The IPMI Journal

Foreword

It is with great pleasure that we announce the availability of this second 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, 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.

The second issue of the Journal contains eight total contributions that include six historical contributions in the fields of precious metals chemistry, assay, refining, sampling, and marketing and two new contributions. We plan continue to use this format in the issuance of the Journal on an annual basis.

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
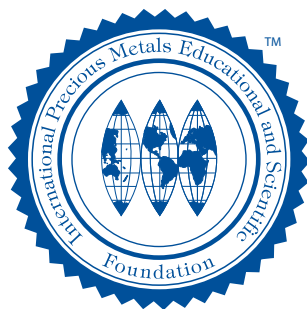
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The International Precious Metals Educational and Scientific Foundation

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 and Dr. Bob Ianniello 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 second 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

The secret to getting ahead
is getting started.

PMR
Catalytic Converter Recycling

The International Precious Metals Educational and Scientific Foundation Board of Directors

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The IPMI Journal - A Publication of the International Precious Metals Educational and Scientific Foundation - https://ipmi.org

NORNICKEL

The Palladium Challenge

Presented by the IPMI Educational and Scientific Foundation and Sponsored and Promoted by Nornickel

Palladium is one of the Platinum Group Metals (PGMs), known for its catalytic capabilities and valuable properties. It is widely utilized in the automotive industry as an essential part of catalytic converters. Palladium is also used in: chemical and petrochemical catalysts; electronic devices production (especially MLCC's and connectors); as well as dental restoration and jewelry.

Nornickel is the global leader in palladium production. As the largest palladium producer, Nornickel feels responsible for developing the palladium market and promoting metal use in new areas. That is why Nornickel would like to encourage professionals worldwide to take a more detailed look at palladium and its potential applications in their research areas. In order to do that, Metal Trade Overseas SA, affiliate of Nornickel, in collaboration with IPMI, launches the "The Palladium Challenge", is an award granted to individuals and institutions who come up with the most promising technological solutions that may generate substantial demand for palladium.

Areas of Research

Projects from any field of science and technology can participate in the competition. However, palladium applications in the hydrogen economy (including hydrogen storage and cleaning films, catalysts for electrolyzers and fuel cells, and hydrogen sensors), battery technologies (with palladium as a battery energy density booster), sensors, industrial catalysts or alloys are seen as the most promising areas of the research.

Who Can Participate

Participation in The Palladium Challenge is not restricted. All laboratories, universities, individual scientists, engineers, and entrepreneurs with a great idea are encouraged to participate.

The Palladium Challenge Criteria

The winner(s) will be determined by a panel of renowned experts in science and technology and the PGM market. The panel's decision will be based on the following key criteria:

1. **The scientific novelty of the proposed project**
2. **Economic feasibility and sustainability of the project**
3. **Minimum annual palladium demand in thousands of troy ounces generated by the proposed application**

Intellectual Property Rights

Subject to the Official Rules of the Palladium Challenge, participants retain any intellectual property, if any, in the submissions and assume all responsibility for any protection thereof. IPMI assumes no responsibility or liability whatsoever for any publication, use or dissemination of any submissions in connection with the Palladium Challenge.

Participant Registration and Official Rules

Participation in the Palladium Challenge is subject to the Official Rules and Participant's agreement to be bound by the terms thereof.

IPMI Disclaimer

IPMI is committed to serving its members and supports education and the sustainable and environmentally responsible expansion of the use of the precious metals in all applications. Subject to the terms of the Official Rules, IPMI makes no representations or warranties regarding the results of the Palladium Challenge and shall remain free and clear of any liability in connection therewith.

The Palladium Challenge Awards

1st place — US$200,000

2nd place — US$100,000

3rd place — US$50,000

Winners to be selected by September 2022

Register

To register, click on the palladium element symbol below. Your completed proposal must be submitted to IPMI by May 31, 2022.

Click Here to Register

PALLADIUM

Pd

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Nornickel retains the right to make changes to the awards and/or decline to grant any specific award In the event the Panel finds that no submission meets the contest criteria.

Recovery of Platinum Group Metals (PGM) From Acidic Leach Solutions Or Strip Liquors By Reduction-Precipitation With A Stabilized Form Of Sodium Borohydride

Permission granted by the author at time of submission to Precious Metals 1990.

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ABSTRACT

Sodium borohydride (SBH) can be used as an efficient agent to reduce the platinum group metals (PGM) such as platinum, palladium and rhodium from aqueous solutions at ambient temperature. The reduction reactions can be performed successfully from highly acidic solutions, e.g. 8 N HC1. The products obtained are agglomerates of very fine black metallic particles as confirmed by XRD and SEM analysis. The reduction reactions are fast; they are complete in less than one minute. Different parameters affecting the reaction are studied namely acidity, SBH and PGM concentration, time, temperature and the solution matrix. The presence in solution of other ions such as Al^{3+}, Zn^{3+}, Pb^{2+}, SO_4^{2-} or NO_3 has no effect on the reduction efficiency of SBH and PGM products obtained from impure solutions are themselves pure. However, the presence of Cu^{2+}, thiourea or thiocyanate ions has a negative effect. Tho process is simple, fast, efficient, selective, safe and economically attractive since it does not require costly capital investments. The barren solutions after PGM precipitation can be recycled. The technology is being patented by CANMET.

KEYWORDS

Platinum group metals (PGM), platinum, palladium, rhodium, sodium borohydride (SBH), agglomerates, reduction, selective.

INTRODUCTION

Separation and recovery of platinum group metals (PGM) has traditionally been achieved through a series of chemical salt precipitation-dissolution steps followed by calcination to produce pure metal sponge or powder. [1] However, these processes are considered inefficient in terms of the degree of separation, the yields obtained and the complexity of the operation. Today newer and more efficient techniques are replacing the usual refining processes in order to satisfy the increasingly stringent demands being made by novel applications outside of the traditional jewellery and investment casting industries. Precious metals have a special physico-chemical properties such as catalytic activity, conductivity and corrosion/oxidation resistance which render them useful in the electronic industries and in catalysts.

One of the most common techniques used for recovering PGM from aqueous solutions is cementation. Cementation can be done by a number of reductants such as Al, Zn and Cu or by a combination of Al with tellurium dioxide which acts as a collector for the precipitate formed [2]. At Outokumpu Pori Refinery, Finland, during the treatment of copper anode slimes, iron bars have been used to reduce platinum metals from solution after gold separation with Na_2SO_3[3].

Precipitation using H_2S or Na_2S is one of the better techniques used to produce a sulphide precipitate of PGM. Although quantitative recoveries are possible, the precipitate is usually highly contaminated. [4,5] Precipitation of palladium and silver from process solutions with thiocyanates and iron cyanides has also been reported. [6]

Chemical precipitations using sodium formate and formic acid as reducing agents have recently been adopted by Noranda, Canada and Sumitomo, Japan for their new precious metal refining flowsheets. [7,8] However, these processes require the adjustment of the pH of PGM bearing solutions to pH 4 and raising of the temperature to 75°C.

Reduction to metallic state from solution can also be achieved with hydrazine [9]; however, its handling requires extreme caution. Hydrogen reduction has been suggested to recover PGM, from aqueous, and organic media originating from solvent extraction processing. [10,11] The reaction in this case requires a special reactor and there is a danger of explosions. [12,13]

Ion exchange using reductive resins containing hydride, for example Amborane resin (Rohm and Haas) has been investigated for the recovery of PGM from the leach solutions. [14,15] The solution pH should be raised above pH 2 and the bulk metal product is recovered after burning of the resin which adds considerably to the process cost.

Electrowinning of platinum and palladium from *aqua regia* solution using titanium cathodes and graphite anodes at 1.4 V and 30 A/m^2 has been reported. [16] A process using the electrowinning of PGM from a leach liquor onto carbon particles has been patented in the USA by Mitsui. [17] The loaded carbon is recovered by filtration, the PGM redissolved and selectively precipitated.

In recent years, solvent extraction technology has supplanted traditional refining practice. Three large refineries based on solvent extraction are currently active. These are INCO Refinery at Acton [18], the Matthey Rustenburg Refinery (MRR) at Royston, UK [19], and the Lonrho Refinery in South Africa [20]. A process for solvent extraction and separation of platinum group metals and gold using organic amines has been briefly described [21]. More recently a Pt-Pd separation process has been developed by CANMET in which 8-hydroxy quinoline derivatives (Kelex 100, Lix 26) were used for their co-extraction followed by selective stripping for their separation [22-24].

The chemical reducing capability of sodium borohydride for precious metals is well known [25]. Actually sodium borohydride is being used for many applications such as silver removal from spent photographic fixing solutions [26], and for the removal of heavy metals from aqueous discharge streams [27]. Platinum Lake Technology Inc. has developed a proprietary leach technique to recover precious metals from spent automotive catalyst. Sodium borohydride in the form of VenMet solution is used to activate the catalyst before leaching by reducing oxidized PGM compounds which would be refractory to acid dissolution [28]. A number of processes have been pantented [17-32] on the use of sodium borohydride in precious metals recovery but none of them have described the process of reducing PGM from leach solutions and liquid streams originating from solvent extraction.

The purpose of this study is to examine the possibility of reducing PGM from highly acidic solutions and to devise a flowsheet for their recovery using sodium borohydride. The factors affecting the reduction efficiency have been examined. In addition examples of the application of the technique to the recovery of PGM from actual plant solutions have been tested.

EXPERIMENTAL DETAILS

Materials

1. Sodium borohydride was used as a stabilized aqueous solution containing 12% by weight $NaBH_4$ and 40% NaOH. It was supplied by Morton Thiokol Inc. under the trade name VenMet solution.
2. Standard solutions of platinum, palladium and rhodium, 1000 mg/L dissolved in 10% HCl were obtained from SPEX Inc., SCP Science Division. Rhodium solution was also prepared from $RhCl_3.xH_2O$ salt supplied by AESAR, Johnson Matthey Inc.
3. Analytical grade reagent acids, NaOH, NaSCN, $ZnSO_4.7H_2O$, $CuSO_4.5H_2O$, $ALC_3.6H_2O$, Na_2SO_4, $NaNO_3$ and thiourea $CS_2(NH_2)_2$ were used.
4. Actual Pt/Pd containing plant solutions tested were obtained from the Royal Canadian Mint, Ortech International and Noranda Inc.

Equipment

The equipment used for measurement and analysis were: pH meter (Metrohm, model 632), Pt electrode vs SCE connected to pH-meter (Fisher model 291), atomic absorption spectrophotometer (IL 551 AAS), X-ray diffraction (XRD) and scanning electron microscope (SEM).

Procedure

Most of the tests were performed in 250-mL beakers containing 100 mL of solution containing 100 mg/L PGM in chloride media at pH = 1 and at ambient temperature. The solution was agitated gently by a magnetic stirrer.

Kinetic studies were performed on 1 L of test solution. Samples were withdrawn at periodic time intervals, filtered and analyzed for the desired metals by AAS. When a mixture of Pt and Pd solution was analyzed, a lanthanum buffer solution was added to both standard and the test solutions to avoid interferences. The effect of temperature was examined in a similar way; 250 mL conical plastic flasks (instead of glass beakers) were agitated in a temperature-controlled shaker-bath. The reaction time was 2 minutes unless otherwise stated.

RESULTS AND DISCUSSION

The most common chloro-complexes of PGM in chloride media are $PtCl_6^{2\bullet}$, $PtCl_4^{2\bullet}$, $PdCl_4^{2\bullet}$, and $RhCl_6^{3\bullet}$.

Their standard potentials in aqueous chloride media are:

$$PtCl_4^{2\bullet} + 2e^\bullet === Pt + 4\,Cl^\bullet \quad +0.73\ V \tag{1}$$

$$PtCl_6^{2\bullet} + 2e^\bullet === PtCl_4^{2\bullet} + 2\,Cl^\bullet \quad +0.74\ V \tag{2}$$

$$PdCl_4^{2\bullet} + 2e^\bullet === Pd + 4\,Cl^\bullet \quad +0.62\ V \tag{3}$$

$$RhCl_6^{3\bullet} + 3e^\bullet === Rh + 6\,Cl^\bullet \quad +0.44\ V \tag{4}$$
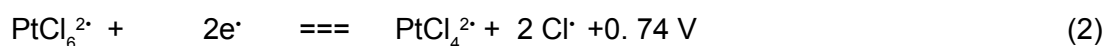
On adding sodium borohydride (as VenMet solution) to their solutions, an immediate drop in potentials was observed (Table 1) and fine black precipitates were formed indicating the efficiency of SBH in reducing PGM.

TABLE 1. Decrease in PGM Chloro-complex Solution Potential with Metal Reduction by SBH

100 ppm PGM, pH= 1, room temperature, 2 min reaction time

Metal	Molar Ratio (SBH/Metal)	Initial Potentials (mV)	Final Potentials (mV)	Recovery (%)
Pt	2	520	-121	95.6
Pd	1	403	-285	99.1
Rh	1	424	-270	99.8

The precipitates were recovered by filtration, air dried and determined by X-ray diffraction to be metallic Pt, Pd and Rh, (Figure 1).
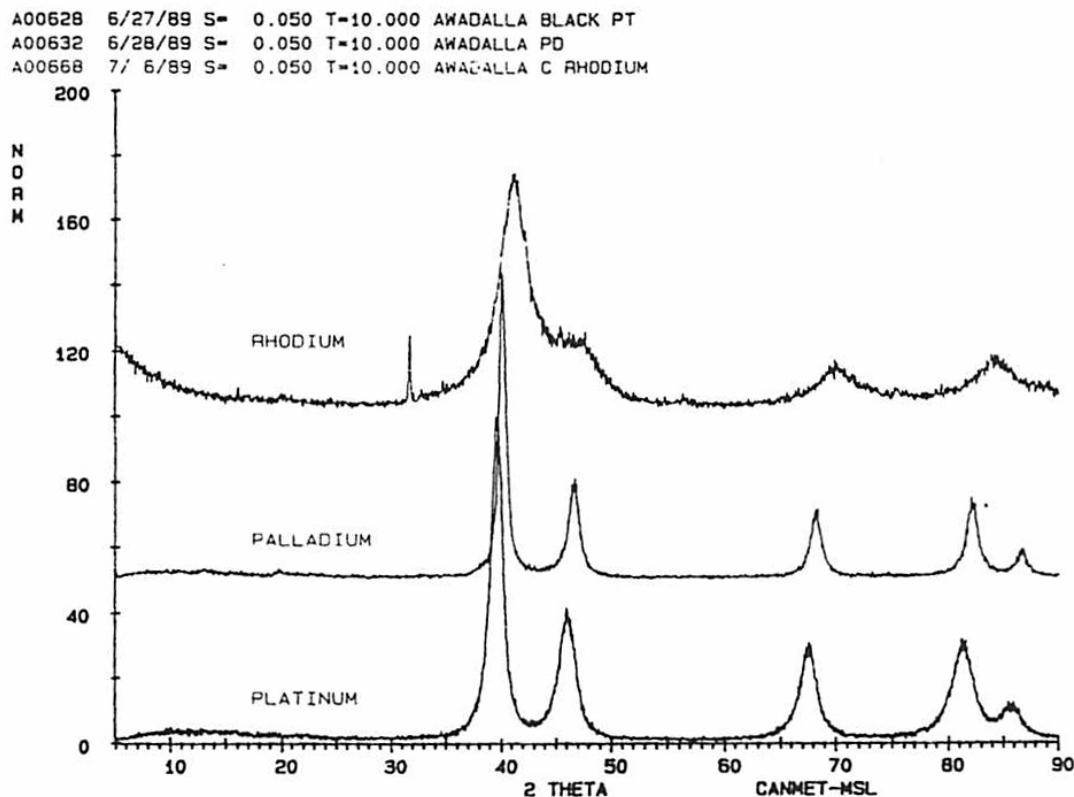
FIGURE 1 - X-ray diffraction pattern for the SBH reduced products
of PGM chloro-comlexes

Scanning electron microscopy also revealed that the particles were very fine crystallites of submicron size, (Figure 2), almost spherical in shape. The fine particles appeared to be agglomerated in the size range 30 to 100 μm (Figure 2).

Pd

Pt

Rh
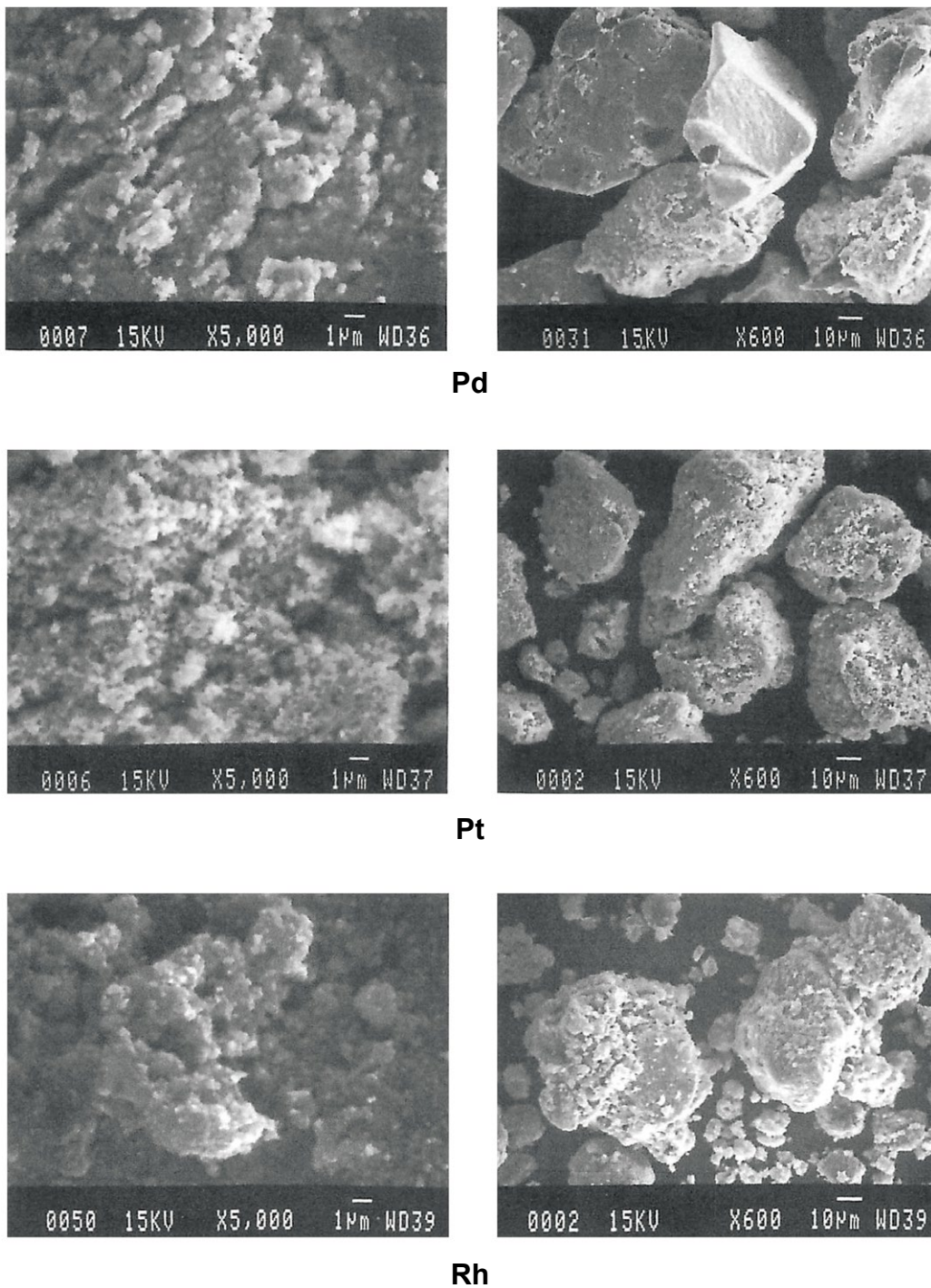
FIGURE 2 - Scanning electron photomicrographs for the products obtained by reduction of PGH chloro-complexes with SBH

Systematic studies were conducted on synthetic solutions of PGM in order to determine the optimum conditions for complete reduction. Parameters studied were pH, PGM concentration, stoichiometry, time, temperature and the solution matrix.

