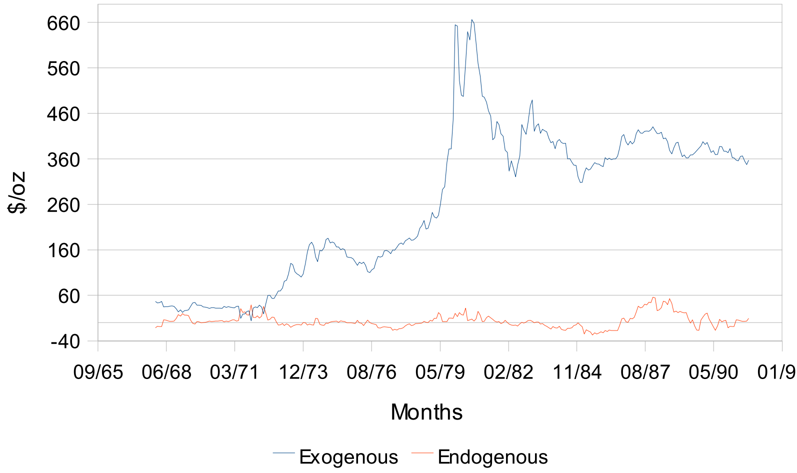
Exogenous Descriptive Statistics for Gold

Min.	1st Qu.	Median	Mean	3rd Qu.	Max.
3.974	182.000	347.000	311.700	394.700	920.600

Figure 14 shows the relative impacts of the two components. The endogenous component accounts for less than 20% of the total price - thus gold prices are highly susceptible to external factors. To illustrate the movement of the endogenous and exogenous portions of price I have normalized both effects in Figure 15. The exogenous and endogenous factors do not move in relation to one another. However when we look at the endogenous portion of the price we can see the series cycle. That is to say that it moves up and down with some type of frequency similar to the pattern see in Figure 4.

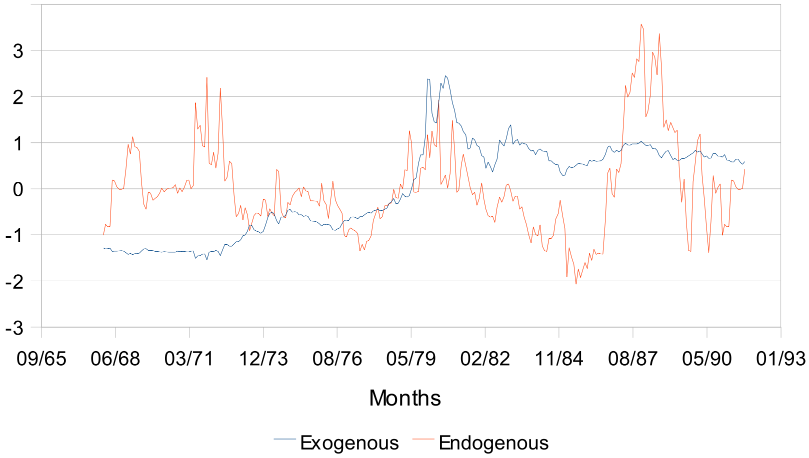
Gold Price Impacts

Figure 14



Normalized Gold Price Impacts

Figure 15



V. DEVELOPING A FUNCTION

The next problem is developing the functional for of the deterministic

(endogenous) data. For the purpose of illustration I will use the logistic functional form that was used at the beginning of the paper. To use the logistic function the data has been scaled into the range for 0 to 1 and then an estimate of the value of the variable of sensitivity alpha is calculated using the method of non-linear least squares. To arrive at convergence for the non-linear least squares method a random term had to be added to the data since the data has had the random comments removed. [4] The results are shown in Table 6 below.

Table 6: NLS Results for Logistic

```
Coefficient  Estimate    Std. Error   T value      Pr(>|t|)
Alpha          3.6386      0.2016      18.0500    2e-16***

Signif. codes:  0 ‘***’ 0.001 ‘**’ 0.01 ‘*’ 0.05 ‘.’ 0.1 ‘ ’ 1
Residual standard error: 0.3212 on 274 degrees of freedom
Number of iterations to convergence: 1
```

We can see that the estimate of the alpha term in the logistic is significant, and the value of 3.64 is inside of the theoretical limit of the logistic function. This shows that the logistic function would possibly be an appropriate determination of the endogenous price component. However there are other function forms that could produce similar results. This illustration shows the complexity in identifying functional form for dynamic data due to the difficulty in determining appropriate tests of functional form.

VI. CONCLUSION:

It is clear that many financial and economic variables exhibit long run dependency and potentially chaotic behavior. This example on gold prices shows that there is more to the story about how these prices behave than just random behavior. As research in this area continues improvements to our understanding of this behavior will increase. Right now we are able to detect the presence of long run dependency, but determining the functional form of the deterministic system is still a challenge. That being said some important implications from this methodology arise. They are that prices today are dependent on a long history of previous prices and are not just brought about by recent events. This means that firms should be wary of how much influence or lack thereof that they have on current prices. The nature of long run dependency implies that takes a rather large mass (firm size) to move prices in a very dramatic way. For the small business it implies that planning for the future means not just looking to the recent past but to 4 or 5 years prior in the case of gold.

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MAXIMIZING THE VALUE OF PRECIOUS METALS INSURANCE: DEALING WITH CARRIERS IN THE EVENT OF A CLAIM

(This paper was originally presented at the 2006 IPMI Conference)

BY MARTIN C. PENTZ[1]

I. INTRODUCTION

For members of the precious metals industry, effective risk management requires unique sophistication. Protection against loss from cash market price fluctuations requires carefully planned hedging investment strategies. Protection against loss from theft, embezzlement, insolvency of consignees and other unique or heightened industry risks requires a specially designed insurance program and innovative policies, such as the so-called “stock floater,” designed to follow your owned or leased metals wherever they go. But even the best risk management design requires diligent follow-through: execution of the often mundane tasks of providing a broker with underwriting information or dealing with a broker or insurer in the event of a loss or claim. A misstep at this stage can cause forfeiture of coverage rights or, at a minimum, place an insurer in a position to delay your recovery or force you into expensive litigation.

To understand why coverage claim prosecution can be so important, one need only consider the nature of the insurance industry. Insurers are in business to collect and invest premiums. Whatever their advertising may suggest, the truth is that, for insurers, claims payments are a necessary evil at best; they can only undercut profitability. On the other hand, delay is an insurer’s friend; the longer it takes for a claim to be paid, the longer the insurer has the use value of premium dollars. And litigation – something most business people abhor – is regarded as a tool to avoid or delay claim payments if there is any marginally plausible basis to do so.

Accordingly, the process of dealing with an insurer when a loss has occurred, or when a claim or suit has been filed against your company, can sometimes resemble tip-toeing through a minefield. Insurers often seem to treat the claim submission and communications process as a prelude to a litigation strategy or an opportunity to compile additional bases to refuse coverage. Policyholder businesses must recognize this and approach the process with diligence and savvy. The objective of this paper is to provide the reader with practical guidance in techniques for dealing with insurers that can help move the insurance recovery effort to a swift and satisfying conclusion.

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II. INSURER NOTIFICATION AND RESERVATIONS OF RIGHTS

A. Notifying the Insurer

In the event of a loss (in the case of property insurance) or of an "occurrence," claim or suit (in the case of liability insurance) the policyholder always will be obliged to notify the insurer, and to do so promptly. In some cases, the timing of the notice (or "report") determines whether the policy applies at all; in others, even though it is the timing of the insured event that determines whether the policy applies, it is still necessary to provide prompt notice to enable the insurer to protect its interests. Simple as this may seem, policyholders fail to give prompt notice of insured events with alarming frequency. There are recurring causes for these failures, nearly all of which are avoidable. Here are few rules to observe to avoid falling into the "late notice" trap:

1. When in Doubt, Notify. We are all familiar with the oft-repeated insurer refrain "read your policy." Ideally, policyholders would do just that, and would come to understand quite precisely the scope of protection they have purchased. Reality is another matter. Businessmen (and women) tend to find policy wordings to be an impenetrable morass of fine print. Responsibility for insurance purchasing and administration may be given to persons with limited relevant training or experience. As a result, unless the company has the resources to employ a well-trained (and supported) risk manager, there may be confusion or misconceptions regarding what is covered and what is not. And all too often this lack of understanding has led to an ill-advised assumption or impression that the company's coverage does not apply to a given type of loss or claim. The insurer is not notified and, when someone later questions the initial inaction and notice is given, the insurer replies that the policy does not apply because the loss was not reported during the policy period or because the insurer was denied an opportunity to handle the matter from its inception.

To avoid a forfeiture of coverage due to late notice, the rule should be "when in doubt, notify." If a loss occurs, or an event takes place that might give rise to a claim against the company, the working assumption should be that there is coverage, the only question being which insurer issued the pertinent policy. If in-house personnel are unable to identify such a policy, then the company's broker should be consulted. Even a broker's "no coverage" reaction should not be taken at face value. Certain brokers will have received an insurer-authored "education" about the scope of the coverages they arrange. The broker should be called upon to explain thoroughly his or her reasons for believing that no coverage exists. If the stakes are high enough, it may even be wise (and cost-effective) to consult an attorney who specializes in representing policyholders in insurance recovery cases.

While neither insurers nor judges tend to show sympathy toward policyholders who delay notification due to an initial, mistaken impression that the coverage did not apply, there is rarely any significant disadvantage to providing notice where coverage is questionable. The insurer itself may provide a satisfactory analysis of non-coverage, and the debate may end there. Or the insurer's analysis may not be convincing, and further consultation with a broker or coverage attorney may be fruitful. While some will raise a concern that claim notifications can result in policy cancellation or "non-renewal," it should be recalled that, from the policyholder's perspective, the purpose of standard insurance is to pay claims; if the policyholder does not intend to actually seek recovery from its insurers, there are other, more cost-effective risk management strategies (self-insurance, fronting policies, etc.) the company should consider.

2. Keep it Simple. Insurer notification need not be daunting from the perspective of content. Keep it simple. If the notice is of an event or condition that may give rise to a claim (under liability insurance), a very brief description (who, what, when, where and not why) gets the ball rolling. If the insurer wants more information (or is even entitled to it under the policy), its claim representative will know how to ask. If the notice is about a property loss, an equally brief description should suffice: there will be plenty of opportunity for excruciating detail when the proof of loss comes due. If the notice is of a claim or suit, enclose copies of the papers. Insurers rarely, if ever, defeat otherwise meritorious coverage claims because the initial notification omitted some detail the insurer was entitled to know.

It is helpful, though not required, to be specific about identifying the person with whom the insurer should correspond, providing contact information, and to request that the insurer immediately notify that person of the claim number assigned to the matter and the identity of the claim representative, with contact information. The claim number is particularly important because claim representatives are a notoriously transient lot; one often ends up dealing with a series of claim representatives before an insurance recovery is finally realized.

If there is anything more an initial notice should contain – and even this should be unnecessary – it is a demand for performance under the policy. This can be as simple as a reference to the policy number in the subject clause of the letter and a request that the insurer provide an indemnity for the loss, or a defense to the suit, as the case may be. This should be unnecessary because the insurer knows what it promised to do when it issued the policy; it may be helpful because insurers have been known (disingenuously) to treat a notice as "informational" absent a demand for performance.

3. Notice Must Reach the Insurer. Many policyholders are inclined to employ the services of a broker to handle insurer notification. Some brokers do this quite well. Others less so. The important point to remember is that insurance policies require notice by the policyholder to the insurer. Notice to a broker is not notice to the insurer. Even if the policyholder has no choice but to provide notice through a broker (as in the case of coverages placed at Lloyd's of London), it is always prudent to require the broker to furnish some evidence of an acknowledgement of notice from the insurer. The good brokers will pass along the acknowledgment without being asked. The notice task should not be considered complete until the acknowledgment is in hand.

4. Institutionalize. One common scenario that can lead to delayed notification is that in which company personnel who are aware of an event or loss are not sensitized to the potential for insurance coverage. It is beyond the scope of this paper to provide detailed risk management program recommendations, but the hallmark of an effective claim notification component of such a program is to identify company personnel who are likely to become aware of losses or liability engendering events and to advise them (and remind them, repeatedly) of the company point of contact (risk manager, chief financial officer, etc.) they should notify in the event of a loss. And they too can be advised that, when in doubt, they should let that person decide whether the event or loss is potentially covered.

5. All is Not Lost (if Notice is Delayed). Finally, important as it may be to avoid a "late notice" debate with an insurer, it is also important not to assume that all hope of coverage is lost because notice has been delayed. Once the potential for coverage is recognized, notice should be given, notwithstanding that it is indisputably delayed. The courts of many states will refuse to find a forfeiture of coverage based on late notice unless the insurer can prove that the delay substantially undermined its ability to investigate, adjust or defend the claim. Insurers also have been known occasionally to overlook late notice issues. Late notice makes the pursuit of coverage more of an uphill battle than it would have been otherwise, but in many cases the reward will still be worth the effort.

B. Insurer Reservations of Rights

The insurer's response to a policyholder's initial notice of a loss or claim frequently is in the form of a "reservation of rights" letter. Such a letter typically will include: (i) an acknowledgement of receipt of notice from the policyholder; (ii) a statement that the insurer is starting an investigation of the claim or loss; (iii) a list of specific bases on which the insurer may later decline or limit coverage; and (iv) a catch-all reservation of a claimed right to raise other questions about coverage in the future. "Reservation of rights" letters are employed by insurers to in an attempt to prevent the policyholder from claiming that the insurer's actions (or inaction) in response to a claim stop it from taking what seem to be inconsistent positions in the future. It is important for policyholders to understand that reservation of rights letters are not magic; that they do not always preserve all options for the insurer; and that they may in fact create rights the policyholder otherwise would not have. It is also important for policyholders to understand that "strategic letter writing" is not solely the province of the insurer.

1. Independent Counsel Rights. In the context of liability insurance, an insurer typically makes two promises: that it will defend the policyholder in any lawsuit alleging liability of a kind falling within the coverage, and that it will pay on behalf of the policyholder any amount for which the policyholder is held liable, so long as the basis of the liability is within the coverage of the policy. When your company is sued, it is often the case that the allegations of the lawsuit will fall partially within and partially outside the scope of the coverage. The classic example is the lawsuit that alleges that your company intentionally caused harm or, if the injury was not intended, then it was at least the result of negligence. Liability for an intentionally caused injury would not be covered, whereas liability for negligence would.

In such cases a liability insurer often will agree to provide the policyholder with a defense (because of the negligence allegations) but reserve the right to refuse to pay the claimant on behalf of the policyholder if it is ultimately determined that the injury was intended. The insurer's reservation is proper, but it comes at a price. Generally speaking, liability policies give the insurer the right to control the defense – the right to choose the lawyer who will defend the policyholder, to determine defense strategy, and to decide whether to settle or go to trial. Most courts hold, however, that this right of control is lost when an insurer reserves a right to refuse to satisfy any liability that may be imposed. The insurer must cede control because it cannot be allowed to adopt a defense strategy that is dictated by its own financial interests. So, for example, it cannot hire a lawyer and tell her to defend the case in such a way as to assure that, if liability is imposed, it is imposed only on a non-covered ground.

In these circumstances, courts say that the policyholder is entitled to "independent" counsel – a lawyer who has no relationship with the insurer. This means that the policyholder gets to choose the lawyer – whether or not he or she is someone the insurer would have chosen – and the insurer must pay the lawyer's bills, so long as the charges are reasonable. This lawyer's duty of loyalty will extend to the policyholder alone, and it will be perfectly appropriate for this lawyer to defend the case in a way that maximizes the likelihood that any liability imposed will be within the coverage of the policy – and the insurer will be required to pay. The insurer's "reservation of rights" thus can ultimately work in the policyholder's favor – if the policyholder recognizes and asserts its right to independent counsel. This is one reason why it is usually wise to show an insurer's reservation of rights letter to the company's lawyer.

2. Reservations of Rights and Inconsistent Positions. Just because a "reservation of rights" letter says the insurer is reserving all of its rights under the policy does not mean the insurer will actually succeed in doing so, regardless of its actions. For example, property policies often have very formal and strict requirements for submission by the policyholder of a "proof of loss" (detailing the nature and claimed amount of the loss). Often, the policy will say that the policyholder must submit the proof of loss within, say, 120 days from the event. In responding to the claim, however, the insurer might behave in a variety of ways that are inconsistent with insisting upon strict compliance with this requirement. Perhaps the insurer and personnel of the policyholder will be in the midst of a series of meetings discussing the loss when the policy "proof of loss" deadline arrives. If the insurer's actions have reasonably led the policyholder to believe that the insurer has chosen a different approach to adjusting this loss than the procedure contemplated by the policy, the "proof of loss" deadline will be held to have been waived. And it will not matter that the insurer asserted a "catch all" reservation of rights in response to notice.

Courts also increasingly refuse to sustain inconsistent positions insurers often take, regardless of what the insurer may have said in a "reservation of rights" letter. For example, suppose that, in response to notice of a loss, the insurer sends a reservation of rights, including a right to refuse coverage on the basis that the policyholder's notice of the loss was late. Suppose further that, after taking a harder look at the loss, the insurer concludes that it falls entirely outside the scope of the coverage of the policy and refuses coverage outright. So the policyholder sues the insurer and the court says the insurer was wrong: The loss is within the scope of coverage. Can the insurer still try to defeat coverage based on late notice, pointing to its reservation of a right to do so? Many courts have said "No." As mentioned above, in most states, an insurer cannot avoid paying a claim based on late notice unless the delay somehow undermined the insurer's position. Many courts have said that, if the insurer was just going to refuse coverage on some other ground, it cannot contend that it was harmed by late notice – all that earlier notice would have done was lead to an earlier coverage denial. So if an insurer's "we don't cover that type of loss" position is overturned, "late notice" will not provide rearguard protection.

3. Two Can Play the Letter-Writing Game. A final point to understand about "reservation of rights" letters is that there is nothing magic about them. These letters are just a "papering of the record" to permit the insurer maximum flexibility. Policyholders can play the same game just as skillfully. For example, one of the most frustrating things about dealing with insurers is how slowly they move toward resolving claims. In the liability context, often the most cost-effective way to resolve a claim against your company is to make a quick, practical settlement. Yet insurers are set up in such a way as to make it next to impossible to strike such a settlement with insurer funds. The adjusters they assign to the case typically have next to no experience and next to no authority. They also tend to move on to greener pastures and get replaced with stunning frequency. This is not a recipe for agility or decisiveness.

Yet it still may be that the best thing for your company is that quick settlement. Here is where the policyholder letter-writing campaign comes in. In a situation such as this, the policyholder should write a series of letters making quite clear that quick action is crucial, that the insurer is not actually handling the claim – but rather forcing the policyholder to do the work – and that, ultimately, it was the insurer's inaction and indecisiveness that have forced the policyholder to take the reins and resolve the case. If the policyholder makes a record that the claim actually took such a course, in spite of repeated requests that the insurer live up to its obligations, then in a subsequent suit to recover under the policy, the policyholder's letters likely will carry the day, and the slothful insurer's "reservation of rights" will be for naught.

III. THE DUTY TO COOPERATE

A. Assisting the Insurers' Investigation or Defense

Insurance policies almost invariably contain "conditions" that require the policyholder to cooperate with the insurer in the event of a claim or loss. In the liability context, the insurer is entitled to reasonable assistance from the policyholder in conducting its investigation or settlement of the claim and defense of any lawsuit. If the policyholder has unique access to information about the claim (for example if its personnel witnessed pertinent events), it must share that information with the insurer. If the policyholder's personnel are called to testify in a deposition or at trial, they must prepare with insurer-appointed counsel, show up at the event, and testify truthfully. In the property insurance context, the insurer is entitled to learn whatever the policyholder knows about the circumstances of the loss. All of this makes a great deal of sense, and it is rare that business policyholders run into problems providing this type of cooperation.

But insurers will not hesitate to use cooperation clauses to help them maneuver toward defeating a coverage claim or to develop an additional ground to avoid coverage for a claim to which they are hostile from the start. For example, insurers often will cite a cooperation clause as a basis to demand information from the policyholder that is not relevant to the insurer's investigation of the underlying claim or loss, but only to the question whether the coverage applies. In other words, insurers often will try to force the policyholder to offer up the very information the insurer will then rely upon in denying coverage. In other circumstances, an insurer who has decided to resist coverage may seek to impose cooperation burdens so heavy that the policyholder inevitably will fail to fully comply, thus providing the insurer with an additional ground to deny coverage – a "failure to cooperate." When insurers engage in such tactics, the insurance recovery process again becomes a game the policyholder can play to win.

1. Statements/Examinations Under Oath. In the property insurance context in particular, insurers are entitled to take statements from policyholder personnel with knowledge of the circumstances of the loss. The inquiry may take the form of an examination under oath. In the liability insurance arena, insurers sometimes will send an adjuster to conduct one or more interviews, and the interviews usually will be recorded. Generally speaking, compliance by the policyholder is mandatory. But just because the examination typically cannot be avoided does not mean that the policyholder cannot exercise a measure of control over process and content. Unfortunately, policyholders do not always understand what is at stake at this stage and make critical – and unnecessary – errors that may defeat coverage or create an issue that will steer the matter toward expensive and uncertain litigation. It is imperative, therefore, that policyholders appreciate the potential significance of the examination and approach it with the utmost seriousness.

The policyholder may or may not be permitted to designate the person who will sit for the examination. If the company is permitted to make the choice, the person it selects should be knowledgeable, both regarding the loss – what the company does and does not know – and regarding the nature and scope of the coverage, including potentially applicable policy exclusions. If the insurer designates a particular individual to be examined, then that person must be educated. The key is preparation, and the insurer will have little choice but to allow the company a reasonable time to prepare. Careful preparation will permit the person examined to portray most accurately the information available to the company and to do so in a way that does not unnecessarily compromise the company's prospects for an insurance recovery.

In the precious metals industry, for example, the nature of the property interest the company has in the metal that is the subject of the insurance may vary, or may be affected by transfers or commingling. The person being examined by the insurer after loss must understand the nature and intended effect of any transactions that may have occurred before the loss and how the insurance was intended to apply to the metal in light of those transactions. This is not to suggest that the assistance of an attorney will be necessary in every case, but participation by the company's risk manager or insurance broker may be advisable to assure the best possible outcome. A person who understands how the coverage works is much less likely to describe the circumstances of the loss in a way that is both inaccurate and coverage-defeating.

That said, it is important to understand that the company is entitled to have the assistance of an attorney in responding to a request for an examination. If the stakes are high and the insurer seems reluctant to confirm that the coverage applies, it may make sense to retain an attorney to assist in preparation for the examination. This will make the attorney-client privilege applicable to what is said during preparation while the attorney is present. The policyholder also has the right to have the attorney attend the examination itself. Of course, the attorney will not be the one answering the questions, but he or she can help to make sure that the questions are not misleading or unclear; he or she can help

the witness "examine the examiner" to make sure there is no misunderstanding or inadvertent mistake. While attorneys are expensive, and will not always be necessary, this area can be one in which an ounce of prevention is indeed worth a pound of cure. If an insurer approaches an examination with an anti-coverage agenda, the policyholder must still cooperate, but should do so understanding that an adversarial relationship may already have arisen, and should act accordingly.

2. Burdensome Requests for Information. Another potentially difficult task in the realm of cooperation with the insurer is compliance with written requests for information or documents. Again, assuming the insurer has not yet declined coverage, there is little choice but to comply. And this is true even though the insurer may be transparently hostile. Indeed, hostile insurers tend to employ requests for information as a tool to discourage the policyholder from further pursuing coverage, or as a means to concoct a "failure to cooperate" coverage defense. Here as well, the trick in parrying the insurer's tactics lies in how compliance is achieved. The key is to show a willingness to comply, but to do so in a way that compels the insurer to assume much of the burden. If this is done effectively, either the insurer's requests will be satisfied without inordinate effort by the policyholder or (as occurs with impressive frequency) the insurer will simply drop its demands.

A typical, deliberately burdensome insurer request for information will ask the policyholder company to provide copies of numerous categories of documents and written answers to a long list of questions. Unless the policyholder business has capable employees with plenty of time on their hands – a rare circumstance, to be sure – this sort of request tends to get "back burner" treatment. The time and effort that will be required to respond seems stifling, and there will be no immediate reward for compliance. At a minimum, the insurer's interest in delaying payment will be served, and the policyholder may begin to view the road to recovery as long and uncertain. What should the policyholder company do?

The key point to understand is that the insurer's right is only to have access to information. The courts do not require the policyholder to toil endlessly to satisfy the insurer's demands. Thus, it is not necessary for the policyholder to locate and copy at its own expense every document in which the insurer may express an interest. Instead, the policyholder's response to a request for documents can be simply to invite the insurer's adjuster to visit the company's place of business and inspect its business records. The policyholder need not grant the adjuster access to every document it possesses; rather it can set aside a conference room and place in it just those files that are reasonably likely to contain documents responsive to the insurer's requests. The adjuster can be told to place a marker (such as a post-it "flag") on the documents he or she wants copied, and to identify a copying service with which the insurer has an account. The policyholder then can make a record (or an extra set of copies) of the documents the insurer has requested – so that it knows what the insurer has. And most of the effort and expense will have been borne by the insurer.

Similarly, the policyholder need not provide a lengthy written narrative in response to the insurer's questions. Where the answers can be derived from a review of documents, it is enough for the policyholder to tell the insurer so and then follow the procedure just outlined. If the information is not available in documentary form, then the insurer can be invited to speak with knowledgeable persons and – so long as they are prepared as discussed in the preceding section – the insurer will get the information to which it is entitled without undue burden on the policyholder and without adverse consequences to the policyholder's position. Insurers know that a practical response such as this is sufficient, and they will go along. And when their own personnel are forced to devote time and effort to get the information they are seeking, it can be quite striking how much more practical and reasonable their requests become.

B. Non-Covered "Voluntary Payments"

In the liability insurance context, another aspect of the policyholder's duty to cooperate is its obligation to let the insurer decide whether to make

payments or assume obligations. If the policyholder acts independently, the insurer may brand any outlay the policyholder makes a non-covered "voluntary payment." Worse, the insurer may claim that the making of the payment undercut its ability to defend the case as a whole and it may deny coverage outright. When the insurer is actually on the scene, actively (and competently) handling defense and settlement opportunities, problems of this sort are not common. When the insurer is not constructively engaged, however, the policyholder may feel compelled to act in its stead. Again, there are ways to deal with such situations that can maximize the likelihood of an insurance recovery.

1. The Do-Nothing Insurer. In the discussion above concerning reservation of rights letters, we examined the potential value of a letter-writing campaign to force the hand of a slow-acting insurer – or at least to make a record of its behavior. Part of the reason for such a campaign is to prevent the insurer from successfully claiming at a later date that payments made by the policyholder when the insurer failed to act were non-covered "voluntary payments." In such a situation, the policyholder arguably is forced to substitute itself for the insurer in handling the claim, and any payments it makes cease to be "voluntary."

Sometimes an insurer's inaction will stem from hostility toward the claim, sometimes from pure ineptitude of its personnel. In such circumstances "making a record" through letter-writing may be all that is necessary. On other occasions, however, the insurer's inaction may be due to adherence to an inflexible claim-handling model. The insurer's preferred approach may be to pay little heed to pre-suit written demands by claimants; to force the claimant to file suit (against your company) and to defend the case on every plausible basis. Meanwhile, your company may see and wish to take advantage of opportunities for creative approaches to early settlement. Given that the policy does in fact provide the insurer with the right to control defense and settlement of claims, what (besides writing letters) can the policyholder do?

The key thing to understand here is that courts do not allow insurers to exercise their right of control unreasonably. Many states have "unfair claim settlement practices" laws that require insurers to settle claims against their policyholders where liability is reasonably clear. Those states often provide for the policyholder's recovery of multiple damages and attorney's fees if the insurer fails to settle with the claimant despite the fact that liability is reasonably clear. Moreover, if in such a case the insurer's refusal to settle at a time when it can do so within policy limits causes the liability to reach a point beyond policy limits, courts will hold the insurer liable for the entire amount, regardless of policy limits.