Stoichiometry

SBH is a strong reducing reagent; it supplies eight electrons per mole to achieve the reduction. The reduction reactions can be represented as follows:

$$PtCl_6^{2-} + NaBH_4 + 2H_2O \longrightarrow 2Pt° + NaBO_2 + 8HCl + 4Cl^- \tag{5}$$

$$PtCl_4^{2-} + NaBH_4 + 2H_2O \longrightarrow 4Pt° + NaBO_2 + 8HCl + 8Cl^- \tag{6}$$

$$PdCl_4^{2-} + NaBH_4 + 2H_2O \longrightarrow 4Pd° + NaBO_2 + 8HCl + 8Cl^- \tag{7}$$

$$^8/_3RhCl_6^{3-} + NaBH_4 + 2H_2O \longrightarrow ^8/_3Rh° + NaBO_2 + 8HCl + 8Cl^- \tag{8}$$
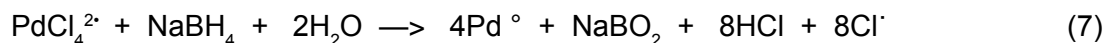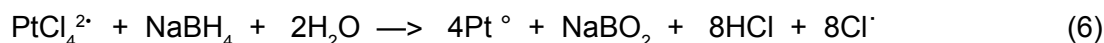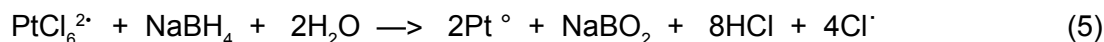
According to the above reactions, one mole of SBH can reduce 2 moles of Pt(IV) or 4 moles of Pt(II) or Pd(II) and 2.7 moles of Rh(III). Figure 3 shows that in the case of Pd(II) and Rh(III) ions, the stoichiometric amounts of SBH were enough to attain complete reduction. For platinum the quantities of SBH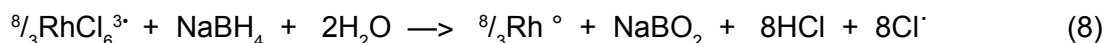 required were greater than the stoichiometric amounts calculated assuming that all the platinum is present as Pt(II). This is consistent with a large fraction of the platinum being present in the tetravalent oxidation state which requires more SBH (Pt(IV) —> Pt° = -1.47 V). However, the amount of SBH required to complete the reduction reaction is also dependent on other factors such as pH and PGM concentrations as discussed below.
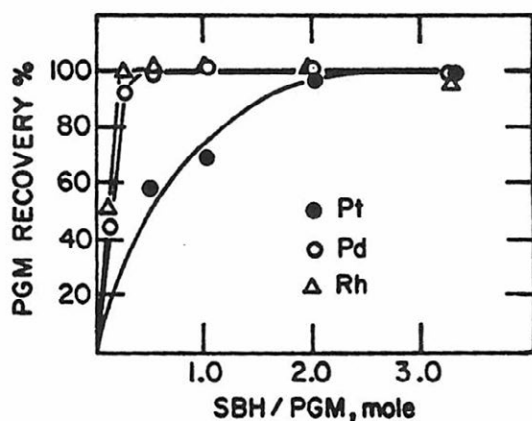
FIGURE 3 - Effect of SBH/PGM molar ratio on reduction of PGM from chloride solution (100 ppm PGM, pH = 1, room temperature, 2 min reaction time)
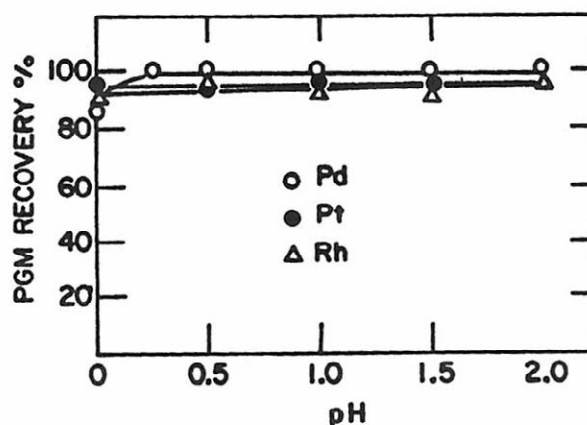
FIGURE 4 - Effect of initial pH on reduction of PGM chloro-complexes by SBH (100 ppm EGM, molar ratio (SBH/PGM) = 1 for Ed, Rh, 2 for Pt, room temperature, 2 min reaction time)

Effect of Initial pH

SBH was found effective for reducing PGM in highly acidic solutions. Figure 4 shows the effect of pH on the reduction efficiency of SBH. As shown by this figure, the reduction efficiency of Rh and Pd is slightly reduced at pH=0. Further increasing the acidity to 4M HCl did not substanitally change the reduction efficiency for these metals. The reduction efficiency for Pt did not decrease when the pH was lowered to 0 but with 4M HCl it was seen to drop to 68%.

However, the reduction efficiency also depends on the metal concentration. Increasing the concentration of Pt ion (100 ppm to 1000 ppm Pt) at an acidity of 4M HCl resulted in an increase of its reduction efficiency (84.5%). Furthermore, when the amount of SBH added was increased (molar ratio of SBH/Pt = 6) Pt recovery increased to 93.0%.

The reducing ability of SBH in highly acidic solutions of PGM may be explained by an autocatalytic mechanism [33] whereby the reduced PGM e.g. Pd, homolytically splits the hydrogen gas produced by SBH hydrolysis to form an active (H) which can then in turn reduce another chloro-complexed PGM. The reactions can be represented as follows:

$$2Pd \ + \ H_2 \ \longrightarrow \ 2Pd(H) \tag{9}$$

$$PdCl_4^{2-} \ + \ 2Pd(H) \ \longrightarrow \ 3 \ Pd° \ + \ 2HCl \ + \ 2 \ Cl^- \tag{10}$$
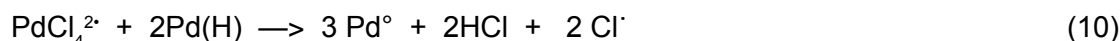
Kinetics

The reduction of PGM by SBH is fast. The reaction was completed in less than one minute (Figure 5). The reduced products were stable over a period of time of at least 12 hours. Due to the rapid PGM reduction kinetics with SBH, the effect of heat on the reaction rate could not be studied using the available techniques.
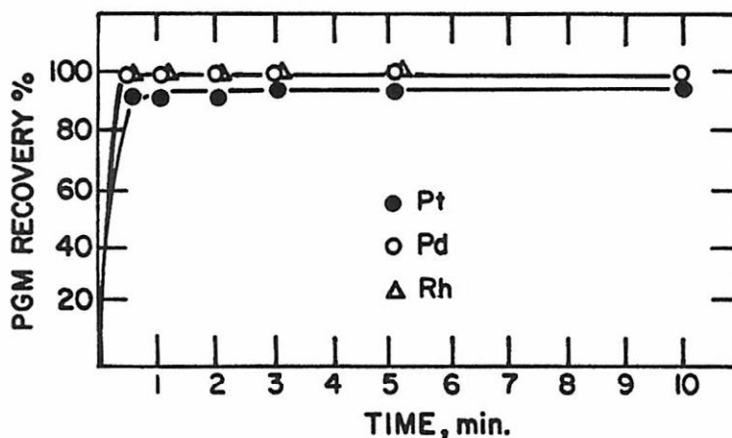
FIGURE 5 - PGM reduction, kinetics with SBH (100 ppm PGM, pH = 1, molar ratio (SBH/PGM) = I for Pd, Rh, 2 for Pt, room temperature)

PGM Concentration

SBH reduction was tried over a wide range of PGM concentrations (5 ppm - 1000 ppm). As shown by Figure 6, the reduction was efficient at lower PGM concentrations. However, under the conditions investigated, the reduction efficiencies decreased slightly at concentrations below 25 ppm. This may be a reflection of the decreased probability of SBH metal contact at lower concentrations. Longer contact times might be expected to improve the recoveries but it was also found that a competing redissolution can take place with prolonged mixing as the SBH is decomposed.
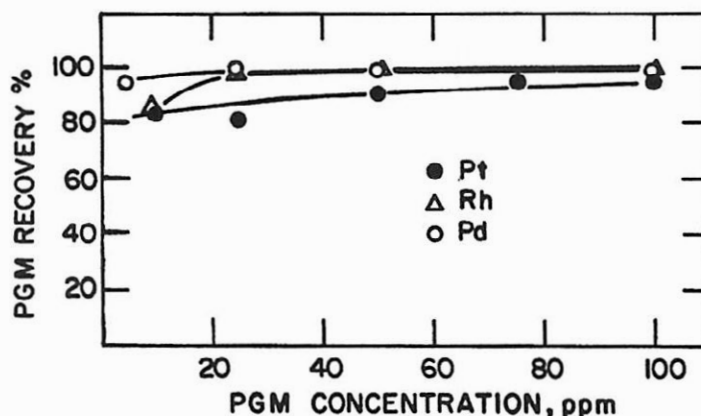
FIGURE 6 - Reduction with SBH of various concentrations of PGM chloro-complexes
(pH = 1, molar ratio (SBH/PGM) = l for Pd, Rh, 2 for Pt, room temperature, 2 min reaction time)

Effect of Temperature

Reduction of Pt, Pd and Rh ions were performed at different reaction temperatures (25°C - 60°C). It was found that increasing the temperature increased the reduction efficiency of Pt while no effect was observed for Pd and Rh (Table 2). This is probably a result of the fact that a deficient amount of SBH was used for the Pt recovery while sufficient amounts were available for Pd and Rh. Additional tests will be carried out using less than the required quantities of SBH for Pd and Rh and this should show the temperature dependency of the reduction of these metals.

TABLE 2. Effect of Temperature on PGM Reduction

100 ppm PGM, pH = 1.0, molar ratio (SBH/metal) = 1, 2 min reaction time

Temperature (°C)	PGM Recovery (%)		
	Pt	Pd	Rh
25	69.0	99.70	99.80
35	74.0	99.77	99.92
50	90.0	99.77	99.14
60	95.0	100.00	99.93

Effect of Foreign Ions

In secondary PGM bearing materials such as automotive exhaust catalytic converters, other catalyst materials and metal scrap, the PGM are typically contaminated with other metals. A study was made of the effect that a number of these contaminant cations, nam ely Al^{3+}, Pb^{2+}, Cu^{2+} and Zn^{2+} would have on the reduction with SBH.

The feed solution was doped with foreign ions, one at a time. The presence as foreign ions of Al^{3+}, Zn^{2+}, or Pb^{+2} in concentrations ranging 25-250 ppm had no effect either on the PGM reduction efficiency or on the kinetics of the reactions. The PGM product was not contaminated by Al^{3+} and Zn^{2+} ions as indicated by a comparison of the solution analysis before and after reduction. However, there was evidence that Pb^{2+} coprecipitated (Table 3).

TABLE 3. Reduction of PGM Chloro-complexes in Presence of Pb2+

100 ppm PGM, pH = 1, molar ratio (SBH/Metal) = 2 for Pt, 1 for Pd and Rh, room temperature, 2 min reaction time

Pb^{2+} Ion (ppm)	PGM Recovery (%)			Pb Coprecipitated* (ppm)		
	Pt	Pd	Rh	Pt	Pd	Rh
25	97.2	96.6	99.4	10.6	all	23.8
50	97.1	97.6	97.3	12.2	28.1	29.6
100	96.7	98.6	98.9	14.4	20.3	40.5
250	96.4	98.1	95.2	27.5	20.8	75.0

*Difference in solution concentration after reduction.

On the other hand the presence of Cu^{2+} ion in the solution matrix of PGM had a negative effect on the recovery of PGM with SBH (Figure 7). The effect was greatest in Rh, less in Pt and Pd was the least sensitive to the presence of copper. The amount of copper coprecipitated is shown in Table 4.
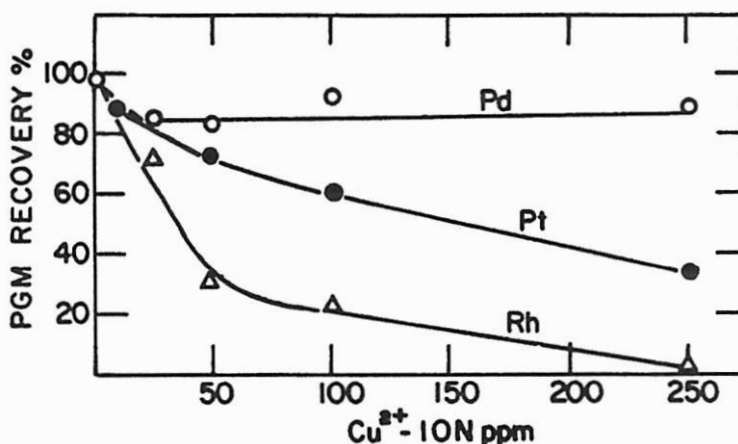
FIGURE 7 - Effect of copper on reduction of PGM chloro-complexes by SBH (100 ppm PGH, pH = 1, molar ratio (SBH/PGH) = l for Pd, Rh, 2 for Pt, room temperature, 2 min reaction time)

TABLE 4. Copper Coprecipitated during PGM Chloro-complex Reduction

100 ppm PGH , pH = 1, molar ratio (SBH/Metal) = 2 for Pt, 1 for Pd and Rh, room temperature, 2 min reaction time

Cu^{2+} Ion (ppm)	Cu Co-precipitated* (ppm)		
	Pt	Pd	Rh
25	14	21.3	14.7
50	7	23.4	7.7
100	17	32.5	7.2
250	36	38.7	15.3

*Difference in solution concentration after reduction.

The Cu^{2+} ion acts as an active catalyst for the hydrolysis of borohydride ion and rapidly liberates hydrogen before complete reduction of PGM takes place. However, the negative effect of Cu^{2+} ion could be overcome either by pH increase of the treated solutions or by increasing the SBH/PGM molar ratio as illustrated for Pt in Figures 8 and 9. In both cases the amount of Cu^{2+} ion coprecipitated reaches a maximum value of around 20% of the original amount added to Pt solution. This maximum is reached at considerably lower pH or SBH/Pt mole ratio than where the Pt recovery peaks.
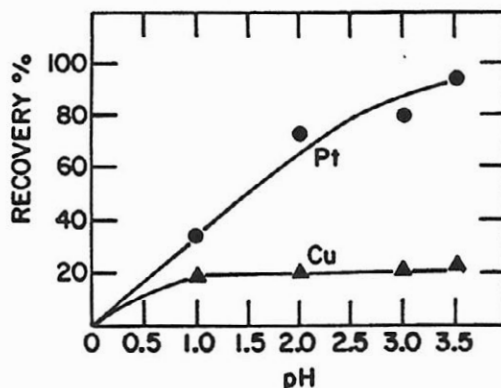
FIGURE 8 - Effect of pH on reduction of platinum chloro-complexes by SBH in the presence of copper
(100 ppm Pt, 250 ppm Cu, molar ratio SBH/Pt = 2,room temperature, 2 min reaction time)
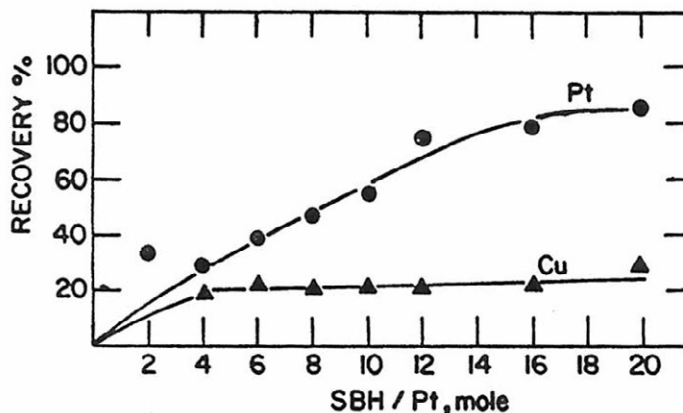
FIGURE 9 - Effect of SBH/Pt molar ratio on reduction of platinum chloro-complexes by SBH in the presence of copper
(100 ppm Pt, 250 ppm Cu, pH = l, room temperature, 2 min reaction time)

When up to 50 g/L of anions such as NO_3 and SO_4^{2-} were added to PGM-containing solutions, the reduction efficiency of SBH remained the same for Rh and Pd while a small decrease was observed for Pt. (Table 5).

TABLE 5. Effect of $NO_3^{\cdot}$ and SO_4^{2-} Ions on Reduction of PGM Chloro-complexes

100 ppm PGM, pH = 1, molar ratio (SBH/Metal) = 2 for Pt, 1 for Pd and Rh, room temperature, 2 min reaction time

SO_4^{2-} or NO_3^- conc.(g/L)	Pt Recovery (%) (in presence of)		Pd Recovery (%) (in presence of)		Rh Recovery (%) (in presence of)	
	SO_4^{2-}	NO_3^-	SO_4^{2-}	NO_3^-	SO_4^{2-}	NO_3^-
0	84.8	84.8	99.79	99.70	99.97	99.97
10	68.4	78.0	98.76	98.88	99.96	99.60
25	66.4	79.0	98.65	98.65	99.16	99.40
50	67.3	70.0	98.03	98.56	98.00	98.50

The reduction of PGM by SBH was greatly affected by the presence of thiourea in solution. Practically no reduction was obtained for 100 ppm PGM at pH = 1 on adding an excess amount of SBH (SBH/metal up to 6) in the presence of 3 g thiourea/L . However, the Pd reduction was improved when the pH of a solution containing 3g/L thiourea, 100 ppm Pd, was increased using a molar ratio of SBH/Pd = 3 (Table 6). At pH = 2.5 complete reduction was obtained. Table 7 shows the effect of thiourea concentration on the Pd reduction efficiency of SBH under otherwise favourable conditions. Little effect was obtained below 30g/L thiourea. In contrast to Pd, reduction of Pt in thiourea solution is possible only when an excess of SBH as raising the pH to useful levels without precipitating a Pt compound is not possible.   For example in a 1000 mg/L Pt solution containing 38g thiourea/L reduction is only achieved at SBH/Pt = 12. In Rh solution containing thiourea the reduction is completely inhibited under any conditions of pH or excess SBH additions.

TABLE 6. Effect of pH on the Reduction of Pd^{2+} in Presence of Thiourea

30 ppm Pd, thiourea = 3 g/L, molar ratio (SBH/Pd) = 3.0, room temperature, 2 min reaction time

pH	Pd Recovery (%)
1.0	0
1.5	9.3
2.0	13.8
2.5	99.6
3.0	98.0

TABLE 7. Effect of Thiourea Concentration on Reduction of Pd^{2+}

30 ppm Pd, pH = 2.5, molar ratio (SBH/Pd) = 3.0, room temperature, 2 min reaction time

Thiourea (g/L)	Pd Recovery(%)
1	98.0
3	98.0
5	99.6
10	99.97
30	96.2
50	75.2

In thiocyanate solution, Pt reduction was also adversely affected. For 500 mg/L PGM in the presence of 1 M thiocyanate ion, no reduction was obtained on adding up to 0.2 mL VenMet solution (SBH/Pt^{2+} = 2.5) at pH = 1. Upon addition of a further 0.2 mL, the pH increased to 9 but only about 14% of the Pt was recovered.

SBH loses its reduction power for PGM in the presence of thiourea and thiocyanate because these anions strongly complex PGM consequently hindering their reaction with SBH.

The Proposed Flowsheet

PGM containing material is leached with HC1 in the presence of an oxidising agent. The residue from which silver can be recovered is removed by filtration. The filtrate containing gold and PGM is treated with SO_2 gas for gold recovery by precipitation. After separation of gold powder, PGM containing solution can, if required be concentrated by solvent extraction or ion exchange. The loaded organic phase (or resin) can be selectively stripped (or eluted) to produce a rich aqueous stream of Pt or Pd. PGM can be recovered directly from leach solution or from the enriched aqueous streams with the stabilized form of SBH. The PGM powder precipitated is separated by filtration and the barren solution can be recycled to the upstream process (Figure 10).
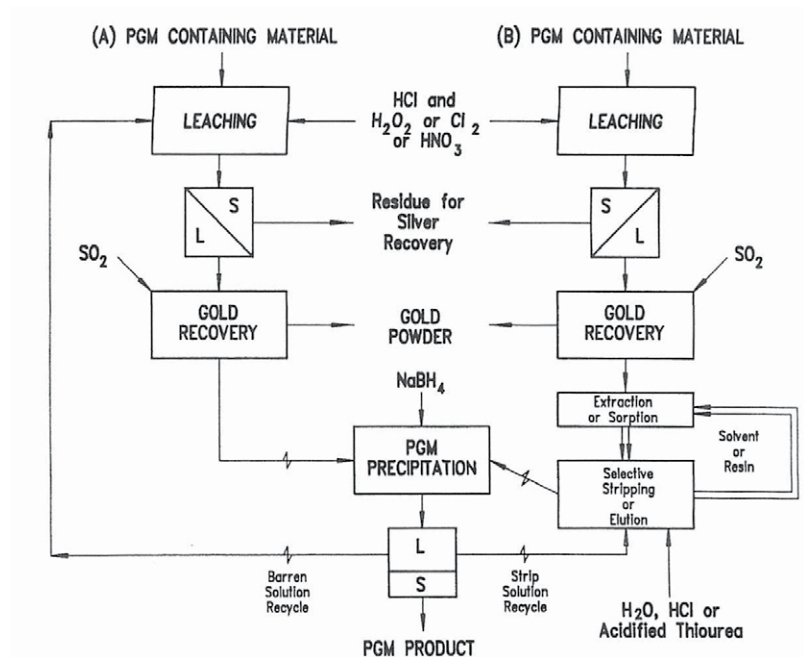

FIGURE 10 - Flowsheets for the recovery of PGM by SBH reduction

The process of precipitating PGM by SBH has many advantages over other similar processes. It is simple, efficient and safe. No intermediate pH adjustment step is required. The reduction is selective, fast and can be conducted at ambient temperature. The PGM precipitate product is less contaminated. The amount of SBH added is small and the boron discharged in effluents as boric acid or borates is environmentally acceptable as boron is an element vital to many life processes and is widely distributed in nature. [34]

Precipitation of PGM from Real Solutions

Real solutions containing PGM such Pt, Pd and Rh, obtained from the Royal Canadian Mint, Ortech International, and Noranda Inc. were tested to recover their PGM content using SBH reduction. The solution from the Mint was a sample of spent gold chloride electrolyte from which the gold had been removed by treatment with SO_2. Noranda provided a high acid containing (8N HC1) Pd strip solution from a solvent extraction circuit. The sample from Ortech was produced by chloride leaching of spent automobile exhaust catalyst.

Fifty mL of each solution was treated with VenMet solution, added dropwise, over a 3 to 15 minutes time period while agitating the solution with a magnetic stirrer. The reaction was conducted at room temperature. A change in the colour of the treated solution to colourless was taken to indicate the end of the reaction.

Precipitates, in the form of black agglomerates, were immediately produced. They were readily by filtration or decantation. The results of these tests were summarized in Tables 8 and 9.

TABLE 8. Precipitation of Pt and Pd from Royal Mint Solution

Feed: 2277 ppm Pt, 915 ppm Pd, 2.0 g Cu/L initial pH = - 0.08, 5 min reaction time

Initial pH	VenMet Sol'n (mL)	Recovery (%)				Product Purity (%)			
		Pt	Pd	Rh	Pb	Pt	Pd	Rh	Pb
0.86	0.25	88.7	96.7	9.1	8.5	38.4	33.8	1.6	26.1
0.86	0.20	89.1	96.7	9.2	10.2	36.6	32.1	1.5	24.7
1.10	0.20	89.7	96.7	9.3	8.9	38.2	33.3	1.6	32/3
1.72	0.15	90.0	96.7	9.2	11.6	35.4	30.7	1.5	32.3
2.00	0.10	90.7	96.7	9.2	9.8	37.5	32.2	1.6	37.0

As shown in Table 8, the amount of Pt and Pd removed from the Royal Mint Solution being treated at its natural pH (- 0.08) increased with increasing additions of VenMet solution. Increasing the initial pH of the solution to 1.0 enabled complete removal of Pt, Pd and Cu ions at a dosage of 0.5 mL of VenMet solution to 50 mL of PGM solution.

TABLE 9. Precipitation of PGM from Ortech Solutions.

Feed: 243.3 ppm Pt, 196.6 ppm Pd, 11.1 ppm Rh, 1726 ppm Pb, 9650 ppm Al, 15 min reaction time

VenMet Solution (mL)	Recovery (%)			Product Purity (%)		
	Pt	Pd	Cu	Pt	Pd	Cu
0.1	17.9	32.8	1.2	55.7	41.1	3.2
0.2	20.3	38.3	7.4	48.1	36.5	15.4
0.3	16.7	49.1	8.4	46.3	45.0	16.8
0.5	35.0	88.4	21.1	39.3	39.9	20.8
0.7	57.0	98.7	38.3	43.8	30.4	25.8

Table 9 gives the data from the precipitation of PGM from the Ortech solution. At the natural pH of the feed sample , the amount of VenMet solution required to achieve 97% Pd, 90% Pt and 9% Rh recovery with about 10% Pb coprecipitated is 0.2 mL VenMet per 50 mL feed solution. The VenMet solution requirement can be halved if the initial pH of the PGM feed is adjusted to 2.0.

The data obtained with synthetic solutions discussed above had indicated that Pd recovery was relatively insensitive to solution pH. This was confirmed when it was possible to effect almost complete removal of PGM from the Noranda Pd strip liquor sample treated at its natural acidity (8N HCl) at a dosage of 0.5 mL VenMet solution to 50 mL of feed. The initial concentrations in this feed solution were 12.67 g Pd/L 32.3 ppm Pt and 75 ppm Cu, and recoveries of 99.9% Pd , 89 .5% Pt and 99.7% Cu were attained. The purity of the product obtained is 99.2% Pd, 0.2% Pt, and 0.6% Cu.

CONCLUSIONS

1. PGM can be precipitated by SBH from highly acidic chloride solutions e.g. 8 N HCl at ambient temperature.

2. PGM precipitation with SBH from chloride solutions is efficient over a range of PGM concentrations from less than 10 ppm to several grams per litre.

3. From a pH = 1 solution stoichiometric amounts of SBH are sufficient to completely precipitate Pd and Rh ions (0.25 mole SBH/mole Pd or Rh) while amounts of SBH greater than the stoichiometric requirement are needed to precipitate Pt ion (2 moles of SBH/mole of Pt).

4. The reaction of PGM with SBH is fast; it is completed in less than one minute.

5. The presence of Al^{3+}, Zn^{2+}, Pb^{2+}, SO_4^{2-}, and NO_3^- has no effect on the reduction efficiency of PGM by SBH from chloride solutions and therefore the products obtained are not contaminated by these ions.

6. Cu^{2+} has a negative effect on the reduction efficiency of PGM by SBH. However, changing the pH and SBH/PGM ratio can eliminate this negative effect and a complete precipitation of metal ions can be effected.

7. The presence of thiourea and thiocyanate hinder the reduction of PGM by SBH. However, a complete recovery of Pt in presence of thiourea can be achieved by increasing the SBH/Pt molar ratio while with Pd increasing the molar ratio or the starting pH are both effective. The reduction of Rh ion in the presence of thiourea was not possible.

8. The process can be applied successfully to recover PGM from real plant solutions.

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Induction Furnace Sampling and Sample Preparation Methods

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ABSTRACT

Noranda copper is dedicated to providing the best service possible to its clients in the precious metal scrap business. One prime objective,therefore, is to be and continue to be the best in scrap sampling, preparation and treatment. As a result of Noranda's commitment, an extensive development program was initiated to ensure that sampling and sample preparation methods, procedures and practices are the "best-available-technology".

Precious metal scrap represents a large fraction of precious metal input to the Horne smelter. As a custom smelter, the Horne must determine the metal contents of all scrap for settlement with suppliers. It is, therefore, essential that a sample taken is representative of the scrap and is cost-effective. Several sampling and preparation methods were proven for various types of scrap. One such development is induction furnace melting and homogenizing of scrap for subsequent sampling. This paper summarizes tests conducted to: (i) prove the homogeneity of the molten bath; (ii) determine the best melt sampling method; and (iii) develop a cost-effective sample preparation device.

KEYWORDS

>   Scrap; sampling; precious metals; induction furnace; bath homogeneity; bar-sawing;
>   pintube; precision; accuracy

INTRODUCTION

Noranda copper is dedicated to providing the best service to its clients in the precious metal scrap business. One prime objective, therefore, is to be and continue to be the best in scrap sampling, preparation and treatment. Noranda is committed to continually evaluate its sampling and sample preparation methods and practices at all scrap sampling locations. This is done to ensure the equipment, methods and practices employed are "best-available technology" and, where warranted, improved.

The Horne smelter, a division of Noranda Minerals Inc., is situated in Rouyn-Noranda,Quebec, Canada, approximately 650 km northwest of Montreal. Scrap is a significant part of the Horne smelter's business and represents a large fraction of the smelter's precious metal (PM) input. It purchases scrap from North America,

Europe and Asia. Most of the scrap is smelted in the Noranda Process reactor [1] along with copper concentrates. Some scrap is also treated in the reverb furnace and converters. The types of scrap treated include:

Copper wires, sheets, pipes and ingots, motors, armatures, copper spills, brass turnings, radiators, electronics, computers, telephones, printed circuit boards, integrated circuit chips, mattes, slags, ashes, residues etc.

As a custom smelter, the Horne must determine the metal contents of all scrap for settlement with suppliers. Most of the high-PM scrap, such as electronics, are sampled at two other Noranda-owned companies: Noranda Sampling in East Providence, Rhode Island, and Micro Metallics in San Jose, California. The Horne smelter samples copper scrap, low-PM materials and some high-PM materials that can be melted or remelted in an induction furnace, such as ingots and chopped wires.

This paper describes the Horne smelter induction furnace sampling and sample preparation practices. It also summarizes the development work conducted to: (i) prove the homogeneity of the molten bath; (ii) determine the best melt sampling method: and (iii) develop a cost-effective sample preparation device.

SCRAP SAMPLING AT THE HORNE

It is necessary that a primary sample is representative of the entire lot. Over a period of time, several sampling and sample preparation methods have been proven for the various types of scrap received. After the primary sample is taken, its particle size and sample mass must be reduced to obtain a representative sample for laboratory analysis.

Reducing the particle size and/or sample mass of some materials like ashes and mattes can readily be achieved by successive crushing, screening, mixing and dividing procedures. For other materials such as chopped wires, motors, radiators etc., mechanical reduction methods to obtain a laboratory sample mass are inadequate or impossible. An induction furnace is therefore used to melt the primary sample, which is further sampled and reduced, to provide a final laboratory sample mass and particle size. This procedure ensures that a laboratory sample is still representative of the original lot.

The induction furnace is also used to prepare scrap samples containing electronics, plastics or ceramics. In these cases, a matteing process developed in-house is used. The overall Horne scrap sampling scheme is shown in Figure 1.

For reference, all figures may be found at the end of this article.

INDUCTION FURNACE

Description

The Horne smelter presently uses two 1.5-ton Inductotherm VIP (Variable Induction Power) induction furnaces equipped with an afterburner (Figure 2). A recently-built scrap building, with truck and rail car unloading bays, houses the furnaces as well as scrap shredder [2]. These production furnaces were also used for conducting the development testwork which is described below. Two additional induction furnaces will be added in the near future. The additional furnace capacity will allow the Horne to melt or re-melt an entire lot, if necessary. Typically, a 500 lb. charge of ingots is melted in 2-3 hours at a power of 300-350 kW.

Induction furnaces are used to melt Cu and PM scrap so that representative samples can be taken from the molten bath. One practice of sampling the induction furnace bath is to cast the entire furnace charge into ingots. The ingots, Figure 3, are then sawn and the sawings comprise the laboratory sample.

Another sampling method is to take pintube samples (Figure 4) of the molten bath which is continuously mixed by inductively-induced convection currents. Pintube samples are taken at several bath levels. The pintubes are then cut into small pieces for analysis.

DEVELOPMENT PROGRAM

Testwork

Recently, particular attention has been focused on the induction furnace sampling of high-PM materials such as ingots and wires. The major factors that determine the most suitable sampling method and sample preparation procedure are: bath homogeneity, precision and accuracy. A development program was initiated to determine the bath homogeneity of various high-PM materials, and the precision and accuracy of alternate bath sampling methods. Some of the test results are presented below.

Bath Homogeneity

Tests were conducted on several ingot lots of various sizes, shape and compositions. Each lot was divided into several sublots of equivalent weight - the sublots were not necessarily equivalent in composition. The sublots were melted in the induction furnace, and pintube and bar samples were taken at three bath levels: top, middle and bottom. The samples were analyzed for Au and Ag.

Test results for three lots are summarized in Tables I to III. For lots A and B (Table I and II), it was found that the differences in the Au and Ag contents among the three bath levels were not statistically significant at the 95% confidence level.

TABLE I. Bath Homogeneity Tests - Lot A

Melt	Gold			Silver		
	Top	Middle	Bottom	Top	Middle	Bottom
1	26.47	26.30	26.43	589.4	569.4	572.9
2	23.15	23.40	23.12	274.1	279.7	282.3
3	23.47	23.62	23.94	444.0	449.9	440.6
4	19.15	19.31	19.61	928.3	931.5	947.3
5	22.37	22.66	22.97	438.4	449.7	459.1

Induction furnace molten bath was homogeneous, i.e. no segregation among top, middle and bottom levels.

TABLE II. Bath Homogeneity Tests - Lot B

Melt	Gold			Silver		
	Top	Middle	Bottom	Top	Middle	Bottom
1	23.77	23.84	23.04	5.33	5.49	5.30
2	16.20	15.90	16.10	14.30	14.28	14.30
3	32.70	32.25	33.04	0.94	0.89	0.91
4	27.21	26.99	26.97	16.25	16.68	16.74
5	27.76	28.09	27.51	14.20	14.14	13.84

Induction furnace molten bath was homogeneous, i.e. no segregation among the top, middle and bottom levels.

TABLE III. Bath Homogeneity Tests - Lot C

Sample	Gold			Silver		
	Top	Middle	Bottom	Top	Middle	Bottom
1	8.632	8.803	8.319	675.7	683.3	672.1
2	8.712	8.857	8.880	700.6	703.5	698.9
3	8.630	8.787	8.618	703.2	698.6	690.3
4	8.836	8.573	8.542	686.1	687.9	680.0
5	8.721	8.821	8.549	675.3	683.5	681.9
6	8.774	8.818	8.770	700.9	689.1	690.2
7	8.878	8.827	8.883	701.7	695.2	696.6
8	8.763	8.633	8.775	683.1	689.3	687.6

Induction furnace molten bath was homogeneous, i.e. no segregation among the top, middle and bottom levels.

In lot C (Table III), eight samples were taken at each level of one charge, it was found that there was no significant difference between the mean Au and Ag content among the three levels.

A homogeneity test was also conducted with silver wires (copper wires coated with 65 oz/ton Ag). The wire-melting results confirmed previous ingot-melting results that no significant differences in metal content exist between the three bath levels. All these results showed that there was no significant segregation in the induction furnace bath.

Sampling Methods Precision

In this paper, the overall precision is expressed by the coefficient of variation (CV) which is defined as one standard deviation as a percentage of the mean assay. The CV, therefore, accounts for the variance contributed by sampling, sample preparation and analysis.

In each induction furnace test, the overall precision of the sampling method was determined. The overall precision of pintube versus bar-sawing (one-cut) methods for Lot A are compared in Table IV. It is evident that pintube sampling of the molten bath (at three levels) was more precise than one-cut bar-sawing. If one considers the CV as an indication of the monetary risk associated with sampling, sample prenaration and analysis, then pintube sampling has significantly lower risk. For Lot A, the overall monetary risk by pintube sampling was less than half that of bar sawing ($260/ton as compared to $684/ton, respectively).

TABLE IV. Pintube and Bar-sawing Precision

Metal	Pintube		Bar Sawing	
	C.V., %	$ / ton	C.V., %	$ / ton
Au	0.94	130	2.2	310
Ag	1.6	85	5.5	290
Pd	1.4	35	2.4	62
Cu	0.66	10	1.4	22
Overall		260		684

An analysis of variance was done to determine the main contributing factor to the overall sampling, preparation and analysis variance. A summary of an analysis of variance of a typical melt sampling test is shown in Table V. An F-test is used to determine whether a factor is a significant contributor to the overall variance at 95% confidence level. It is evident that the laboratory sample was the main contributing factor to the overall variance.

Sampling Methods Accuracy

A sampling and preparation scheme has to be accurate as well as precise. Since the true Au and Ag contents of commercial lots were not known, copper-doping tests were conducted in the induction furnace to evaluate the accuracy of pintube and bar-sawing sampling schemes. Initial tests were conducted with 4 charges of cathode copper with varying Au (4 to 40 oz/ton) and Ag (40. to 400 oz/ton) contents.

TABLE V. Typical Analysis of Variance

Error Source	Number	Sum of Squares	Degrees of Freedom	Mean Squares	Variance
Level	3	0.56555	2	.2828	0
Side	2	2.68625	3	.8954	0
Section	4	6.76231	18	.3757	0
Laboratory	4	24.4354	72	.3394	.339
Total	96	34.4495	95	.3626	.339

Pintube samples were taken from the left and right sides at the top and bottom bath levels. For bar-sawing, 10 bar samples were taken. The bar samples were prepared by using one-cut and eight cut sawing methods The test results, Table VI, showed that for cathode copper there were no statistically significant differences in the recoveries of Au and Ag for the three methods. The results confirmed expectations that no significant segregation in cathode copper occurs at these Au and Ag contents. Further doping tests are planned for alloyed copper to compare recoveries for the different sampling schemes.

PINTUBE SAMPLE PREPARATION DEVICE

The induction furnace development testwork produced many pintube samples which had to be prepared for the laboratory. It became evident that manual cutting of pintube samples to acceptable sizes for the laboratory was inadequate and time consuming.

A novel device to reduce the pintube samples into fine particles for the laboratory was developed by Noranda. The device has been tested on several metals including copper, brass and aluminum. The typical particle size of the reduced sample for copper pintubes (Figure 5), Table VII, showed that it is possible to obtain 90% less than 1 mm-size particles for the laboratory sample. This device reduced the pintube sample preparation time and produced a more representative final laboratory assay sample. The net benefits are lower sample preparation costs and potentially lower laboratory variances. Noranda intends to patent the novel pintube sample preparation device developed.

TABLE VI. Cathode Copper Doping Test - Recovery

| Metal | Charge | Bar Sawing | | Pintube | | |
		1-cut	8-Cut	Top	Bottom	Mean
Au	A	1.008	0.998	1.018	1.014	1.016
	B	1.000	1.000	1.000	1.004	1.002
	C	1.008	1.003	1.000	0.994	0.997
	D	1.001	0.999	1.003	1.005	1.004
Ag	A	0.996	0.959	0.950	0.966	0.958
	B	0.971	0.974	0.992	0.984	0.988
	C	0.965	0.963	0.980	0.976	0.978
	D	0.972	0.972	0.984	0.984	0.984

All three sampling methods were accurate for sampling cathode copper.

TABLE VII. Reduced Copper Pintube Sample Typical Particle Size Distribution

| size. mm | | Distribution, % | | |
		Coarse	Medium	Fine
	+1.4	2	2	2
-1.4	+1.0	48	10	11
-1.0	+0.8	37	35	30
-0.8	+0.5	10	39	36
-0.5		3	14	21

FUTURE DEVELOPMENT WORK

Further Au and Ag doping tests will be conducted with alloyed copper (alloyed with Fe, Ni, Zn and Al) to evaluate the effects of impurities on the induction furnace molten bath. These tests will also include evaluation of the best method for sampling alloyed copper.

CONCLUSIONS

The development tests conducted showed that:

    (a) Melting PM scrap in the induction furnace produces a homogeneous melt, i.e. no PM segregation in the bath.

    (b) Pintube sampling provided more reproducible metal assays than bar-sawing and was accurate.

    (c) The small scatter in the metal assays was due mainly to laboratory sample.

A pintube sample preparation device was developed which reduces the monetary risk associated with sampling of high PM scrap, and sample preparation costs.

ACKNOWLEDGEMENTS

The success of the development program is due to the contributions of many people at the Horne smelter and the Noranda Technology Centre. Their work and cooperation are appreciated. The authors also wish to thank the management of the Horne Division for its commitment to the program and permission to publish this paper.

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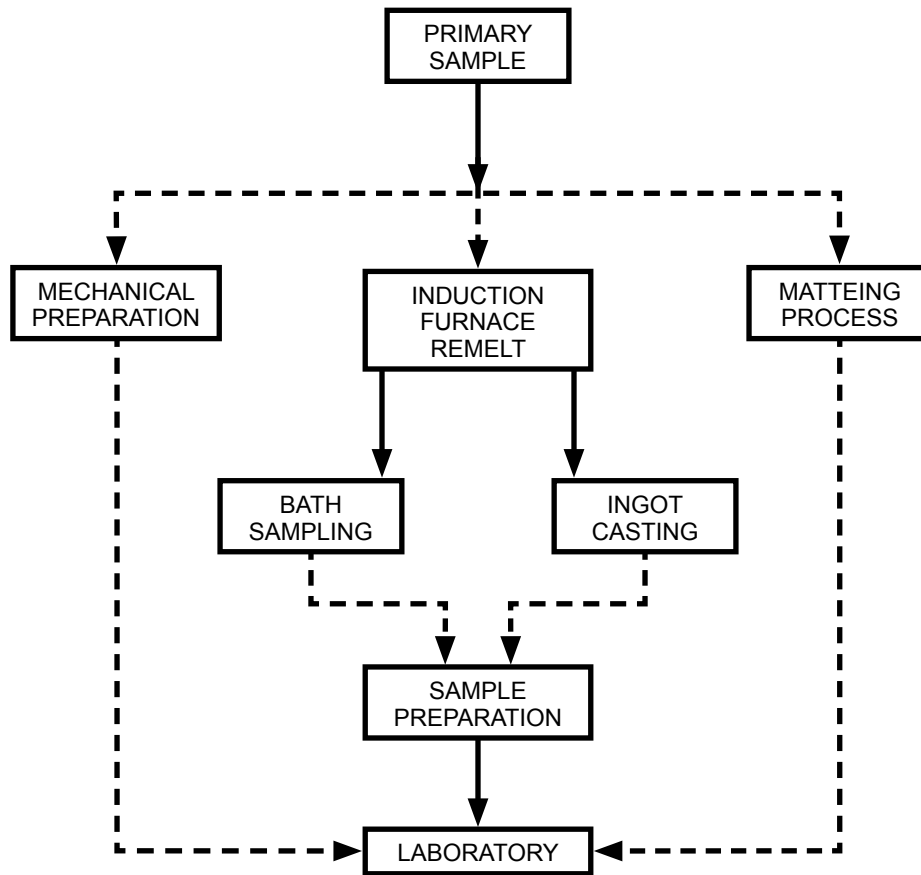**FIGURE 1** - Overall scrap sampling scheme at Horne Division.

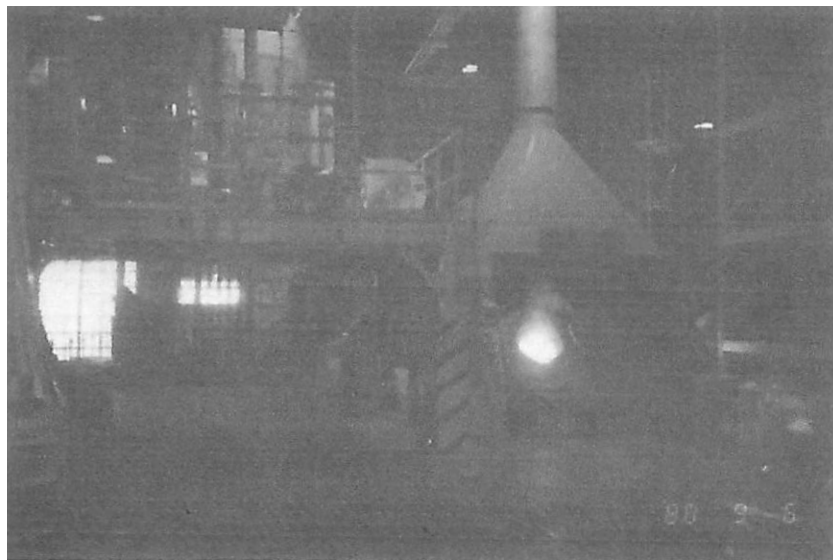**FIGURE 2** - 1.5 ton Inductotherm VIP induction furnace.

FIGURE 3 - Sawn induction furnace ingot. (Note: proper method is to cut ingot half way and cuts must be equally spaced, unlike the above ingot).
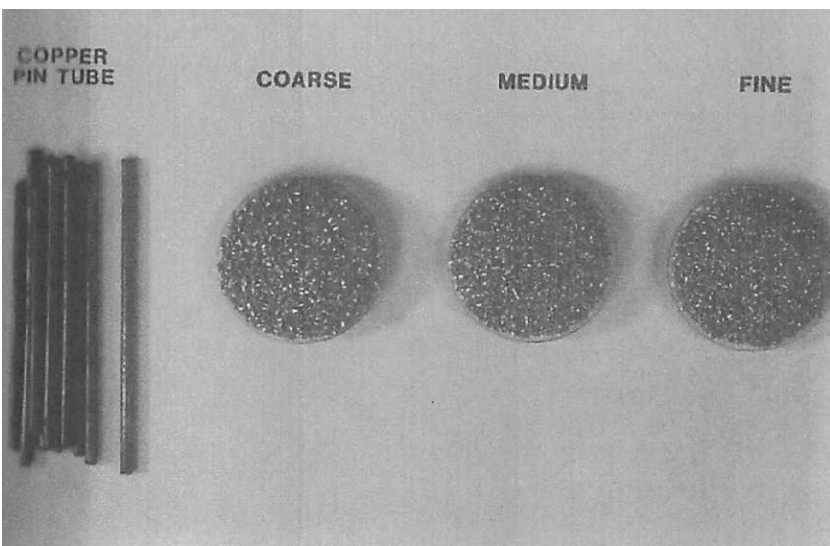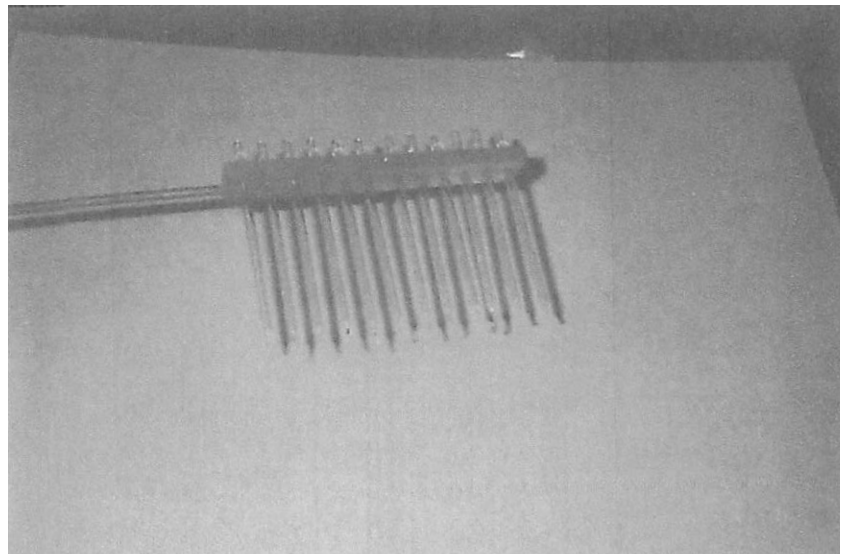
FIGURE 4 - Pintube sampling apparatus.