Knowing that these rules and enforcement mechanisms exist, policyholders can adopt various strategies to help ensure a satisfactory result. A couple of examples should illustrate the concept. One approach might be described as taking the letter-writing campaign to the next level. The policyholder can actively solicit settlement demands and pass them on to the insurer. The policyholder can arrange a meeting with the claimant to which the insurer's adjuster is invited. The idea is to "rub the insurer's nose" in the settlement opportunities that exist, if it would just take out its checkbook. Insurers may resist these efforts – in which case it's just another way of making a record – or, once in a while, they may actually wake up, engage, and do the right thing.

Another strategy is to retain a "personal" lawyer, not paid by the insurer, to monitor the insurer's handling of the case and to exert pressure on the insurer to settle within policy limits when the time is right. This attorney need not devote a great deal of time to the matter, but his or her communications can be an effective means of pushing the insurer to act. Often the approach will be to have the attorney prepare a liability and settlement analysis, recommend settlement within policy limits, and remind the insurer of its potential liability in excess of policy limits if it fails to enter into a settlement. Such communications often will yield results, particularly if they are based on a more careful analysis than the insurer (or its appointed counsel) has performed.

2. <u>"Pre-Tender" Costs</u>. Sometimes a policyholder's "voluntary payments" may be made even before the insurer has been notified and asked to defend. As discussed above, delayed notification happens. And when it does, the policyholder may already have spent substantial sums on attorneys and consultants before realizing the claim may be covered. Insurers will just about always refuse to reimburse these expenses when notice finally is given. There is little in the way of practical advice to give on this issue, other than to point out that, in a number of states, the courts will not sustain the insurer's refusal, so long as the expenses were reasonable and prudently incurred, and the actions taken before notification did not undermine the insurer's position. So, the good news is that these costs may be recoverable; the bad news is that the company likely will have to sue the insurer for a recovery to be realized.

IV. INSURER "SUBROGATION" RIGHTS

A. Subrogation Principles

In the event of a claim or loss, your company may have both insurance coverage rights and rights over against other parties. For example, in the case of an embezzlement loss, the company may have both coverage under a crime insurance policy, and a right to sue the dishonest employee. In the case of a liability claim, the company may have both coverage under a liability insurance policy and an entitlement to be indemnified by a third party. Under most – though not all – insurance policies, the fact that the policyholder may have rights against others does not relieve the insurer of its coverage obligations. Instead, once it has paid the claim, the insurer will have the right to "step into the shoes" of the policyholder and pursue the policyholder's claims against others. In these circumstances, the insurer is said to be "subrogated" to the rights of the policyholder. The policyholder is referred to as the "subrogor" and the insurer is referred to as the "subrogee."

The subrogation relationship generally is beneficial to the policyholder. The value of rights of recovery against third parties is limited by their financial worth. For example, the former employee embezzler may have squandered the embezzled funds on a gambling habit. The insurer effectively assumes that risk, and that's one of the good reasons to buy insurance. Also, if the insurer pursues the rights, then the policyholder avoids costs of litigation. Nevertheless, insurer subrogation rights can be a source of frustration and friction where the insurer is hostile to the claim or fails to deal with it in timely fashion. Here too, careful strategic thinking and action on the part of the policyholder may be required.

B. Duty to Preserve Insurer Subrogation Rights

Insurer subrogation rights can arise with or without express recognition in the policy language. What is almost always in the policy is an "anti-impairment" provision. An anti-impairment clause is a promise by the policyholder that it will do nothing after loss that would impair the insurer's subrogation rights. The idea is that, if the insurer covers the loss, it should then be in a position to maximize its own recovery from third parties, and should not be limited in that respect by anything the policyholder has done. Perhaps the most common example of impairment of subrogation rights is the policyholder releasing its rights against a third party. In most circumstances, the release given by the policyholder will also destroy the insurer's subrogation rights.

Difficulties with "anti-impairment" provisions can arise when the insurer does not promptly acknowledge coverage or pay the claim. For example, the insurer may be slow in conducting an investigation and deciding whether or not to provide coverage, and the insured may have reason to believe that a liable third party is in the process of putting assets out of reach. In such a circumstance, the policyholder may feel compelled to sue the third party and attach its assets or to strike a quick settlement, and all the while the insurer claims it is not ready to commit. The policyholder seemingly is caught in a dilemma: pursue the claim and be subjected to post-hoc criticism for impairing subrogation rights, or let it go, only to learn at a later date that the insurer will not be providing coverage.

Again, a rule of reason will apply, and effective communication is critical. If claims that may involve insurer subrogation rights must be resolved before the insurer has taken a position, then the insurer will not be permitted to stand in the way. When the policyholder comes to perceive the need for prompt action on the third-party claim, this fact, and the underlying reasons, should be explained to the insurer – in writing. If quick action is indeed necessary and the insurer does not take it, then the policyholder can proceed itself, and the insurer will be bound by the reasonable actions taken – including settlements with third parties – regardless of any "anti-impairment" clause in the policy. The main purpose of the policy is to protect the policyholder against loss; the courts do not subordinate that purpose to potential insurer subrogation rights when the insurer has yet to pay the claim.

V. CONCLUSION

For most companies, insurance premiums are a major expense. The precious metals industry is no exception. But paying premiums, standing alone, does not guarantee that the company will get the coverage it expects. To get the most out of the policy, the company also must be prepared to pursue its coverage rights in an energetic and sophisticated way. At times, this can resemble something of a chess game. But it is a game the policyholder can win.

A DYNAMIC SIMULATION MODEL FOR EXAMINING THE IMPLICATIONS OF LIMITED MATERIALS AVAILABILITY*: THE CASE OF PLATINUM*

(This paper was originally presented at the 2008 IPMI Conference)

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ABSTRACT

Recent South Africa power shortages have demonstrated the risks of source concentration within the platinum supply chain. High market concentration is one of a number of metrics that can be used to signal the presence of material scarcity risk to firms. This paper describes the development and application of a simulation model to examine scarcity risks to firms reliant upon platinum suppliers. The model strives to capture the dynamics of platinum market supply, demand and price. The detailed structures of supply and demand are key features of the model. Results show that risk-mitigation strategies available to downstream firms are increased emphasis on recycling, source relocation and material substitution.

INTRODUCTION

Platinum prices have recently increased significantly relative to historic prices. Between 1999 and 2007, demand outpaced supply and the net movement in stocks has been negative (see Figure 1). In early 2008, power shortages in South Africa led to a further increase in pressure on primary supply and prices have risen from less than $1500/oz in January to over $2000/oz in May [1]. As economic theory states, increasing prices indicate materials scarcity: conditions where demand exceeds supply and shortages occur.

Economists have noted that demand decreases and supply increases in response to high prices [2, 3]. A number of mechanisms underlie these responses, including price elasticity, material substitution, technological development, and increased capital investment. As a result, such price increases have typically been short-term, lasting only a few years.

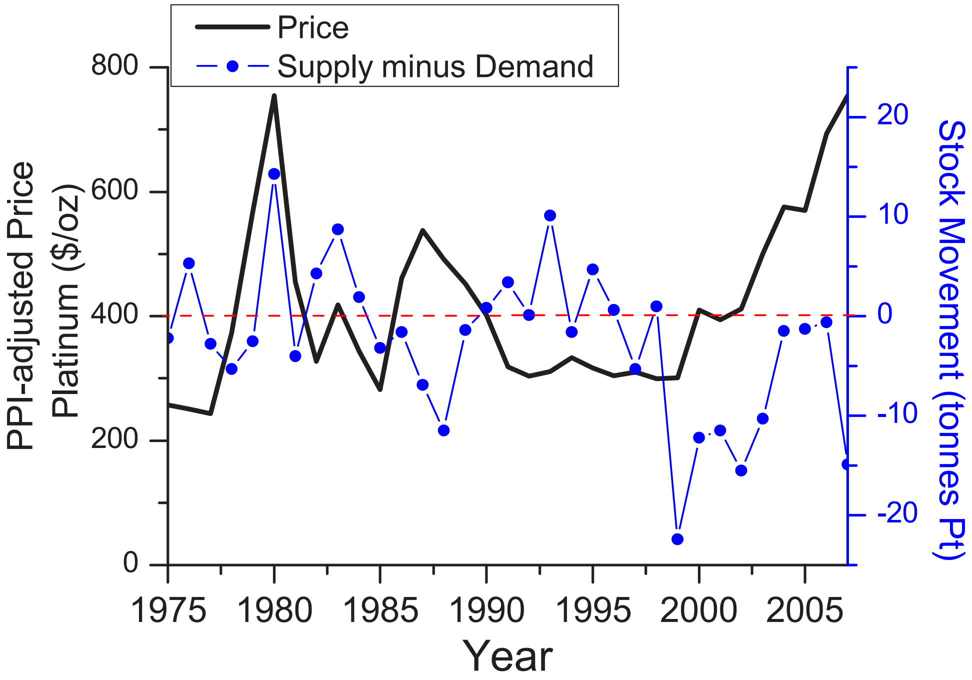

Figure 1: 1975 to 2007 data: platinum prices (adjusted by the commodity producer price index) are plotted with black line (left axis) and the net movement in stocks (supply minus demand) is plotted with the dotted blue line (right axis) [1, 4, 5].

This assessment has been made from a global market-oriented perspective, but not on a regional, localized or firm level. In fact, although supply shortages and their resulting price spikes may be temporary, an historical case-study of the cobalt shortage in the 1970's has shown that there were technical, operational and geographic outcomes for firms that could easily be permanent [6]. Examples of outcomes observed during the 1978 cobalt crisis are:

- Technical: substitution, increased efficiency of use
- Operational: increased recycling, stockpiling
- Geographic: source relocation

Stakeholders in the platinum group metal (PGM) supply chain have also experienced materials shortages in the past, for example, the palladium shortages in the late 1990's. The shortages were partially attributed to shipment delays and other uncertainties in supply from Russia, which in 1997 produced 43% of global palladium. Skyrocketing demand, in particular a 38% annual growth in the automotive industry and speculative demand, far outpaced supply of palladium [7]. As a result, prices quadrupled over the three-year period between 1998 and 2001. This dramatic price increase led to equally dramatic changes in demand: demand in 2002 was almost halved from 1999 peak levels [5]. 2007 demand remained below 1999 levels, despite relatively healthy growth (see Figure 2).

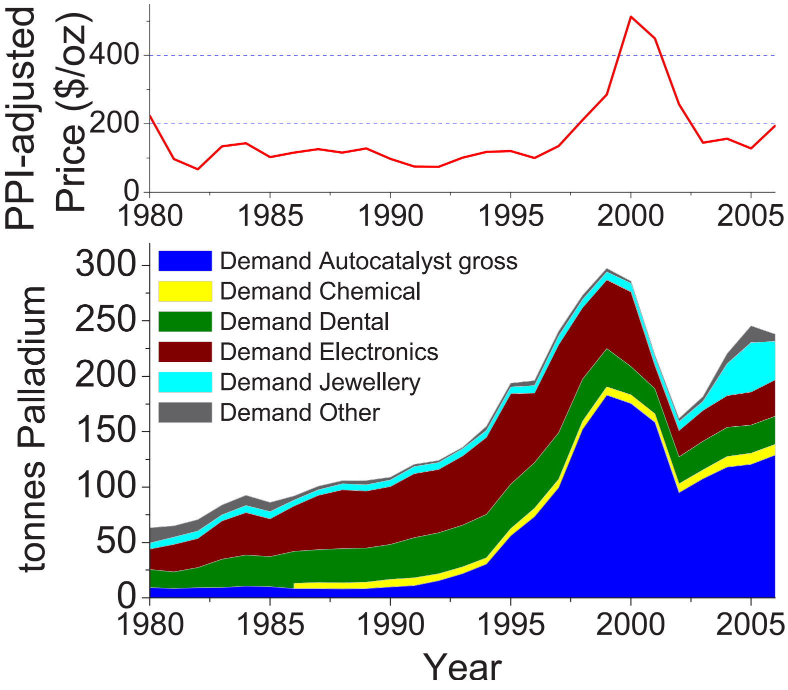

Figure 2: Historical palladium demand response as a result of price increases [5].

The cobalt and palladium disruptions exemplify the risks of materials scarcity due to supply concentration in a single country. In both cases, a large percentage of world supply of a given metal depended on a single country's production and global markets were severely impacted when local supply interruptions occurred.

These historical examples highlight the need for better consideration of the risks of unexpected materials scarcity for firms reliant on their upstream material suppliers. Firms' strategies in the face of price increases require time to implement and therefore reacting only post facto to increasing prices is a poor mode of managing risk [6]. The long term outcomes for downstream firms and the time required to respond to scarcity motivate the need to answer two questions:

- What material systems are at risk for scarcity?
- What actions should firms take to mitigate that risk?

Numerical measures of risk for scarcity, including metrics for platinum scarcity, have been examined in previous work as a way to screen material systems, identifying those that are at risk for scarcity [6, 8]. In the cases where metrics identify the need to address scarcity, firms need to have on hand effective strategies to mitigate their risks. This paper discusses recent work which examines the dynamics of the platinum market and focuses on addressing the question of which actions firms can take to mitigate risk.

THE CASE FOR PLATINUM

Three aspects of the platinum market are most likely to pose greater risk of unexpected future increases in platinum scarcity.

The first risk is for market inefficiency arising as a consequence of a high concentration of platinum supply measured on both a firm and geographic basis. Primary supply of platinum is concentrated in South Africa (75% of production, 88% of reserve base) [9] (see Figure 3). Five companies (Anglo Platinum, Norilsk Nickel, Implats, Lonmin and Inco) control most of the supply [10].

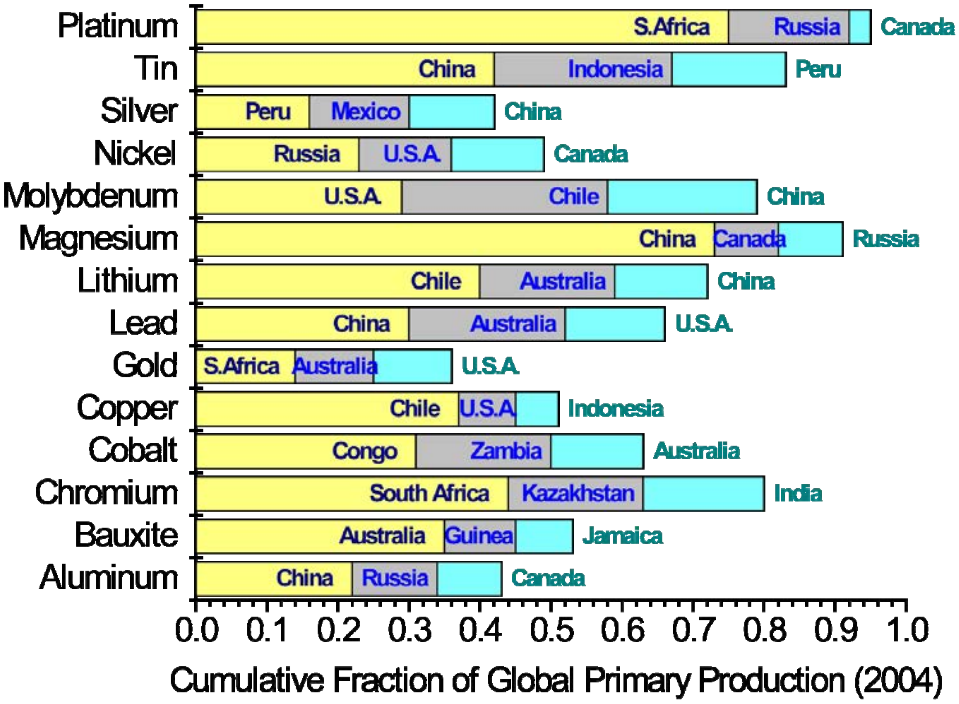

Figure 3: Country distribution of primary production [9].

There is also the potential for a large increase in demand for platinum if proton exchange membrane fuel cells become a key component for reducing greenhouse gas emissions in the transportation sector. PEM Fuel cell technologies typically use platinum to catalyze the electrochemical reaction that produces electricity. Estimates of platinum requirements for a typical fuel cell car range between 15 and 100g/car, significantly more than the platinum used for a typical catalytic converter (~5g/car) [11]. Presently, there are poor substitute options for platinum in PEM fuel cell applications. Potential substitution options are other platinum group metals, such as palladium, which are mainly mined alongside platinum.

The third risk is that cost of extraction is more susceptible to energy price increases than that of most other metals because of typical platinum ore grades. Platinum ore grade is 3 orders of magnitude lower than copper, nickel, tin, zinc or lead (see Table 1).

Platinum reserves relative to primary production are much larger than those of other metals (Reserves/Production in Table 1). Geophysical supply of platinum is abundant relative to demand for the metal. Although much of the literature examining materials scarcity examines geophysical scarcity, which is a long term concern [2, 12-15], scarcity also occurs through market inefficiency, as in the cases for cobalt and palladium. Regardless of its drivers, scarcity's long term impacts and the conditions indicating risk of platinum scarcity motivate this work.

Table 1: Comparison of metrics of scarcity for metals. References are: Ore grade [16], price (monthly average for October 2007, www.metalprices.com), energy (Simapro, Ecoinvent database), Reserves/Production [9].

Metal	Ore grade (wt %)	Price ($/tonne)	Energy (MJ/kg)	Reserve/ Production (years)
Magnesium	70-95% $MgCO_3$, brine 3% Mg	2938	257	Very large
Aluminum	35-50% Al_2O_3	2391	201	157
Iron	30-65% Fe	645	12	112
Lead	4-8% Pb	3227	21	21
Zinc	2-4% Zn	2881	85	23
Copper	0.2-5.0% Cu	7773	64	32
Nickel	1.5% Ni	30,748	195	44
Tin	0.5% Sn	15,023	324	23
Cobalt	0.4% Co, byproduct of Cu, Ni, Ag	65,725	132	134
Silver	0.006% Ag, byproduct of gold and base metals	415,080	Not available	14
Platinum group metals	0.0003-0.002% PGM, sometimes a byproduct of Ni-sulfide ores	42,331,189	196,000-846,000	332

METHODOLOGY

A material market is a complex system comprising many stakeholders and dynamic feedback mechanisms that influence price, supply and demand over time. A decision by a stakeholder or an event occurring in one part of the market can affect global market dynamics, e.g. the historical cobalt and palladium cases [6].

For this work, system dynamics simulation is used. The platinum system is described by a set of non-linear first order differential equations. The model numerically simulates the behavior of key material market actors to study the impact of changing market conditions on changing material scarcity over time. Although market forces (especially price) ideally lead to a balance between supply and demand, market actors (suppliers, consumers, and market-makers) can choose to take actions that can lead to increased imbalances, sometimes arising from imperfect information or poor understanding of the appropriate strategies.

Systems with complex feedbacks such as material markets and the supply chain have been studied previously using system dynamics with ordinary differential equations [17- 21]. The model uses established system dynamics building blocks for a commodity market with a supply chain and product aging chains [22].

Figure 4 is a model structure diagram. Supply, demand and price are endogenous variables to the model. Supply and demand depend on a number of exogenous variables. Exogenous variables that determine primary supply are the rates of change of ore grade and technology, the delays involved in adjusting the production capacity, and the desired rate of returns (cash flows). Exogenous variables that determine secondary supply are product lifetimes, delays for changing recycling capacity, and the sensitivity of collection rates to price.

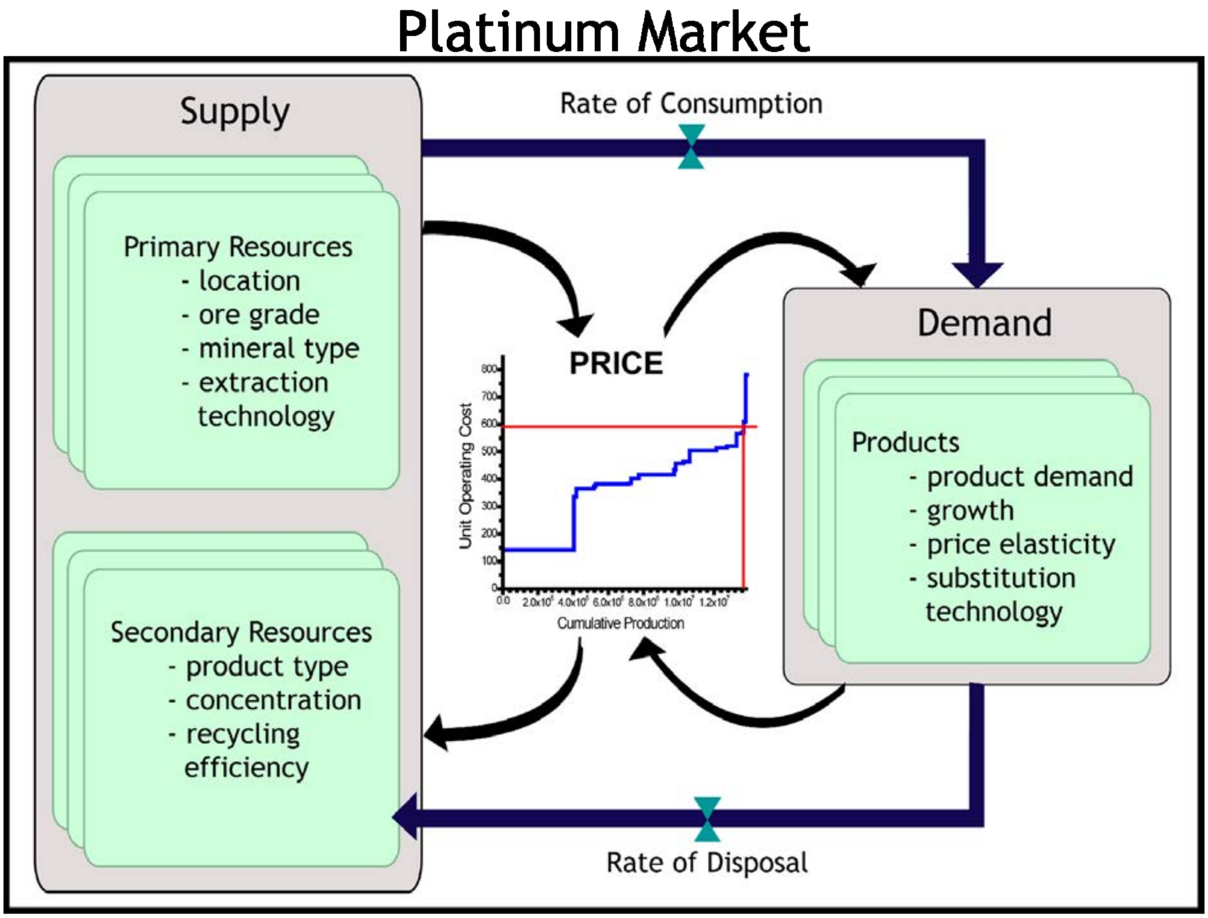

Figure 4: Market model structure diagram.

Material supply is the sum of primary (mined metal) and secondary (recycled metal) supply. The primary supply curve is modeled using the aggregated production from six major platinum-producing regions, with each willing to offer a set quantity of the material at a given price, depending on production cost and capacity. The secondary supply is modeled using estimates of product lifetimes, amounts of platinum in each product, collection rates and recycling efficiency. The model tries to capture cost and capacity based on resource data from platinum producers, recyclers and geological studies [5, 7, 23-30]. The six regions included for primary production are: Merensky reef, UG2 reef, Platreef, Great Dyke, J-M reef, Norilsk Nickel mines.

The aggregated demand for platinum is derived from demand for products such as jewelry, hard disks, automotive catalysts, and petrochemical catalysts. The demand model uses price elasticity and growth expectations for products that use platinum [5, 11].

The model dynamically determines the supply curve at any point in time by determining how much platinum is produced at any given operating cost (see Figure 5). The recycled metal is included here in the supply curve as the first point to show how it increases the total supply of platinum. It is assumed that the cost of recycling platinum is lower than for mining platinum and limited to the amount of platinum that can be collected and recovered. The model shifts price when there are imbalances between supply and demand. The model price can be greater or less than the marginal operating cost.

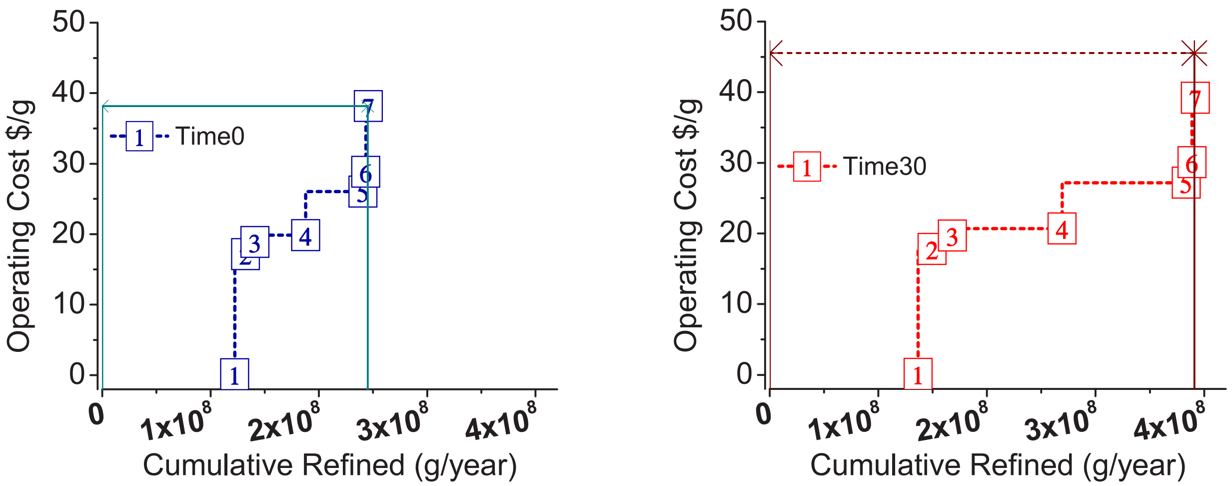

Figure 5: Dynamic supply curve at time 0 and 30 years under a case with some expected growth in demand for products that use platinum. Price and demand are identified by the vertical and horizontal lines that cross the x and y-axes in each figure.

PLATINUM MARKET MODEL INPUTS

This model tries to capture the complexities of the platinum supply and demand structures. This is achieved in part by using as much platinum supply and demand data and information about material market behavior as was available to the authors. Also, the model defines separate mining regions with different ore bodies and separate platinum applications with different demand behavior. This section describes some of the data underlying the model supply and demand sectors. There is still ongoing work in improving the model behavior to reflect platinum market behavior including continuing data collection.

SUPPLY SIDE

Platinum primary supply in 2005 was 206.8 tonnes with most of the world's primary platinum (77%) produced in South Africa's Bushveld region [5, 7]. The Bushveld region is rich in platinum group metals and contains about 80% of global platinum reserves [9, 31]. Data on global secondary supply were difficult to obtain, except in the case of autocatalysts, where it has been reported that 24 tonnes were recovered [5].

Five mining companies dominate primary platinum supply: Anglo Platinum, Norilsk Nickel, Implats, Lonmin and Inco [24]. The highly concentrated market structure of platinum is an advantage for modeling because there are fewer market actors to be modeled and from which data are needed.

Each company has a number of mines and smelting and refining operations. Data from individual mines were collected from company financial reports [5, 23, 25-28, 30]. Cash operating cost per gram of platinum and tonnes of platinum refined data were obtained where available and incorporated in the supply curve shown in Figure 6. Unfortunately, data on costs were not found for all mines, most notably Stillwater Mines in the US, and Sudbury and Lac-des-Iles mines in Canada. The mines that are included in this supply curve account for 70% of total 2005 platinum supply.

Norilsk Nickel reported the lowest costs ($1.19x107/tonne Pt or $369/oz Pt) and produced about 23.4 tonnes in 2005. Marula and Modikwa mines reported the highest costs, but these mines had not yet reached full production capacity. The cash operating cost per gram of platinum does not take into account other metals mined along with platinum, such as other platinum group metals, gold, nickel and copper and therefore is only an upper bound measure of the cost of mining platinum.

Price in 2005 fluctuated between $2.71x107/tonne Pt and $3.25x107/tonne Pt and averaged at $2.89x107/tonne Pt. For most mines, the cash operating costs per tonne of platinum were below the maximum price of platinum.