FIGURE 5 - Typical particle size of reduced copper pintube samples.

The Kinetics of the Pyrometallurgical Purification of Pt and Pt-Alloys

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ABSTRACT

Refining of metals by distillation in a vacuum is a well known procedure for separating undesirable components from heavy metals, rare-earth metals, iron group metals, alkaline-earth metals, for the distilling separation and refining of Al, Mo, Ti, Cr, Nb, V and so on. Less practical experience is known for the distilling treatment of precious metal melts. Theoretical models have been combined with results from distilling refining-experiments of vacuum induction melted platinum- and platinum-alloy-scrap. These materials contain elements like Fe, Ni, Sb, As, Al, W, Zr, Y, Co, Cu, Cr,... which have to be separated to get a desired matrix-purity > 99,9 %.

Results from VIM-experiments in a zirconia-crucible show a high discrepancy to the theoretical prediction - especially for the refining-rate - for the investigated elements Fe, Sb, Cu and Al. Minimum concentrations < 100 ppm can be achieved for Cu and Sb, Al and Fe are difficult to remove, a limit-concentration could be found for those, beneath no further separation is possible. Fe is the most problematic element of all the considered, as the experimental refining rates are lowest and even refining with oxygen has no positive effects. The experiments also show, that the raffination-success is influenced by the used crucible material.

INTRODUCTION

The process of vacuum induction melting is widely used in the precious metal industry for the removal of selected impurities from secondary platinum and Pt-alloys. These processes features several advantages over the traditional methods of raffination PGM's by chemical processes like extraction and precipitation/calcination. The most important one is, that for a lot of industrial applications only the removal of detrimental impurities to certain low levels is necessary. Process times and fixing of material weight are low. With chemical methods, the removal is more complete and usually a purity of the matrices of >99,95 or 99,99% can easily achieved, and material bonding and process times are generally higher.

Platinum and Pt-alloys with high demands on degree of purity are successfully in use for the production of high-quality glasses, like optical glass-products or fiber-optic cables, where highest demands on transparency and optical dispersion have to be fulfilled. During the contact of the glass-melt with Pt-construction parts, the concentration of some elements are increased by diffusion-processes and are enriched in the matrix with increasing process-time and continuing process-cycles. These construction-parts loose important mechanical properties with increasing impurity-concentration and can contaminate new glass-melt charges melted therein. If those parts have to be renewed or replaced by uncontaminated or undeformed ones, they undergo a pyrometallurgical purification-process under vacuum, where the impurities are removed to a desired residue concentration.

The effect of raffination in the VIM-process is based on the physical properties of the participating elements, namely the vapor pressure, rate of vaporization and reaction with slags or crucible materials. Generally limited information exists in literature on experimental and theoretical results of the refining of secondary Pt-, and Pt-alloy-melts by VIM.

THEORETICAL MODELS

Theory of Vacuum Raffination:

The vacuum metallurgical removal of impurities from a melt is only possible if the general criteria, stated by the ratio of the evaporation-rate of the dissolved element to that of the solvent is larger than that of the corresponding concentrations, this is described as:

$$\left(\frac{J_i}{J_{Pt}} \right) > \left(\frac{N_i}{N_{Pt}} \right)$$

(1)

J_i - molar flux impurity-element [mol.cm^{-2}.s^{-1}]
J_{Pt} - molar flux platinum [mol.cm^{-2}.s^{-1}]
N_i - molar .fraction of solute i (impurity-element)
N_{Pt} - molar fraction of platinum

Equation (1) can also be described [4] by:

$$\alpha = \frac{\gamma_i p_i}{\gamma_{Pt} p_{Pt}} \left(\frac{M_{Pt}}{M_i} \right)^{1/2} > 1$$

(2)

α - relative volatility coefficient
γ_i - activity coefficient of solute i (impurity)
p_i - vapor pressure of pure solute i (impurity) [Pa]
M_i - molecular weight of solute i [g.mol^{-1}]
γ_{Pt} - activity coefficient of platinum
p_{Pt} - vapor pressure of platinum [Pa]
M_{Pt} - molecular weight of platinum [g.mol^{-1}]

The driving force of the purification is expressed by the value of the α coefficient [4]. In any case, the rates of the raffination are a kinetic phenomena, which is dominated by the mass transfer in the system. In principle, elements with a high α -value can be removed easier. Elements with a value of < 1 cannot be removed by vacuum raffination at all. Assuming the activity coefficients as unity, the α-coefficient in the case of refining platinum-melts can be calculated (*Table 1*). It can be seen, that almost all elements can be separated from such Pt-melts, except the elements Zr, Mo, W, which have a high oxygen-affinity.

TABLE 1: Relative Volatility Coefficient a/or the Vacuum Taffination of Typical Impurities in Platinum Melts at 2100 K

element	As	Cd	Zn	Pb	Mn	Sb	Ag	Al	Cu	Sn	Cr
α	9,9E10	7,5E8	5,3E8	3E6	1,1E6	6,2E5	3,9E5	8,2E4	3,9E4	2,8E4	1,3E4

element	Fe	Ni	Co	Si	Y	Ti	Pi	Zr	Mo	W
α	4,1E3	2,1E3	1,9E3	5,4E2	3.7E2	1,7E2	1	5,9E-2	5,5E-3	1,4E-7

Besides that, the kinetics of the material transport influences the success of such a treatment essentially. The mechanism can be described by the following process-steps [5]-[8]:

- heat and material transport in the metal to be distilled and of the dissolved atoms in the liquid phase to the liquid-gas interface
- evaporation
- materials transport through the gas space
- condensation

or can be described by a mass-transport-coefficient K_i:

$$\frac{1}{K_i} = \frac{1}{K_L} + \frac{1}{K_E} + \frac{1}{K_U} \qquad (3)$$

K_L - liquid phase mass-transfer coefficient [cm.s^{-1}]
K_E - evaporation mass-transfer coefficient [cm.s^{-1}]
K_U - gas-phase mass-transfer coefficient [cm.s^{-1}]

The rate of distillation is governed by the slowest of the process-step, which is—according to experience—the evaporation-step. Based on this the model "binary system", "multicomponent-system", "binary-time-system" and model "oxidation" have been developed and are described in the following sections.

"Binary System":

In this simple system only the vapor-pressures of the participating components are considered and are supposed to be decisive for the selective remove of a impurity element, the time-dependence of the mass-transport is not taken into consideration. If the partial-pressure of the platinum reaches the one of the refining element, the limit of the remove at a given temperature is obtained. In the ideal binary system platinum / impurity-component , the partial pressure of the elements is direct proportional to the mole fraction in the solution according to Raoult's law and the assumption of the partial-pressure of the platinum and the impurity-component i are being equivalent:

$$p_{Pt} = p_i \qquad (4)$$

$$(l - x_i)\, p_{DPt} = x_i\, p_{Di} \qquad (5)$$

p_{Pt} - partial pressure of platinum
p_i - partial pressure of element i
p_{DPt} - vapor pressure of platinum
p_{Di} - vapor pressure of element i
x_i - mole .fraction of element i
$(l - x_i)$ - molar fraction of platinum

From equation (5) theoretical concentrations can be calculated, which values for the most relevant elements are listed in Table 2 for the temperatures of 2100 and 2300K. The results show for some impurities an concentration-increase with increasing temperature. The results are the better, the lower the process-temperature is.

TABLE 2: Theoretical Concentrations Calculated with Model "Binary System"

T = 2100 K: **element i / c_i [ppm]**

As	Cd	Zn	Pb	Mn	Sb	Ag	Al	Cr	Cu	Sn	Au
6,25E-6	1,01E-3	1,10E-3	3,41E-1	4,99E-1	1,28E-0	1,91E+0	4,52E+0	3,90E+1	1,46E+1	2,82E+1	2,87E+2

Fe	Pd	Ni	Co	Y	Si	Ti	Rh	Zr	Ir	Mo	W
1,29E+2	3,03E+2	2,58E+2	2,84E+2	1,80E+3	7,06E+2	2,97E+3	1,86E+5	9,21E+5	9,94E+5	9,92E+5	1,00E+6

T = 2300 K: **element i / c_i [ppm]**

As	Cd	Zn	Pb	Mn	Sb	Ag	Al	Cu	Sn	Cr	Au
4,81E-5	8,36E-3	8,45E-3	1,85E+0	2,06E+0	5,31E+0	7,02E+0	1,31E+1	4,11E+1	8,32E+1	8,80E+1	6,78E+2

Fe	Pd	Ni	Co	Y	Si	Ti	Rh	Zr	Ir	Mo	W
2,71E+2	6,86E+2	4,71E+2	5,26E+2	3,39E+3	1,27E+3	4,50E+3	1,84E+5	8,98E+5	9,90E+5	9,86E+5	1,00E+6

Multi-component System:

Similar to the binary system model, equation (4) and (5) can be further developed to a multi-component system under the assumption, that the partial pressures of all impurity-elements are equivalent (equation (6)) and are dependent from the molar fraction (equation (7)), as well as the sum of all partial pressures of all impurities reach the partial pressure of platinum.

$$p_1 = p_2 = p_3 = \cdots = p_i \qquad\qquad (6)$$

$$x_1\, p_{D1} = x_i\, p_{Di} \qquad\qquad (7)$$

$$p_{Pt} = p_1 + p_2 + p_3 + \cdots + p_i \qquad (8)$$

$$[1 - (x_1 + x_2 + x_3 + \cdots + x_i)] \, p_{D_{Pt}} = n x_1 p_{D_1}$$

$$[1 - (x_1\frac{p_{D_1}}{p_{D_1}} + x_1\frac{p_{D_1}}{p_{D_2}} + x_1\frac{p_{D_1}}{p_{D_3}} + \cdots + x_i\frac{p_{D_1}}{p_{D_i}})] \, p_{D_{Pt}} = n x_1 p_{D_1}$$

$$[1 - (x_1 p_{D_1} \sum \frac{1}{p_{D_1}}] \, p_{D_{Pt}} = n x_1 p_{D_1}$$

$$x_1 = \frac{p_{D_{Pt}}}{p_{D_1}[\, n + p_{D_{Pt}} \sum \dfrac{1}{p_{D_i}} \,]} \qquad (9)$$

p_i - partial pressure of element i

$p_{D_{Pt}}$ - vapor pressure of platinum

x_i - molar fraction of element i

p_{Pt} - partial pressure of platinum

p_{D_i} - vapor pressure of element i

n - number of elements

Again, from these equations the theoretical concentration of the impurities at the temperatures of 2100 and 2300 K can be calculated. It can be seen (Table 3), that with this model the calculated impurity-concentration increases with increasing process-temperature and almost all elements—except W—can be removed. In comparison to the model "binary system", the values of the multi-component model are lower and express generally minimum values.

TABLE 3: Theoretical Concentrations Calculated with Model "Multi-Component System"

T = 2100 K: element i / c_i [ppm]

As	Cd	Zn	Pb	Mn	Sb	Ag	Al	Cu	Sn	Cr	Au
8,80E-13	1,42E-10	1,55E-10	4,80E-8	7,03E-8	1,80E-7	2,70E-7	6,36E-7	2,05E-6	3,96E-6	5,49E-6	4,04E-5

Fe	Pd	Ni	Co	Y	Si	Ti	Rh	Zr	Ir	Mo	W
1,82E-5	4,27E-5	3,63E-5	4,00E-5	2,54E-4	9,95E-5	4,20E-4	3,22E-2	1,65E+0	2,32E+1	1,79E+1	1,00E+6

T = 2300 K: element i / c_i [ppm]

As	Cd	Zn	Pb	Mn	Sb	Ag	Al	Cu	Sn	Cr	Au
3,28E-11	5,71E-9	5,77E-9	1,26E-6	1,41E-6	3,62E-6	4,79E-6	8,96E-6	2,80E-5	5,68E-5	6,01E-5	4,63E-4

Fe	Pd	Ni	Co	Y	Si	Ti	Rh	Zr	Ir	Mo	W
1,85E-4	4,69E-4	3,22E-4	3,60E-4	2,32E-3	8,70E-4	3,09E-3	1,53E-1	6,02E+0	6,84E+1	4,66E+1	1,00E+6

<u>Time Dependence of the Mass-Transport, Model "Binary-Time-System":</u>

Considering the mass-transfers, also the time-component has to be taken into account. Therefore the molar mass-flux can described in dependence of time [7]:

$$(pct_i)_t = (pct_i)_0 \exp\left[-K\frac{A}{V}(t - t_0)\right] \qquad (10)$$

$(pct_i)_0$ - bulk concentration of solute i in melt at t = 0 [wt-pct]
$(pct_i)_t$ - bulk concentration of solute i in melt at time t [wt-pct]
K - overall mass-transfer coefficient
V - volume of melt [cm^3]
A - melt surface area [cm^2]

The coefficient K in equation (10) represents the overall mass-transfer coefficient for solute i K_i due to equation (3). Due to the above formula, the concentration decreases exponentially with time, after infinite time minimal concentration can be obtained. Equation (10) can also described by (11) under the assumption of the step of evaporation having the biggest influence on the vacuum raffination. (For a real system the influence of the different rates of evaporation of the impurities are significant) [6], [9], [10]:

$$w = p_D A(M / 2\pi RT)^{0,5} \qquad (11)$$

$$W = 4,4 p_D (M / T)^{0,5} \qquad (12)$$

w - evaporation rate [g.s^{-1}]
A - crucible surface [m^{-2}]
R - gas constant [J.mol^{-1}.K^{-1}]
W - evaporation rate [g.m^{-2}.s^{-1}]
p_D - vapor pressure [Pa]
M - molar mass [g/mol]
T - temperature [K]

The molar fraction for one (impurity) element can be simplified by:

$$x1 = \frac{\dfrac{m_1}{M_1}}{\dfrac{m_1}{M_1} + \dfrac{m_{Pt}}{M_{Pt}}} \cong \frac{m_1 M_{Pt}}{m M_1} \qquad (13)$$

x_1 - molar fraction of impurity element
m_1 - mass of impurity element [g]
m_{Pt} - mass of platinum [g]
M_1 - molar mass of impurity element [g.mol^{-1}]
M_{Pt} - molar mass of platinum [g.mol^{-1}]
m - total mass of melt [g]

Applying Raoult's law to (13), equation (14) follows:

$$p_1 = x_1 p_{D_1} = \frac{m_1 M_{Pt}}{m M_1} p_{D_1} \qquad (14)$$

Combining equation (14) and (8) for the vapor pressure of the impurity p_D and instead of x, equation (13), equation (15) follows:

$$w = \frac{4{,}4 m_1 M_{Pt} A\, p_{D_1} (M_1 / T)^{0,5}}{m M_1} \qquad (15)$$

after inserting $w = dm_1/dm_1$:

$$\int_0^t \frac{dm_1}{m_1} = \int_0^t \frac{4{,}4 m_1 M_{Pt} A\, p_{D_{11}} (M_1 / T)^{0,5}}{m M_1}\, dt \qquad (16)$$

After integration and under the assumption of (17), the change of the molar fraction of the impurity-element with time can finally be calculated by equation (18):

$$\frac{x_t}{x_0} = \frac{m_t}{m_0} = \frac{m_t}{m} \qquad (17)$$

$$x_{(t)} = x_0 \exp\left[\frac{-4{,}4 M_{Pt}\, p_{D_1} A t (M_1 / T)^{0,5}}{m M_1}\right] \qquad (18)$$

$x_{(t)}$ - molar fraction of the impurity element after time t
x_0 - starting molar fraction of the impurity element
A - melt surface area [m^{-2}]
T - temperature [K]
M - molar mass [g.mol^{-1}]
p_D - vapor pressure [Pa]
t - melting time [s]
m - total mass of melt [g]

The concentration decreases exponentially with time and is due to equation (18) mainly dependent from the vapor pressure, temperature, mass of melt and the free evaporation surface. Theoretically after infinite time a concentration x = 0 for each impurity-element can be obtained. In practice, lower melting process-times are aimed for, as with long process times—besides high costs—high metal-losses and impurity accumulations from the crucible material can occur. For elements which are difficult to refine, it is important to find a time-limit at specific conditions—like temperature, pressure, atmosphere, crucible material, alloy composition—where the process can be abandoned, if the concentration keeps stable and cannot be decreased furthermore. The expected theoretical raffination behavior calculated from equation (18) at a temperature of 2300 K for some relevant elements is represented in Figure 1. A starting concentration of 1000 ppm, a free melt surface of 15 cm^2,

a melt-mass of 1400g, as well as two different temperature—2100 K and 2300 K—and a maximum time of 3000 sec have been chosen for the calculations. The subsequent figures show, that for the raffination of most elements only short process-times should be necessary. For the elements Fe, Si, Y, Ti longer refining times should be expected. As expected, the elements Ir, Rh, W, Mo and Zr cannot be vacuum-refined from platinum-melts.

FIGURE 1: *Influence of Time on Impurity-Concentration, Calculated by Model "Binary-Time-System"*
(T = 2300 K, c_o = 1000 ppm, A = 15 cm^2; m = 1400 g)
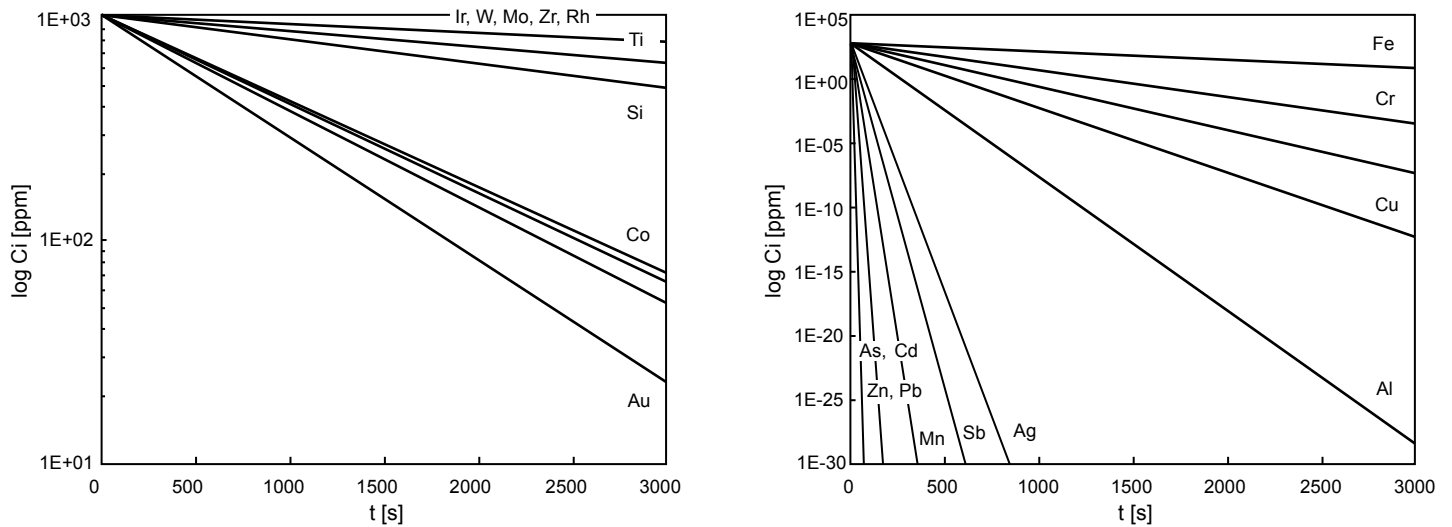
TABLE 4: Theoretical Concentrations Calculated with Model "Binary-Time-System",w
t= 3000 s; c_o = 1000 ppm, A = 15 cm^2; m = 1400 g (small crucible)

T = 2100 K: element i / c_i [ppm]

As	Cd	Zn	Pb	Mn	Sb	Ag	Al	Cu	Sn	Cr	Fe
0	0	0	0	3E-93	2E-53	2E-31	4,1E-5	3,0E-1	3,2E+1	6,5E+1	4,2E+2

Au	Pd	Ni	Co	Si	Y	Ti	Rh	Zr	Ir	Mo	W
4,8E+2	6,0E+2	6,4E+2	6,7E+2	8,9E+2	9,3E+2	9,7E+2	1,0E+3	1,0E+3	1,0E+3	1,0E+3	1,0E+3

T = 2300 K: element i / c_i [ppm]

As	Cd	Zn	Pb	Mn	Sb	Ag	Al	Cu	Sn	Cr	Fe
0	0	0	0	0	0	0	3E-29	3E-13	3,7E-8	2,9E-4	6,4E+0

Au	Ni	Pd	Co	Si	Y	Ti	Rh	Zr	Mo	Ir	W
2,2E+1	5,1E+1	6,3E+1	6,9E+1	4,7E+2	6E+2	7,6E+2	9,9E+2	1E+3	1E+3	1E+3	1E+3

Figure 2 shows the influence of the process-temperature on the raffination behavior of Fe. To raise the temperature from 2100 K to 2300 K will significantly reduce the time of refining for a starting concentration of 1000 ppm Fe and 1400 g of melt.
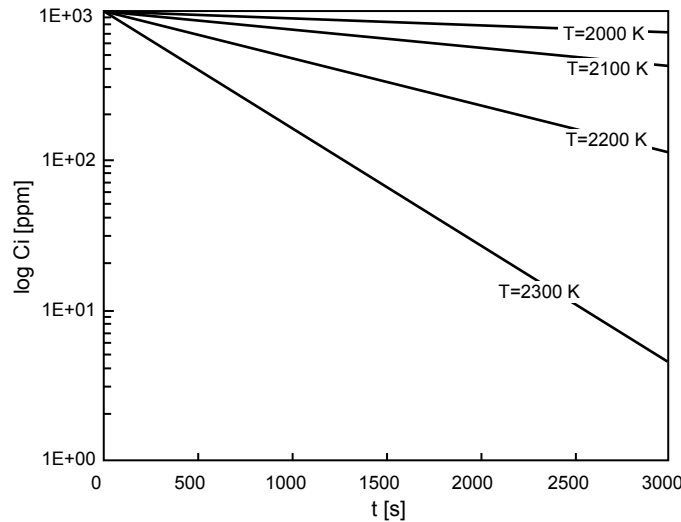

FIGURE 2: *Influence of Time and Temperature on Fe-Concentration*
(c_0 = 1000 ppm, A= 15 cm^2, m = 1400 g)

By the means to obtain 20 ppm of iron, the influence of the crucible geometry on the theoretical refining behavior at 2300 K is shown in Figure 3, where the starting concentration is 1000 ppm Fe. The diagrams show, that with a melt surface of 50 cm^2 and a total melt weight of 5000 g, the concentration of 20 ppm Fe in the casting should be obtained after 1400 seconds, with a melt weight of 10000 g, this limit will be raised to about 5000 seconds. Increasing the melt surface to 100 cm^2 (at 5000 g melt) will reduce the process-time to 1000 sec significantly.
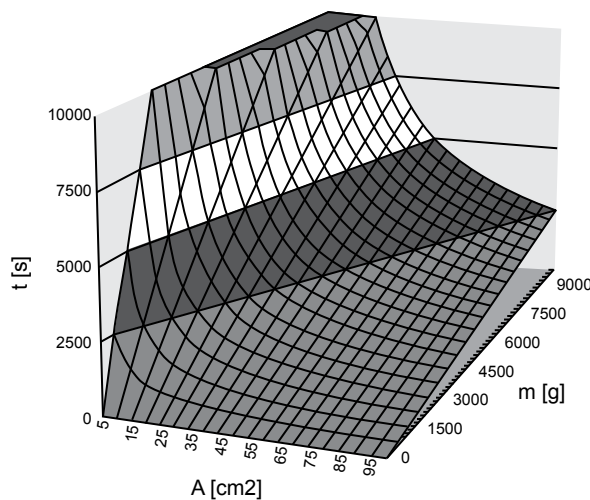
FIGURE 3: *Influence of the Melt Mass and the Melt Surface on Time to Obtain 20 ppm Fe*
(c_0 = 1000 ppm, T = 2300K)

Refining by Oxidation, Model "Oxidation":

Besides the refining of platinum melts by vacuum, some of the elements could be better removable by a oxidation process, especially for those elements with a high affinity to oxygen, like W, Mo, Zr, Ti (Table 1). The remove of the oxides could be via slag-forming or by subsequent evaporation of the formed oxides under vacuum. Using the free enthalpy of formation for the oxides [11], the residue concentration of the impurities in the casts can be calculated, provided that all oxides developed from the impurities having a smaller enthalpy of formation than platinum oxide:

$$\Delta G_{PtO_2} \geq \Delta G_{Me_mO_{2n}} \tag{19}$$

$$\Delta G = \Delta G° + RT \ln K \tag{20}$$

ΔG - free enthalpy of formation: ΔG_{PtO_2}
$\Delta G_{Me_mO_{2n}}$ - free enthalpy of formation for PtO_2, Me_mO_{2n}
$\Delta G°$ - standard Gibbs energy of formation

$$\Delta G°_{PtO_2} + RT \ln \frac{\alpha_{PtO_2}}{\alpha_{Pt}\alpha_{O_2}} \geq \Delta G°_{Me_mO_{2n}} + RT \ln \frac{\alpha_{Me_mO_{2n}}}{\alpha_{Me}^m \alpha_{O_2}^n} \tag{21}$$

α - activity: α_{PtO_2} - PtO_2 activity, $\alpha_{Me_mO_{2n}}$ - Me_mO_{2n} activity etc.
α_{Me} - activity of the element Me: $\alpha_{Me} = x_{Me}$
x_{Me} - molar fraction of the element Me (from element i, $x_i = x_{Me}$)
αO_2 - oxygen-activity: $\alpha O_2 = pO_2$
pO_2 - partial pressure of oxygen

The obtainable theoretical concentration for the elements have been calculated with equation (21) under the assumption of the oxygen-activity being equivalent to the oxygen partial pressure and that the activities of the oxides and of platinum are also equivalent. The relevant values are presented in Table 5.

The calculations are made with the assumption of an oxygen partial pressure of 21000 Pa. Reducing it to a lower level would result in lower concentrations for a few elements like Pd, Ag, Cu, Co, Ni, Sb, Zn. For all others, a higher partial pressure is preferable for their remove through oxidation. Generally it can be stated, that it is impossible to refine the PGM's (Pd, Ag, Rh, Ir) by oxidation, the elements Cu and Cd are almost impossible to remove. All other elements show a more or less good refining behavior. The calculated concentrations also tend to decrease with decreasing temperature.

TABLE 5: Theoretical Concentrations Calculated with Model "Oxidation"

T = 2300 K, p_{O2} = 21 000 Pa: **Element i / c_i [ppm]**

Y	Zr	Si	Al	Ti	W	Sb	Mo	Cr	Sn	Co	Mn
1,1E-26	4,7E-14	1,8E-10	6,7E-8	1,6E-7	3,6E-4	1,3E-4	2,3E-3	3,5E-3	3,0E-1	5,7E-1	1,0E+0
Ni	**Fe**	**Zn**	**Pb**	**As**	**Cu**	**Cd**	**Pd**	**Ag**	**Rh**	**Ir**	
4,3E+0	2,0E+1	2,1E+1	8,3E+1	5,2E+2	1,8E+3	4,5E+3	3,4E+4	1,4E+5	3,0E+5	-	

T= 2100 K, p_{O2} = 21 000 Pa: **Element i / c_i [ppm]**

Y	Zr	Si	Al	Ti	Sb	W	Cr	Mo	Sn	Mn	Co
3,4E-31	9,IE-17	8,0E-13	6,9E-10	2,8E-9	2,4E-5	3,9E-6	1,3E-4	1,8E-4	8,4E-3	7,8E-2	1,0E-1
NI	**Zn**	**Fe**	**Pb**	**As**	**Cu**	**Cd**	**Pd**	**Ag**	**Rh**	**Ir**	
6,2E-1	1,1E+0	2,7E+0	2,0E+1	9,7E+1	8,8E+2	1,8E+3	8,5E+3	8,3E+4	5,8E+5	-	

EXPERIMENTAL PROCEDURE

For studying the raffination behavior of Platinum by vacuum-refining techniques, the elements Al, Cu, Fe and Sb had been chosen as impurities. Due to the theoretical models as well as from practical problems under production-conditions these elements had been identified to be critical as having non-expected behavior during vacuum refining.

In order to compare the experimental results with theoretical models and their prediction, The binary system as well as multicomponent-systems have been investigated. Therefore melts with Platinum as matrix and one additions of one of the critical elements, as well as experiments with additions of all components have been prepared. All samples has been prepared by powder metallurgical techniques, which means the matrix have been produced by a wet-chemical purification process (precipitation and calcination process [1]), and the impurity have been introduced as elemental powder by mixing, pressing and sintering of the powder mixture. The sinterbodies have been introduced into a ZrO_2 - crucible and melted under Ar-atmosphere to prevent oxidation and evaporation of the impurity component before the melting point of the matrix has been reached. After reaching the melting point, vacuum was applied. Melt-weight was 1300 g, after different process-times small samples have been casted, and analysed for the residue-concentration of the impurity-element by WXRF and ICP-AES/CSN.

A 11 kHz fixed medium-frequency generator have been used, lowest chamber-pressure in the cold condition was $1 \cdot 10^{-3}$ Pa. Metal-vapors have been condensated by a water-cooled Cu-condenser. The crucible was an 85 ml ZrO_2-crucible with a free melt-surface of about 13 cm^2. Temperature was measured by a 2-color-pyrometer.

RESULTS AND DISCUSSION

The raffination behavior of the elements Cu and Sb in Figure 4 and Figure 5 shows the desired behavior. These elements own a satisfactory high vapor-pressure at the considered temperature in order to remove them under vacuum within a realistic period. Even from a starting concentration of 5000 ppm a final-concentration of 70 ppm Cu can be achieved after three hours, a pressure of $5E^{-3}$ Pa and a temperature of 2223 K. Reducing the concentration in the starting material to 1000 ppm, even only 20 ppm can be detected in the casting. On the other hand a slightly different behavior can be measured, if a multicomponent alloy - Pt-matrix with Sb, Cu, Fe and Al - is investigated. The simultaneously existence of all impurities results in a similar decrease in concentration with time, but the raffination proceeds slower. With slightly increasing raffination-time; similar final-concentrations of Cu can be expected. With Sb, a similar behavior was found. After 6 hours under vacuum treatment at 2223 K and a starting concentration of 5000 ppm, 100 ppm of Sb are left in the casting. Reducing the concentration again to 1000 ppm leads to a minimum of 6 ppm Sb after 6 hours of vacuum raffination. The investigated multicomponent system Pt-SbAlCuFe shows no significant difference to the binary system.

FIGURE 4: *Raffination Behavior of Cu Under Vacuum at 2223 K*
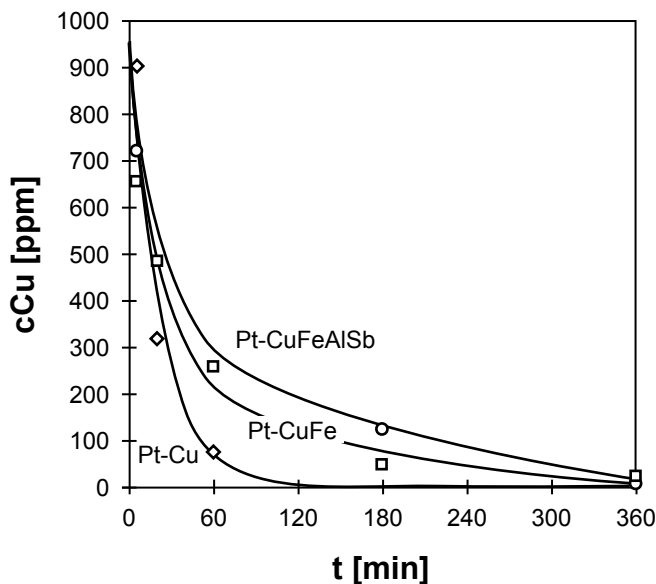
FIGURE 5: *Raffination Behavior of Sb Under Vacuum at 2223 K*
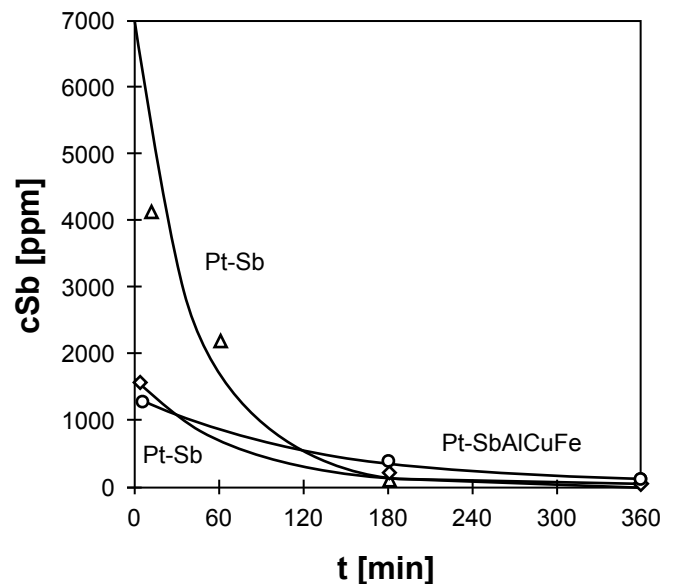
Compared to the theoretical model and its calculated minimum achievable concentrations, the elements Cu and Sb show a slightly different behavior to the predicted one. Model "multicomponent", as well as "binary-time", have a bigger discrepancy to the experimental results, than the simple "binary"-model. Especially from the calculations by model "binary-time" higher refining rates were expected.

The impurities Al and Fe form the other group amongst the four investigated elements. They show lowest refining rates and no differences in their raffination behavior between the corresponding binary, ternary or multicomponent-systems (Figure 6 and Figure 7). Starting from a concentration of about 1600 ppm Fe in a binary PtFe-melt, a residue of 1325 ppm Fe can be measured in the casting after 6 hours of vacuum treatment at 2223 K. Almost the same refining rate can be observed for the Fe in the ternary Pt-FeCu or the Pt-FeAlCuSb multicomponent alloy, even if the starting concentration of Fe is reduced to 1100 ppm. After 6 hours, the Fe-content has only been reduced to about 850 ppm. Even oxidation by applying pure oxygen onto the surface of the melt, has no positive effect on the reduction of the Fe-content.

In the refining of Al, a marked decrease at the starting period of the vacuum-process can be seen. The concentration drops from about 1000 ppm rapidly to about 600 ppm within the first 20 minutes. From that time, the concentration decreases only slightly to 500 ppm, the raffination almost comes to a standstill. Similar behavior can be observed for the Al in the multicomponent alloy Pt-AlCuFeSb, although compared to the binary PtAl-sample, the refining rates are even lower.

FIGURE 6: *Raffination Behavior of Fe Under Vacuum at 2223 K*
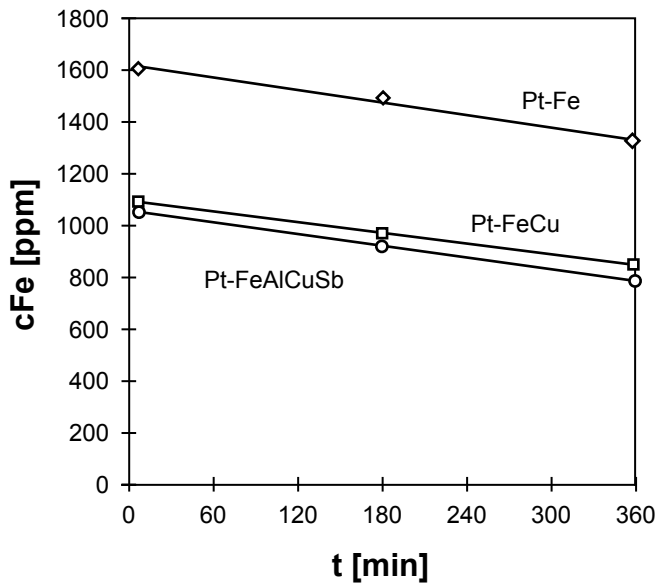
FIGURE 7: *Raffination Behavior of Al Under Vacuum at 2223 K*
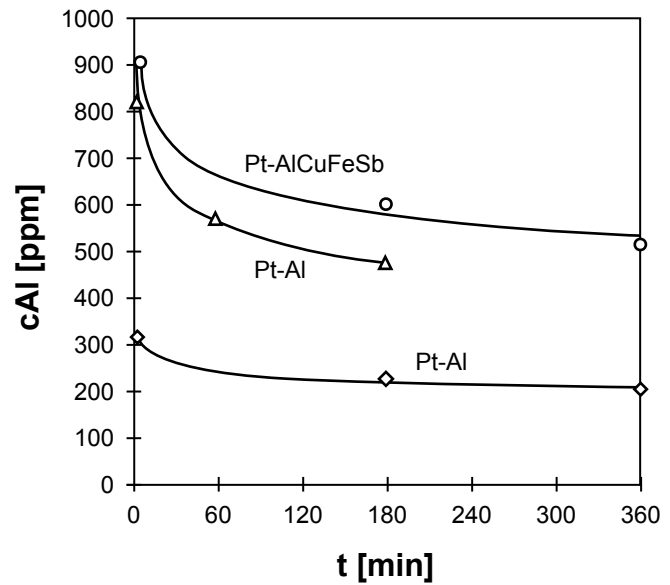
The rapid decrease within the first process-time can be explained by a reaction between the Al-containing melt and the crucible. This reaction is manifested by a visible melting of the inside crucible-surface and can be observed in all samples containing Al. After the largest part of the reaction is completed, the further refining behavior of Al is dominated by the liquid-vapor transition and is characterized by a very slow process of the Al-remove from the melt.

Comparing these results with the calculated ones from the presented models, it can be seen, that the theoretical behavior quite differs from the experiments and do not reflect the real situation.

Additionally the behavior of the crucible has been studied. The experiments show, that in all samples—independent from composition—an increase of Zr happens. As the crucible consists of ZrO_2 and its stabilizers CaO and MgO, and also of SiO_2, Fe_2O_3 and Al_2O_3, these elements can be detected in the castings, as they react with the Pt-melts as well. In Figure 8 the increase of Zr in a Pt-sample (without any additional impurities) can be seen clearly, after 6 hours of vacuum melting at a temperature of 2223 K a Zr-concentration of almost 400 ppm can be measured. A different behavior can be observed for the Pt-Al samples. These are marked by high Zr-contents at the beginning and a rapid decrease with increasing process-time. In the Pt-sample with 500 ppm Al, about 600 ppm Zr can be detected. In the 1000 ppm Al sample, the Zr-concentration is even 1300 ppm. A rapid decrease follows, but the content after 6 hours is still clearly above the one of the Pt-sample.

FIGURE 8: *Reaction Between ZrO$_2$-Crucible and Pt- and PtAl-melts Under Vacuum at 2223 K*
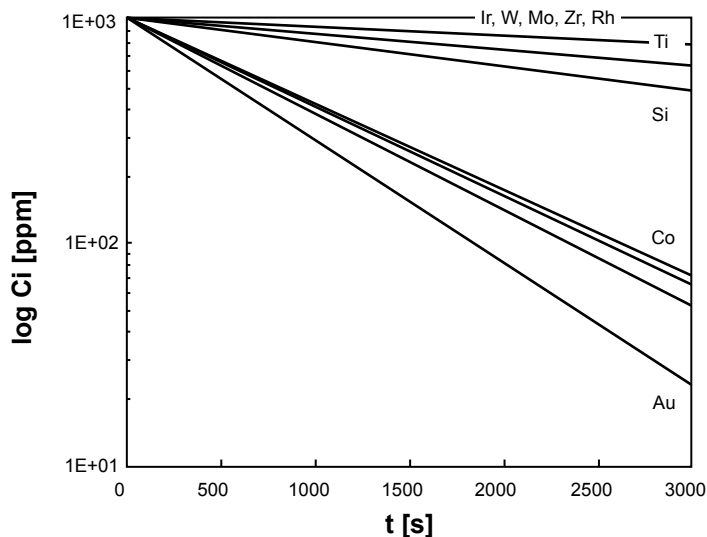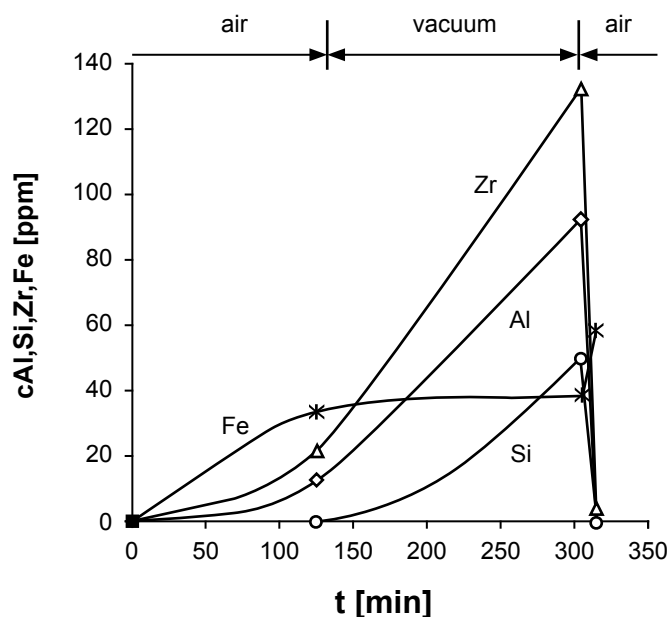

FIGURE 9: *Enrichment of Zr, Al, Si, Fe from Crucible in a Pt-melt Under Different Atmospheres at 2223 K*

In Figure 9 the increase of Al and Si is represented, but in contrast to the samples in Figure 8, this sample (Pt) was treated first under air, then under vacuum and followed by a repeated flooding of the vessel with air. The lines show small increases for the melting under air and the expected rapid increase of Zr under vacuum. A similar behavior is shown by Si and Al, both components arising from the crucible. By way of contrast, the Fe-content from the crucible increases during melting under air, keeps more or less constant under vacuum and increases again under air. Whereas Zr, Al and Si show an immediate decrease, if the vessel is flooded with air. The concentrations of these elements can reduced to almost zero.

This is of certain use for the explanation of the different refining behavior of the investigated elements Fe and Al. Contrary to the simultaneous refining of these elements, a reaction between the crucible and the melt occurs, which results in an enrichment of Zr, Fe, Si and Al in the casting. Therefor the refining behavior under vacuum is influenced by this event, and the refining e.g. of Fe, Si, Al - elements which have to also to be removed from the melt - is only possible to that level which is given by the enrichment from the crucible. The reason for the enrichment of Zr, Al, Fe and Si from the crucible and the possible removal by flooding the vessel with air for a short period, is actually not clear. It is quite possible, that Zr, Al and Si are simply (re-)oxidized and removed by forming a slag, but with increasing time again an increase should be expected, if furthermore melted under air.

CONCLUSION

Based on theoretical considerations about vacuum metallurgical raffination and thermodynamics, four models have been developed, from where theoretically achievable concentrations of impurities in a platinum matrix melt after a vacuum treatment or after an oxidation treatment can be calculated for different temperatures. The models give either maximum values (model "binary-system"), minimum ones (model "multicomponent-system") or should reflect a realistic situation, where the time has to be taken into consideration (model "binary-time-system"). Also the influence of melt mass, as well as melt surface can be simulated with this model. Additionally a model "oxidation" have been developed, in which the refining behavior under an oxidizing treatment of the melt has been simulated.