Mill head grades were also collected and found to vary between 1g PGM/t and 16g PGM/t. The percentage of total PGM that was platinum varied between 12 and 60% of PGM weight, with lower values for Stillwater mines and Norilsk Nickel and higher values for Bushveld region mines. Where historic data were available, mill head grade was found to have decreased with mine cumulative production over the past decade or so (see Figure 7).

USGS estimates indicate that reserves for platinum group metals are 71 thousand tonnes and that the reserve base is 80 thousand tonnes [32]. Mines also publish their estimated reserves and resources. Although gathered data only accounted for one third of USGS's estimates, they indicate that expected PGM grades for future production from these mines are between 1g/t and 20g/t.

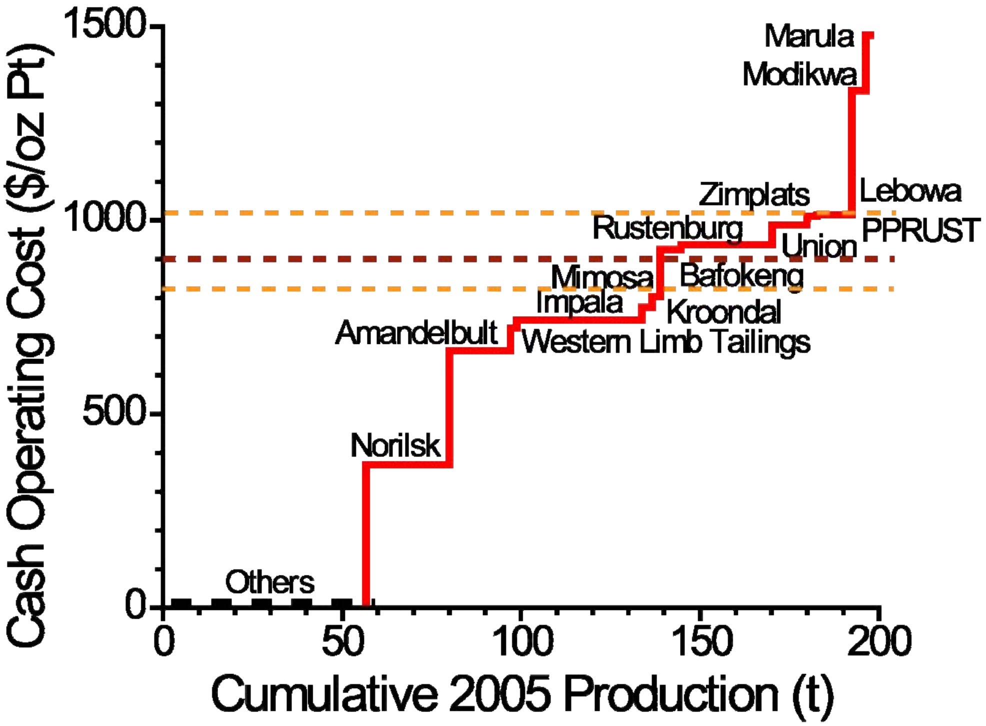

Figure 6: Platinum supply curve (70% covered, rest identified as "Others") with minimum, average and maximum prices marked by the dashed lines [5, 23, 25-28, 30].

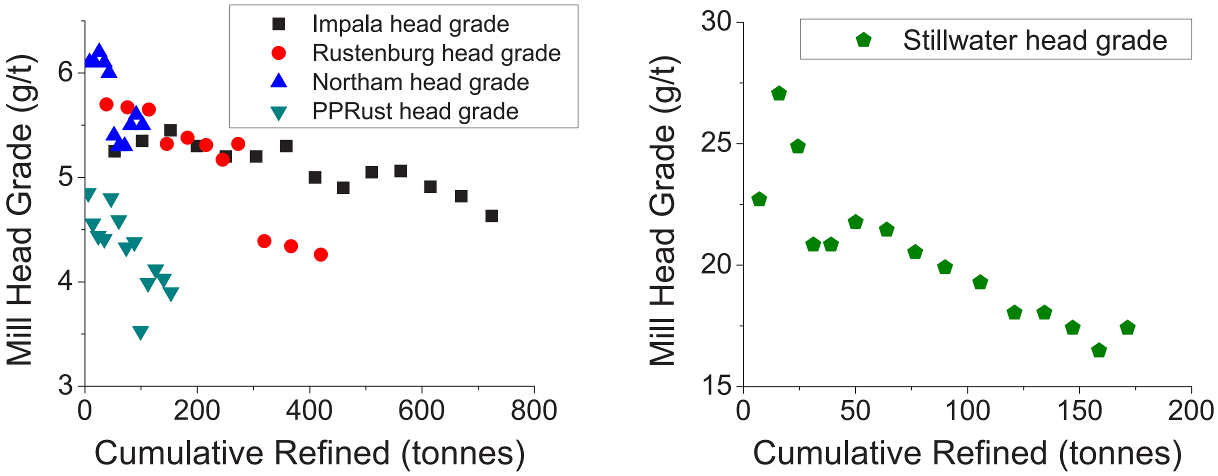

Figure 7: Decreasing trend for mill head grade (g PGM/tonne ore) over the life of four South African mines and Stillwater mines (USA).

DEMAND SIDE

Demand for platinum has been steadily increasing since the early 1980's. Two industries dominate demand: the jewelry and automobile industries (see Figure 8). In particular, platinum is desired for its catalytic properties, especially for diesel engines in cars sold in Europe where autocatalysts are needed to meet increasingly stringent environmental regulations. In fact, in 2007, Europe accounted for more than 82% of world platinum demand.

In the autocatalyst application for platinum, minimal substitution (except to other platinum group metals) is possible. Automotive platinum demand is considered relatively inelastic, whereas for jewelry, where gold and silver readily substitute for platinum, it is relatively elastic [11].

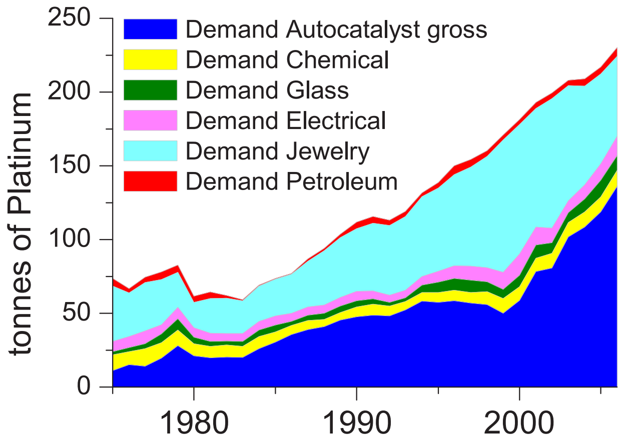

Figure 8: Demand for platinum from 1975 to 2006 [5].

DESCRIPTION OF MARKET FEEDBACKS

The model contains hundreds of variables and equations. The main stocks, flows and causal loops are shown in Figure 9. There are four main stocks (represented by rectangles): material resources, inventory of refined platinum, platinum in products that are in use and platinum in products that have reached end-of-life and can be recycled.

The platinum flows in the model are described here. Platinum starts out as a material resource in ore bodies found in Earth's crust. Primary extraction and recycling processes (flow rates represented by arrows and valves) make platinum ready for use in products. Manufacturers take the refined platinum and use it in products for consumer use

(consumption rate). Finally, when products reach end-of-life, they are made available for collection. Products not collected immediately, may accumulate in landfills for example.

Modeling the behavior of market actors involves answering questions such as: "On what basis does each market actor make a decision?" Feedback loops attempt to represent this behavior.

As prices increase, primary and secondary producers are motivated to increase production either through increasing capacity or increasing collection of end-of-life products. These actions help bring prices back down (balancing feedback loops B1 and B2). In the short term, primary producers may also try to take advantage of high profits to process lower grade, higher cost ores (reinforcing feedback loop to maintain cash flow R1). Increasing production also has the undesired consequence of depleting the mine's resources and increasing future costs of extraction. Technology improvement can offset those future cost increases, but requires time and money to develop.

On the demand side, high prices force consumers to consider alternatives and over time, high prices will lead to a decrease in demand which will help balance price (balancing feedback loop B3). Demand determines consumption of platinum and present consumption determines future availability of secondary materials (reinforcing feedback loop R2).

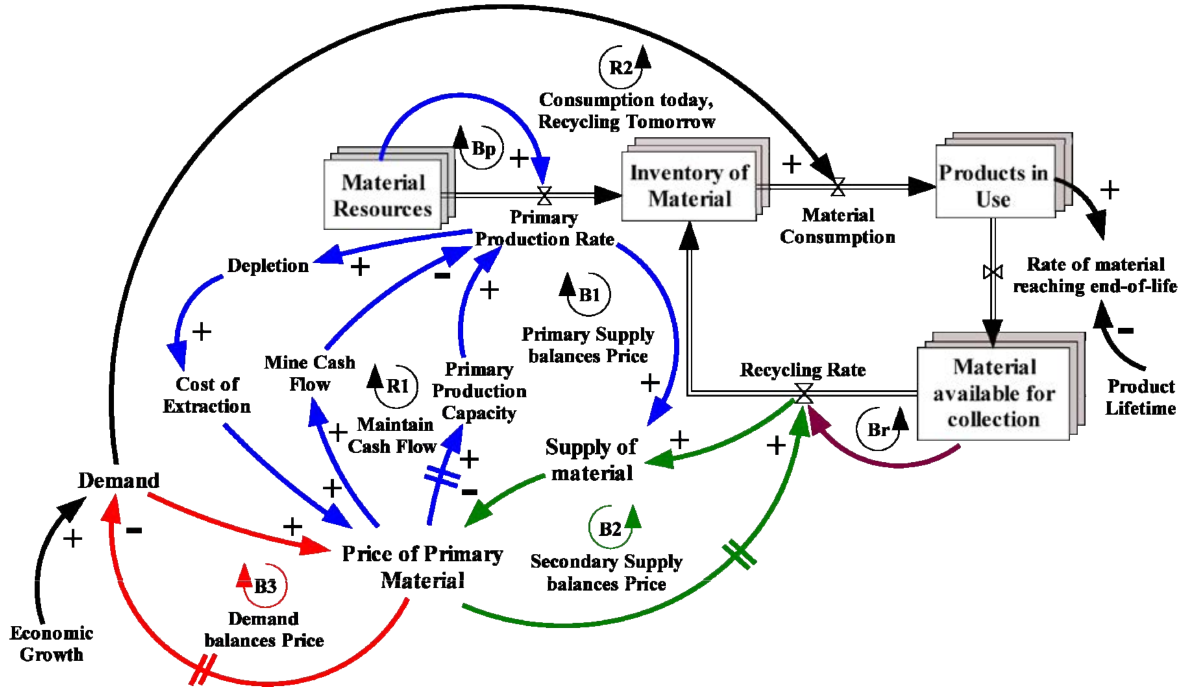

Figure 9: Causal loop diagram: schematic of feedback dynamics captured in the model.

MODEL RESULTS AND DISCUSSION

The model results are not attempts to predict future platinum prices. The model is designed as an experimental platform for examining the dynamics of metal markets in the face of risks for scarcity. Where possible, the model uses average platinum industry data such as mill head grade, operating costs, and price elasticity. However, the model has not yet been calibrated and the results provided are qualitative not quantitative.

The base case conditions for the model are:

- 50 year time frame, with 0.03125 year simulation time step
- 6 primary supply groups (mining regions), 4 demand groups,
- no exogenous product demand growth,
- initial demand: 245 tonnes/year,
- initial recycling rate: 50%.

For the following analyses, four simulation scenarios were examined with conditions outlined in Table 2.

Table 2: Description of conditions for simulation scenarios.

Scenario	Recycling	Perturbation
A	Base case	None
B	Half of base case	None
C	Base case	Largest supply group shuts down in year 10 for 1 year
D	Half of base case	Largest supply group shuts down in year 10 for 1 year

NON-PERTURBED SYSTEM

Scenarios A and B examine the effects of continued use of platinum in a market without growth in demand for products that use platinum and where unexpected exogenous perturbations do not occur. The no-growth scenario is a simplified case where effectively, suppliers can accurately predict future demand. This type of market is described as a well-behaved market.

The model shows that effects in a well-behaved market are straight-forward. As expected, the main driver for price is increasing marginal operating costs due to depletion of ore grade outpacing technological improvements in extraction. Recycling simply slows down depletion since it reduces the demand for primary metal (see Figure 10). Substitution away from platinum would also have the same effect.

The results of the two scenarios show that there are no significant increases in costs This is consistent with the platinum geological data showing that there are more than 300 years of known reserves relative at present extraction rates and that much of the reserves have similar ore grade to presently milled ores.

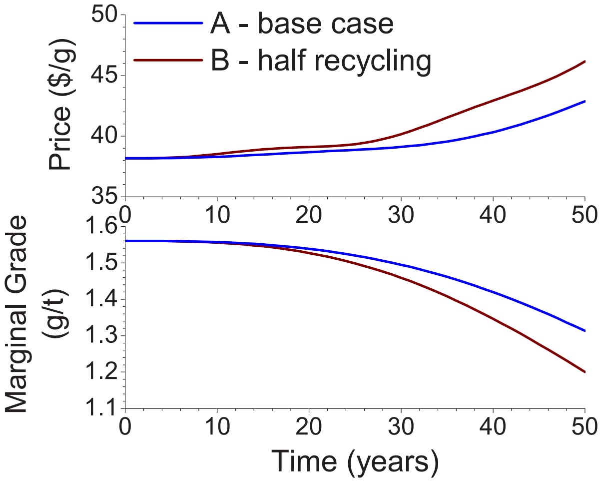

Figure 10: Comparison of modeling results for scenarios A and B. Price and marginal grade are plotted for the 50-year simulation period.

PERTURBED SYSTEM

The conditions for scenario C differ from scenario A in that the largest primary supply group is forced to shut down for 1 year. This exogenous model perturbation is very large since the largest supply group accounts for 43% of primary supply.

The impact of the unexpected 1 year shutdown on modeled price is dramatic as supply is unable to meet demand and inventory levels drop to make up the supply shortfall. The price increases and remains above base case prices (scenario A) for almost a decade (see Figure 11).

When prices do drop, they drop below levels of the base case. As shown in the Figure 11, primary capacity following the mine shutdown increases above base case scenario following a delay of a few years. The capacity overbuild occurs after the high prices motivated capital investment and the delay is a result of the time required to install the new capacity. Inventory levels rise to levels that are considered high and take a number of years to return to target levels.

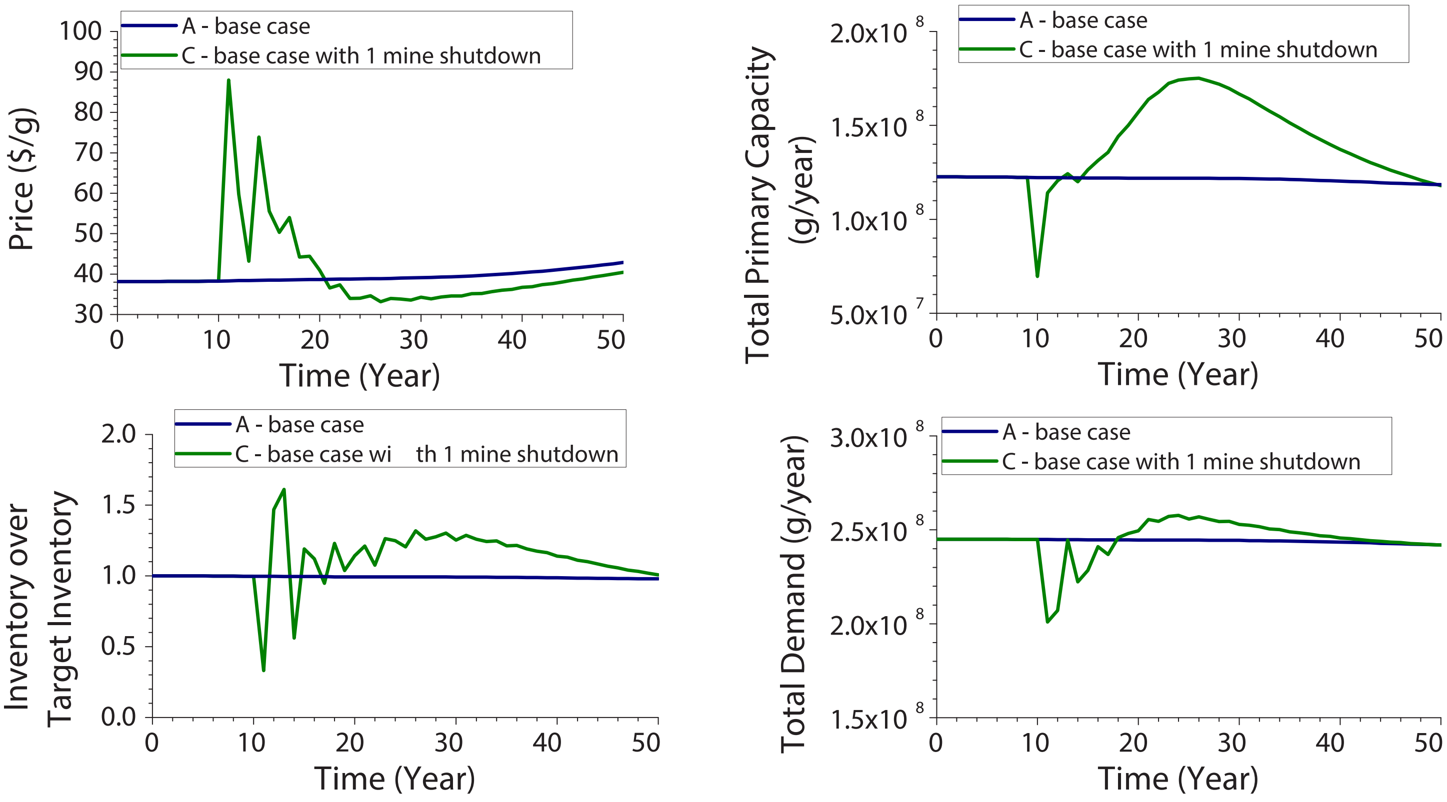

Figure 11: Perturbation (C) and non-perturbation scenarios (A) comparison. Price, total primary capacity, inventory levels relative to target levels (ideally = 1), and total demand are plotted as a function of time for the 50-year simulation period.

During the period of varying prices, demand is also affected. Demand decreases as a result of the high prices and increases during the period of low prices before recovering to pre-perturbation levels.

The results show that the modeled price, demand, and supply respond dynamically to the supply shortfall. The multiple feedback loops, identified previously in Figure 9, act to produce the results observed.

The model behavior in the case of a forced mine shutdown also can indicate possible strategies for firms to mitigate the risk of materials scarcity. Three strategies are identified and discussed in the next sections:

- Source relocation
- Material substitution
- Recycling

SOURCE RELOCATION

The high prices, although temporary, last long enough to encourage the remaining supply groups to increase their capacity (see Figure 12). As a result of the perturbation, there is a permanent change of production capacity for each of the supply groups. The previously highest producing mining region is replaced in size by the previously second largest producer.

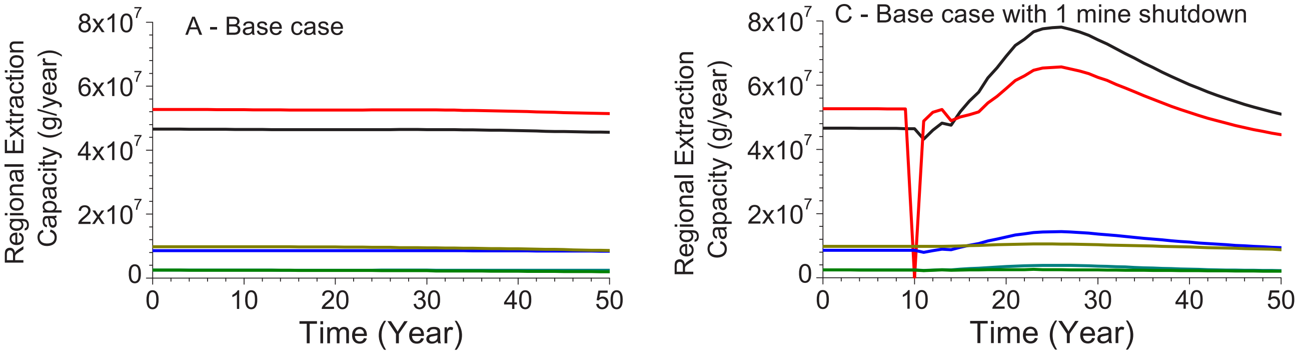

Figure 12: Extraction capacity for each of the six primary supply groups in the case of no perturbation and with a perturbation (scenario A and C).

This result indicates a potential need for downstream firms that use platinum to relocate parts of their supply chain in the case of future scarcity.

SUBSTITUTION

In scenario C, the case of a single supply group shutdown, demand responds to price but not equally among the different demand groups (see Figure 13). In the case of jewelry, gold, palladium and silver are easy substitutes for platinum. Also, demand for platinum jewelry is elastic to the price of the platinum, since the price of platinum essentially determines the price of the jewelry. As such, the demand platinum for jewelry decreases significantly as a result of the price spikes.

On the other hand, demand for platinum for use in autocatalysts and electronics is hardly changed as a result of the price increase. This is due in part to the lack of alternative materials for these applications and in part to the fact that the demand for cars and hard disks do not strongly depend on the price of platinum (price inelastic).

The impact to downstream firms of the price increase is therefore different depending on whether or not they can change their platinum demand behavior, through substitution for example, when scarcity occurs. Those who can, spend less on platinum over time, as observed in the case of jewelry.

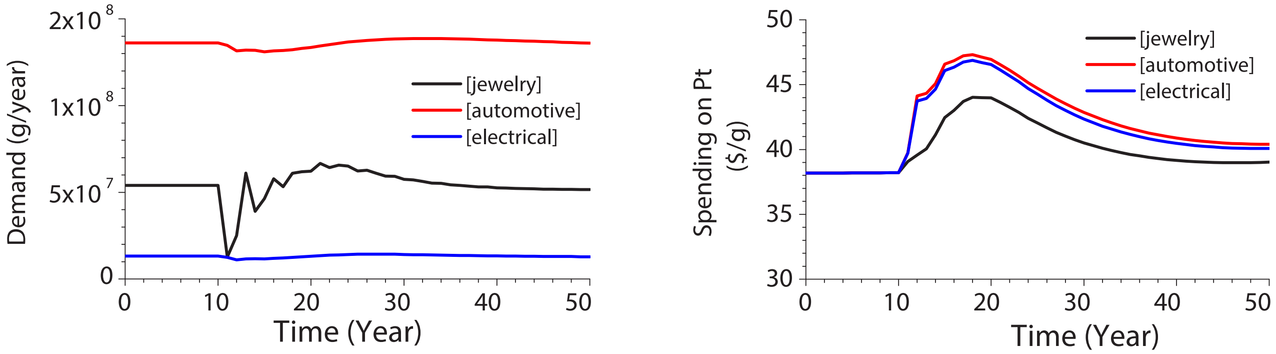

Figure 13: Demand and spending for three of the four demand groups in the case with a perturbation (scenario C).

RECYCLING

Scenarios C and D examine the impact of recycling on market model behavior in the case of a perturbation. In scenario D, recycling amounts of scenario C are cut by half.

Recycling is able to dampen the price spike since it reduces the dependence on primary suppliers (see price plotted in Figure 14). In the case of platinum, where recycled materials can be used interchangeably with primary materials, downstream firms that use both recycled platinum and primary platinum have increased the robustness of their supply chain by having two suppliers. Downstream firms are therefore less affected by the mine shutdown when there is more recycling and their average spending per gram of platinum is less over time.

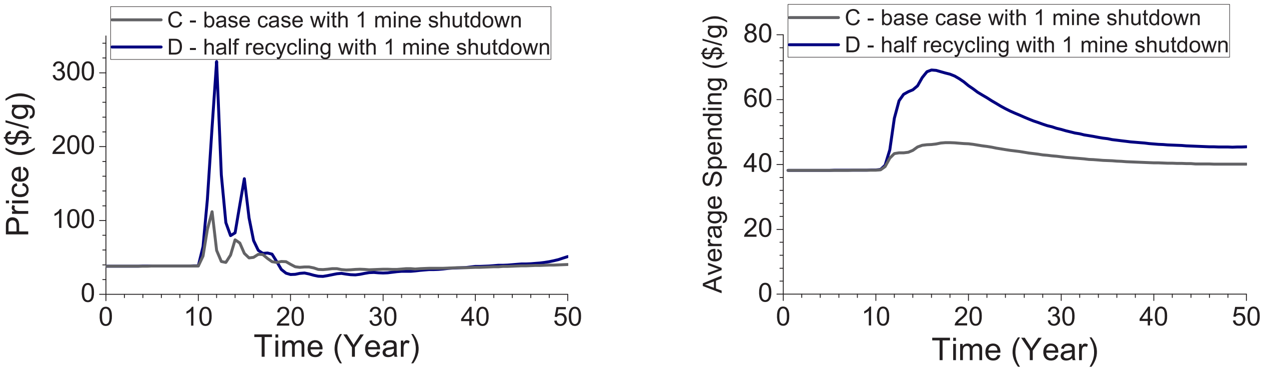

Figure 14: Price and spending comparison with a mine shutdown in year 10. The recycling rate is varied between base case recycling and half recycling (scenarios C and D).

CONCLUSIONS AND FUTURE WORK

The price of platinum has more than tripled in recent years: these prices impact downstream firms that use platinum whether these increases are temporary or permanent.

A platinum market model has been built to examine the implications of firm actions in the face of materials scarcity. The model is a simulation based on a system on non-linear first order differential equations that describe the causal feedbacks between supply, demand and price. Platinum market data were used where available.

The simulation provides an experimental platform for examining scenarios of platinum scarcity. The model results from a number of hypothetical scarcity scenarios, including one with a supply group shutdown, were analyzed. Three strategies were suggested in the face of risks for scarcity:

- **Source relocation:** scarcity may require firms to move their supply chains
- **Recycling:** use of both recycled and primary materials can dampen price increases
- **Substitution:** industries that can substitute to other materials are less impacted by scarcity

There is still much work to be done to improve the model. In particular, input from stakeholders in the platinum market is desired to improve the model's representation of market behavior. The model should capture all important drivers of market behavior (Figure 9 is a schematic of the feedback dynamics represented in the present model).

Also, additional model behavior analysis should be conducted. Model sensitivity analysis is important for determining the variables that have the most significant impact on the model behavior. Sensitivity analysis can also be used to examine the limitations of potential firm strategies, including the three suggested in this paper.

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FAST THROUGHPUT ANALYSIS OF PRECIOUS METALS IN CERAMIC AUTOMOTIVE CATALYSTS BY XRF OR OES

(This paper was originally presented at the 2006 IPMI Conference)

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ABSTRACT

To meet the demands for short throughput time in the analysis of precious metals in spent automotive catalyst, the analytical laboratory of Umicore Precious Metals Refining developed 3 alternative methods.

The first method consists of analysis by X-Ray Fluorescence Spectroscopy (XRF) with a portable INNOV-X instrument. The calibration with in-house standards makes it possible to analyse Pt, Pd, and Rh and some base metals on site with a precision of 10% and maximum offset of 10% relatively compared to the analysis with Nickel Sulphide fire assay collection. The method is applied to obtain on site reliable indications of precious metals content in no time.

Until 2005, the preferred method to analyse Pt, Pd and Rh in spent automotive catalysts in the UPMR laboratory is the NiS collection. Since it is a time-consuming method that additionally needs special health precautions, our laboratory developed a faster method with XRF resulting in an comparable precision and reliability. In a co-operation with the University of Antwerp, a preparation and measurement method was set up for the analysis of precious metals in 40-40-10 automotive catalysts (40% Al2O3, 40% SiO2, 10% MgO) by energy-dispersive XRF with the PANalytical Epsilon 5 instrument. This instrument, new on the market since 2004, combines the speed of traditional XRF with lower detection limits. Simultaneously a method was developed by lead collection and measurement by spark Optical Emission Spectroscopy (spark OES). Combining different wavelengths for each precious metal and specific regression lines for ceramic automotive catalysts, a method with accuracy and precision equal to the NiS collection was obtained. In this way, we are able to report precious metals results in automotive catalysts for customer settlement within 48 hours!