Four elements have been investigated in the experimental procedure: Cu, Sb, Al and Fe. The refining behavior under vacuum at 2223 K of samples of binary Pt-matrix-melts, as well as samples, where all of these elements participate have been studied. The results show for the elements Cu and Sb a satisfactory remove under vacuum, the elements Al and Fe can only removed to small extent. Depending on the starting concentration, as low as 20 ppm Cu or 6 ppm Sb can be achieved after 6 hours at 2223 K. Tendency shows slightly lower refining rates, if multi component alloy are investigated in contrary to binary systems. If any Al is in the samples, a reaction between the ZrO_2-crucible and the melt occurs,

which is manifested by a visible melting of the inside crucible surface. As a consequence, the Al-concentration decreases rapidly at beginning of the experiment, but after the reaction has consumed most of the Al, the residue Al in the melt can be removed just to small extent. The refining rate for Fe from binary PtFe-melts, respectively Pt FeSbCuAl multicomponent melts, is comparably low. After 6 hours of vacuum treatment the residue concentrations are still too high to justify a new use in the process as a new construction-part. Increasing the process-times is not useful as this would increase costs. Under these aspects a maximum of 6 hours should be applied.

Additionally the influence of the crucible has been investigated. The experiments show a reaction between the melt and the substances contained in the ZrO_2-crucible. An increase of Zr, Al, Si and Fe can be observed, but the enrichment of these elements can be controlled and navigated by the used atmosphere during the melting process. It could be shown, that after the vacuum treatment, the content of these elements decrease rapidly, if the sample is cast under air.

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Options

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Good afternoon ladies and gentlemen. I would like to personally welcome you to the IPMI Conference. This afternoon I was supposed to talk to you about a consumer's view of the market and particularly about how consumers can use options. But, after looking over the list of attendees, I decided to talk in more general terms instead of a particular segment of the industry.

 The paper will be broken down as follows:

> (A) The risk of basic hedging
> (B) What is an option
> > (a) How do they work
>
> (C) Option trading strategies
>
> (D) Exotic option programs

HEDGING

Hedging is the activity by which producers, processors and marketers of actual physical commodities lock in the price of a future delivery or sale.

The essence of hedging is to take a position in the future market opposite that of the cash or "physical" market. If a silver consumer purchases 100,000 T/O of physical silver, he is now "long" silver and at risk for any downward price movement. In order to protect his profit, he should sell 100,000 T/O in the silver market. Since cash and future prices tend to move in tandem, only gain or loss in the future market is usually off-set by gain or loss in the physical market. But, there are also risks involved in basic hedging:

SELLING

> (1) Selling hedge in a normal market followed by a narrowing of the basis.
>
> (2) Selling hedge in a normal market followed by a widening of the basis.
>
> (3) Selling hedge in an inverted market followed by a narrowing of the basis.
>
> (4) Selling hedge in an inverted market followed by a widening of the basis.

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BUYING

    (1) Buying hedge in a normal market followed by a narrowing of the basis.

    (2) Buying hedge in a normal market followed by a widening of basis.

    (3) Buying hedge in an inverted market followed by a narrowing basis.

    (4) Buying hedge in an inverted market followed by a widening of the basis.

So what's a person to do? If you are like most, you go searching or researching for a market timing signal to get you in at the top and out at the bottom. The answer is to use options to help offset some of the risk in hedging. Options by no means replace basic hedging. They can act as an enhancement to hedging.

    (B) What is an option? Following are two descriptions of an option. The first is a relatively standard definition. The second may make it easier to see what is really going on.

        (1) An option is the owner's , but not the obligation, to buy (in the case of a call option) or to sell (in the case of a put option) a particular item at a predetermined price know as the "strike" price on or before a specific date usually called the "expiration" date. The amount paid for an option is called the premium.

        (2) An option is a forward or futures contract that may be canceled prior to maturity if one of the two parties involved so chooses. The party who has the cancellation privilege is the buyer of the option.

    The decision to purchase or sell either a put or a call is based upon two primary factors.

        (1) The belief that the option is at least fairly priced.

        (2) and, the expectation that the underlying market will move in the anticipated direction.

    (C) Options trading strategies

        Bullish Strategies
- Buy call
- Bull spread
- Sell put
- Buy instrument/buy put
- Buy call/sell put

        Stable Prices
- Sell straddle
- Sell strangle
- Ratio write
- Short butterfly
- Ratio spreads

Bearish Strategies

- Buy put
- Bear spread
- Sell call
- Sell instrument/buy call
- Buy put/sell call

Volatile Prices

- Buy straddle
- Buy butterfly

Time Decay Help

- Short call
- Short put
- Short straddle
- Covered call write
- Covered put write

Time Decay Mixed

- Bull spread
- Bear spread
- Long butterfly
- Short butterfly

Time Decay Hurts

- Long call
- Long put
- Long straddle

Profit/Loss Characteristics

Strategy	Profit	Loss
Buy call	Open	Limited
Buy put	Open	Limited
Short a call	Limited	Open
Short a put	Limited	Limited
Bull spread	Limited	Limited
Bear spread	Limited	Limited
Long butterfly	Limited	Limited
Short butterfly	Limited	Limited
Calendar spread	Open	Open
Long straddle	Open	Limited
Short straddle	Limited	Open

<u>Buy Call</u>

Buying a call a is bullish strategy that requires a price rise in the underlying instrument. Nonetheless, the most critical factor in trading calls profitably is an ability to predict the future price moves of the underlying instrument.

<u>Synthetic Call</u>

A synthetic call can be created by buying a put and buying the underlying instrument.

<u>Risk/Reward</u>

The maximum profit potential is theoretically unlimited. If the price moves above the premium paid, the profit becomes unlimited.

<u>Bull Spread</u>

This is a bullish strategy with both limited risk and profit potential. It is not as bullish as buying a call or selling a put, but the risk is generally lower than buying a call and is significantly lower than selling a put.

> A bull spread is either:
> - Long a lower strike call and short a higher strike call, or
> - Long a lower strike put and short a high strike put.

<u>Stable Prices/Neutral Strategy/Volatile Prices</u>

There are two types of straddles: <u>long</u> and <u>short</u>. They are constructed as follows:

> **Long Straddle** = Long Call and Long Put
>
> **Short Straddle** = Short Call and Short Put

<u>Straddles</u> are generally considered neutral strategies because the put and call are usually both at-the-money options. This means the long straddle will profit if the price of the underlying instrument moves significantly in one direction or the other.

The <u>short straddle</u> will profit if the price of the underlying instrument stays in a narrow range.

<u>Strangle</u> is a purchase (or sale) of a call and a put different strike levels. The strangle is the same as a straddle. The only difference is that th option in a strangle are struck at different prices.

<u>Butterfly Spreads</u>

Butterfly spreads are usually considered neutral strategies.

> A long butterfly is constructed by:
> > Buying one low-strike option
> > Selling two medium-strike options
> > Buying one high-strike option
>
> A short butterfly is constructed by:
> > Selling one low-strike option
> > Buying two medium-strike options
> > Selling one high strike option

<u>Ratio Spreads</u>

There are two types of ratio spreads - long and short.

A long ratio spread is constructed by buying a low strike call and selling a larger quantity of higher strike calls or buying a high-strike put and selling a larger quantity of lower strike puts.

<u>Calendar Spreads</u>

Calendar spreads are constructed by buying or selling a put or call in one expiration month and taking the opposite position in a further expiration month. Calendar spreads can be constructed to be either bullish and bearish. Also, there are two ways to construct neutral calendar spreads.

A neutral calendar spread can be constructed by selling a nearby at-the-money option and buying a longer-dated contract with the same strike. This strategy is used when one is looking for prices to remain stable in the near term, but want to capture the time decay of the nearby option.

A second type of neutral calendar spread, called a reverse calendar spread, is constructed by buying the nearby option and selling the longer option. A large price move in the underlying instrument is required before reverse calendar will profit.

A bullish calendar spread can be constructed by using a strike price above the current market price.

A bearish calendar spread can be constructed by using a strike price below the current price of the underlying price.

<u>Exotic Option Programs</u>

> (I)   Participating Sales Program
> (II)   Min-Max Program
> (III) Average Price Option
> (IV)   Compound Options
> (V)   Up and outs (Knock-out} Barrier
> (VI)   Zero Premium

Barrier (APO)

An APO is like a standard option, except that it settles against the average of spot price over its lifetime, rather than spot at expiration. The average can begin at any point in the option's life and spot readings can be taken at any interval and frequency. In general, the cost of an APO will be less than a standard option, partially because the average process effectively smoothes out the volatility of the underlying commodity.

Compound (option on an option)

A compound option gives the holder the right to purchase an option on a preset date for a preset premium, called the strike premium. The more initial premium paid upfront, the more favorable the strike premium. If the first option is exercised, the underlying option functions as a standard option throughout its lifetime. If the first option is not exercised the compound option expires and the holder does not recoup the initial upfront premium.

Zero Premium (Contingent Premium)

No premium is required upfront for this option. The payment of the premium is contingent upon the option finishing in-the-money. If the option finishes in-the-money at expiration, then the premium must be paid. If the option finishes either at-the-money or out-of-the-money, the option holder pays no premium at all. If exercised, the cost of the contingent option will be higher than a standard option.

Barrier

A barrier option differs from a standard option in that an "out strike" or "in strike" must be selected in addition to the normal strike price. The outstrike marks the level at which the option will cease to exist if it is reached or crossed by the spot exchange rate at any time during the life of the option. Conversely, the instrike marks the level where the option will come into existence. The price of a barrier option will be less than the price of an equivalent standard option because it may expire prior to its normal expiration date.

Lookback

A lookback option allows the holder to look back at expiration and set the strike at the most favorable level achieved by spot during the life of the option. For a lookback call, the strike is set at the minimum spot level, thus allowing the holder to buy at lowest level reached during the period. For a lookback put, the strike is set at the maximum spot level and the holder has the right to sell spot at the highest level attained over the life of the option. Because the lookback option always finishes in-the money or at-the-money, the premium will be higher than a standard option.

Participating Forward

This is a forward sale, some of the proceeds are used to finance the purchase of calls. The seller usually gives up the forward contango which is used to pay for the calls. This creates downside protection (forward sale) and upside participation (call purchase).

Examples of Strategies

(I)   Position: Call Ratio Backspread (sell lower strike call, buy more of a higher strike call)
        Outlook: Very bullish
        Risk: Limited. Worst case if at expiration, the futures price is at the level of the calls bought.
        Reward: Unlimited
        Time: Works for position
        Volatility: Works for position

(II)   Position: Long straddle. (Buy put and buy call each at same strike price.)
        Outlook: Volatile market in either direction.
        Risk: Limited
        Reward: Unlimited
        Time: Works against position
        Volatility: Works for position

(III)   Position: Long strangle. (Buy put and buy call each of out-of-the-money.)
        Outlook: Very volatile market in either direction.
        Risk: Limited to premiums paid
        Reward: Unlimited
        Time: Works against position
        Volatility: Works for position

(IV)   Position: Short butterfly (sell one in-the money call, buy two at-the-money calls,
        sell one out-of-the money call)
        Outlook: Expect the market to move sharply in either direction.
        Risk: Difference between middle strike and one of the outer strikes
        Reward: Limited to net credit (premium from option sales)
        Time: Usually works against position
        Volatility: Helps position to the extent that trader wants price to move

(V)   Position: covered call write. (Buy the futures and sell a call)
        Outlook: Mildly bullish, expecting lower volatility
        Risk: Unlimited, if purchased futures fall substantially, premium taken in will not cover future loss.
        Reward: Limited
        Time: Works for position
        Volatility: Works against position

(VI)   Position. Ratio spread (buy call, sell more calls at a higher strike price.)
        Outlook: Slightly bullish, maximum profit at call written (sold).
        Risk: Unlimited
        Reward: Limited
        Time: Works for calls written, against call bought. Overall, time works for position.
        Volatility: Works against position

(VII)   Position: Short strangle - (Sell call and sell put each out-of-the-money.)
        Outlook: stable market
        Risk: Unlimited
        Reward: Limited to the amount of premium received
        Time: Works for position
        Volatility: Works against position

(VIII) Position: Short straddle. (Sell call and sell put each at the same strike price.)
        Outlook: Expect lower volatility with very little price movement.
        Risk: Unlimited - major losses can occur if prices soar or collapse.
        Reward: Limited to the amount of premium received
        Time: Works in favor of position
        Volatility: Works against position

(IV)   Position: Bull call spread (Buy lower strike, sell higher strike).
        Outlook: Moderately bullish
        Risk: Limited to net premium outlay
        Reward: Limited to the difference in strikes used.
        Time: Depends
        Volatility: This position is more concerned with direction of the market than the volatility.

(X)   Position: Bull put spread - (Sell a higher strike put, and buy a lower strike put).
        Outlook: Expect the market to become less volatile with slight price increase.
        Risk: Limited
        Reward: Limited to net premium taken in
        Time: Depends upon strike selected
        Volatility: Works against position (depends on strike).

(XI)   Position: Bear put spread (buy higher strike put, sell lower strike put).
        Outlook: Moderately bearish
        Risk: Limited to net up-front cost for put
        Reward: Limited to difference in strikes
        Time: Depends on strike selected
        Volatility: Work against position.

(XII)   Position: Bear call spread (buy a higher strike call and sell a lower strike call).
        Outlook: Expect the market to become less volatile with a slightly bearish tone.
        Reward: Limited to net credit received. Maximum profit happens when, at option expiration, futures
        are below strike sold.
        Time: Depends upon strike
        Volatility: Works against position, but of more concern is the direction of the underlying price.

(XIII) Position: Long butterfly (buy one in-the money strike call; sell two at-the-money strike
        calls; buy one out-of-the-money strike call.)
        Outlook: Expect little price movement over a fairly long period of time (more than a month).
        Risk: Limited to initial debit
        Reward: Limited. Best case scenario occurs when futures expire at the level of calls written.
        Time: Works for position
        Volatility: Hurts position.

(XIV)   Position: Long calendar time spread. Sell nearby option and buy longer-term option both
        at the same strike price.
        Outlook: Neutral if both done at-the money. Bullish if call strikes are out-of-the-money. Bearish if
        puts strikes are out-of-the-money
        Volatility: Stable - Volatility hurts.

HEDGING

To hedge, take a position in futures that is opposite to the cash position

	CASH POSITION	FUTURES POSITION
To Hedge	LONG	SELL
At Offset	SELL	BUY

FULL HEDGE

Fully protects cash position

REWARD — Offset any adverse move in underlying cash positions

RISK — Opportunity cost

BUYING

    (1) Buying hedge in a normal market followed by a narrowing of the basis

    (2) Buying hedge in a normal market followed by a widening of basis

    (3) Buying hedge in an inverted market followed by a narrowing basis

    (4) Buying hedge in an inverted market followed by a widening of the basis

SELLING

    (1) Selling hedge in a normal market followed by a narrowing of the basis

    (2) Selling hedge in a normal market followed by a widening of basis

    (3) Selling hedge in an inverted market followed by a narrowing of the basis

    (4) Selling hedge in an inverted market followed by a widening of the basis

CALL: The right (not obligation) to buy a future at a specific price for a specific period of time.

PUT: The right (not obligation) to sell a future at a specific price for a specific period of time.

OPTION BUYING

CALL: The right to buy a future at a specific price for a specific period of time.

PUT: The right to sell a future at a specific price for a specific period of time.

OPTION SELLING

CALL: The obligation to sell a future at a specific price for a specific period of time.

PUT: The obligation to buy a future at a specific price for a specific period of time.

EXERCISING OPTIONS

CALL

Buyer — Long Future
Seller — Short Future

PUT

Buyer — Short Future
Seller — Long Future

RISK PARAMETERS

OPTIONS vs. FUTURES

RISK	Buyer	Seller
OPTION	Limited to Premium	Unlimited
FUTURE	Unlimited	Unlimited

REWARD	Buyer	Seller
OPTION	Unlimited	Limited to Premium
FUTURE	Unlimited	Unlimited

HEDGE — LONG CASH

BULLISH TO NEUTRAL — A.) Long cash, long put
B.) Long cash, short call

REWARD — A.) Profit increase as cash position increases
B.) Profit limited to premium received on call

RISK — A.) Loss limited to premium paid for put
B.) Limited to call premium received plus difference between cash and call price

HEDGE — SHORT CASH

BEARISH — A.) Short future/long call
B.) Short future/short put

REWARD — A.) Profit increases as cash position declines
B.) Profit limited to premium received on put

RISK — A.) Loss limited to premium paid
B.) Limited to premium received plus difference between Future Price & Put Price

EXOTIC OPTION PROGRAMS

  (I)   Participating Sales Program

  (II) Min-Max Program

  (III) Average Price Option

  (IV) Compound Options

  (V) Up & Outs (Knock-Out) Barrier

  (VI) Zero Premium

SELL PUT

  BULLISH

  REWARD — Profit limited to premium

  RISK — Unlimited less premium

BULL SPREAD

  BULLISH —   Buy Option With Lower Strike
               Sell Option With Higher Strike

  REWARD —   Calls — Profit Limited to Difference Between Strikes Less Premium Paid
               Puts —   Profit Limited to Premium Received

      RISK —   Calls — Loss Limited to Premium Paid
               Puts —   Loss Limited To Difference Between Strikes Less Premium Received

BUY CALL

  BULLISH

  REWARD — Profit increases as future rises

  RISK — Loss limited to premium paid

BUY FUTURE / BUY PUT

  BULLISH

  REWARD — Profit Increases As Future Rises

  RISK — Loss Limited To Premium Paid

BUY CALL / SELL PUT

(SYNTHETIC LONG FUTURE)

BULLISH

REWARD — Profit increases as future rises

RISK — Loss increases as future declines

BUY PUT

BEARISH

REWARD — Profit increases as future declines

RISK — Loss limited to premium paid

BEAR SPREADS

BEARISH —   Buy option with higher strike
Sell option with lower strike

REWARD —   Calls — Profit limited to premium received
Puts — Profit limited to difference between strikes less premium

RISK —   Calls — Loss limited to difference between strikes less premium
Puts — Loss limited to premium paid

SELL CALL

BEARISH

REWARD — Profit limited to premium

RISK — Unlimited less premium

SELL FUTURE / BUY CALL

BEARISH

REWARD — Profit increases as future declines

RISK —   Loss limited to premium paid

BUTTERFLY SPREAD

A.) LONG BUTTERFLY — Stable Market —
                Long 1 Call (Put) 400
                Short 2 Call (Puts) 390
                Long 1 Call (Put) 380

B.) SHORT BUTTERFLY — Stable Market —
                Short 1 Call (Put) 400
                Long 2 Call (Puts) 390
                Short 1 Call (Put) 380

REWARD — A.) (Long Butterfly) — Maximum Profit if Future Settles At Striking Price Of Short Call (Put)

               B.) (Short Butterfly) — Maximum Profit Limited To Premium Received

RISK — A.) (Long Butterfly) — Maximum Loss Limited To Premium Paid

               B.) (Short Butterfly) — Maximum Loss If Future Settles At Striking Price Of Long Call (Put)

BUY PUT / SELL CALL

(SYNTHETIC SHORT FUTURE)

BEARISH

REWARD — Profit increases as future declines

RISK — Loss increases as future rises

BUY STRADDLE

VOLATILE MARKET — Buy call, buy put — Same striking price, same expiration date

REWARD — Unlimited less premium paid

RISK — Loss limited to premium paid

BUY FUTURE / SELL CALL

STABLE MARKET

REWARD — Profit limited to premium received on call

RISK — Unlimited less premium received

TIME SPREADS

STABLE MARKET — Buy call (put), sell call (put), same striking price, different expiration month

REWARD — Allow time to erode value of the near-term option at a faster rate than for the longer-term option.

RISK — Significant Increase or decrease in the underlying future will result in losses.

NEUTRAL SPREADING

(RATIO SPREADING)

STABLE MARKET — Buy call (put), sell call (put), same expiration month, different exercise prices, in usual ratio of 1:3 or less. All done to initial delta neutrality. Short call at higher strike than long call. Short put at lower strike than long put.

REWARD — CALL SPREAD — Profit maximized if future settles at exercise price of short call.

— PUT SPREAD — Profit maximized if future settles at exercise price of short put.

RISK — CALL SPREAD — Unlimited on upside because of excess short calls.

— PUT SPREAD — Unlimited on downside because of excess short puts.

SELL FUTURE / SELL PUT

STABLE MARKET

REWARD — Profit Limited To Premium Received On Put

RISK — Unlimited Less Premium Received

SELL STRADDLE

STABLE MARKET — Sell call, sell put — Same striking price, same expiration date

REWARD — Profit limited to premium received — Maximized if future settles at strike price

RISK — Unlimited less premium received

Solidification Fundamentals of Jewelry and Dental Casting

1982 IPMI Distiguished Achievement Award Address

Permission granted by the author at time of submission to Precious Metals 1982.

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Professor Emeritus of Metal Science
Polytechnic Institute of New York

PREFACE

The Planning Committee for the Sixth International Precious Metals Conference appropriately chose the theme to be "Precious Metals Serving Mankind Today and Tomorrow." It was clear to those in attendance that the fundamental changes are taking place not only in the precious metals community but also in the industry it serves and the Society dependent upon both. The role these metals play in offering mankind better life has been expanding at a rapid pace over the past few years. Today, one cannot think of an industry not dependent upon precious metals in on form or another.

Sessions of this Conference were thus planned to reflect this awareness and to present to the attendees and readers of this volume papers on a variety of technical innovations in the application of precious metals. Obviously, we did not neglect the main-stay topics of advances on recovery and refining and analysis of precious metals. Following the wide swing in the precious metal prices experienced over the past two years, hedging and inventory protection became timely topics. The financial sessions covered these topics well. Heap leaching is the most recent treatment for low grade ores. Therefore, a comprehensive discussion on this technique was included. The aforementioned are only a sample of what the reader will encounter in this volume.

The Distinguished Achievement Award was presented to Dr. John P. Nielsen, a co-founder and Executive Director of the IPMI. His lecture representing results of years of investigations is thus included in this volume of proceedings. The Henry J. Albert Award for excellence in the field of Physical Metallurgy of Precious Metals was presented to Mrs. Joseph Tuccillo for his work on Gold Alloys. Moreover, the Gemini Industries Research Grant was presented to John B. Wiley of California State University to carry out research on "Precious Metal Complexes of Macrocyclic Ligands."

ABSTRACT

A series of casting hulls were produced of jewelry and dental castings in which the liquid fraction was centrifuged off the partially solidified casting 1 to 12 seconds after mold filling. Marked differences were found between the coarse and fine grained type of alloys. Vertices, edges, etc. in the pattern configuration were sources of solidification nucleation. These nuclei appeared to burst into existence very rapidly and in turn were the sources of new nucleation, producing nucleation chains penetrating into the liquid region. These nucleation chains were in effect fingers of solid enmeshing with other fingers, occasionally entrapping pockets of liquid metal. Entrapped liquid pockets also occurred when hot spots were produced in the regions of hot metal impingement on some local point on the mold wall.

KEYWORDS

Jewelry casting, dental casting, mode of solidification, nucleation of solid, nucleation chains, hot spots, grain size.

INTRODUCTION

In order that the best sprue design and casting procedure are followed to make a good jewelry or dental casting, it is of considerable help to have a good idea of the mode of solidification. The ideal mode of solidification that is continually being sought by the caster is to have the casting begin to solidify at the tip of the casting, opposite the sprue, with the solid-liquid front progressing steadily toward the sprue, entrapping no liquid metal pockets en route. The caster uses certain devices in attempting to achieve this. The sharp tips of a pattern are usually placed in the mold away from the sprue, these being the points of first solidification, and his spruing will generally be at the heavy portion of the pattern, this being the last portion generally to solidify. However, he can hope for only limited success. Complicated designs sometimes frustrate the application of these principles, and also, it is rather difficult to get feedback to check on some sprue design he has in mind. He must work pretty much in the dark counting considerably on intuition and experience.

This paper describes some fundamental experiments to elicit the mode of solidification for a very small casting using the investment casting procedure. The results of this experiment lead to some basic conclusions as to how very small castings solidify. These conclusions in turn lead to some recommendations for casting techniques, and for future research work.

SOME CASTING CHALLENGES

The casting of precious metals into jewelry has been going on for centuries, and it is a tribute to the artists and craftsmen involved that some remarkably good castings have been made. What is interesting is that rather little basic technology has been applied. Some casting shops today look no different from what they must have been like hundreds of years ago. Some interesting challenges confront the jewelry and dental caster. Figure 1 shows some jewelry cast in 22 kt gold, going back to ancient times. Figure 2 is a modern design of a ring depicting the rather fine detail that can be cast in a gold alloy. Figure 3 shows some wax patterns of two items; a 32-tooth mustache comb (about one inch in length), and a ring for the tennis buff showing a tennis racquet of 5 strands crossing each other. At first glance it might seem that these are very difficult to cast. They are in fact being made every day, and are really not too difficult to cast. The reason for this is that alloys, when once heated clearly above the liquids, have a rather low kinematic viscosity, so that with the aid of centrifugal force, it is not difficult to get the metal to fill a thread of, say, 1/2 millimeter thick and 1 cm in length before solidification sets in.
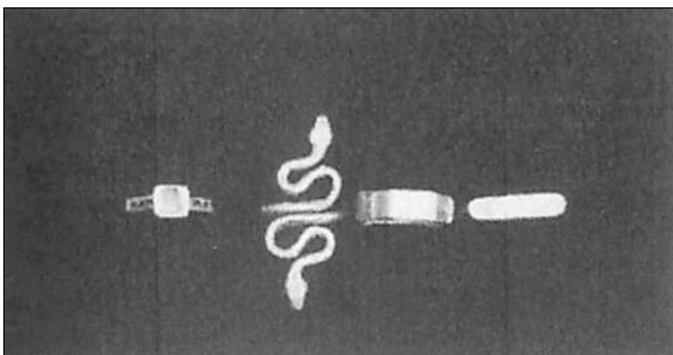
FIGURE 1. 22-kt cast jewelry of ancient design.
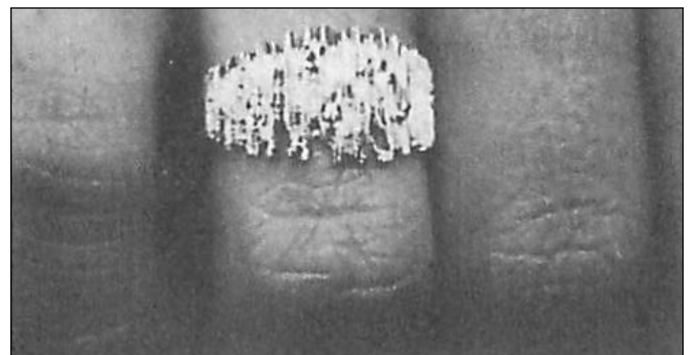
FIGURE 2. S. African gold jewelry, present-day design.
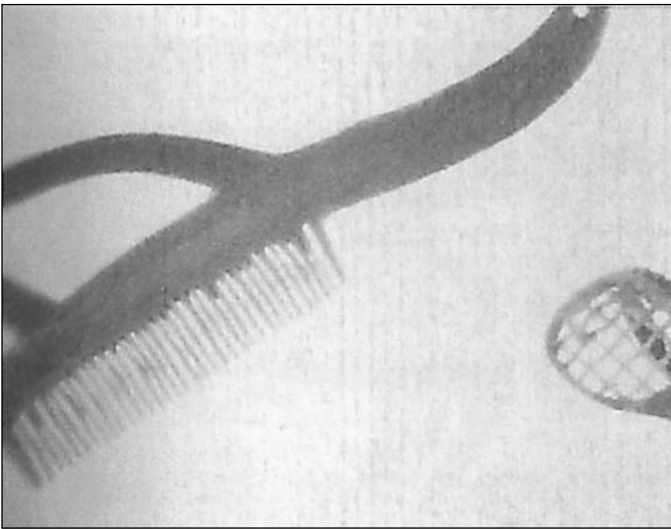
FIGURE 3. Wax patterns of a 32-tooth mustache comb, and a tennis racquet ring, both for gold casting.
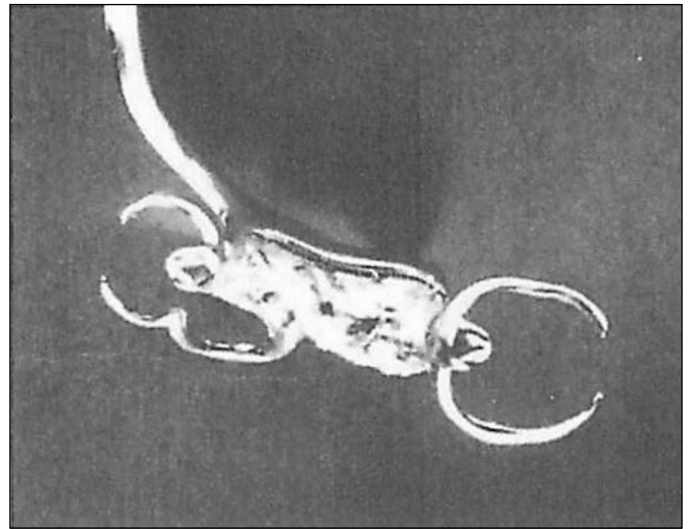
FIGURE 4. Gold alloy dental casting showing clasps requiring high dimensional precision.
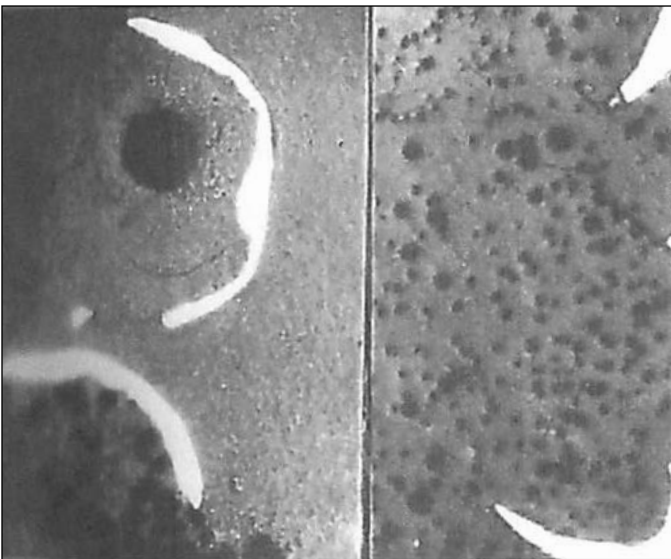
FIGURE 5. Cross sections of dental crowns showing sharp margins and thin wall requirements.
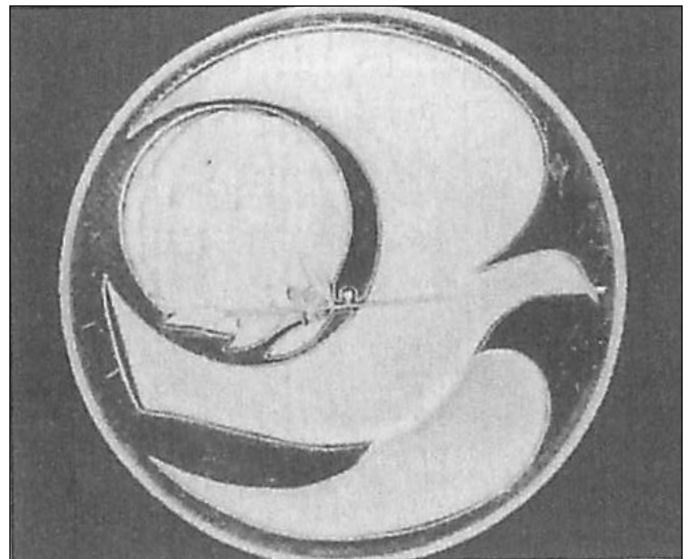
FIGURE 6. Bronze medallion in satin and mirror finish which are difficult to reproduce by casting.

Figure 4 shows one end of a dental restoration cast in a gold alloy. The significance of this design is not so much in the fine detail, there is no problem with this, but in the dimensional precision; the clasps must fit with a tolerance less than 0.005". Figure 5 shows some cross sections of gold cast crowns. The pointed tips of the crowns are called margins and they require considerable sharpness with precise dimensions. One wedge angle of a margin in this photo is about 15°, with a tip radius of about 1/10 mm. A wall thickness at a narrow constriction is about 1/3 mm.

There is one deterrent to the successful filling of extremely fine detail, the limitation imposed by surface tension of the liquid metal that does not "wet" the mold material, as is the case for investment casting. (If the metal were to wet the mold material a tenacious bond would occur between metal and investment, and castings would be extremely difficult to finish). The surface tension effect is that of the tendency of a metal to "ball up" when in small droplet form, much like a mercury droplet resting on glass. If a wax pattern were to be made of a razor blade, the liquid metal would not penetrate into the sharpest crevice of the blade root. However, this imposes a minor limitation on most castings, as such fine detail is not called for by the designer. An interesting challenge

for the caster is to try to produce a mirror finish on a casting. Figure 6 shows a stamped medallion. The white background is in satin finish while the black is in mirror finish. When this medallion is converted into a wax pattern and then cast the mirror finish is lost, and the entire casting comes out with the roughness of the satin finish. This is partly due to the surface tension effect, the metal not penetrating the interstices of the mold material, and also to the granular texture of the mold material imposing its surface roughness.

EXPERIMENTAL PROCEDURE

The customary procedure to determine the mode of solidification for industrial casting is by "bleeding" the castings, i.e. turning over the mold upside down to pour off the liquid fraction leaving behind the solidified casting hull. Figure 7 shows a series of 5 bled casting hulls after 5 sec., 1 min., 2 min., 4 min., and 6 min. after mold filling. The casting was presumably of several pounds in weight, and cast for example in cast iron. In examining the hulls it can be observed that the cylindrical surfaces develop a wall thickness rather uniformly with time, with the smaller radii surfaces slightly thicker than the larger radii ones for the same time interval. The edges, as seems reasonable, draw heat away from the metal faster than the cylindrical walls, as the regions at the edges are the thickest portions of the castings, while the reentrant angle regions are the thinnest.
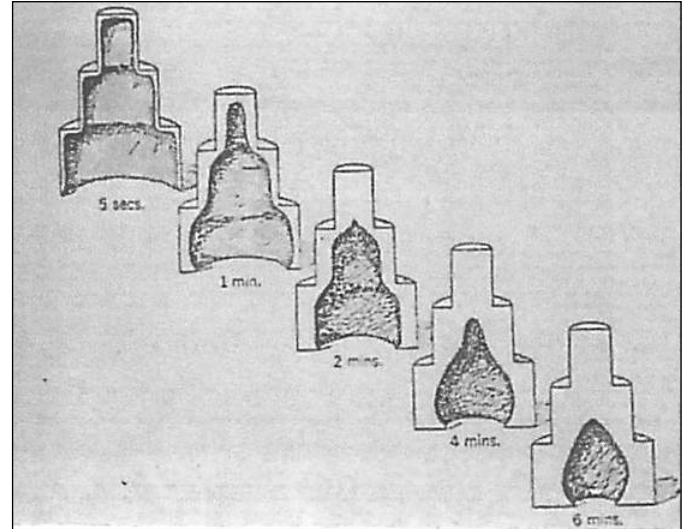
FIGURE 7. Schematic drawing of a sequence of bled castings from 5 seconds to 6 minutes delay from mold filling.

Castings in the 1/4 to 1 oz (5 to 10 dwt) as is generally done in jewelry and dental casting freeze far faster than the casting described above, usually in matters of a few seconds. A cast wedding band may for example take no more than five seconds to solidify. In order to construct the mode of solidification for such size castings a special centrifuge was designed. Figure 8a shows a dental casting machine with a resistance-wound melting furnace. The casting flask is in place but with one special feature, it may pivot around a vertical pin (seen just inside the casting ring) mounted on the rotating arm. The rocker arm above (seen better in Figure 8b) holds the flask in place while the casting is allowed to solidify and as the machine is still rotating. At a desired instant after the mold filling the plunger is pressed down releasing the flask to rotate outward around the rear pin, by centrifugal force.
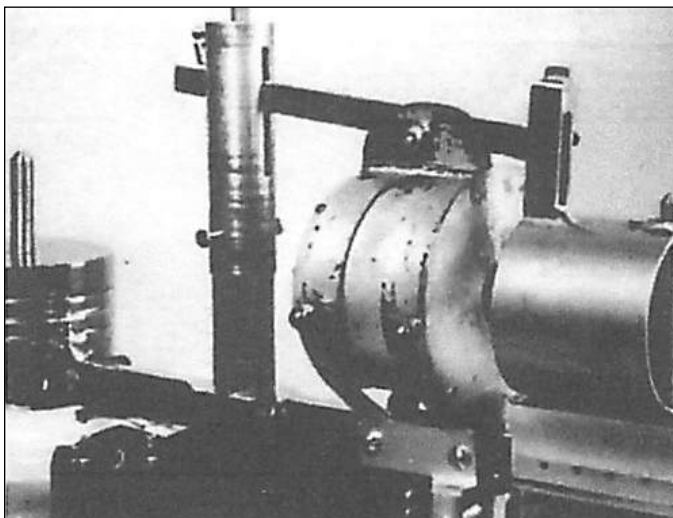
FIGURE 8A. Centrifuge modification of a dental casting machine with casting flask positioned to receive metal.
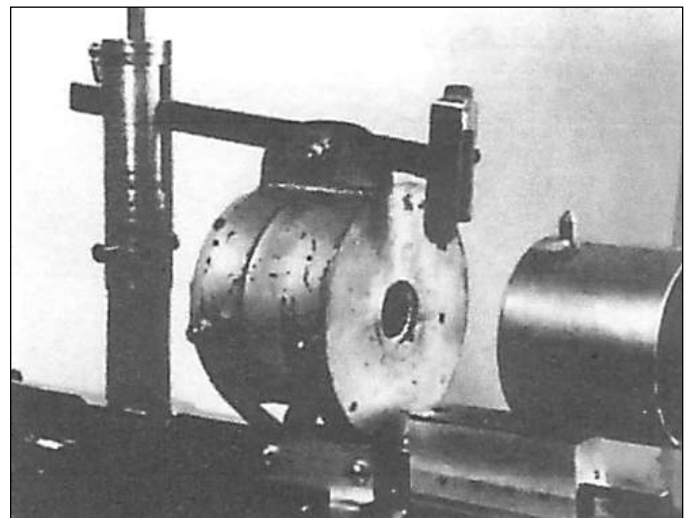
FIGURE 8B. Centrifuge as above with casting flask swung out by centrifugal force to eject liquid fraction from casting.

The unsolidified fraction of the casting is centrifuged off to splash against the metal skirt surrounding the casting machine. Figure 9 shows a trace of this splash striking a sheet of paper lined along the metal skirt. Knowing the speed of the machine rotation and the size of the splash smear, it was calculated that the separation of the liquid metal from the solidified interface was approximately one millisecond. Figure 10 shows the interface of the dentrites of the solidification front depleted of the liquid that had been centrifuged off. It was found that it was not difficult to spring the centrifuge at any desired second after filling, to within ± 0.5 seconds. Thus centrifuging was done in intervals after casting of 1, 2, 2 1/2 secs., etc. Various metals were cast: coarse and fine-grained 14 kt. jewelry alloys, 42% gold dental alloys, casting brass, jewelry bronze, and Cerro Bend, a low melting alloy which permitted casting without preheating the mold. To date some 200 casting hulls have been produced. A large variety of shapes have been experimented with.
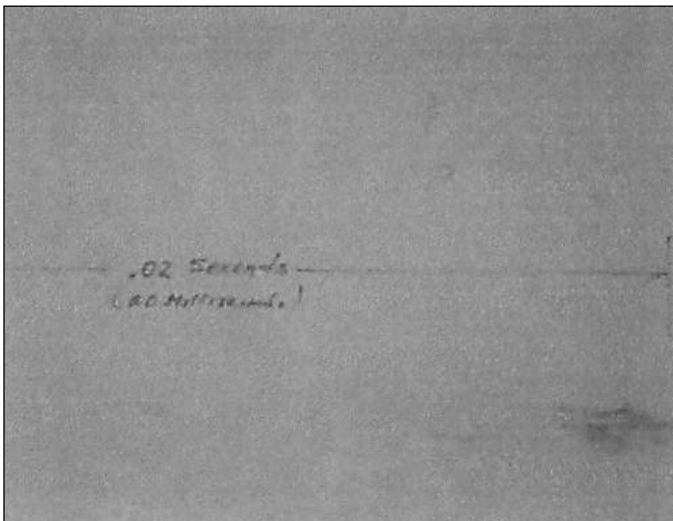
FIGURE 9. Smear of ejected liquid on a paper liner around casting machine.
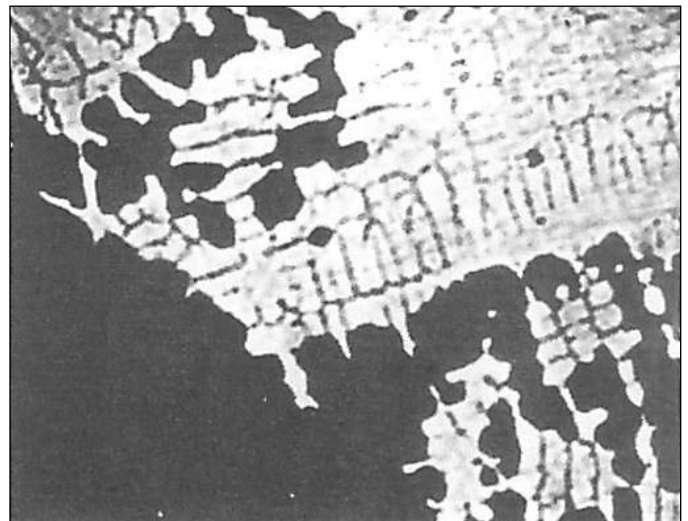
FIGURE 10. Coarse grained dentritic frame-work after liquid fraction has been centrifuged off.
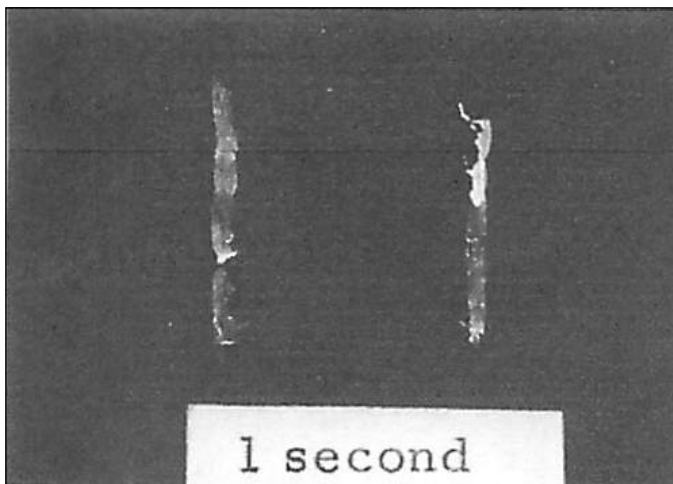
FIGURE 11. Two-edged razor blade casting monitor cast in brass showing edges formed in one second.
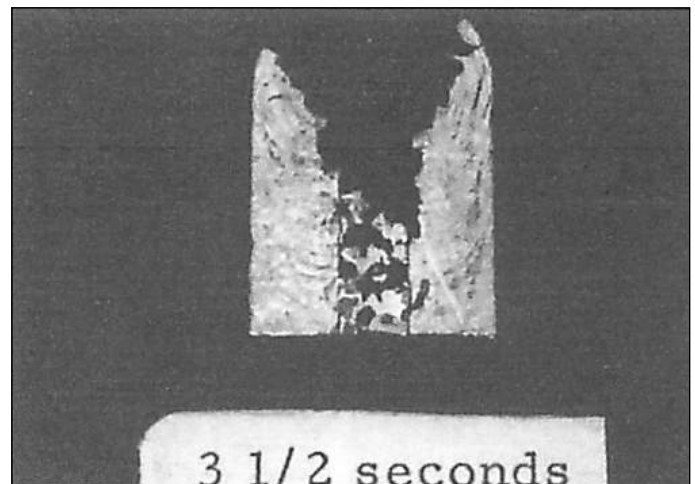
FIGURE 12. Same as above after centrifuging in 3 1/2 seconds. Note the inter-meshing of the solid fingers in the central region.