INTRODUCTION

Umicore Precious Metals Refining is a world market leader in recycling complex materials containing precious metals. The plant in Hoboken is designed to recover precious and non-ferrous metals from a broad range of industrial by-products and secondary precious metals bearing raw materials from sectors such as electronics, photography and catalysts. The feed includes drosses, mattes, speiss, tankhouse slimes, cements and sulfates from non-ferrous plants, spent automotive and petrochemical catalysts, electronic scrap, residues from the photographic industry, sweeps and bullions.

In the analytical laboratory, there is a continuous research for enhanced, reliable and automated analysis methods. Key drivers are high quality, optimised lead times and customer-oriented solutions.

One of the major research topics of the last year is the analysis of spent automotive catalysts. The method applied for several years as the official analysis method for the determination of precious metals in car catalysts is collection in Nickel Sulphide, and final determination by ICP-OES. This method is not only time consuming, but needs specific health precautions due to the risk of Nickel allergy. Other methods applied in the UPMR laboratory, for indicative results, are pressed pellets, analysed by WDXRF (Wavelength Dispersive XRF) and pre-assay by Lead collection and spark OES. The introduction of the PANalytical Epsilon 5 instrument gave opportunities for the analysis of precious metals in automotive catalysts by XRF with a high accuracy. Research was performed to optimise the preparation method and the measurement conditions, in a close co-operation with the University of Antwerp. In-house, the method of lead collection and measurement by spark OES was optimised for ceramic car catalysts. On the other hand, a method was developed to analyse precious metals in ceramic car catalysts outside the laboratory, with a portable XRF instrument, resulting in a fast and reliable pre-assay. This paper presents the results of the research on the sample preparation and on the measurement conditions of these three methods and the comparison with the reference method by NiS collection and ICP-OES analysis.

1. Reference method: NiS collection and ICP-OES

The analysis method applied for several years in the UPMR laboratory to determine the precious metals content in spent car catalysts consists of the collection of Pt, Pd, and Rh in Nickel Sulfide by fire assay at 1250° C. The crushed NiS bead is dissolved in HCl and filtered. Subsequently, the PM residue is dissolved in aqua regia and the measurement is done by ICP-OES. This method is the reference method for our laboratory, to which all new methods are compared. Working with NiS implies the use of gloves and a mask (Piccola FFP3.SV) or air-stream helmet because nickel-compounds can cause allergenic reactions and above all some are carcinogenic. Next to the strict health precautions, this method is time-consuming. For quality reasons, each sample is prepared in four fold, at 2 different days, by 2 different persons, resulting is a mean lead time for this method of 5 working days.

The accuracy of this method is better than 1% relative.

2. Optimised spark OES method on Lead beads for customer settlement within 48 hours

A new application was developed in the laboratory of UPMR for the analysis of Pt, Pd, and Rh in spent ceramic automotive catalysts by Lead collection and measurement by spark OES.

2.1 Sample preparation

5 grams of the sample is mixed with flux (Na2CO3, Na2B4O1, PbO, (4HsO5K). Fire Assay at 1100° C is performed on the sample, resulting in a Pb button of approximately 65 grams. Prior to measurement by spark OES, the button is surfaced.

2.2 Measurement conditions

Both sides of the button are analysed by spark OES (Spectrolab S), on 2 different days, to minimise the influence of instrument variations. The 2 measurement are performed in two different calibrations. Before each analysis of real samples, reference samples are analysed. If the results, plotted on a SPC chart, differ too much from the real value, a calibration of the instrument is performed. Before and after each set of 12 samples, blanks and reference samples are measured, to be able to correct for drift. At least 3 spark analyses are performed on each side. The accepted difference between different spark analyses is maximum 1 % relative.

Homogeneity tests are performed by analysing 32 buttons (of 16 samples) on both sides. The mean relative difference of the results of both sides is 0.12% for Pt and for Rh and 0.21 % for Pd. Statistical analysis of these data by t-test shows that for Pt, Pd, and Rh the concentrations on both sides of the button are comparable. Thus, these precious metals are homogeneously distributed in the Lead button. However, to overcome errors due to segregation of elements in the Lead button, we analyse the Lead buttons on both sides. The measurements of 2 buttons on 2 different days are also statistically comparable, as proved by the results of the two-tailed t-test, shown in Table 1. The average values, the standard deviation and the relative standard deviation of the 4 measurements are presented in Table 2. The average relative standard deviation for Pt is 1 %, for Pd 0.6% and for Rh 0.8%.

	Pt	Pd	Rh
t Stat	0.70	1.48	0.65
t Critical two-tail	2.04	2.04	2.04

Table 1: Results of the t-test (at 95% confidence level) of the analysis results of Pt, Pd, and Rh on two different days.

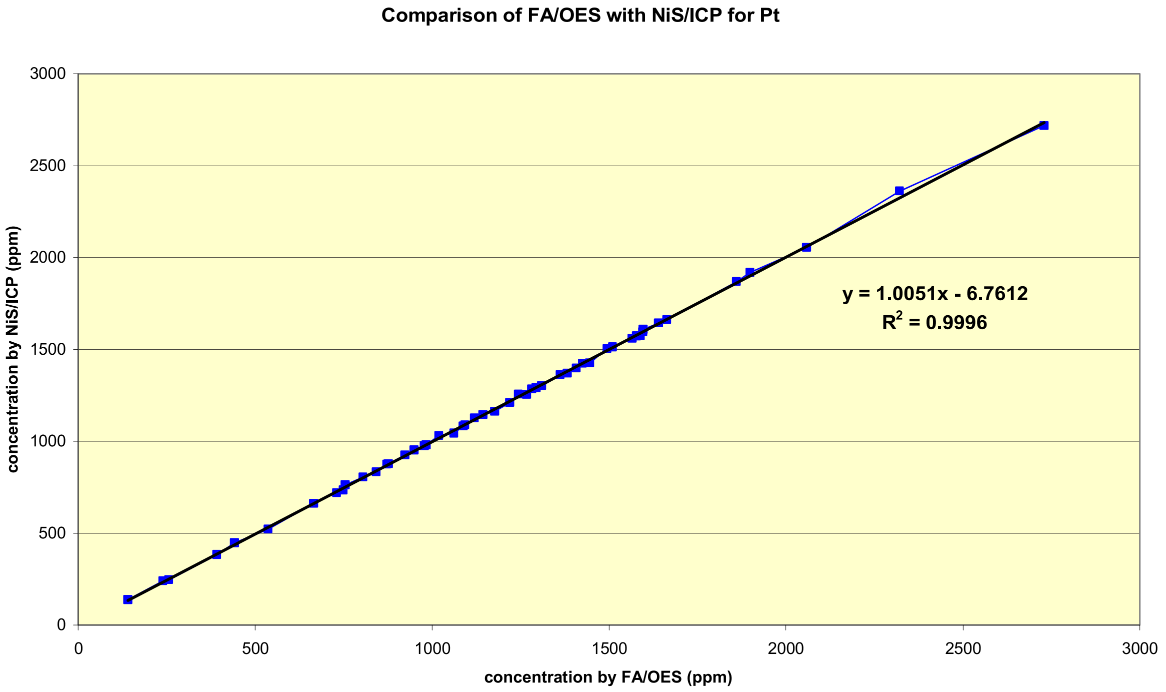
sample	Pt			Pd			Rh		
	average	SD	RSD (%)	average	SD	RSD (%)	average	SD	RSD (%)
1	2912	59	2.0	543	2.1	0.4	580	4.3	0.8
2	2974	63	2.1	1210	8.3	0.7	572	5.3	0.9
3	1351	15	1.1	260	1.7	0.7	280	1.8	0.7
4	2866	40	1.4	1211	6.1	0.5	594	1.0	0.2
5	723	4	0.6	264	2.9	1.1	89	0.8	0.9
6	2215	57	2.6	2224	38.9	1.8	530	9.6	1.8
7	1513	2	0.1	499	2.2	0.4	107	1.0	0.9
8	1423	9	0.6	528	2.9	0.5	284	1.7	0.6
9	1410	9	0.6	286	1.4	0.5	289	1.7	0.6
10	1398	8	0.6	329	0.8	0.2	289	1.4	0.5
11	1492	6	0.4	193	1.0	0.5	277	2.2	0.8
12	1365	4	0.3	216	1.3	0.6	276	2.4	0.9
13	1360	13	0.9	733	5.1	0.7	246	1.5	0.6
14	1246	9	0.7	526	1.0	0.2	238	1.7	0.7
15	1101	2	0.2	934	3.3	0.4	304	2.2	0.7
16	1210	12	1.0	888	8.1	0.9	147	1.7	1.2
average RSD			1.0			0.6			0.8

Table 2: Average, standard deviation (SD) and relative standard deviation (RSD) of 4 measurements of Pt, Pd, and Rh. Results of the lower Lead button side and the upper Lead button side, both analysed on 2 different days.

2.3 Comparison with the reference method

In total 55 samples of spent car catalysts of different origin were analysed by the reference method, NiS/ICP, and by the described method, FA/OES. As shown in the graphs in Figure 1, the correlation between the two methods is better than 99.9% for Pt, Pd, and Rh.

a)



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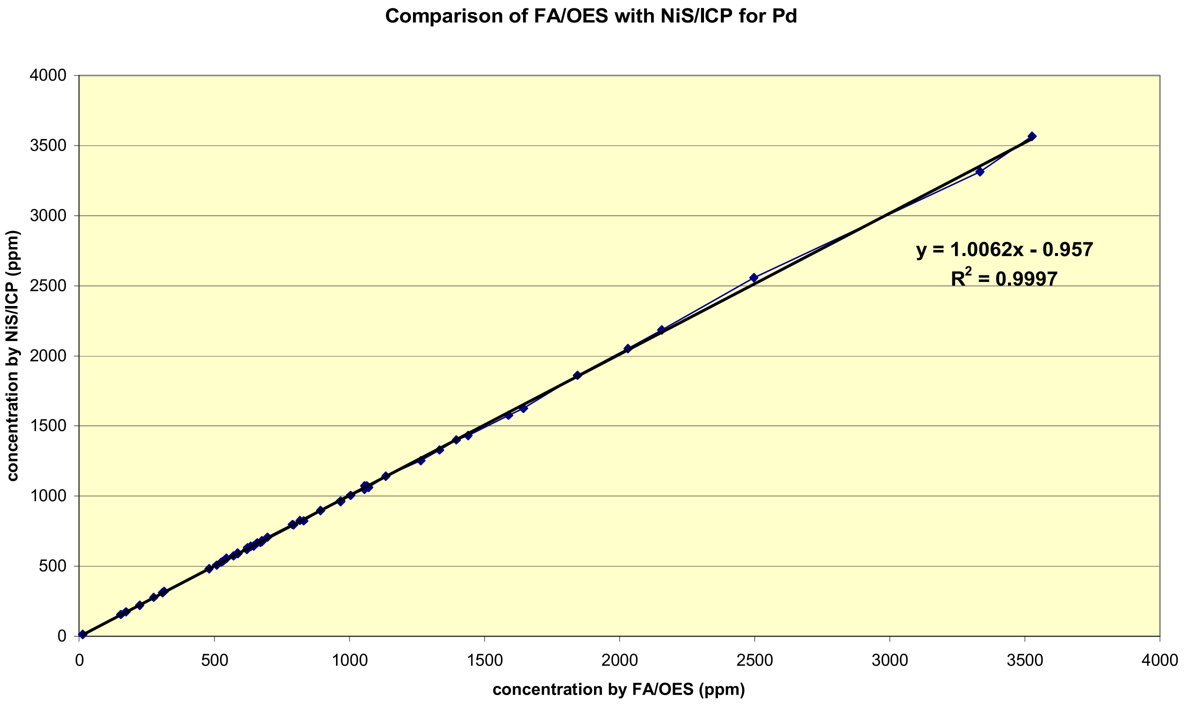


c)

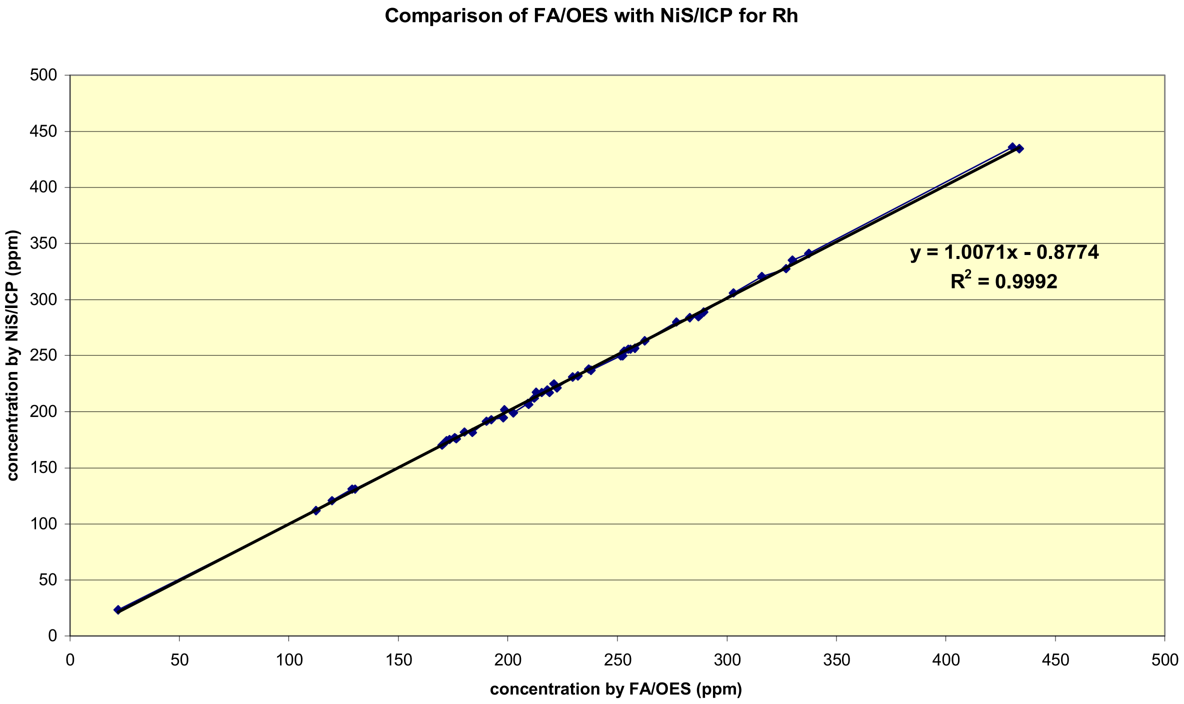


Figure 1: Comparison of the results of FA/OES and NiS/ICP for a) Pt, b) Pd, and c) Rh

2.4 Conclusions

A new method is developed to determine Pt, Pd, and Rh in spent automotive catalysts by Fire Assay. The precious metals are homogeneously collected in the resulting Lead button. The latter is analysed by spark OES. Comparison of the results of this method to those of the reference method, Fire Assay with Nickel Sulphide and analysis by ICP-OES, shows that both methods produce comparable results. In this way, we are able to generate reliable results within 48 hours instead of 5 working days.

3. Fast and reliable pre-assay by portable INNOV-X XRF instrument

A portable INNOV-X instrument was tested to obtain fast pre-assay results, both on field and in laboratory environment. In close co-operation with INNOV-X, we set up different calibrations to analyse precious metals (Pt, Pd, Rh) content in spent ceramic automotive catalysts of different origin. The customer made application contains the analysis of the elements Ag, Au, Pt, Pd, Rh, Pb, Cu, Bi, Ni, Co, As, Sb, Sn, Zn, Fe, Cr, Ce, In, K, Mn, Mo, P, Re, Se, Sr, Ta, Ti, W, Zr, Ba, Ca, Cd, Hf, Hg and the sum of light elements (such as Al2O3, CaO, SiO2, MgO). The instrument works with a W X-Ray tube, at 35 kV, with up to 5 selectable filters.

3.1 Sample preparation

Since particle size can influence results of X-ray analysis to a large extent, sample preparations tests were performed, with variable particle size. The following tests were compared:

A) For a sample with grain size less than 6 mm, 3 test cups were filled. Each cup was measured threefold, during 300 seconds. Each cup was, after measurement, manually crushed in a mortar with pestle and measured again during 3 x 300 seconds. After those measurements, each cup was ground in a ring mill and measured again as above.

B) The totality of A was then manually crushed in a mortar with pestle. 3 test cups were filled and measured during 3 x 300 seconds. After those measurements each cup was ground in a ring mill and measured as described above.

C) B was sieved through a 112 µm sieve, resulting in 2 fractions: a fraction with coarse material (± 75%) and a fine fraction (± 25%) Of each fraction, 3 test cups were filled and measured during 3 x 300 seconds.

D) The 2 fractions of B were mixed together again and then ground in a ring mill. Again 3 test cups were filled and measured during 3 x 300 seconds.

Table 3 shows all the analysis results of these tests. We conclude that to obtain representative figures, at least three sample test cups have to be measured. Grain size is an important influencing factor: sieving tests told us that the standard deviation is improving drastically when reducing the particle size (especially for Pt). Milling and screening on 112 µmis recommended. The ratio of coarse to fine fraction has to be at least 75/25.

				Pt				
	target	- 6 mm	RSD (%)	man.crushed	RSD (%)	sieved 112µ	RSD (%)	RD target (%)
		test A		test B		test C		
	ppm	ppm		ppm		ppm		
	1045	1005	5	906	4	981	2	-6
	1029	1070	11	862	15	1092	2	6
	526	523	13	503	4	602	3	15
	931	940	20	887	9	1027	2	10
	1415	1407	7	1141	4	1455	2	3
average	***989***	***989***	***11***	***860***	***7***	***1031***	***2***	***5***
				Pd				
	target	- 6 mm	RSD (%)	man.crushed	RSD (%)	sieved 112µ	RSD (%)	RD target (%)
		test A		test B		test C		
	ppm	ppm		ppm		ppm		
	504	395	18	459	14	513	4	2
	654	523	21	545	14	674	2	4
	697	557	21	579	3	681	4	-3
	271	201	12	243	5	271	4	0
	640	456	17	503	7	610	2	-7
average	***553***	***426***	***18***	***466***	***9***	***550***	***3***	***-1***
				Rh				
	target	- 6 mm	RSD (%)	man.crushed	RSD (%)	sieved 112µ	RSD (%)	RD target (%)
		test A		test B		test C		
	ppm	ppm		ppm		ppm		
	240	217	6	219	3	240	5	0
	196	177	12	165	11	191	5	-3
	257	206	17	213	4	248	2	-4
	102	74	2	87	3	115	10	18
	172	163	13	124	13	162	2	-6
average	***193***	***167***	***10***	***162***	***7***	***191***	***5***	***1***

Table 3: Results by INNOV-X of the samples prepared by different grinding and sieving tests. Results of tests A, B, and C are listed (RSD = relative standard deviation of the 3 measurements on the same sample) and compared to the target value (RD target = relative difference of the results of test C to the target value).

3.2 Precision and accuracy of the analytical method

The measuring limit of the device is set at 60 ppm, and detection limits of about 100 ppm are to be considered. Correlation coefficients (target versus INNOV-X analyzer) for Pd and Rh are excellent (>0.995), and acceptable for Pt. Pt is the weakest element, due to his longer wavelength, and more affected by slight differences in particle size distribution of the sample.

Reproducibility was tested by performing during 9 days measurements on 1 sample at random time. As presented in Table 4, the results meet the expectations, the deviation was better than 10% relative.

			InnovX	**InnovX**	**InnovX**
number	**day**	**hour**	**Pt**	**Pd**	**Rh**
1	10-Oct	11:00	320	1668	294
2	11-Oct	9:00	339	1719	278
3	11-Oct	12:00	305	1791	336
4	11-Oct	13:30	301	1694	277
5	11-Oct	15:40	325	1679	295
6	19-Oct	8:30	274	1664	297
7	19-Oct	9:00	272	1652	264
8	19-Oct	13:15	275	1688	319
9	19-Oct	14:40	317	1652	282
10	20-Oct	7:50	276	1748	335
11	20-Oct	13:10	298	1527	223
12	20-Oct	14:50	279	1653	256
13	20-Oct	17:00	312	1719	275
14	21-Oct	8:10	305	1695	321
15	21-Oct	13:50	308	1695	275
16	21-Oct	15:30	266	1625	276
17	24-Oct	8:00	320	1609	273
18	24-Oct	10:40	282	1647	286
19	24-Oct	12:40	259	1673	259
20	24-Oct	14:15	282	1659	266
21	24-Oct	15:45	261	1618	264
22	25-Oct	7:50	301	1670	245
24	25-Oct	10:10	273	1617	261
26	25-Oct	11:50	308	1614	232
28	25-Oct	15:15	286	1693	284
29	26-Oct	7:55	284	1619	279
30	26-Oct	11:10	303	1636	313
31	26-Oct	14:40	318	1719	279
32	26-Oct	17:50	293	1615	262
33	26-Oct	20:30	288	1661	276
34	27-Oct	7:50	302	1649	300
35	27-Oct	10:15	271	1570	264
		average	**294**	**1661**	**280**
		SD	**20**	**49**	**26**
		RSD (%)	**6.9**	**3.0**	**9.5**
	target value (ppm)		**327**	**1603**	**273**

Table 4: Results of the reproducibility test of the INNOV-X instrument by the measurement of the same sample during 9 days at random times.

The accuracy of the method was determined by measurements of 20 quality samples, prepared in our Sampling Department. Results were satisfactory, as illustrated by the results in Table 5 and Figure 2.

	Pt			**Pd**			**Rh**		
	target	**INNOV-X**	**RD (%)**	**target**	**INNOV-X**	**RD (%)**	**target**	**INNOV-X**	**RD (%)**
test nr	**ppm**	**ppm**		**ppm**	**ppm**		**ppm**	**ppm**	
1	**327**	294	10.1	**1603**	1675	-4.5	**273**	289	-5.9
2	**1430**	1274	10.9	**4729**	4631	2.1	**1326**	1347	-1.6
3	**1193**	1011	15.3	**570**	540	5.3	**180**	191	-6.1
4	**221**	184	16.7	**702**	644	8.3	**84**	110	-31.0
5	**962**	869	9.7	**174**	182	-4.6	**192**	218	-13.5
6	**148**	133	10.1	**3743**	3601	3.8	**320**	346	-8.1
7	**951**	772	18.8	**613**	572	6.7	**223**	213	4.5
8	**579**	503	13.1	**795**	695	12.6	**236**	236	0.0
9	**1557**	1456	6.5	**647**	646	0.2	**179**	213	-19.0
10	**1605**	1715	-6.9	**565**	626	-10.8	**122**	151	-23.8
11	**1552**	1638	-5.5	**574**	694	-20.9	**125**	188	-50.4
12	**363**	307	15.4	**976**	890	8.8	**117**	130	-11.1
13	**353**	307	13.0	**1905**	1803	5.4	**320**	325	-1.6
14	**3079**	3156	-2.5	**2519**	2495	1.0	**689**	689	0.0
15	**710**	605	14.8	**865**	752	13.1	**175**	191	-9.1
16	**681**	679	0.3	**246**	232	5.7	**157**	217	-38.2
17	**1060**	1061	-0.1	**201**	196	2.5	**94**	132	-40.4
18	**1297**	1217	6.2	**344**	300	12.8	**163**	164	-0.6
19	**1168**	995	14.8	**665**	553	16.8	**139**	163	-17.3
20	**1334**	1251	6.2	**338**	336	0.6	**243**	273	-12.3
average	***1029***	***971***	*5.6*	***1139***	***1103***	*3.2*	***268***	***289***	*-7.8*

Table 5: Results of the accuracy tests: comparison of INNOV-X results to target values of 20 samples (RD = relative difference of INNOV-X result to target value).

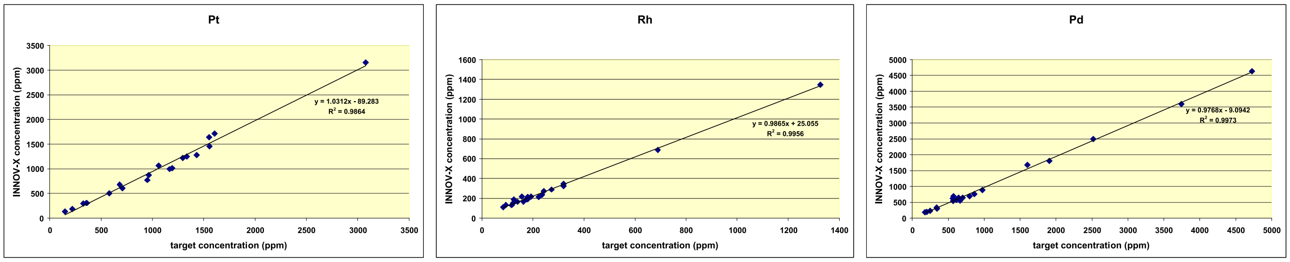


Figure 2: Comparison of the results of the INNOV-X instrument to the target values for Pt, Pd, and Rh.

3.3 Conclusions

Different sample preparation steps were evaluated to obtain optimal results with the INNOV-X instrument for the analysis of Pt, Pd, and Rh in spent automotive catalysts. The best conditions are:

- On field: manual milling of grab samples with mortar and pestle, combined with a manual screening into two fractions with a 112 µm screen (depending on the desired quality of results), followed by the measurement in triplicate of each fraction.
- Laboratory conditions: milling in the small ball mill (milling time to be determined). Check the grain size for at least 25% of fines .”As is” measurement or measurement after sieving are both options in triplicate.
- The best results, with small influence of particle size, are obtained after manual milling and screening on 112 µm. Milling and screening on 112 µm is recommended. The ratio of the coarse to the fine fraction has to be at least 75/25.

Important remark: one has to take caution that some matrix elements could influence the results, which can lead to wrong interpretation of results. Especially the presence of Ti, Zr, Cr, and Fe has to be controlled.

4. NEW EDXRF METHOD COMBINING LIMITED SAMPLE PREPARATION WITH HIGH ACCURACY

4.1 Optimisation of the sample preparation

A sample preparation method working directly on the ground material was optimized. The material was pressed as a pellet using wax as a binder; no internal standard was added. The pellet thickness and amount of sample needed, the grain size, the pressure and the time to press the pellets are parameters that are varied to obtain optimal sample preparation conditions. The optimised sample preparation consists of:

- the sample is ground in a ring mill during 6 minutes
- minimum 15 grams of sample are mixed with wax, the sample to wax ratio equals 5:1
- the ground mixture is pressed in an Al cup at 20 tonnes during 10 seconds.

4.2 Measurement conditions

An Epsilon 5 instrument energy dispersive XRF instrument (PANalytical, Almelo, The Netherlands) was applied for the XRF analyses. It has a 600W Gd tube with a maximum voltage of 100 kV, giving the possibility of high-energy excitation. Its three-axial Cartesian geometry using secondary targets provides a low background signal and the possibility to choose to most sensitive excitation-condition for each element. A polarised beam is generated by the secondary target being in a triaxial geometry with the tube, sample and detector. When applying CsI as a secondary target, it became possible to excite the Pd- and Rh-K-lines. For the determination of Pt, a Zr-target was chosen to excite the Pt-L-series. The reproducibility of the XRF-analysis appeared to be better than 0.5%, while the precision of the whole method was approximately 1 %. The accuracy was investigated using ICP-OES as a reference and similar performances were obtained. When irradiating 500 seconds for the CsI-target as well as for the Zr-target, detection limits for Pt, Pd, and Rh proved to be better than 5 ppm.

The measurement conditions of the Epsilon 5 instrument applied for this study are shown in Table 6.

Secondary target	Voltage (kV)	Filter	Element and analytical line
Zr	90	Cu	Pt (Lα)
CsI	70		Pd (Kα), Rh (Kα)
Mo	100	Cu	Pb (Lα)
Ti	35		Al_2O_3 (Kα), SiO_2 (Kα), P (Kα), S (Kα), K_2O (Kα), CaO (Kα)
Al	25		MgO (Kα)
W	100		CeO2 (Kα), BaO (Kβ)
Ge	65		Other elements

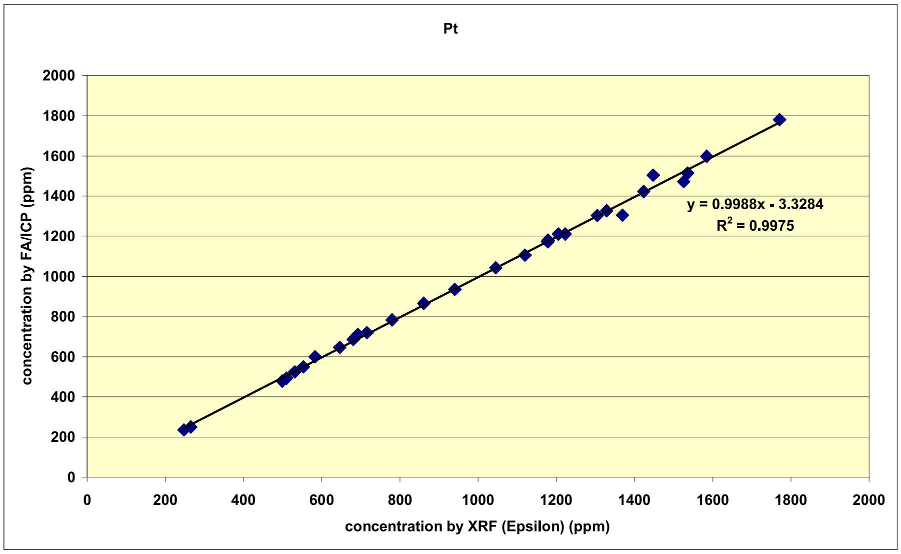
Table 6: Measurement conditions of Epsilon 5 EDXRF instrument applied for the analysis of spent car catalysts

The standards used for this application were automotive catalysts, prepared in the same way as the unknown samples. The concentrations of the precious metals in these standards were verified with ICP-OES. For this purpose the samples were preconcentrated using NiS Fire Assay.

4.3 Comparison with the reference method

In total 29 samples of car catalysts were analysed with the described method and with the reference method (FA/ICP). For Pt, Pd, and Rh, the results are comparable, as shown in Figure 3. Table 7 lists the results of the t-test applied to compare the results of XRF with those of FA/ICP. It shows that the results from both methods are comparable.

a)



b)

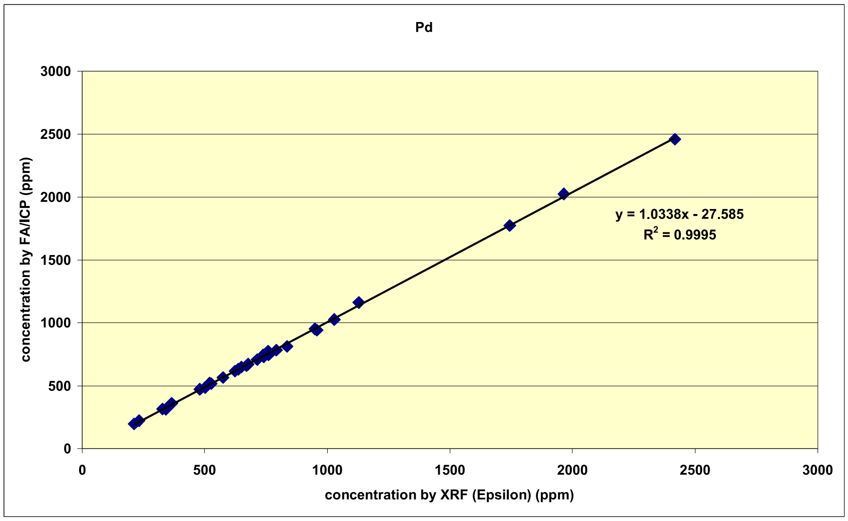


Figure 3 : Comparison of the analysis of a) Pt, and b) Pd in spent car catalysts by XRF with Epsilon 5 and by the reference methode FA/ICP.

c)

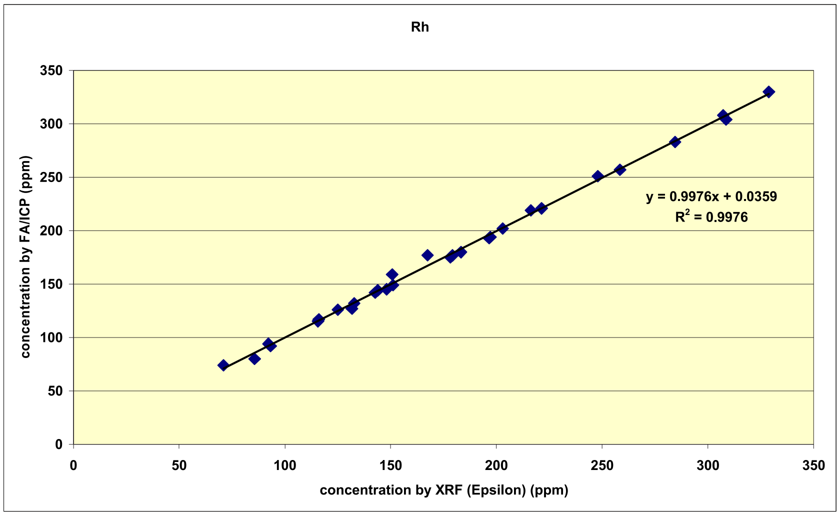


Figure 3 c): Comparison of the analysis of Rh in spent car catalysts by XRF with Epsilon 5 and by the reference methode FA/ICP.

	Pt	Pd	Rh
t Stat	1.13	0.25	0.61
t Critical two-tail	2.05	2.05	2.05

Table 7: Results of the t-test (95% confidence level) of the analysis results of Pt, Pd, and Rh by XRF with Epsilon 5 and by FA/ICP.

4.4 Conclusions

A sample preparation method was optimised for the analysis of spent car catalysts by the EDXRF instrument Epsilon 5. The optimal preparation conditions are:

- the sample is ground during 6 minutes
- 15 grams of sample are mixed with wax in a ratio of 5/1
- the mixture is pressed in an Al cup for 10 seconds at 20 tonnes

The reproducibility of the analysis method, both preparation and measurement, was quantified by preparing the same sample at 10 different days, by 10 different people and by the measurement of the same sample at different times the same day and at 10 different days. These tests prove that the analysis method has a reproducibility better than 1 %.

5. Conclusions

Three different alternative methods were developed to analyse Pt, Pd, and Rh in spent automotive catalysts. Comparing the methods to the reference method of collection in NiS and analysis by ICP-OES shows that all methods generate statistical equal results.

The method of spark OES on Lead buttons gives in 48 hours reliable results, the portable INNOV-X instrument is able to generate instant results on field and the new EDXRF method combines limited sample preparation with high accuracy.

HIGHLY SELECTIVE SEPARATION AND RECOVERYAT HIGH PURITY OF PALLADIUM AT THE BOLIDEN RÖNNSKÄR COPPER SMELTER USING MOLECULAR RECOGNITION TECHNOLOGY™(MRT™)

(This paper was originally presented at the 2022 IPMI Conference)

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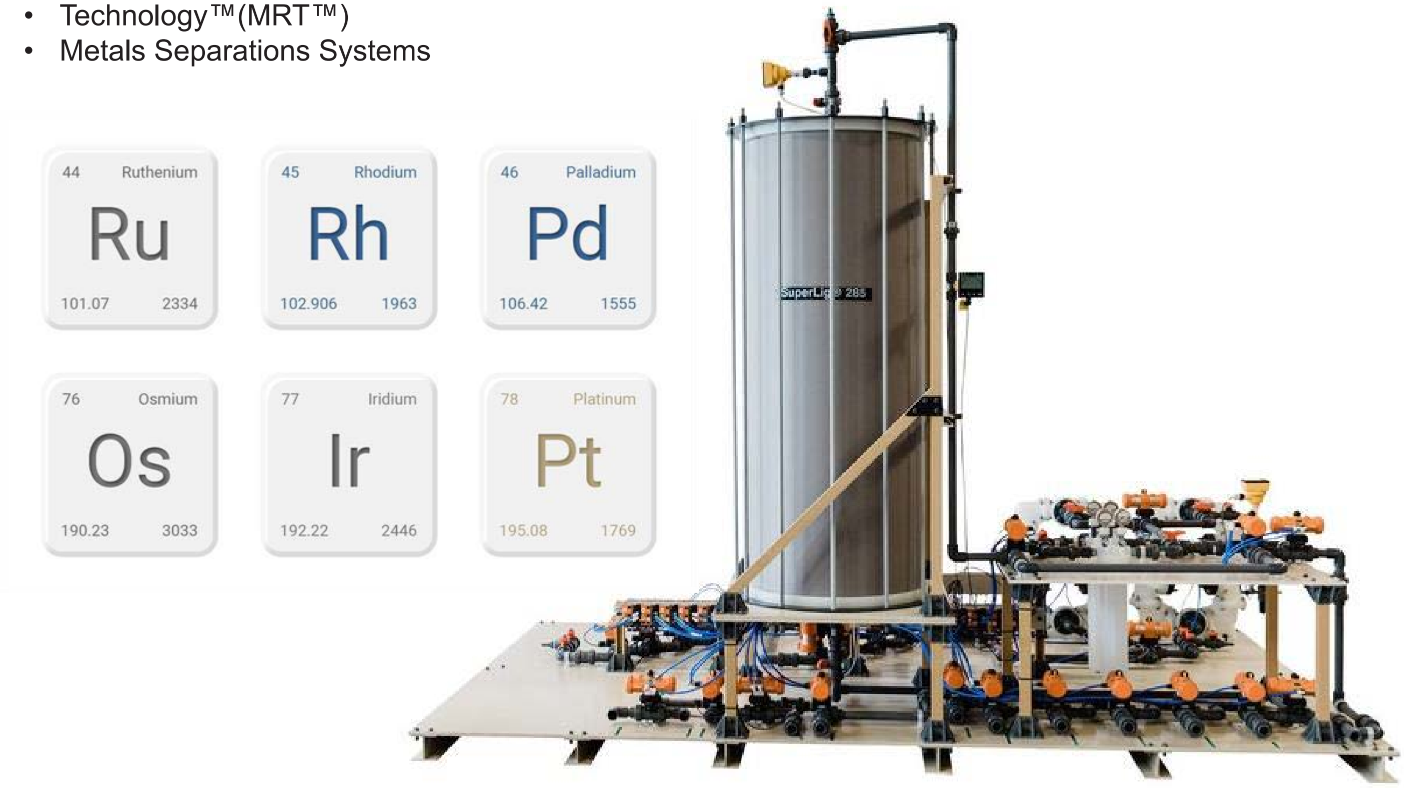
BOLIDEN RÖNNSKÄR, SWEDEN *WORLD LEADER IN RECYCLING ELECTRONICS*

- One of the world's most efficient copper smelters
- Receives deliveries of copper and lead concentrates from Boliden's own mines and from external suppliers
- Primarily extracts copper, lead, gold and silver
- Biggest private employer in the region

IBC ADVANCED TECHNOLOGIES, INC.

- Highly Selective
- Molecular Recognition
- Technology™(MRT™)
- Metals Separations Systems



BOLIDEN AND IBC HAVE A SHARED INTEREST IN GREEN TECHNOLOGY IN METAL PRODUCTION

Boliden Rönnskär

- Company purpose is to provide the metals essential to improve society for generations to come
- Company vision is to be the most climate-friendly and respected metal supplier in the world
- Long-term goal is to reach net zero carbon emissions by 2050

IBC Advanced Technologies, Inc.

- Green chemistry and green engineering are at the core of IBC's highly metal-selective SuperLig®Molecular Recognition Technology™(MRT™) products
- Energy, infrastructure, water, chemicals, labor, space, and time are conserved in MRT™worldwide separation systems
- Minimal waste is generated, no organic solvents are used, zero carbon footprint is achieved
- Separation rates and purity of recovered metals approach 100% leading to a circular economy and individual metal sustainability

BOLIDEN AND IBC SHARE A COMMON GOAL OF SELECTIVE SEPARATION AND RECOVERY AT HIGH PURITY OF METALS FROM SPENT SECONDARY SOURCES

Boliden Rönnskär

- Extracts metals from mined raw materials and recycles secondary materials
- One of the world's largest recycling plants for electronic wastes is located at Rönnskär(crushed electronics, printed circuit boards, other)
- Contribution to metal production from recycled materials at Boliden in 2020: gold (32%), copper (26%), silver (25%)
- Printed circuit boards –copper, gold, silver, and palladium are recycled
- Residues originating from catalytic converters –palladium and platinum are recycled

IBC Advanced Technologies, Inc.

- Highly selective industrial-scale green chemistry separations and recovery of individual platinum group metals at purity levels approaching 100%
- Commercial MRT™systems for PGM separations operate at numerous global locations
- IBC has extensive, decades-long industrial experience using MRT™systems for separation and recovery of platinum, palladium, and rhodium from spent catalytic converters and electronic wastes

LIMITATIONS OF TRADITIONAL SEPARATION TECHNOLOGIES PRECIPITATION, SX, IX

- Profligate in use of energy, water, chemicals, labor, space, and time
- Low target metal selectivities lead to need for complex engineering to treat contaminated, impure, and/or dilute solutions downstream
- Result: extensive waste generation, large capital and operating expenses, and high environmental consequences requiring large control costs

GREEN CHEMISTRY AND GREEN ENGINEERING SUPERLIG® MRT ™ SYSTEMS: EFFICIENT, SUSTAINA BLE AND CIRCULAR ECONOMY RECYCLING OF METALS

- Paradigm shifts:
    - From organic solvents to green chemistry
    - From high complexity to simplicity in green engineering separation systems
    - From low to high selectivity processes in metal separation and recovery
    - From low to high recovery rates to minimize wastage

- Higher production levels per dollar spent
- Significant cost reduction during processing
- >99% first pass recovery rates
- Minimal environmental impacts–minimal waste generation

MRT™: SELECTIVE SEPARATIONS TECHNOLOGY

GREEN CHEMISTRY AND GREEN ENGINEERING

Positive ESG Impact

- SuperLig ® MRT ™products combine simplified, rapid green engineering column separations with highly selective green chemistry materials for efficient metal separation and recovery from primary and secondary sources
- SuperLig ® MRT ™processes consume minimal energy and water and do not use organic solvents or harsh chemicals
- Number of process steps, labor, chemical cost, and space requirements much lower than with traditional technologies
- Ambient temperature, atmospheric pressure
- Zero carbon footprint, minimal waste is generated
-

INSTALLATION OF AN MRT™ SYSTEM FOR PALLADIUM SEPARATION AND RECOVERY AT RÖNNSKÄR PRECIOUS METALS PLANT

- Previously, all platinum group metals in the process solution after gold extraction were precipitated as a concentrate and refined elsewhere
- A SuperLig® 2MRT™system for palladium has been incorporated into the Rönnskär process flowsheet as an intermediate refining step
- Palladium product purity is around 99.95%.
- Palladium recovery (feed --> product solution) is of the order of 99.99%

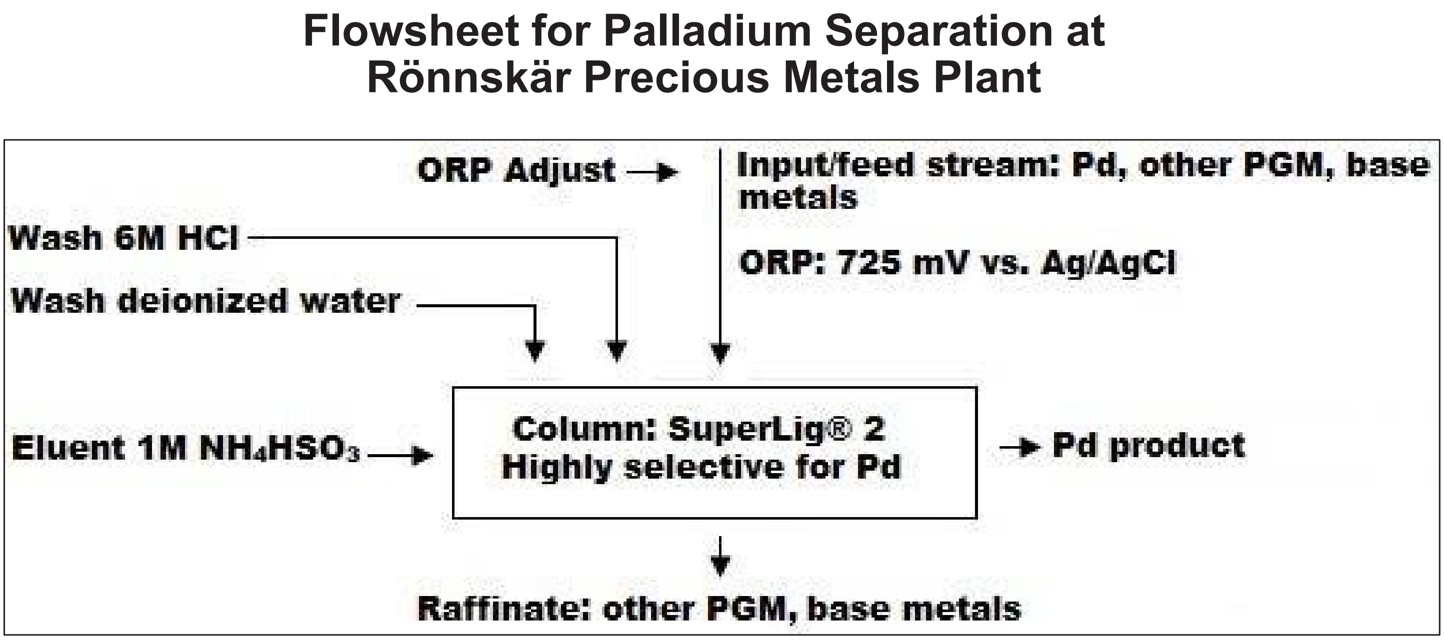
MRT™ PALLADIUM SEPARATION SYSTEM AT RÖNNSKÄR PRECIOUS METALS PLANT

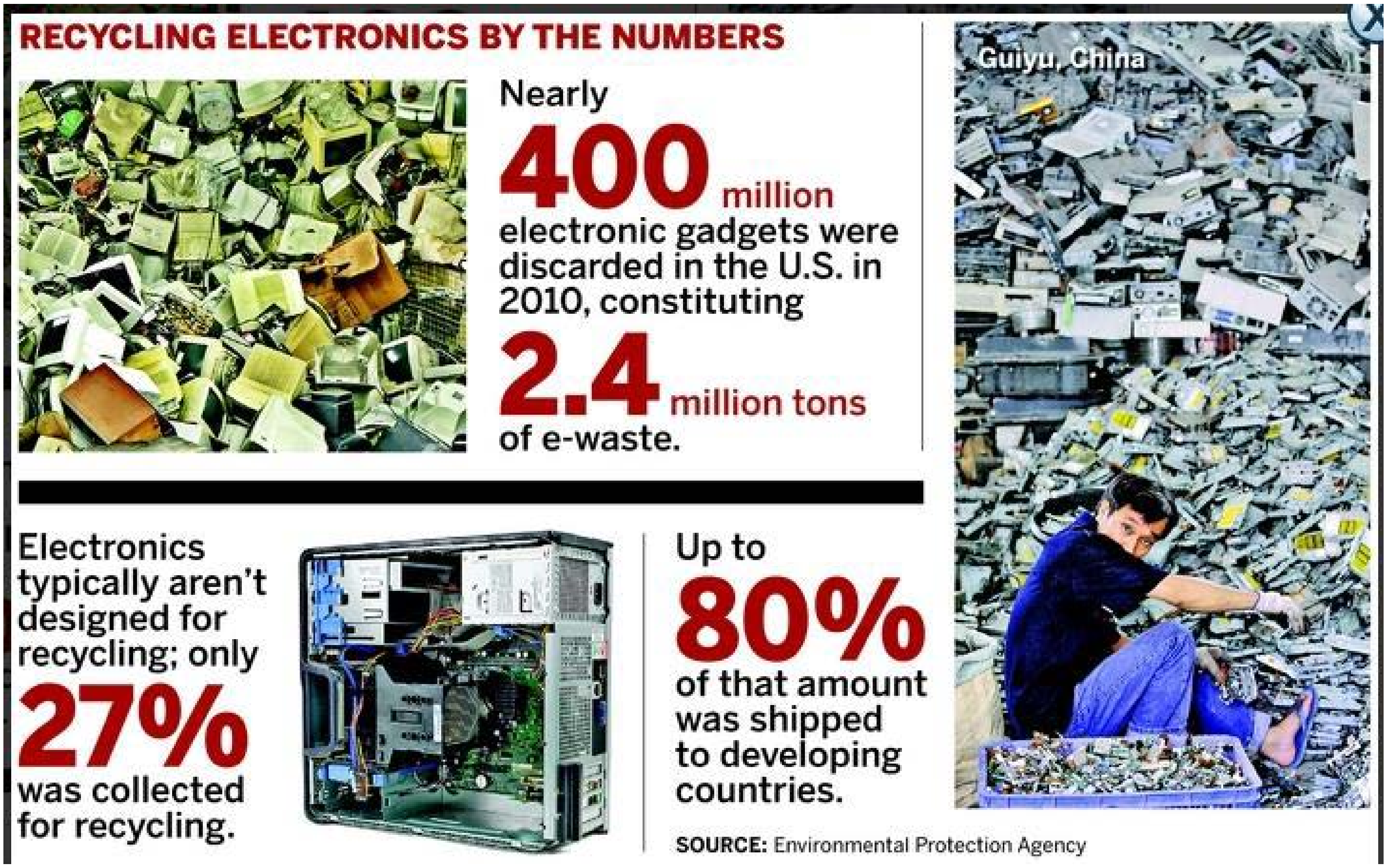
Left: Column packed with SuperLig® 2

Right: Column loaded with palladium

Figure 1

FLOWSHEET FOR PALLADIUM SEPARATION AT RÖNNSKÄR PRECIOUS METALS PLANT




RECYCLING ELECTRONICS BY THE NUMBERS

Nearly 400 million electronic gadgets were discarded in the U.S. in 2010, constituting 2.4 million tons of e-waste.

Electronics typically aren't designed for recycling; only 27% was collected for recycling.

Up to 80% of that amount was shipped to developing countries.

Guiyu, China

SOURCE: Environmental Protection Agency

Source: Ritter, S.K., *C&EN*, April 1, 2013. pp.41-43

PALLADIUM: GLOBAL SUPPLY-DEMAND 2021 (‘000 OUNCES)

- Gross Demand: 10,097 -Automotive, 8340 (83%); Industrial, 994 (9.8%); Electrical & Electronics, 655 (6.5%), Other, 108 (1%)
- Supply: Mined Ore: 6794 -Russia, 2689 (40%); South Africa, 2652 (39%); Other, 1453 (21%)
- Recycled: 3363 (49% of mined ore)
- Global Palladium Use: Catalytic Converters (80%); Electronics (16%)
- Most recycled palladium comes from spent catalytic converters (approximately 50%)
- Global recycling of palladium from electronic wastes (5-10%)

Approximately half of mined palladium is irretrievably lost to landfills and other places

Sources: Johnson Matthey, PGM Market Report May 2022; Izatt, S.R. et al., in preparation

PALLADIUM: GLOBAL SUPPLY DEMAND ISSUES MANDATE A GREATER RECYCLING EFFORT

- Projected growth in demand will require significant additional supply
- Increased supply is unlikely to come from mined ore due to increased cost of mining as ore grades diminish, ore becoming more difficult to access and potential for supply disruptions increase
- Increased recycling of palladium is a viable alternative to mining higher grades, more reliable supply, much less waste generation, many fewer geopolitical and labor issues, simple well defined matrices, availability of large quantities of spent catalytic converters and electronic wastes that contain palladium in amounts much larger than those found in ore bodies

CHALLENGES FOR PALLADIUM RECYCLING FROM SECONDARY SOURCES

- Spent catalytic converters and electronic wastes must be collected and transported to the few global integrated refineries available
- Electronic wastes contain palladium at low (ppm) levels in individual units (iPhone, circuit board) that are not easily or economically collected
- Catalytic converters contain palladium at higher concentration levels but still must be transported
- Classical technologies (solvent extraction, ion exchange) are not efficient in recovering metals technologically or economically from secondary sources, especially at low concentration levels in complex matrices

SUMMARY OF ADVANCES FOR PALLADIUM RECOVERY FROM SECONDARY SOURCES USING MOLECULAR RECOGNITION TECHNOLOGY™

- Highly selective, single step separation of palladium with near-100% recovery eliminates expensive downstream processing
- No organic solvents or harsh chemicals are used in MRT™processes eliminating a host of problems associated with their use
- Minimal waste generation minimizes potential environmental and social concerns
- 100-fold or more concentration in the elution step enables economic recovery from formerly inaccessible, low palladium level solutions
- Rapid binding and release kinetics permit inclusion in plant operation on a real time basis
- Compact MRT™systems conserve space, labor, time, chemicals, energy and infrastructure significantly reducing Capex and Opex values
- Acircular economy in palladium is attained with achievement of palladium sustainability and zero carbon footprint

SUPERLIG® MOLECULAR RECOGNITION TECHNOLOGY™

Highly Selective Green Technology for the 21stCentury

ELECTROCHEMICAL STUDIES ON PLATINUM DISSOLUTION FROM AG-AU-PT ALLOY IN DILUTE NITRIC ACID

(This paper was originally presented at the 2006 IPMI Conference)

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ABSTRACT

The electrochemical studies on pure Pt and Ag-Au-Pt alloy were investigated. The corrosion behavior of Pt in Ag-Au-Pt (10:3:1) wt % ternary alloy was studied. Corrosion studies were conducted using potentiodynamic polarization technique with a three electrode arrangement. The Ag-Au-Pt ternary alloy was used as working electrode. The experiments were conducted in 50 wt% HNO_3 at 65°C. Samples were analyzed before and after the corrosion studies using SEM and EDAX. Corrosion rate of 0.26 and 4.69Å~10^6 micrometers per year were observed for pure Pt and ternary alloy, respectively.

The surface of the corroded alloy was composed of individual grains. Different concentrations of platinum were observed on the grain surface, grain edge, and bottom of the grain. Concentration of Pt on top of the grain and at the edge of the grain is 10.09 and 15.55 wt%, respectively. Platinum content of 4.68±1 wt % observed in the EDAX analysis of corrosion product confirmed the corrosion of Pt from Ag-Au-Pt alloy in 50 wt% HNO3. It can be concluded that dissolution of Pt from the sample is due to bulk as well as grain boundary diffusion.

INTRODUCTION

Platinum is inert in most of the aqueous corrosive environments [1]. Dissolution of platinum from precious metal scrap is not well understood. It has been well known to the skilled fire assayers that an alloy of platinum prepared with gold and silver, such that it contains (a) gold three times the amount of Pt and (b) silver at least three times the amount of gold, then platinum and silver in the resulting alloy will dissolve in dilute nitric acid (due to the parting of silver) whereas gold will not.

Dissolution of Pt in NaCl, HCl solutions [2], and potentiostatic studies of PtO [3, 4], Pt^{2+}

compounds [5] under more severe electrolytic conditions with varying potential were investigated. Since the observed dissolution rate of Pt is very small, no systematic studies on the dissolution of Pt from alloys was reported. In the present study dissolution of platinum from Ag-Au-Pt (10:3:1) wt % alloy using potentiodynamic polarization technique was investigated. The reaction products were analyzed using SEM and EDAX. Corrosion rate of Pt in Ag-Au-Pt alloy was determined.

EXPERIMENTAL PROCEDURE

Potentiodynamic polarization tests were conducted using three-electrode method consisting of working electrode, counter electrode, and a reference electrode. The working electrodes are pure Pt and Ag-Au-Pt alloy. Platinum foil and saturated calomel were used as counter and reference electrodes, respectively. The samples were mounted in an epoxy mould. Electrical contact was made by using single stranded copper wire soldered to the sample along with silver conductive paint for better electrical contact. The mounted sample was ground with 240-grit emery paper and further polishing was carried out with 400, 600, 800, 1000, and 1200 grit emery papers. Final polishing was done on the cloth polisher (Struers Inc.) using water suspended silica/alumina polishing media to obtain mirror like finish. Furthermore, the samples were degreased using methanol, washed with double distilled water and dried just before corrosion test. Sample preparation and cleaning was followed as per ASTM standard: G1-03.

The electrolyte used in this study was 50 wt% HNO_3 and tests were conducted at 65°C temperature. The counter electrode was platinum foil spot welded to platinum wire sealed in Pyrex. Accumet™ saturated calomel reference electrode was placed in a Pyrex tube outside the cell. The Pyrex tube having a Luggin capillary at one end was filled with saturated KCl solution. The mounted sample was then placed just above the tip of the Luggin capillary (approximately 1 mm). A conductive gel (Agar gel) was applied on the tip of the Luggin capillary to prevent contamination of KCl and electrolyte (50 wt% HNO_3). A hot plate was used to maintain the temperature of the corrosion cell. The tests were conducted using an EG&G Princeton Applied Research Potentiostat/Galvanostat (Model 273A) and analyzed with EG&G Version corrosion software. Experimental setup along with the Potentiostat/Galvanostat is illustrated in Figure 1. Argon was purged through the electrolyte solution for 1 hr before the start of experiment. The scan rate employed was 10 mV s^{-1}. It was observed that alloy dissolved in the electrolyte as soon as test was started. Morphology of the corroded sample was analyzed using SEM. The corrosion product in the solution was filtered and its composition was determined using EDAX.

(A) (B)

Figure 1. (A) EG&G PAR A273 potentiostat/galvanostat and (B) corrosion cell used for corrosion studies.

RESULTS AND DISCUSSIONS

Corrosion Rate of Ag-Au-Pt (10:3:1) Alloy

Potentiodynamic polarization test were performed to analyze the dissolution of platinum from Ag-Au-Pt alloy in 50 wt % HNO_3 solution at 65 °C. Figure 2 shows the potentiodynamic polarization curves of both Ag-Au-Pt alloy and pure platinum. The corrosion current and potential were determined by Tafel extrapolation method. Corrosion rate (r) for uniform corrosion can be expressed as following equation [6]:

$$r = \frac{3.27 i_{corr} W_i}{\rho}$$

where *r* is corrosion rate in micrometers per year, W_i is equivalent weight of the alloy, ρ is density of the alloy (g/cc) and i_{corr} is corrosion current density (μA/cm^2). Equivalent weight of the alloy was determined using atomic mass fractions and valency of each of the alloying elements [6]. Equivalent weight of the Ag-Au-Pt (10:3:1) wt % alloy is 94.19 and density of the alloy was assumed as 12.13 g/cc.

From Figure 2, it can be seen that Ag-Au-Pt alloy exhibited very high current density compared to that of pure platinum. For Ag-Au-Pt alloy current density did not vary when the voltage increased above 1.4 V as can be seen in the figure 2. However for pure platinum active anodic dissolution was observed with increasing voltages. Corrosion potential of 1.074 and 0.838 V vs. SCE was observed for platinum and Ag-Au-Pt alloy, respectively.

Table 1 illustrates the corrosion current density (icorr), corrosion potential (Ecorr) and corrosion rate of pure platinum and Ag-Au-Pt alloy. It can be seen that corrosion rate of the alloy is almost 18Å~10^6 times higher than that of pure platinum. The alloy corrodes immediately after inserting in to the solution which clarifies the high corrosion rate.

However, adequate measures were taken in determining the corrosion current considering the above difficulties. After the corrosion test, both the corroded sample and corrosion product were analyzed using SEM and EDAX.

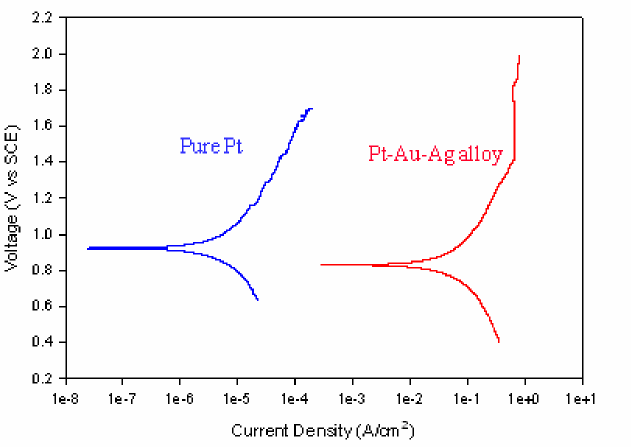


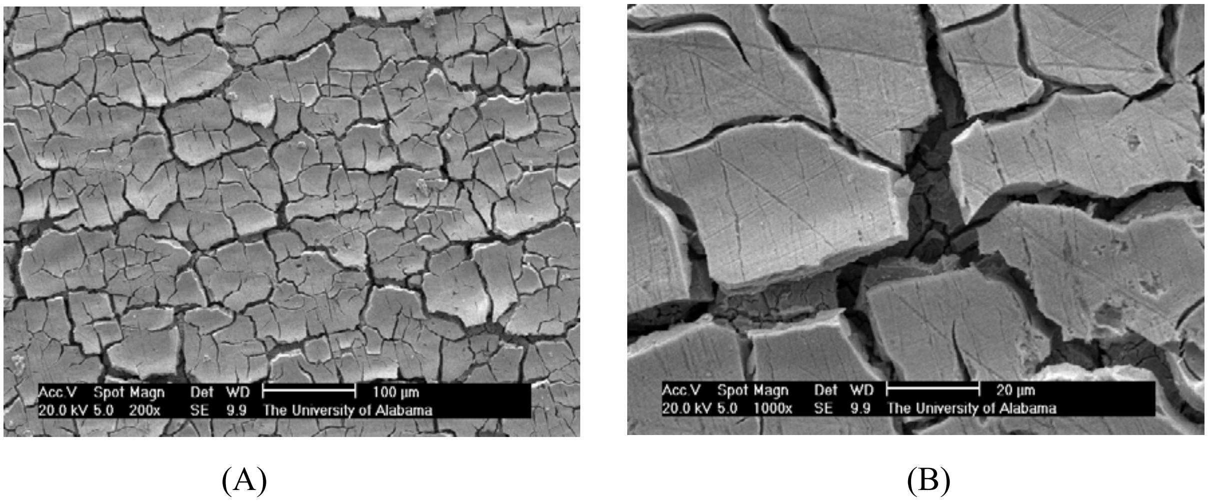
Figure 2. Potentiodynamic polarization curves of pure Pt and Ag-Au-Pt alloy in 50 wt % HNO_3.

Table 1: Corrosion current density (i_{corr}), corrosion potential (E_{corr}) and corrosion rate (r) for Ag-Au-Pt alloy and pure Pt

Material	E_{corr} (volts vs. SCE)	i_{corr} (A/cm^2)	Corrosion rate (r) micrometers per year
Ag-Au-Pt Alloy (10:3:1) wt %	0.838	0.1861	4.69×10^6
Pure Platinum	1.074	1.8×10^{-8}	0.26

Microstructural and Compositional Analysis of Corrosion Products

Figure 3 shows scanning electron micrographs of the surface of corroded samples. Surface of the corroded alloy was composed of individual grains as can be seen from Figure 3A. Cracks all over the surface may be due to the preferential dissolution of one or more components of the alloy. This resembles a commonly observed phenomenon of intergranular corrosion in austenitic stainless steels. At higher magnifications, a separate layer of the sample was observed below the grains as shown in Figure 3B. This indicates that dissolution of one of the components from within the alloy has developed a layer separation. Compositional analysis of the corroded sample using EDAX was performed to elucidate the mechanism involved in corrosion of the alloy.



(A) (B)

Figure 3: SEM images of the surface of corroded Ag-Au-Pt alloy at different magnifications.

Figure 4 shows the SEM images of the as received alloy and corroded sample. Figure (4A) corresponds to topography of the as received alloy, and figures (4B), (4C) and (4D) illustrate the top of the grain, bottom of the grain, and edge of the grain on the corroded alloy sample, respectively. The corresponding compositional analysis is shown in Table 2. It can be seen that concentration of Pt and Au in the corroded alloy has increased compared to the initial alloy, while Ag content has decreased. Enrichment of Pt, Au in the corroded sample is due to the dissolution of Ag, because Ag is more active compared to both Pt and Au. Ag is dissolving from top of the grain and from bottom of the grain through the edge, since less amount of silver is observed at the bottom than on edge of the grain. In the corroded sample, concentration of Pt is increasing from top to bottom of the grain and that of Au is decreasing. A small increase in the concentration of Pt in the corroded sample despite a large decrease in the concentration of Ag indicates that Pt is certainly corroding. Moreover, compositional analysis of the corrosion product will make it evident.

Table 2. EDAX compositional analysis of the as received alloy and different regions of the corroded alloy as shown in Figure 4

Element	As received alloy composition (Wt %)	EDAX alloy composition (A) (Wt %)	Top of the grain (B) (Wt %)	Bottom of the grain (C) (Wt %)	Edge of the grain (D) (Wt %)
Pt	7.14	10.21 (±0.5)	10.09 (±0.3)	11.33 (±0.5)	15.55 (±0.5)
Au	21.42	25.69 (±2)	84.95 (±2)	83.89 (±1)	73.14 (±2)
Ag	71.42	64.10 (±2)	4.96 (±0.5)	4.78 (±0.3)	11.31 (±1)

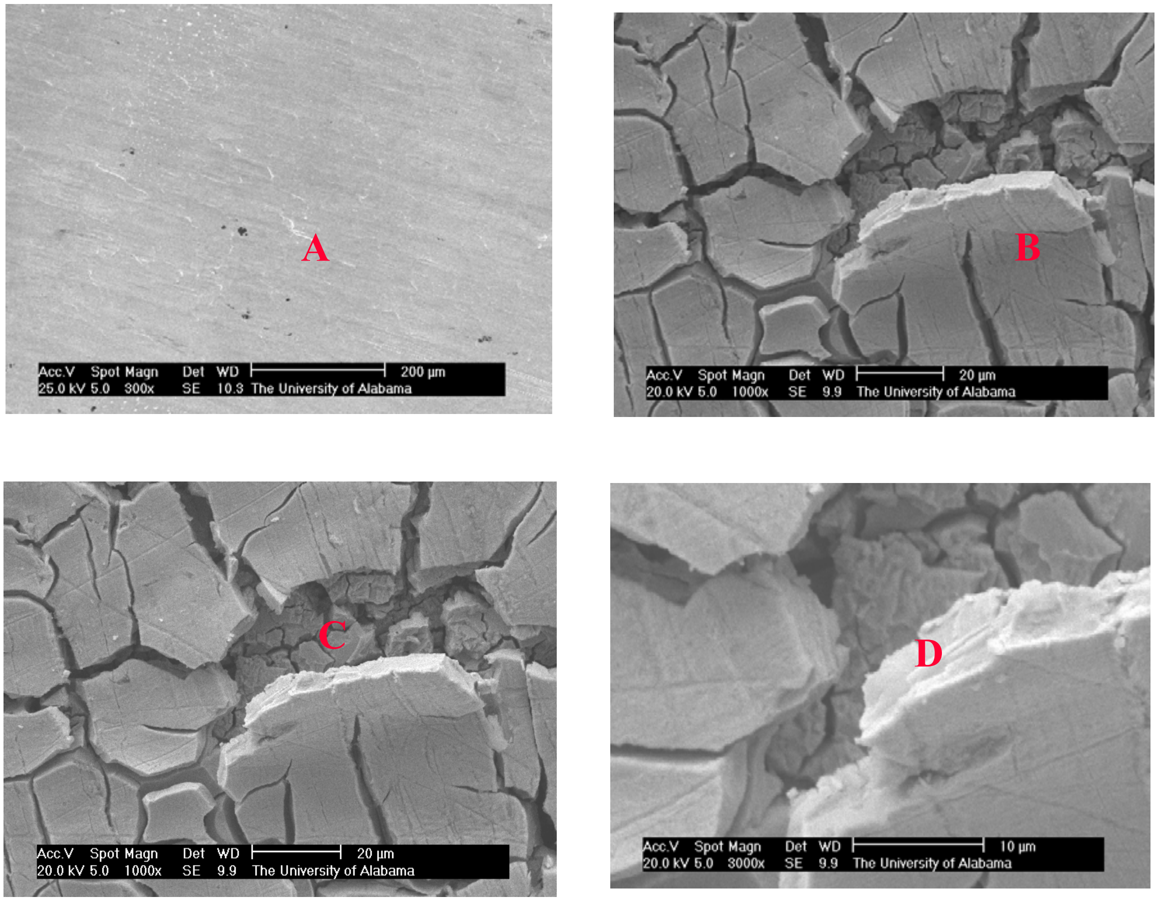
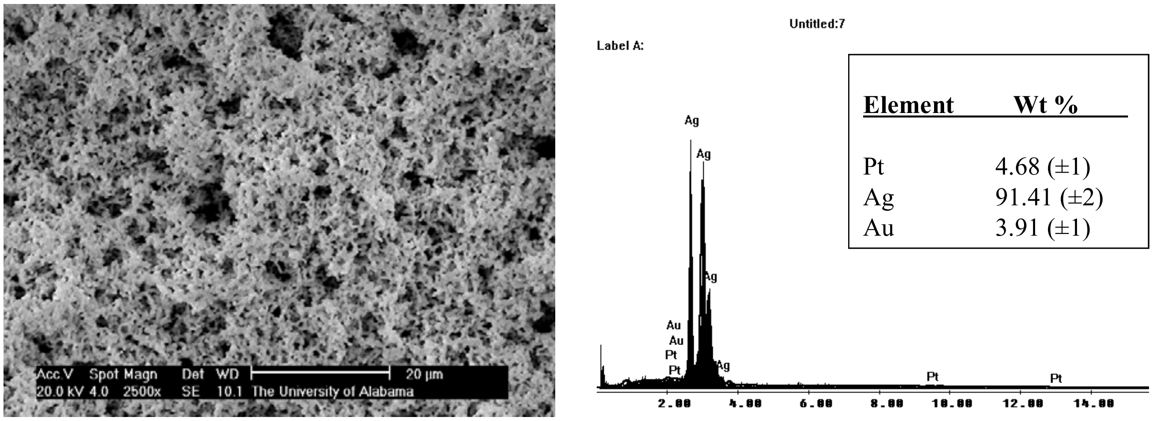


Figure 4. SEM pictures of the as received alloy and corroded sample at different regions. (A) As received alloy surface, (B) top of the grain, (C) bottom of the grain, and (D) edge of the grain.



Element	Wt %
Pt	4.68 (±1)
Ag	91.41 (±2)
Au	3.91 (±1)

(A) (B)

Figure 5. (A) SEM picture of the corrosion product after filtration, (B) EDAX and quantitative analysis.

SEM image, EDAX, and quantitative analysis of the corrosion product are shown in Figure 5. Corrosion product is mainly composed of silver (91.41±2 wt %) and small amounts of Au (3.91±1 wt %) and Pt (4.68±1 wt %). Presence of platinum in the corrosion product confirms the observation that Pt corrodes in 50 wt % HNO3. Moreover, it can be concluded that dissolution of Pt from the sample is due to bulk as well as grain boundary diffusion.

CONCLUSIONS

Electrochemical studies on pure Pt and Ag-Au-Pt alloy were investigated. Corrosion behavior was studied using potentiodynamic test and corroded surface was analyzed using SEM and EDAX. Ag-Au-Pt (10:3:1) wt % alloy corroded instantaneously in 50 wt % HNO_3 solution at 65 °C. Corrosion rate of 0.26 and 4.69Å~10^6 micrometers per year were observed for pure Pt and ternary alloy, respectively. SEM images revealed that the surface of the corroded sample was composed of individual grains generated due to the dissolution of one of the components of the alloy. Platinum concentration in the corroded sample differs from that of the initial alloy. Concentration of Pt on top of the grain and at the edge of the grain is 10.09 and 15.55 wt %, respectively. Presence of 4.68±1 wt % of Pt in the corrosion product concludes that Pt corrodes due to bulk as well as grain boundary diffusion.

ACKNOWLEDGEMENTS

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ELECTROCHEMICAL PRINCIPLES AND REFINING

(This paper was originally presented at the 1981 IPMI Symposium on Recovery, Refining, Reclamation and Refining of Precious Metals)

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ABSTRACT

The basic electrochemical principles of importance in hydrometallurgy are reviewed. The process of electrorefining is described with its application to the precious metals. The design of cells for the refining of silver and gold is discussed with examples from current practice.

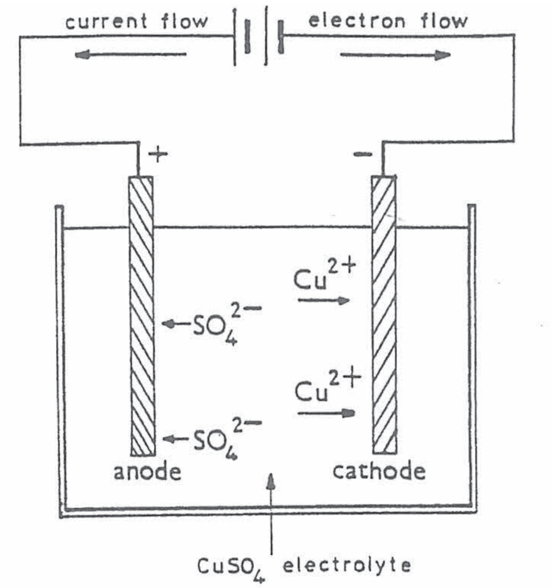
INTRODUCTION

Extractive metallurgy relates to the recovery and refining of metals from their ores and both pyrometallurgical and hydrometallurgical processes are used. In both cases chemical reactions are employed in which oxidation and reduction steps take place. These chemical reactions require energy input either to allow thermodynamically unfavourable reactions to proceed or to speed up thermodynamically favourable ones for maximum process efficiency. This energy is often provided by thermal means using fossil fuels, but electricity offers an alternative energy supply. In both pyro- and hydrometallurgy electrical energy is widely used indirectly with arc furnaces, induction furnaces, solution heating, etc., but it can also be used directly in electrolytic processes.

PRINCIPLES OF ELECTROLYSIS

An electrolytic cell consists essentially of a positive electrode (anode), a negative electrode (cathode) and a conducting solution (electrolyte). The passage of current through the electrolyte is associated with the directional movement of ions, positively charged metal ions (cations) being attracted towards the cathode and negatively charged non-metallic ions (anions) migrating to the anode. On arrival at the cathode, the cations take up electrons and become metal atoms, while at the anode the anions lose electrons to become neutral radicals.

Figure 1 Electrolyte Cell



The passage of current through an electrolyte is not conducted in a similar manner to that flowing through a wire in which the current is carried by electrons. The electrical potential applied to the electrodes of an electrolytic cell is maintained by the flow of ions and is indicated by the solution of metal at the anode and deposition of metal at the cathode and also frequently, by evolution of gas bubbles. The electrical and chemical changes which occur during electrolysis are represented by electrochemical equations in which the ions carry charges equal to their chemical valency. Thus, the dissociation of a copper sulphate solution can be represented as:-

$$CuSO4 \rightarrow Cu^{2+} + SO4^{2-} \qquad (1)$$

On electrolysis with a copper anode, the cations migrate to the cathode where the copper ions accepting electrons are neutralised, to deposit copper atoms.

CATHODE REACTION $Cu^{2+} + 2e \rightarrow Cu$ (2)

At the anode $SO4^{2-}$ ions lose electrons and become radicals

ANODE REACTION $SO4^{2-} \rightarrow SO4 + 2e$ (3)

In order to maintain the cathode reaction, the lose of electrons caused by the neutralisation of the copper ions is made good by electrons obtained at the anode. The electrons travel through the external circuit to the cathode to become available for further copper deposition.

Electrolysis is therefore maintained by simultaneous processes at the anode ans cathode. Reactions taking place at the anode are oxidation reactions, and those at the cathode reduction reactions.

FARADAYS LAWS

The research of Michael Faraday, (1791-1867) led to the discovery of quantitative relationships between the amount of current passed through an electrolyte and the quantity of matter separated at the electrodes, and resulted in two well-known laws:-

1. The amount of chemical decomposition produced by a current is proportional to the quantity of electricity passing through the solution.
2. The amounts of different substances deposited, dissolved or discharged by the same quantity of electricity are proportional to their chemical equivalents.

Thus, if a current of 1 amp is passed through a cell for 1 second (1 coulomb) the weights of different metals deposited will be as shown in Table I, and are known as electrochemical equivalents. The quantity of electricity required to produce 1 equivalent weight in grams of chemical change is known as the Faraday (F) and is the same for all metals at 96,500 coulombs.

TABLE I

ELECTROCHEMICAL EQUIVALENTS

	METAL	ATOMIC	VALENCY	E.C.E. Mg/C
Al	ALUMINIUM	26.97	3	0.09326
Sb	ANTIMONY	121.76	3	0.4206
Cd	CADMIUM	112.41	2	0.5824
Co	COBALT	58.94	2	0.3054
Cu	COPPER	63.57	2	0.3294
Au	GOLD	197.2	3	0.6812
H	HYDROGEN	1.008	1	0.0104
Fe	IRON	55.84	3	0.1929
Pb	LEAD	207.21	2	1.0736
Ni	NICKEL	58.69	2	0.3041
Ag	SILVER	107.88	1	1.1179
Si	TIN	118.7	2	0.6150
Zn	ZINC	65.38	2	0.3388

The amount of metal deposited as shown in Table I assumes a cell efficiency of 100%. In practice, this is never attained because of current leakage, short circuits, gas deposition, etc. The actual current efficiency of an electrolytic process is, therefore, determined by comparing the amount of metal deposited at the cathode with that theoretically possible in accordance with Faradays Laws, and will often be in the vicinity of 90%.

ELECTRODE POTENTIALS

When a metal is in contact with a solution of its ions it has a certain tendency to react,with metal atoms entering solution as ions. The magnitude of this tendency is measured by the electrode potential which is characteristic of the metal and varies with its ionic concentration and with temperature. For example, if the metal is copper then the half cell would be Cu/Cu^{2+} and the electrode potential measures the tendency for the reaction Cu^0--> $Cu^{2+} + 2e^-$ to proceed.

When the solution involved in a cell reaction is at unit activity (i. e. a normal concentration of the metal ions), then the electrode potential for the half cell reaction is called the standard electrode potential. For convenience, the reference point used is the hydrogen electrode H_2/H^+ and a potential of zero is assigned to it, with all other metal electrode potentials being obtained through reference to this standard.

Standard single electrode potentials can thus be determined for all metals with reference to hydrogen and when listed in order of decreasing negativity this is known as the electrochemical series (Table II). The series indicates an order of decreasing reactivity and increasing nobility. The most active metals, and most difficult to reduce, are found at the top of the table whereas the easily reduced but less reactive metals are found at the bottom.

TABLE II

ELECTROCHEMICAL SERIES

Standard Single Electrode Potentials 25°C
(relative to standard hydrogen electrode)

ELECTRODE	E_0(V)	ELECTRODE	E_0(V)
Li, Li^{+}	-3.0	Fe, Fe^{2+}	-0.44
Na, Na^{+}	-2.7	Cd, Cd^{2+}	-0.40
La, La^{3+}	-2.5	Tl, Tl^{3+}	-0.34
Ce, Ce^{3+}	-2.5	In, In^{3+}	-0.34
Mg, Mg^{2+}	-2.4	Co, Co^{2+}	-0.29
U, U^{3+}	-1.8	Ni, Ni^{2+}	-0.25
Hf, Hf^{4+}	-1.7	Sn, Sn^{2+}	-0.14
Be, Be^{2+}	-1.7	Pb, Pb^{2+}	-0.12
Al, Al^{3+}	-1.7	Pt/H_2, H^{+}	0.00
Ti, Ti^{2+}	-1.6	Sb, Sb^{3+}	+0.15
Zr, Zr^{4+}	-1.5	Bi, Bi^{3+}	+0.32
Mn, Mn^{2+}	-1.2	Cu, Cu^{2+}	+0.34
Zn, Zn^{2+}	-0.76	Ag, Ag^{+}	+0.80
Cr, Cr^{2+}	-0.56	Hg, Hg^{2+}	+0.80
Ga, Ga^{3+}	-0.52	Au, Au^{3+}	+1.36

Any metal which is more electropositive (or more noble) than another metal will be replaced in solution. Thus when copper is immersed in a solution of silver nitrate, copper passes into solution as copper nitrate and silver is precipitated as metal. Similarly, copper is precipitated from solution by the even less noble iron or zinc. The practical use of these displacement reactions is known as cementation. When the metals shown in Table II are in contact with solutions of their respective ions in concentrations other than unit activity, the resulting electrode potentials are related to the standard electrode potentials (E^0) by the Nernst Equation:

$$E = E_0 - \frac{RT \ln a}{zF} \qquad (4)$$

where z is the valency of the metal ion
F is the Faraday
a is the activity of the metal ion
R is the Gas Constant
T is the absolute temperature.

CELL VOLTAGES

In any electrolytic cell, a definite potential difference must be established before the electrodes are disturbed from their equilibrium potential and current can flow. This excess potential varies for each metal and electrolyte, and once reached current will flow, with metal being deposited according to Faradays Laws.

The excess potential required, can be made up from various factors:-

a) The voltage required to overcome the resistance of the electrolyte. This is subject to Ohms Law, and will alter proportional ta electrode spacing.

b) The voltage required to effect compound decomposition. Unlike current relationships with metals which are subject to Faradays Laws, no exact correlation exists between the metal deposited and the voltage, which varies from solution to solution. Thus the decomposition voltage of a solution of zinc sulphate is 2.55 volts, whereas that of zinc chloride is only 1.38 volts. Approximate decomposition potentials for some metal solutions are shown in Table III,

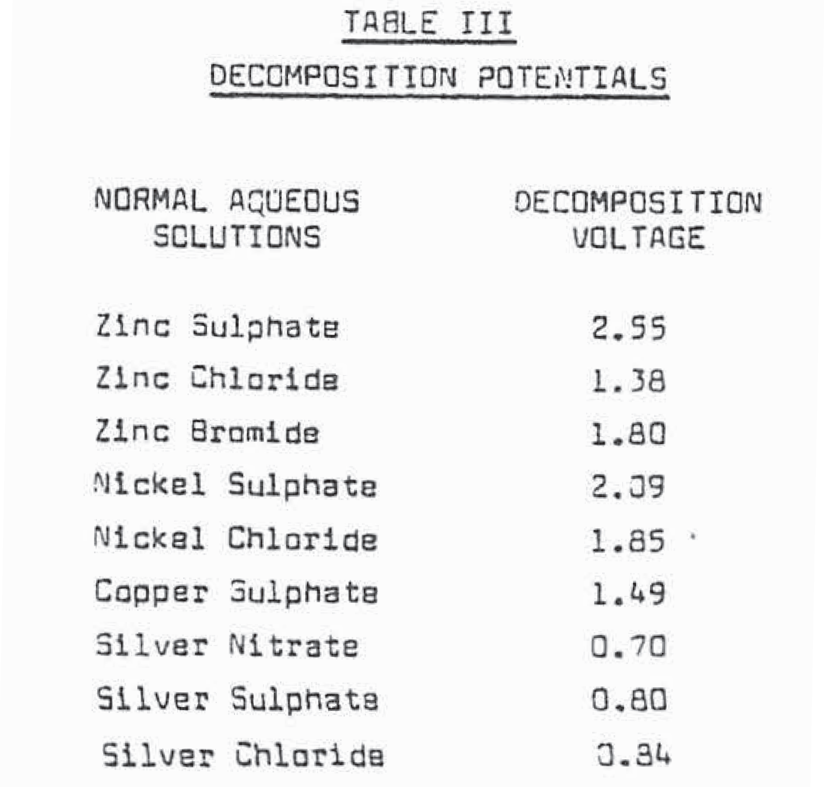


TABLE III

DECOMPOSITION POTENTIALS

NORMAL AQUEOUS SOLUTIONS	DECOMPOSITION VOLTAGE
Zinc Sulphate	2.55
Zinc Chloride	1.38
Zinc Bromide	1.80
Nickel Sulphate	2.09
Nickel Chloride	1.85
Copper Sulphate	1.49
Silver Nitrate	0.70
Silver Sulphate	0.80
Silver Chloride	0.34

c) Polarisation

Polarisation relates to the slowness of one or more processes occuring at the electrodes resulting in a change of ion concentration and/or an accumulation of electrolysis products at the electrodes.

Concentration polarisation is caused by the fact that the speed with which ions can travel through any particular electrolyte is limited. At the interface between the cathode and electrolyte there becomes a deficiency of metal ions as they deposit faster than they can diffuse through the solution. The opposite effect prevails at the anode. This depleted area adjacent to the cathode face is known as the Nernst or diffusion boundary layer. Concentration polarisation is an important factor in the electrorefining of metals. If the current per unit area is increased until the rate of metal deposition according to Faradays Laws surpasses the rate of diffusional supply of reacting ions through the Nernst layer, then the concentration of metal ions at the cathode will reduce to zero. This point is called the limiting current density and further increases of potential will not allow more current to flow unless another electrode reaction begins to take place. Furthermore, as the solution within the Nernst layer is depleted of positively charged ions the pH will rise and unwanted basic salts of electrolyte impurities can be precipitated, polluting the refined metal product.

The limiting current density can be raised and concentration polarisation effects reduced by any means which will assist the diffusion of ions through the electrolyte, such as stirring, circulation, increase in temperature, etc.

When the electrode reaction products are gaseous then significant gas overvoltages can occur. Hydrogen and Oxygen are the most common gases discharged and H_2 evolution at the cathode surface is a particularly important factor in electradeposition from aqueous solution. Molecules of gas accumulate at the electrode face and the resistance of these gas accumulations is higher than the normal resistance of

the electrolyte. This requires a higher electrode potential and can also prevent the arrival of fresh ions. The difference between the equilibrium value and that potential which caus, evolution of hydrogen gas bubbles is known as the Hydrogen overvoltage.

Values vary with the nature of the metal, law melting point metals generally showing the highest hydrogen overvoltage. The nature of the electrode surface can also have influence.

Hydrogen avervoltages can be large with respect to certain metals (sea Table IV) and it is because of this that some metals, such as nickel, zinc and cadmium whose standard electrode potentials are negative, can be refined by electrolysis.

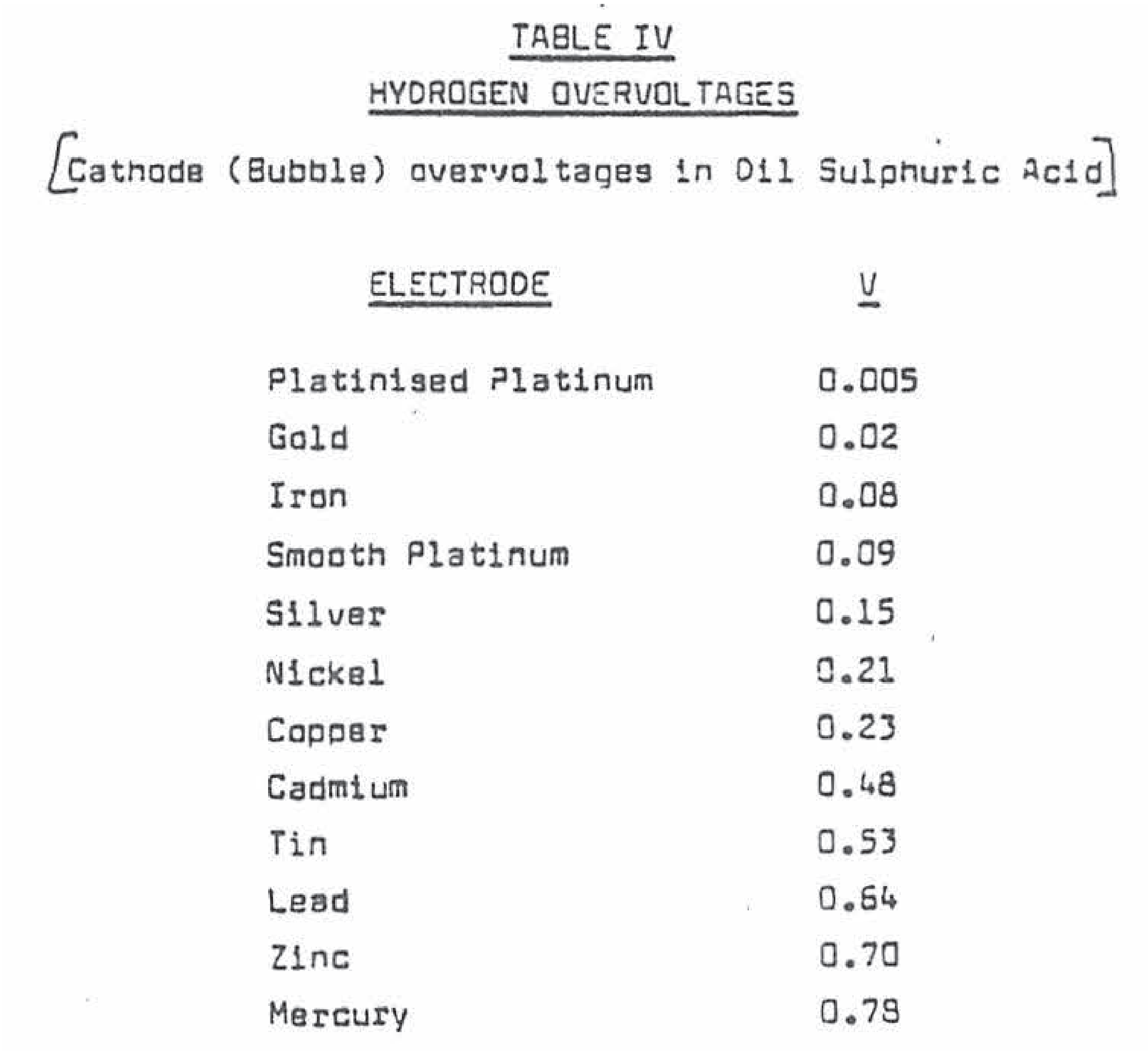


TABLE IV

HYDROGEN OVERVOLTAGES

[Cathode (Bubble) overvoltages in Dil Sulphuric Acid]

ELECTRODE	V
Platinised Platinum	0.005
Gold	0.02
Iron	0.08
Smooth Platinum	0.09
Silver	0.15
Nickel	0.21
Copper	0.23
Cadmium	0.48
Tin	0.53
Lead	0.64
Zinc	0.70
Mercury	0.78

ELECTROREFINING

Metals are often placed in solution, by chemical means, and recovered through electrowinning using inert or insoluble anodes. However, this process is not generally applicable to the precious metals which are widely recovered and refined using electrorefining processes with soluble anodes.

Process design must always start with the infeed material and any flow sheet developed must take into account all economic and operating factors to choose the best route. Electrorefining is just one available process which the designer can use. Electrorefining is a particularly flexible process in that it can often produce a refined metal product whilst, at the same time, separate and concentrate important and valuable by-products.

Examples of this are in the copper, cnickel and lead industries where these major non-ferrous metals are often bulk electrorefined to a high purity state and during the electrolytic process, precious and other important metals are separated and recovered in a form amenable to further refining treatments.

All these various electrorefining processes are reasonably well documented, and with such a wide varying number of influencing factors to process design it is the fundamentals which are best considered, especially where relating to precious metals.

SILVER

The introduction of electrolytic processes on an industrial scale through the latter part of the 19th century generated considerable interest and a great deal of work was done ta determine suitable electrorefining systems far the precious metals.

Early attempts by Wohlwill and others using a variety of electrolytes including sulphates met with many difficulties and were superceded when Dr. Moebius patented a process in 1884 using a silver nitrate solution as the conducting media. The first industrial plant was commissioned in 1885 and, in principle, the process has remained unchanged ever since.

Silver to be refined electrolytically can-contain many impurities such as gold, platinum group metals, copper, lead and other base metals. These impurities can vary considerably from plant to plant both in number and concentrations and Silver electrorefining cells are designed specifically to meet requirements.

When impure silver anodes are placed in a cell containing a silver nitrate electrolyte and a current passed, the silver will dissolve at the anode and deposit onto a suitable cathode in the form of pure silver crystals. Base metals mainly pass into and remain in solution, whilst gold and many platinum group metals will remain undissolved at the anode and fall as a slime.

The objects are:-

a) to remove the silver crystals from the cathode for washing, malting and market sale as pure silver.

b) to remove the anode slimes (containing as little Silver as possible) for further treatment to recover values such as gold and platinum group metals.

c) to maintain the electrolyte in as pure a condition as possible.

d) to perform all these operations at maximum speed and minimum operating costs, especially where labour related.

In practice, like most successful processes, the silver electrorefining system is found to be a series of compromises which are adjusted in relation to each other dependent on the particular anode metal.

The rate of production of Silver crystal is controlled by Faraday’s laws of electrolysis and for unit area of cathode relates to current density. The size and shape of the silver crystals produced, which will affect ease of removal and washing, is dependent mainly on current density, electrolyte composition and temperature.

Concentration polarisation can occur at high current density causing precipitation of polluting base metal impurities onto the silver crystal and this effect is also dependent on electrolyte composition, temperature and agitation.

The anode processes are affected greatly by bath current density and electrolyte composition (especially acid content) as well as other minor factors, and the anode processes will, themselves, control the quantity and composition of the anode slimes and the rate of base metal solution which, in time, alters the electrolyte composition.

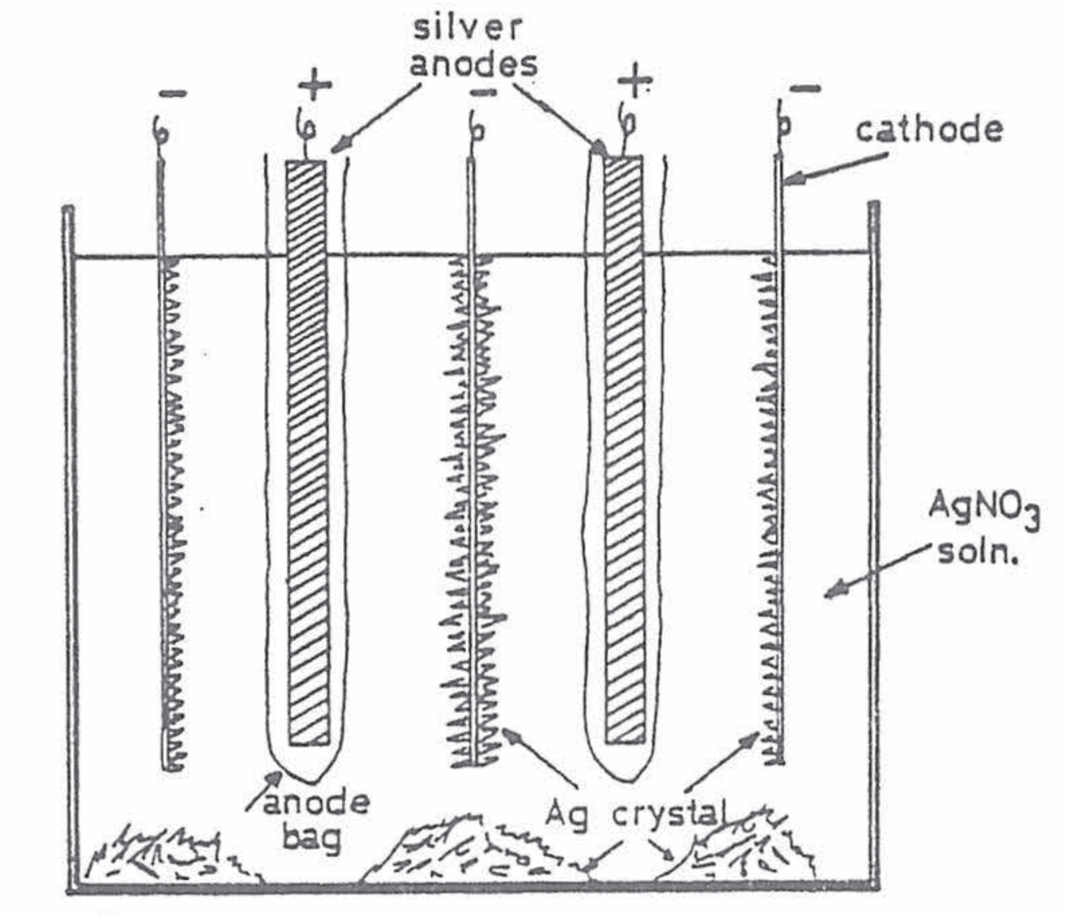
As alteration of the main factors, current density, electrolyte composition, temperature, has apposing effects at anode and cathode, the compromise is inevitable to arrive at a practical operating system.

Some of the problems created by the electrochemical compromise can be alleviated by cell design.

Two basic types of refining cell have found popularity. The original cell developed by Dr. Moebius uses the familiar vertical electrode arrangement and a later cell developed by Balbach and further improved by Thum uses a horizontal electrode configuration. Both cells are widely used today with very little change apart from improvements in general engineering and materials of construction.

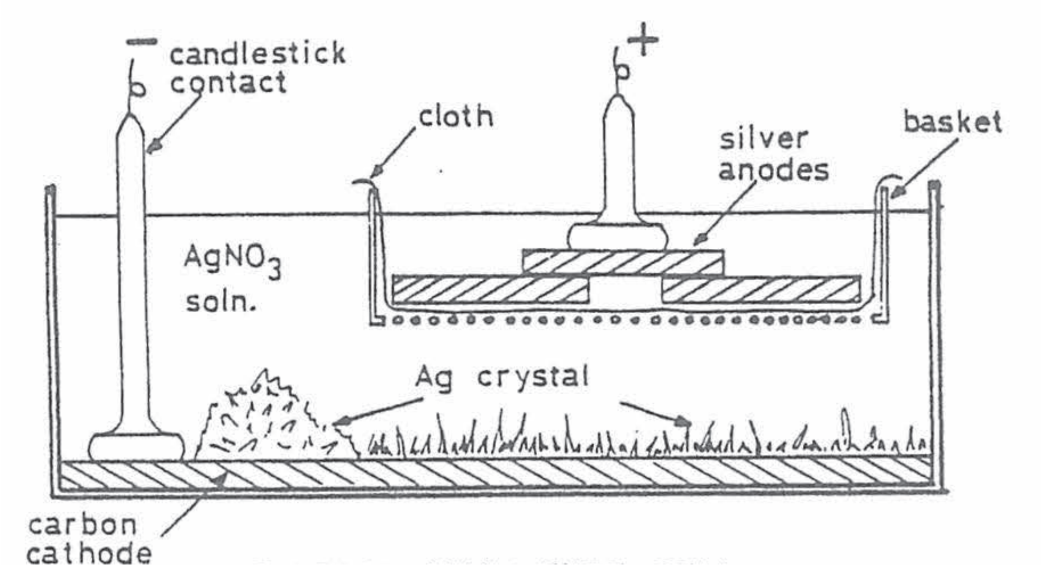
With the Moebius system the anodes are cast, drilled and bolted to hanger bars, before being immersed in the electrolyte. A woven cloth bag of controlled porosity is carefully placed about the anodes ta catch any anode slime produced. It is now usual far the cathodes ta be stainless steel plates upon which the Silver deposits as a coarse crystal which can be easily dislodged. It is common to use mechanically operated scrapers which pass back and forth across the faces of the cathodes to remove the crystal, which then falls to the bottom of the cell from which it is periodically removed. The cells are orten 30 x 30 x 24 inches deep. (see Fig. II).

Figure II Moebius Type Cell



The Balbach-Thum cell consists of a rectangular trough about 48 x 24 x 12 inches deep. The cathode is usually a solid slab of carbon which covers the bottom of the cell and is electrically fed by means of a candlestick type contact mads of silver. An anode basket is suspended in the top of the cell which has an open base fitted with rods across to support the anodes. A woven cloth bag is placed inside the basket and made rigid by a four sided frame, and is not removed unless damaged. A separate cloth is placed in the lined basket to catch anode slimes. Anodes are usually cast plates, but an advantage is that other shapes and smell pieces of silver scrap can also be used. At intervals the anode basket is lifted and silver crystal is scraped, by hand, from the cathode and removed from the call. In this system the anodes are totally consumed. (see Fig. III).

Figure III Balbach-Thum Type Cell



The same end result is achieved by either system and choice often depends upon the particular nature of the silver anode metal used, as there are many advantages and disadvantages peculiar to each type of cell.

A) Anode Scrap. The Moebius cell with its vertical electrodes leaves anorle stumps which must be remelted and recycled to the cells. This can often be as much as a 25% recycle and incurs ‘lock-up’ charges as well as the costs of remelting, etc. The Balbach-Thum cell consumes all of the anode.

B) Cathode Scraping. The Moebius cell allows for the Silver crystal to be continuously removed from the cathode by means of mechanical scraping gear. The cathodes need only be removed and scraped by hand occasionally to remove short, firm, crystal deposits which often build up beneath the scrapers.

The Balbach-Thum cell may have to be hand scraped at about four hour intervals.

C) Anode Slimes. Bags have to be carefully placed about the anodes in the Moebius system. This is laborious and there is always a danger of refined crystal contamination through tiny tears or holes in the anode bags.

The Balbach-Thum cell is doubly protected by filter cloths and the slimes carrying cloth is only removed when the anode slimes build to a significant quantity. There is also far less labour involved in slimes handling than with the Moebius system.

D) Power Requirements. The closer spacing of the electrodes in the Moebius cell offers a lower cell voltage than the Balbach-Thum system. Power is not, however, a significant part of the overall refining costs for operating either system.

E) Floor Space. Silver refineries are always short of floor space due to boundary restrictions imposed by security, etc. The Balbach-Thum cell requires up to five times the amount of floor space for the same production by the Moebius cell.

F) Electrolyte. As with floor space, the Balbach-Thum cell requires a much greater amount of silver nitrate electrolyte than the Moebius cell. This involves considerable extra cost of stock "lock-up." However, there can be an advantege in the larger electrolyte volume. Copper is usually the main impurity in anode Silver and will dissolve and concentrate in the electrolyte. When the copper level reaches a high concentration, the electrolyte must be removed and replaced with fresh low copper silver nitrate solution. With the Moebius system using a smaller electrolyte volume, the anode quality is normally restricted to about 2% impurities to avoid having to change the electrolyte too frequently. The Balbach-Thum cell can therefore be operated practically using a lower quality infeed metal than the Moebius.

G) Platinum Group Metals. Where there are platinum group metals present in the anode metal, the Balbach-Thum cell offers some advantages. The lower anode current density and lack of electrolyte agitation helps to prevent solution of some of these metals, and aids their recovery into the anode slimes.

H) Maintenance. As the Balbach-Thurn cell has no moving parts it is generally easier to maintain than the Moebius.

GOLD

The electrorefining of gold was developed by Dr. Emil Wohlwill and first used at the Narddeutsche Affinenie, Hamburg, in 1878.

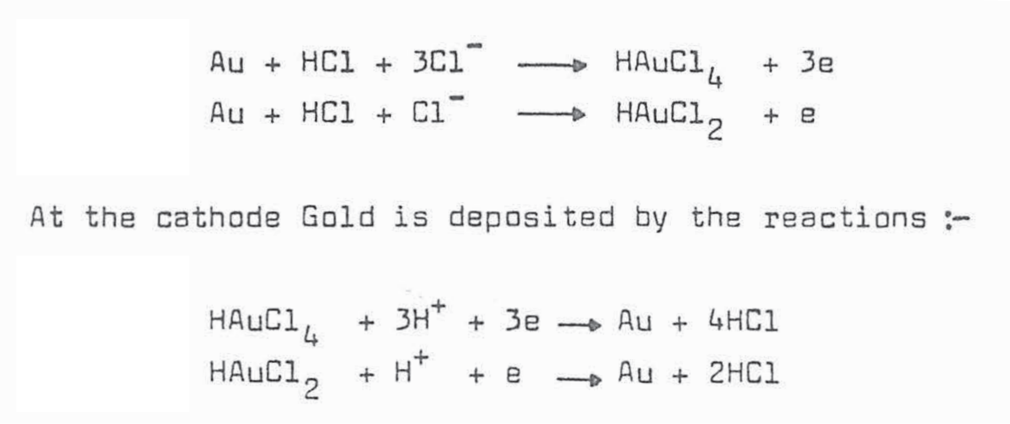
Although widely used throughout the world, the high value of gold has always had influence on refining process choice, and in many situations the economics of pyrometallurgical or chemical refining processes are preferable to the Wohlwill electrorefining system.

The Wohlwill cell is similar in many respects to the Moebius silver cell, using a vertical electrode system and anodes. Cells are generally small, often being about 1 ft. cube, and an Auric chloride electrolyte is used containing free chloride ion.

Thin gold sheet is often used as the cathode material but titanium is also now frequently chosen.

During electrolysis, gold passes into solution as stable anionic complexes by the anode reactions:-

During electrolysis, Gold passes into solution as stable anionic complexes by the anode reactions:-



$$Au + HCl + 3Cl^- \longrightarrow HAuCl_4 + 3e \qquad (5)$$

$$Au + HCl + Cl^- \longrightarrow HAuCl_2 + e \qquad (6)$$

At the cathode Gold is deposited by the reactions :-

$$HAuCl_4 + 3H^+ + 3e \longrightarrow Au + 4HCl \qquad (7)$$

$$HAuCl_2 + H^+ + e \longrightarrow Au + 2HCl \qquad (8)$$

Impurities in the anodes react to form chlorides. Metals, such as copper and zinc, pass into solution but silver and lead impurities farm insoluble chlorides which are left at the anode.

Platinum and palladium dissolve and are periodically recovered from the electrolyte.

If Silver is present in any quantity the silver chloride-formed can coat the anode completely preventing further dissolution. This effect is termed anode passivication and in such a case the silver chloride must be physically removed to allow electrolysis to proceed.

In 1908 Wohlwill proposed an interesting modification to his original patent which made use of a pulsating current obtained by superimposing a low frequency alternating current over the normal D.C. supply. This superimposed A.C. causes the adherent silver chloride film to rapidly flake off the anode and allows both higher silver content Gold to be refined and higher current densities to be employed.

The cathode reactions are considerably speeded up by electrolyte agitation and temperature elevation.

As with silver, the optimum operating conditions are a compromise of the various factors causing apposing effects and are adjusted to suit the particular infeed gold alloy.

GENERAL PLANT DESIGN

Precious metals are unique in that the process designer must consider many important factors which are of lesser importance in the non-ferrous industries. Many of these factors can be attributed to the value and rarity of the precious metals with their peculiar marketing forms dictated by bath industry and investors.

The mast important constraints added to normal process design are all interlinked and are :-

1. Economic
2. Inventory
3. Security
4. Market

1. Economic. The present high market values of the precious metals dictates that cycle time becomes a most important element of process design. Any middle man knows that payment terms given for Gold and Silver bearing materials must equate with payment terms received if a profit is to result. Even primary producers prefer to have money invested or in the bank gaining interest rather than metal tied up for long periods as stock in process. With the present lack of refining capacity throughout the world, caused largely by recant market· price increases, the time factor is becoming increasingly important in both process choice and detailed plant design.

2. Inventory · Apart from the speed of production of the marketable products, the quantity of metals tied up in process as inventory is vital to any good design. Overall inventory can be broken up in to three main areas which are, temporary lock up of metals in process, permanent lock up of metals in solutions, etc. and lock up of metals in by-products which have to be further recycled. Operating costs are all important and, with the precious metals, the amounts of values tied up in process at any point in time becomes a major factor in marginal assessment.

3. Security. Linked directly o the economic and inventory factors is security. Although security can be covered to some extent by insurance, it is often very difficult and costly to prove a loss claim and it can be a good investment to prevent it happening in the first place. Plant and equipment should be designed to minimise the risk of accidental process lass, and also maintain inventory in secure forms which can be easily quantified when required.

4. Market. The marketing of the precious metals is a complete subject in itself, but bath silver and gold are required to meet acceptable standards of quality and appearance in their refined forms.

Good design of electrorefining plant will ensure that the quality standards are met and the physical nature of the final products from the electrolytic cells can considerably assist the transformation into marketable ingots.

CONCLUSIONS ·

The general principles of electrochemistry have been outlined and their application to the refining of metals has been shown with special reference to silver and gold. Some commonly used types of electrorefining cells for the refining of silver and gold have been described with special emphasis placed on the various factors which can affect design.

TO SUM UP:-

A) The most important factor is the infeed metal itself and it must be stressed that all other considerations will relate to the composition cf the anode material.

B) The process designer should not only be an experienced electrachemist, but should also be an accomplished accountant and chemical engineer, with a sound security training and a deep knowledge of commercial and marketing practices.

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SAMPLING: POOR RELATION?

(This paper was originally presented at the 1984 IPMI Analytical Seminar)

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ABSTRACT

The importance of correct sampling as a vital pre-requisite to meaningful analysis is emphasized.

Sampling theory is given brief consideration along with some practical examples in the context of Fire Assaying.

1. INTRODUCTION

The Writer is of the view that Chemists traditionally have divorced their sophisticated activities in the Laboratory from the more mundane activities of the Sampler in the field. Much investment in terms of both manpower and equipment has been made in the analysis of precious metals without a commensurate, parallel investment in the discipline of samplinq. The Chemist continually strives to improve his precision, accuracy and reproducibility (and is succeeding!) whereas without accurate sampling such efforts are simply a waste of effort. Hence the title “Sampling – Poor Relation?”.

2. THE LITERATURE.

A search of the literature serves to highlight the “poor relation” concept: there is a dearth of substantial material .

Computer searches of the commonly available data bases also reveal very little of substance. Government sponsored standards for samplinq (e.g. ASTM, BS , JIS, DIN etc.) are comprised of empirical recommendations (most of them historical - i.e. traditional). Throughout the literature there is very little evidence of definitive studies.

Four publications are of interest.

1) Pierre M. Gy – “Sampling of Particulate Material”

2) 0. J. 0ttley – “The Sampling Slide-Rule”

3) Smith & Jones – “Sampling of Bulk Materials”

4) Springer-Verlag Berlin - “Analyses de Metale”

The latter is written in German. A H Kniqht have arranged a translation into English of the work on behalf of the BIR (Bureau International de la Recuperation).

Gy’s work is the major contribution into the “Principles of Sampling” and this is discussed in more detail later.

3. THE SAMPLING/ASSAY PARADOX

A study of typical relative errors found in the sampling and fire assaying of precious metals has been undertaken.

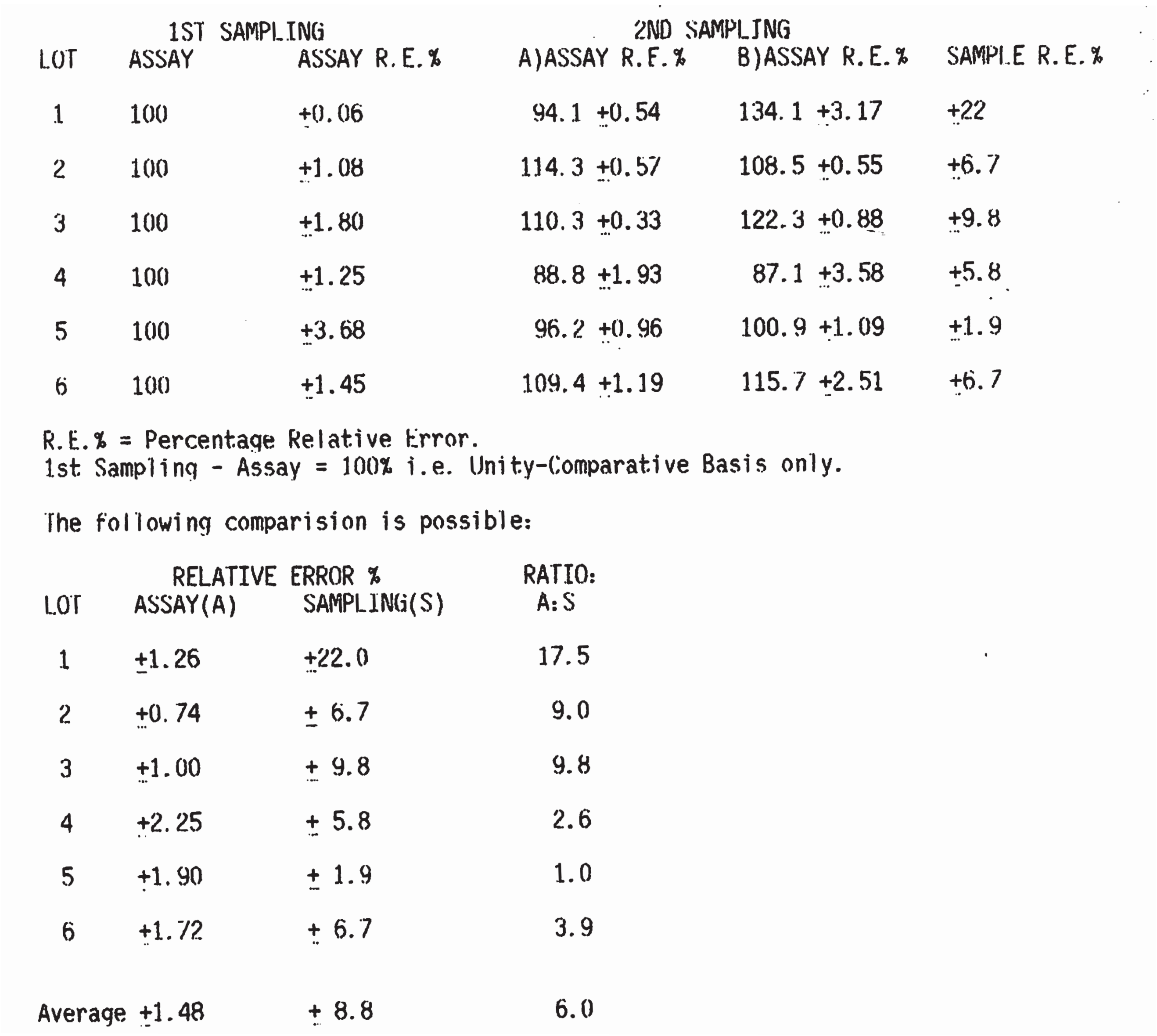
This highlights the gross divergence between the relative errors of the two activities.

A series of granular precious matal bearing materials was sampled by the following method:-

Stage 1	20 tonnes
	I riffle
Stage 2	10 tonnes
	I riffle
Stage 3	2.5 tonnes
	I riffle
Stage 4	1.5 tonnes
	I riffle
Stage 5	.625 tonnes
	I riffle
Stage 6	(A) 300 kgs (B) 300 kgs

These are tabulated below:

Table 1. Sampling Data and Results



	1ST SAMPLING		2ND SAMPLING				
LOT	ASSAY	ASSAY R.E.%	A)ASSAY	R.E.%	B)ASSAY	R.E.%	SAMPLE R.E.%
1	100	±0.06	94.1	±0.54	134.1	±3.17	±22
2	100	±1.08	114.3	±0.57	108.5	±0.55	±6.7
3	100	±1.80	110.3	±0.33	122.3	±0.88	±9.8
4	100	±1.25	88.8	±1.93	87.1	±3.58	±5.8
5	100	±3.68	96.2	±0.96	100.9	±1.09	±1.9
6	100	±1.45	109.4	±1.19	115.7	±2.51	±6.7

R.E.% = Percentage Relative Error.
1st Sampling - Assay = 100% i.e. Unity-Comparative Basis only.

The following comparision is possible:

	RELATIVE ERROR %		RATIO:
LOT	ASSAY(A)	SAMPLING(S)	A:S
1	±1.26	±22.0	17.5
2	±0.74	± 6.7	9.0
3	±1.00	± 9.8	9.8
4	±2.25	± 5.8	2.6
5	±1.90	± 1.9	1.0
6	±1.72	± 6.7	3.9
Average	±1.48	± 8.8	6.0

It can be seen therefore that there is an unacceptable difference between the magnitude of the two relative errors i.e. 6:1. (on average)

The relative error of the assay at 1.48 av (max 2.25) is acceptable: that relating to the sampling is not - 8.8 av (max 22.0%),

This then is the paradox: present assaying techniques give acceptable results already whereas present sampling techniques in some cases do not .

A further paradox is that the Chemist invariably carries out 2 if not 3 assays in parallel with standards whereas the sampler carries out only a single sampling operation! (without standards!)

A paradox indeed.

4. THEORETICAL CONSIDERATIONS

Gy’s basic sampling equation.

Equation 1.

$$M = \frac{Cd^3}{S^2}$$

where

M = mass of subsample (grams).

S = standard deviation (related to unity).

d = largest particle size (cm).

C = sampling constant

$= f \times g \times l \times c$

f = shape factor

g = particle size distribution factor.

l = liberation factor = $\frac{\text{top size } (d)}{\text{liberation size}}$

c = mineralogical composition factor

$= \frac{r}{a}$ where r = density of value.

a = assay value as decimal of unity.

Applying Gy’s formula to the samples itemised in 31 above, an average relative error of 3.11 is calculated with minimum and maximum values of 1.41 and 6.91.

We therefore conclude that theory indicates an expected relative error of 3.11 (951 confidence limits) whereas in practice a figure of 8.8 is found (max 22.01.). This clearly emphasizes the need to carry out a series of full scale samplings to establish the veracity of any indication given by sampling theory.

Theory is only a guideline: practice is the important thing, but at what cost?

5. COSTS OF SAMPLING/ASSAYING

The cost of assaying the series of samples derived in 3 above was:

18 assays at· $66 = $1080

The relative sampling costs were as follows:

1st Sampling	1ST Assaying
$1900	$360
2nd Sampling	2nd Assaying
$2800	$720

Thus the additional costs for duplicate sampling during the 2nd Sampling operation were $900 ($2800 -$1900) i.e. +50%

The costs of probable errors· are as follows: Let us assume material with 2% Ag 120 ton

1) Assaying

Error + 1.48%

120 x 1.48% x 2% x $260,000 = $9235

2) Sampling

error+ 8.81

120 x 8.8% x 2% x $260,000 = $55000

In fact with assaying there is usually an exchange of results between buyer/seller which in most cases would tend to half the error so:

assay error would be+ $4620

In contrast the sample error would remain as ± $55000

i.e. a ratio of 12:1

A comparison of the ratios of costs/ probable errors reveals:

Table 2. Costs and Probable Error Results

	Cost$	Probable Error (PE)$	Ratio (PE/cost)
Assays	360	±4620	13:1
Sampling Once	1900	±55000	29:1
Sampling twice	2800	±27500	10:1

It would be seen therefore that there is a case for dup 11 cate sampling i. e. for a 50% increase in sample cost ($900} the probable error is reduced by soi ($27500) i. e. 30: 1 cost effectiveness.

6.SAMPLING - A COMPROMISE

It would be reasonable to conclude from the above that more spending in sampling is justified.

However as shown, the direct costs of sampling are high compared to assaying.

The indirect costs such as the financial consequences-of delays in extra sampling can be considerable (especially at high current interest rates).

There is therefore an understandable reluctance on the part of buyer/seller to improve the standards of sampling.

A Refinery will use its resources to establish that the installed sampling systems operate without bias to the Refiner errors are to·1erable in a “no-bias” situation in that over the many transactions in which the Refiner is engaged all the errors (both+ and-) will cancel and the aggregate error will tend to zero.

Although the establishment. of such a system gives comfort to the Refiner, such systems will not protect the “small man’ who may conclude 1 or 2 transactions per year.

7. SAMPLING STRATEGY

Historically sampling methods have been evolved by a process of subjective judgements. The writer has already hi the high cost of sampling compared to assaying. However, one area in which correct sampling strategy ·; s of paramount importance is in Geothermic Surveying. Carr (7) has recently demonstrated successful applications of Samplinq. Theory to such a discipline.

In is paper the sampling of gold is considered. He confirms that “fire assay is the only authentic method for gold determination, in that the method is alone in being able to accommodate 150 gm of sample.”

Consider a gold ore:

Assay leve1·2 g/1000 kg - liberation size of gold - 20 microns

Initial thinking imposed by the constraints of sampling equipment was as follows:

Crush whole <0.62mm

Subsample 2.5 kg

Grind <0.21mm

Subsample 1. 25 kg

Grind <0.104mm

Subsample 0. 625 kg

Final Grind <0.076mm

Assay subsample (either 50 or 150 qm)

Application of Sampling Theory: Samplinq errors (for 95% confidence limits).

for 50 qm assay portion 36% Relative Error

for 150 gm assay portion 31% Relative Error

This was considered unacceptable.

The above system involved 4 subsamples and 4 crushing/sieving steps.

A simpler process was designed with only 3 subsamplings and 3 grindings which would give an acceptable sampling error.

Table 3.Sampling Process

Crush Whole <0.152mm

Subsample 2. 5 kg

Grind <0.104 mm

Subsample 1.25 kg

Final Grind <0.0/6 mm

Subsample (50 or 150 gm portions)

The predictable errors are:

for 50 gm assay portion 12%

for 150 gm assay portion 5%

A sampling scheme based in the second option enabled Assay Reproducibility to be maintained at. about. 5% which was acceptable.

Such work is of considerable expense: cost. is justified in that in establishing an ore body for development, mistakes would be obviously horrendously expensive. It is impactable, however desirable, to apply such exhaustive procedures to the sampling of every small lots of “PM” bearing residues. However, it is the view of the Writer that more collective work could be carried out to investigate the various common groups of precious metal bearing materials encountered throughout the industry.

8.CONCLUSIONS

The writer has attempted very briefly to focus the attention of Chemists in the Industry onto a much neglected, but most vital, element of the precious metal quantification process.

Van Loon (5) in his address to the Institute in London in October 1982 stated “it is the present author’s opinion that sampling errors often greatly-overwhelm errors concentrated in the analytical procedures. Great care is essential in developing a proper sampling strategy. In this regard, statistical approaches are probably best.t’ Stewart. (6) at the same meeting appealed to the Institute to sponsor the setting up of an Internationa·1 Standards Committee to consider the sub,1ect of sampling.

The writer endorses these views: If the Industry does not apply itself with equal energy to both assaying and sampling, then any deliberations in isolation about assaying are superfluous.

Is samplinq to remain a “poor relation”?

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SAMPLING PROCESS: HOW TO ENSURE ACCURACY, PRECISION, RELIABILITY & REPRODUCIBILITY

(This paper was originally presented at the 2022 IPMI Conference)

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ABSTRACT

As the recycling industry continues to grow, sampling has become an essential component in determining the value of recyclable materials. Especially when dealing with high-value commodities, such as catalytic converters containing precious metals, sampling methods must be carefully chosen and verified. Although there is a great deal of literature available describing the theory of sampling, the resource-intensive practical aspect of ensuring a representative sample is the responsibility of each company. While Sampling Processes are unique to each company and material type, the process should be thoroughly researched and validated to prevent negative effects on the processors or customers.

This paper will shed some light upon the practical approach Hensel Recycling is taking to ensure a representative sample when processing spent automotive catalysts. Although this method is not applicable to all types of material, it will hopefully demonstrate the challenges and complexity within any Sampling Process and encourages others to take the principles described to find new, creative methods of verifying current systems and procedures.

The questions are: How do we ensure the accuracy and precision of a sample? Is there even such a thing as a representative sample? Is there a way to prove and verify the representativeness of a sample? How can we ensure an unbiased Sampling Process? Once proven representative, how do we ensure the reliability and reproducibility of the process? Let’s find out!

FUNDAMENTALS

It is important to differentiate between the “Sampling Process” and the “Sampling System”. While the “Sampling Process” comprises every process step from receiving the catalytic converters to the final spectroscopic determination, the “Sampling System” describes the equipment (e.g., Ball Mill with an automated Rotary Divider) used to obtain a sample from the bulk material. Since a Sampling System cannot be verified isolated from the process steps to follow, the verification of a Sampling Process accounts for the propagation of uncertainties or random errors at each step.

A “Representative Sample” is an accurate and precise sample representing the bulk material processed. This can only be obtained when a Sampling Process has been verified unbiased and reliability and reproducibility are guaranteed through the implementation of appropriate quality control measures.

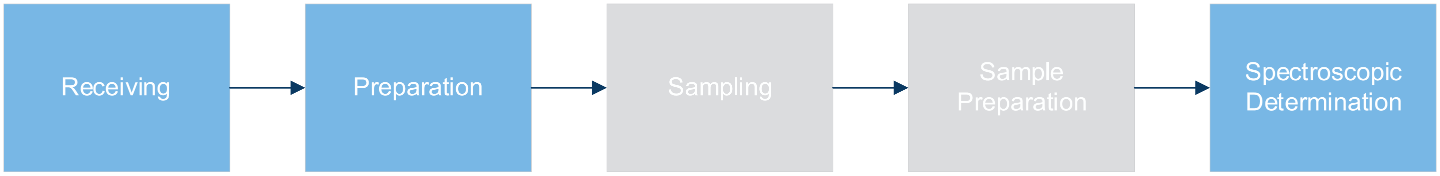

Figure 1: Process Steps

In obtaining a sample from a batch of catalytic converters, a series of process steps must be followed (Figure 1): A catalytic converter must be received, the substrate extracted, the substrate sampled, the sample then prepared, and finally the precious metal content analyzed. Process steps can be combined or further subdivided and differ among companies. As a matter of fact, ensuring a representative sample begins with the awareness of one's own capabilities prior to receiving and accepting recyclable materials.

Before elaborating on the Sampling System, I want to address the Spectroscopic Determination Process and some principles/best practices during the Receiving and Preparation steps.

The verification of the Spectroscopic Determination Process has been the center of much effort and focus in this industry. Frequently performed "Spent Automobile Catalyst Proficiency Tests", a.k.a. Round Robins, help in-house and independent laboratories to benchmark themselves against several other laboratories using a known standard sample provided to all participants [1]. This presents an excellent opportunity for laboratories to identify strengths/weaknesses and potentially calibrate systematic errors – a sophisticated approach to assessing your laboratory proficiency. Nevertheless, this proficiency program assesses the Spectroscopic Determination Process isolated from the rest of the Sampling Process and does not account for potential errors in the processing steps prior. The standard sample used in the Round Robin is subject to a variety of comprehensive homogeneity tests before distribution and does not represent a customer's lot. Each process step leading to the Spectroscopic Determination is therefore subject to the ethics, quality standards, research, and due diligence of the companies involved. What benefit is a confirmed proficiency when the Sampling System is biased by design? In other words, when the sample entering the Spectroscopic Determination Process is not accurately representing a customer's batch, the results are useless.

Checks and balances are essential throughout the entire Sampling Process. Therefore, it is important to have all scales (floor and lab scales) periodically calibrated and certified. In addition to the scale calibrations and certifications, Hensel Recycling performs daily visual scale inspections and uses test weights to verify proper scale functionality by applying statistical analysis. When processing a lot, it is advisable to take weights before and after each process step so discrepancies between input and output can be reacted upon immediately.

RECEIVING & PREPARATION

Receiving and Preparation steps may seem trivial, but solid quality control measures must be implemented to yield the desired outcome. The objective is to ensure the accurate representation of a customer's lot throughout the entire Sampling Process. Thorough, transparent, and complete documentation supports a factual discussion when a customer's expectations and reported results differ.

Without going into too much detail, the following principles can be applied:

- Documentation/Labeling: Proper warehouse material handling is key to an effective and efficient process. Customer's material needs to be clearly identified throughout the entire process.

- Weight/Count Confirmation: Differences in incoming weight and box/bag count requires immediate communication with the customer.

- Production Monitoring: Video footage helps clarify discrepancies. Hensel Recycling is using stationary video cameras at the dismantling stations to trace the processing of every single converter.

Cleanliness and dust extraction play a crucial role in the Preparation step. The machinery involved in this step can include, but is not limited to: alligator shears, shredders, blenders, guillotines, or a combination of different systems - all of which contribute to the formation of dust particles. De-canning equipment and dust control systems must be thoroughly cleaned between lots to mitigate and reduce the risk of cross-contamination. When using a baghouse unit, only one single lot should be processed at any given time. Fine dust, which is usually a multiple higher in value on a per pound basis than the bulk material, cannot be accurately assigned to its respective lot when processing several lots under the same baghouse unit.

SAMPLING & SAMPLE PREPARATION

The Sampling System and the Sample Preparation Process present real challenges as they add complexity and random uncertainties. In short, all materials deal with the issues of heterogeneity, hence, literature suggests reducing the:

- Constitutional Heterogeneity [2] which describes the compositional differences between particles or fragments that can be reduced by milling the substrate to a defined particle size.

- Distributional Heterogeneity [2] which describes the compositional differences between groups within a lot that can be reduced by blending.

Once the material is milled and blended, a composite sample must be taken during a continuous material flow. Automated rotary pipe dividers have been widely accepted as the method of choice. After all literature is digested, and all principles followed, the question persists: Do we have a representative sample?

SOURCES OF ERROR

Unfortunately, up to this point, there is no guarantee the Sampling System or Sampling Process will be accurate, precise, reliable or reproducible as many parameters and factors affect variability and possible bias.

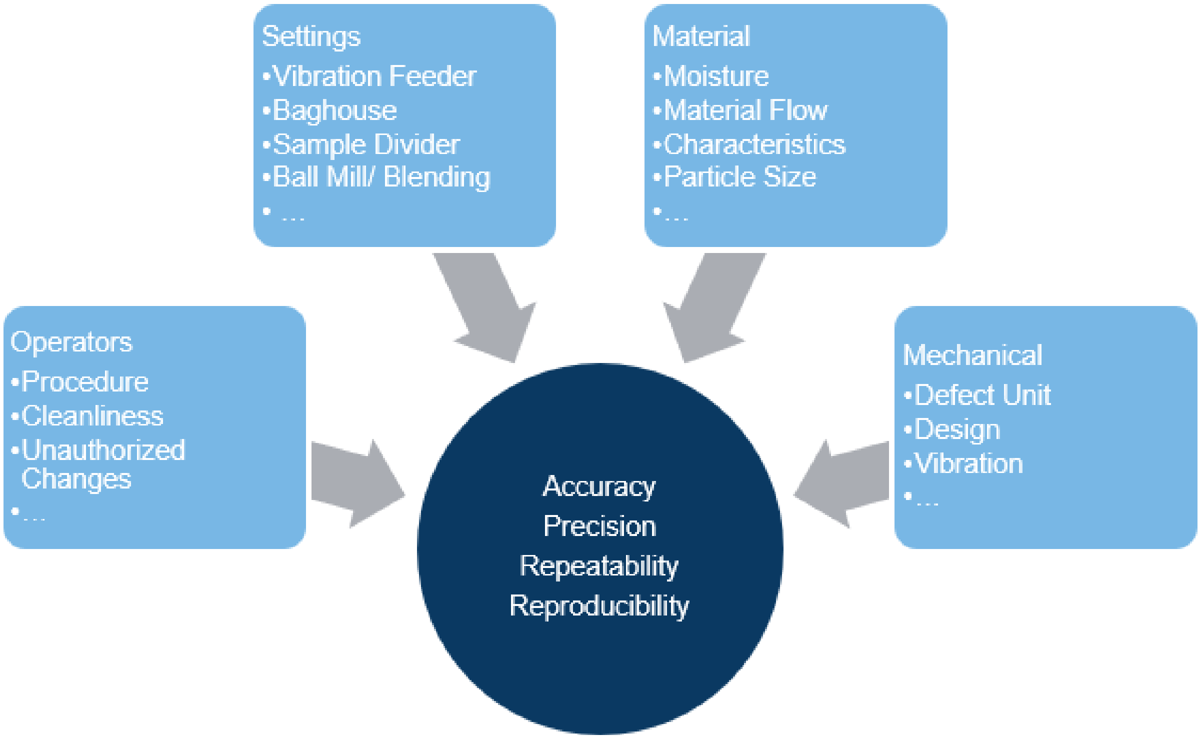

Figure 2 Sources of Error

Figure 2 illustrates the potential sources of error that can affect the sample integrity during the process. Although elaborating on every aspect would go beyond the scope of this paper, I will point out two sources of error that may have the greatest impact on the representativeness of the sample: Procedural Nonconformance and System Design.

Once a sampling process is defined and proven valid, operators need to follow strict procedures to repeat and reproduce the outcome. When operators do not adhere strictly to the same procedures, results could potentially deviate drastically.

An incorrectly designed Baghouse Dust Collection System may create negative pressure in the Sampling System, causing turbulence within the Rotary Pipe Divider which then affects the trajectory of the particles. Although efforts have been made to reduce constitutional heterogeneity, the particle size distribution is still relative in range. Therefore, negative pressure and turbulences have the potential of causing segregation due to particle mass and size.

APPROACHES TO ENSURE A REPRESENTATIVE SAMPLE

A standalone method that satisfactorily answers our questions does not appear to exist. The commonly used Cross-Comparative Analysis is helpful, but still holds a multitude of risks.

- Cross-Comparative Analysis with another Sampling System/Process
  - Results from processing the same lot in two separate and equally designed Sampling Systems/Processes are still inconclusive. The samples can be either unidirectionally biased or deviated significantly. In any case, without having a reference, no conclusion can be drawn as to which is the more accurate result.
  - Results from processing the same lot in two separate and unequally designed Sampling Systems/ Processes lead to the same inconclusive outcome. Results may be indicative, but not definite.

- Cross-Comparative Analysis with downstream Processor/Refiner
  - Comparing results with the downstream Processor/Refiner will not help to find the true value. Results may be indicative but not definite.

It is safe to say: Without knowing the true value of the material processed, results are inconclusive!

Hensel Recycling has developed a Verification Program that helps determine the accuracy and precision of the sample, as well as the reliability and reproducibility of the Sampling Process. A reference sample is obtained during the verification process, allowing for an unbiased comparison between the bulk material and the samples generated throughout the Sampling Process.

When processing a lot through the Sampling System, the bulk material is collected in a barrel. The barrel is then tumbled in a drum tumbler for approximately 10 minutes and spear sampled immediately afterward. To ensure accuracy, a strict spear sample procedure must be followed. The spear sample serves as the reference sample and is compared to the Sampling System's other generated samples (e.g., small, medium, large). Comparing the samples vertically (Figure 3) will provide information about the accuracy and precision of the Sampling System/ Process. Once the first run is completed, the same lot must be processed a 2nd time. Repeating this process n times (2nd run, 3rd run, …) and comparing the results horizontally (Figure 3) provides information about the repeatability of the process. During these runs, the parameters (machine settings, operators, etc.) must not be changed under any circumstances.

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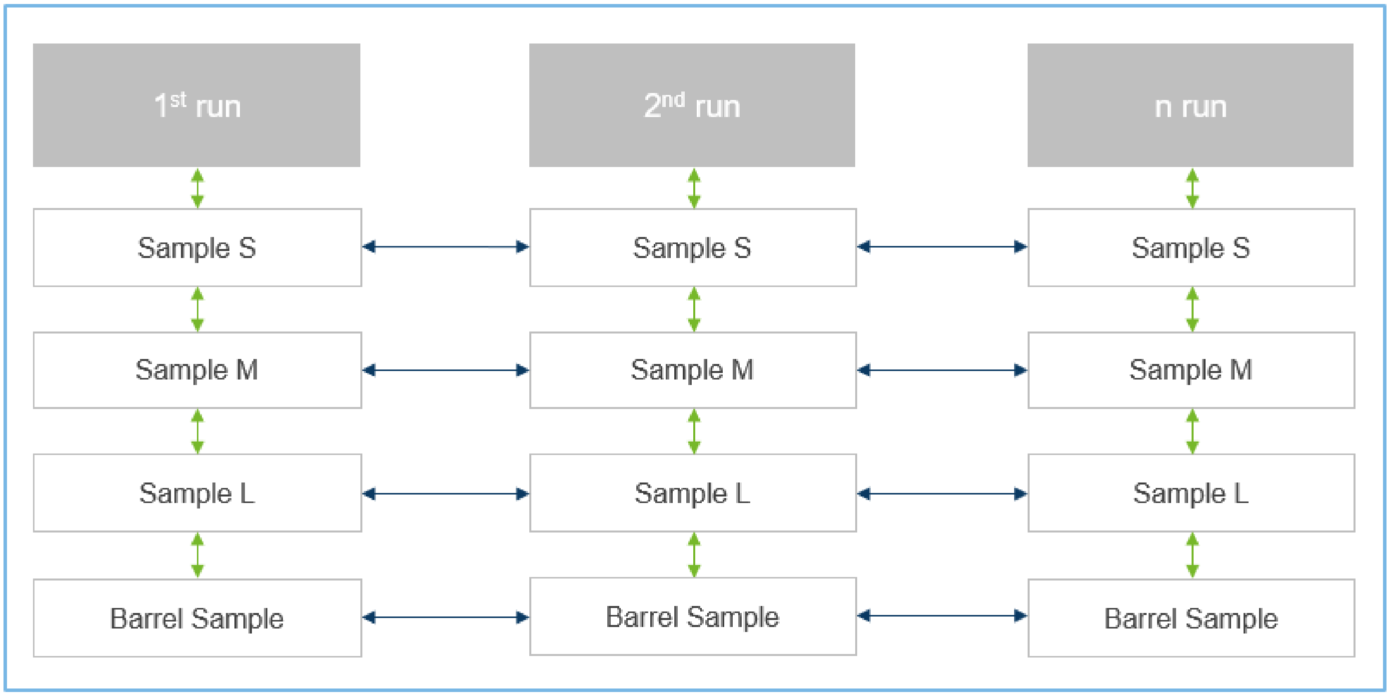

Figure 3 Verification Program

In order to verify the reproducibility of the Sampling Process, another operatork+1 must repeat the process described above (Figure 3). The comparison between the results of operatork and operatork+1 allows for conclusions pertaining to the reproducibility of the Sampling Process.

When a bias is detected, the source of error must be found by eliminating one parameter at a time. When the statistical analysis concludes the sample to be representative, KPIs (e.g., dust-to-bulk ratios and sample size) need to be determined for continuous quality control. Though KPIs do not necessarily yield conclusions about the representativeness of the sample, they serve as a great indication of a proper or faulty process. Tools such as Quality Control Charts (QCC) are easily applied in the day-to-day operation for tracking in-house KPIs [3]. QCCs also trend downstream processors/refiners. The Verification Program must be repeated periodically.

Although this document focuses on the Sampling System Verification, prior efforts must be made to verify the Sample Preparation Process. Similar to the Sampling System, a variety of errors can compromise the integrity of the sample. The sources of error must be identified, the effects empirically determined, errors corrected, and quality control measures implemented. Applying the principles described and illustrated in Figure 4 helps to ensure an accurate, precise, reliable, and reproducible process. Ultimately, the proficiency of every process step must be scientifically verified.

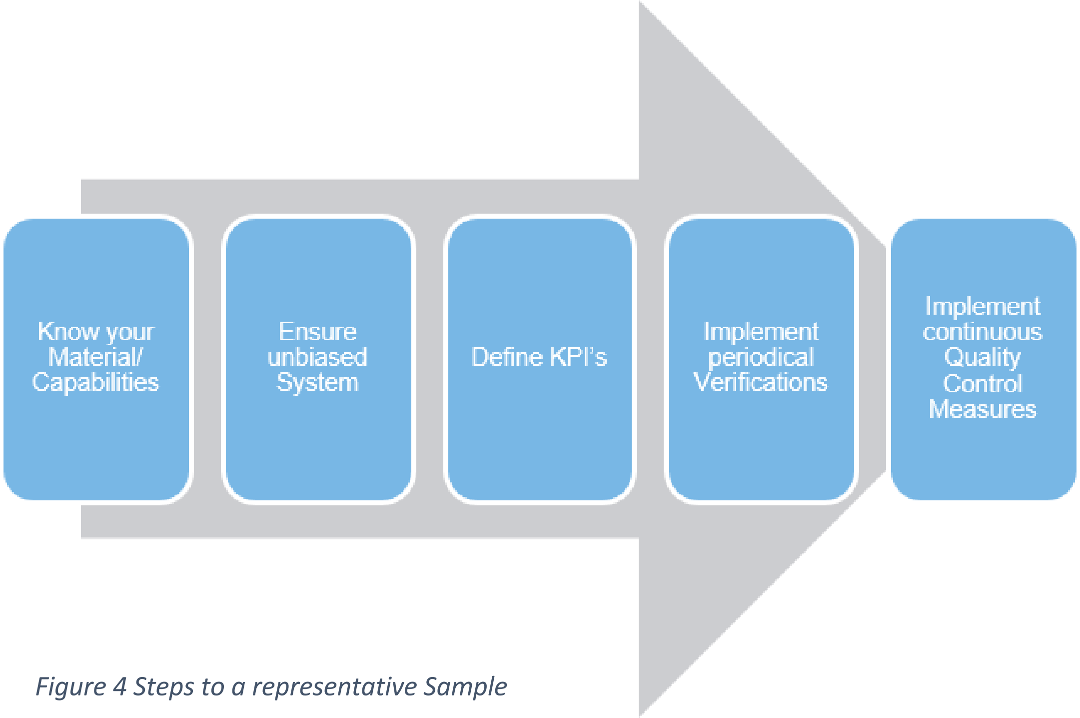

Figure 4 Steps to a representative Sample

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