RESULTS

Figure 11 shows a 2-edged razor blade casting monitor, cast in coarse-grained brass, after one second of centrifuging. The extremely rapid nucleation by the two sharp edges is evident. Figure 12 is the same pattern but after 3 1/2 seconds centrifuging. The central region of the blade (about 1 mm thick) shows, interlacing of fingers of solid coming from the two sides toward the middle. On close inspection especially after etching, it can be discerned that the solid fingers comprise connected grains, some being a connection of as many as five gains, each forming a segment of the solid fingers.

Figure 13 shows a coarse-grained dental alloy cast into a crown pattern but centrifuged after 2 1/2 seconds. Here only the margin edge managed to solidify. The ideomorphic shapes of the solidified grains is clearly evident, an octahedral contour can be seen in the rear. This same crown but centrifuged after 3 1/2 seconds in figure 14 shows about 3/4 of the crown solidified. The liquid pockets are outlined by "rock candy" surfaces indicating the coarse-grained nature of the solidified interface. The liquid pockets were probably the result of solid fingers interlacing as they extended into the liquid region, as in the case of the razor blade.

FIGURE 13. A dental crown case in coarse-grained dental alloy with only the margin region having solidified.

FIGURE 14. Same as to the left after centrifuging at 3 seconds.
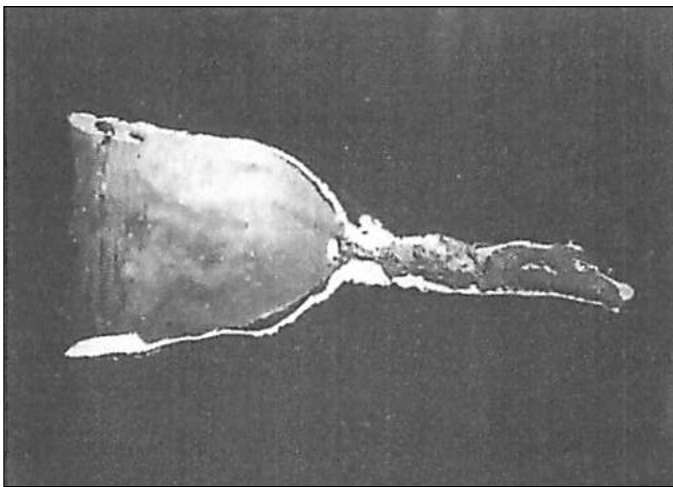
FIGURE 15. Fine-grained dental alloy casting of a crown after 5 seconds. Note the hollow sprue.
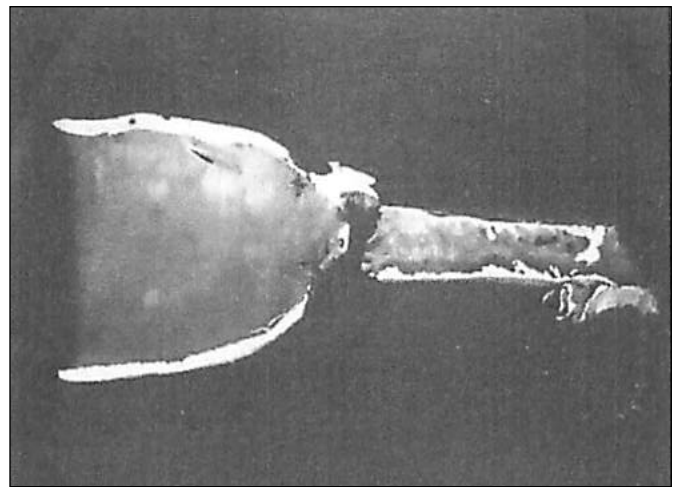
FIGURE 16. Same as above after 7 seconds. Only the outer wall of the crown has formed growing inward to the inner wall.

Figure 15 shows the cross section of a cast crown in a fine-grained dental alloy, centrifuged after 5 seconds. The mode of solidification is quite different here from the coarse-grained case. The margin edges have solidified but only to a short length. Above this there is a build up of the wall thickness, but only from the outer wall, the thickness being about 1/3 of the wall thickness of the crown. The sprue section is hollow. Figure 16 shows the same pattern but after 7 seconds of centrifuging. The sprue wall thickness had increased, almost bridging completely across the sprue cross section.

Figure 17 is a 2-cm long wedge with a triangle cross section, cast in Cera Bend alloy and centrifuged after 12 seconds. A small liquid pocket has been entrapped (or perhaps it is a shrinkage void) after the sprue has completely solidified. Figure 18 is the same pattern after 8 seconds of centrifuging. The roundish nodules are single grains nucleated in the interior of the liquid pocket. In this case it is clear that this is an entrapped liquid pocket. Figure 19 is the same pattern after three seconds centrifuging. The edge that is the longest is that of a less than 60° wedge angle, the others being somewhat larger than 60°. Although this was a coarse-grained alloy, the edges were fine-grained. Figure 20 shows the same pattern but centrifuged after one second. None of the edges is well developed, but the longest one is still that of the less-than-60° angle. The base edges are of course 90° and they all form about equally, with the vertex of the melting of two 90° edges and the 60° one being most developed.
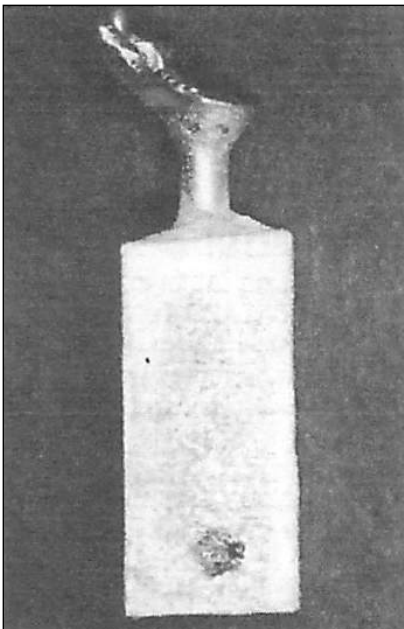
FIGURE 17. A low melting alloy cast into a 2-cm long triangular wedge. A small liquid pocket apparently existed after 12 seconds of solidification.
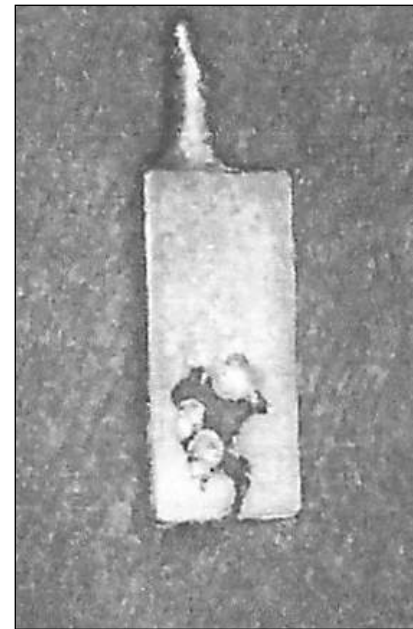
FIGURE 18. Same as to the left after 8 seconds solidification. Note the grain nodules in the interior of what was a liquid pocket.
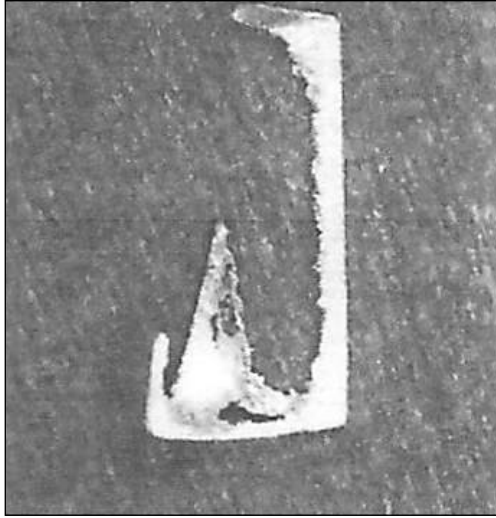
FIGURE 19. Same as in Figure 18 after 3 seconds. The long edge that has formed is fine-grained, and was the sharpest wedge angle of the three angles.
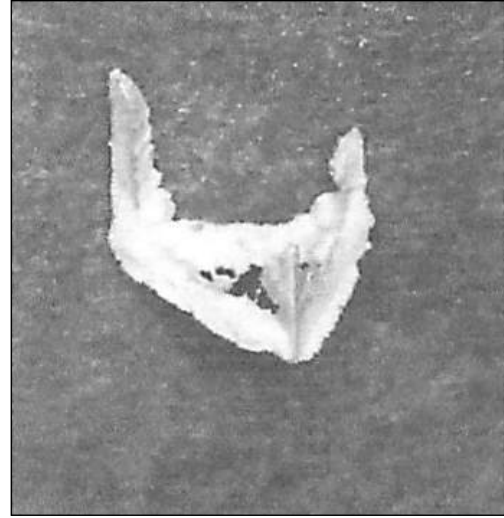

FIGURE 20. Same as to the left after one second centrifuging. The long edge is the sharpest angle of the three upright angles.

DISCUSSION OF RESULTS

Several interesting and rather novel findings emerge from these experiments. The first and most striking observation is that when very small castings are cast, the grain size plays an important role in determining the mode of solidification. Coarse grained alloys, i.e. where the grain size approximated the cross section thickness of the casting in different parts of the casting, apparently produce these grains in sudden bursts to fill size. The concept of a very small nucleus of a grain growing slowly to full size, limited in this growth by encountering other grains is apparently not correct. Once a grain has burst into full size existence it grows no more or very little but rather it stimulates other grain nuclei to form, also bursting into full size existence. The evidence for this is in Figs. 12 and 18. In the razor blade case we can trace a finger of solid emerging from the right side apparently segmented in about five connected grains. A similar connection of five or so grains appear from the left side toward the center. Each of these segments appears about equal in size, suggesting that they burst rapidly into existence, popcorn-like, and each grain then stimulated the occurrence of another connected grain. In the wedge case we see three interior globules, each of about the same size. These apparently are individual grains which had popped into existence, stimulated by a prior grain closer to the surface, or an edge. These fingers of solid penetrating into the liquid region encounter other fingers and proceed to enmesh into a tangle of such fingers. Now and then the enmeshing entraps a portion of liquid denying it contact with further feed from the liquid pool where an attempt is made to show how the mold wall first stimulates a carpet of grains, which in turn nucleate second generation grains, which in their turn stimulate third generation grains, and so on. One suspects that these connected grains forming a solid finger penetrating into the melt are each specially oriented to each other crystallographically. Very likely the common grain boundaries are "special" boundaries with common coincidence sites. This suggests a different mode of formation of equiaxed grains in the center of castings. The customary rationale for the formation of equiaxed grains in the region beyond the columnar grains in chill cast castings is shown in Figure 22, where a chill mold wall on the left side in the figure shows a steady growth of columnar grains. In the series of schematic sketches on the right the columnar grains never get started at all and thus there appear spontaneously nucleated equiaxed grains. The experiments using the centrifuge would suggest that the columnar grains, after ceasing to grow as columnar grains, become the source of nucleation of differently oriented grains, attached to the columnar grains. Thus the grains reaching the middle region of the castings are connected segmentally to the columnar grains.
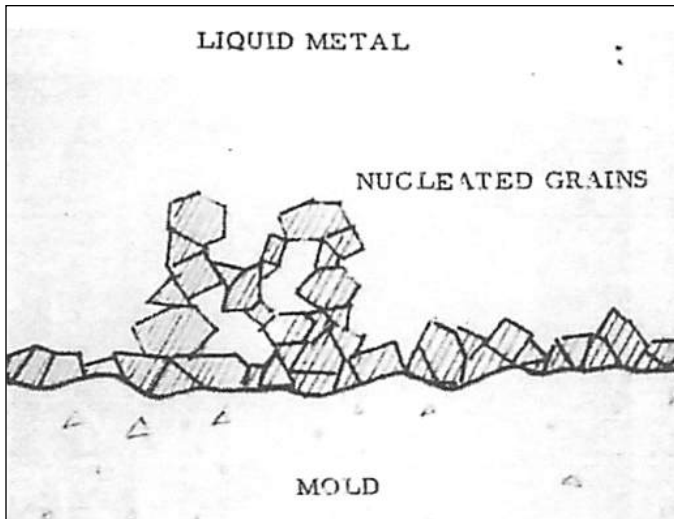
FIGURE 21. Schematic showing grains nucleated by mold wall which in turn nucleate other grains. Special orientations of grains favor rapid chain formation which penetrate into the liquid region.
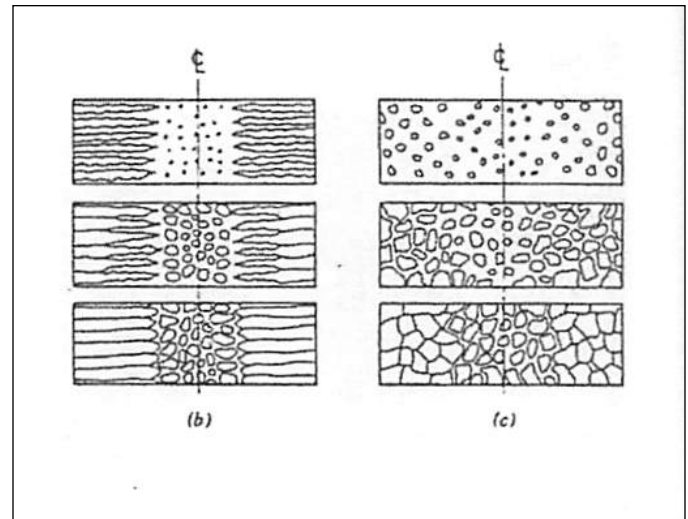

FIGURE 22. Schematic of customary rationale for columnar and equiaxed grain formation in chill casting.

The second striking observation in these experiments is that sharp edges and vertices in the pattern configuration are exceedingly potent in initiating nucleation sites. Thus one must take into account the whole system of vertices, edges, convex surfaces, etc. that make up the pattern configuration to estimate the mode of solidification. The sequence of nucleation can be estimated from the following pattern configuration features, the first in the list being the first to nucleate, with the last in the list being the region where the residual liquid might be found.

SEQUENCE OF GRAIN NUCLEATION SITES

1. Sharp vertices (shaped like the tip of a pointed triangular file, the smaller the included solid angle, the sharper and faster will be the origin of the nucleus, and presumably smaller).

2. Blunt vertices (shaped like the vertices of a cube, for example).

3. Sharp edges (e.g. razor blade type edges).

4. Blunt edges (e.g. the edges of a cube).

5. Sharp convex contours (e.g. the rounded tip of a sharpened lead pencil).

6. Shallow convex contours (e.g. the rounded contour of an egg shell at one of its ends, from inside the egg).

7. Flat surface.

8. Shallow concave contours (the inverse of No. 6 i.e. from outside the egg).

9. Sharp concave contours (the inverse of No. 5 i.e. from outside the pencil lead tip).

10. The inverse of No. 4 (blunt reentrant angle).

11. The inverse of No. 3 (sharp reentrant angle).

12. The inverse of No. 2 (blunt reentrant vertex).

13. The inverse of No. 1 (sharp reentrant vertex).

A third observation that was made from these experiments was that the castings tended to solidify from the far end of the casting toward the sprue. This is probably attributed to the pressure gradient in centrifugal casting, whereby the far end of the casting, i.e. the point furthest from the axis of rotation, experiences the greatest fluid pressure, and hence the greatest heat transfer rate. This of course will not apply to vacuum assist casting where no centrifugal force is used. There is of course some gravity effect, and so in principle the castings should still solidify from the bottom upward, but not so markedly as in the case of centrifugal casting.

A fourth observation was the prevalence of "hot spots". In the heavier castings, where there occurred an excessive impingement became a source of heat for the local region on the mold, making it the last region for the metal to solidify. The far end of the casting in Figure 18 shows a region that was last to solidify. This was apparently due to the impingement of the hot metal at the far end of the casting. This was very much in evidence in the centrifuging of class rings and is described in another paper by this author.

An interesting observation was the tendency for the solid wall to begin at the outer wall shown in Figures 15 and 16. This was puzzling at first glance, since it was suspected that the crown thickness would develop from each wall and meeting in the center. However, shallow convex contours (No. 6 in the nucleation series above) initiate nuclei before shallow concave contours (No. 8).

From these experiments advice can be given to the caster who has the problem of estimating the mode of solidification for a given pattern. He should first note where the vertices, edges, etc. are, which will be the initiators of solidification. As much as possible, these points should be as far from the sprue region as possible. His design of the sprue should be such as to avoid hot spots. The pressure gradient, if it applies, should be taken into account. Of course setting up patterns in christmas-tree mounting will distribute the heat flow such that there will be less flow toward the inner region of the tree. Finally, to avoid liquid entrapment as much as possible, he should favor the use of fine-grained casting alloys.

The experiments described herein will not guarantee a correct estimation of the mode of solidification, but they form a good beginning, and further research of this type should prove rewarding.

ACKNOWLEDGEMENTS

Improving Silver Refining Quality and Quantity: Regenerable Ion Exchange Resin for Highly Selective Palladium Capture in Nitric Acid

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ABSTRACT

Most precious metals refineries produce silver by electrorefining. In the electrolysis process, silver anodes may contain palladium, which is prone to transfer to the electrolyte and the fine silver. The intensity of its transfer is directly dependent on the palladium content and current strength. This represents a loss of valuable palladium and limits the capacity of an electrorefining installation, increasing the lead time of the silver purification process.

In this paper, we show that the use of selective ion-exchange resin and sorption technologies makes it possible to selectively remove Pd from the Ag-electrolyte and, consequently, increase the current of silver electrolysis. In this system, the palladium is recovered for separate refining and resale.

Krastsvetmet's silver electrorefining was upgraded with such ion-exchange purification Upon installation, the electrolyte has become free of palladium increasing the quality of the refined silver and increasing the throughput of the installation. The eluted palladium has been treated in the palladium refining flow-sheet for a full recovery. This paper will cover the practical results from Krastsvetmet's operations with an industrial-scale skid, integrated into silver refining flowsheet.

INTRODUCTION

Pollution of silver with palladium is a general problem for a silver refiner. Depending on where the silver is sourced, high concentrations of palladium can be found in the raw material. The main reason is that the cathodic reduction potentials for silver and palladium are close Therefore, they are difficult to separate prior to or during electrorefining.

When the silver anode contains 0.3% of palladium, only 0.001% is found in the cathode, provided the current density is kept sufficiently low. Such levels of palladium in the cathode are acceptable for 4N silver production. In high palladium silver, 3-5% of palladium can be present, and this is much harder to keep at acceptable low levels on the cathode. The silver must therefore be treated further prior to electrolysis or else the silver refiner will produce out of specification product.

Silver refineries across the world have looked for solutions to this problem. Casting anodes with high and low palladium content raw material is the most obvious method, but this is not very satisfactory, requiring much work and not recovering the palladium. The R&D team at Krastsvetmet joined with the technology start-up AXION have invented a resin-based solution. This was tested, piloted and implemented at the Krastsvetmet refinery, greatly improving the economics of the silver refinery.

EXPERIMENTAL/METHODS

Methods for separating palladium from nitric acid solutions by treating the solution with complexing agents and/or precipitators are already known.

Palladium recovery method by Ginsburg [1] requires an excess of dimethylglyoxime to precipitate palladium. In particular, for every 10 mg of palladium, 25 ml of a precipitant in the form of a 1% alcohol solution is required. Platinum coprecipitation is observed at a level of 5-10% relative to the amount of palladium. As a disadvantage, it should be noted the high consumption of the precipitant for the separation of platinum and palladium.

The method for palladium recovery by Wu at al. [2] suggests the introduction of formaldehyde sulfoxyl sodium salt into a palladium-containing nitric acid solution with an acidity of 0.01-1.4 M, followed by heating the mixture to 70-80 °C, which seems to be impracticable in industrial scale.

The method of palladium recovery mentioned in a Russian patent [3] proposes the precipitation of metallic palladium with carbon monoxide from nitric acid solutions. This operation requires the use of sealed technological equipment and high safety measures due to the use of toxic carbon monoxide.

The listed methods of platinum and palladium recovery from silver electrolyte seem to be inapplicable in the industrial-scale production of silver by the electrorefining method because they have a common significant disadvantage associated with a change in the qualitative composition of the electrolyte. This is due to the use of reagents soluble in the electrolyte, which requires the use of repeated separation precipitation operations.

Also, a group of methods is known for the ion-exchange recovery of palladium from the silver electrolyte.

The method described in a Japanese patent [4] proposes passing a silver electrolyte (Ag 90 g/l, Cu 1.4 g/l, Pd 0.16 g/l) through a fixed bed of activated carbon modified with amine chelate groups. Residual palladium concentrations are less than 1mg/l. Elution is carried out with nitric and hydrochloric acids. The disadvantages of this method are the relatively low peak concentration of palladium in the eluate: about 6 g/l; and also the fact that the eluate contains up to 13 g/l of silver, and, accordingly, requires an additional operation to separate the silver from palladium in the eluate.

The method for the platinum metals compounds production described in a German patent [5] proposes the implementation of ion exchange between the electrolyte and the resin containing iminodiacetic groups. The electrolyte contains Ag 190 g/l, Cu 35 g/l, 1.3 g/l of platinum metals with the acidity of the solution in the pH range from 0.5 to 1.5. Elution is performed with a 2-5% ammonia solution with the addition of 1-3M ammonium/sodium sulfate or nitrate. The disadvantages of the method include the high salt background of the eluate, the presence of a significant amount of silver in the eluate and its accumulation in the circulating eluate, as well as the contamination of the electrolyte with sulfate ions.

Another method for platinum group metals recovery was described [6]. The method suggested treating palladium containing a solution of nitric acid nature with a phosphine-oxide bearing resin known as MPX-310. The main disadvantage of this method is the non-regeneration of the resin.

Since most of the techniques of silver electrolyte cleaning from palladium have disadvantages, their usage becomes excessively complicated. Usually, the palladium content in the electrolyte is controlled below 0.2% which involve special operations varied from a refinery to refinery as well as the limitation on the current of electrorefining process. To eliminate issues on silver electrorefining disadvantages of palladium recovery

techniques described above, the joint team of Axion and Krastsvetmet designed a regeneratable resin for ion-exchange capture of palladium. This allows eliminating the limitation on the palladium content in the electrolyte and electrolysis current as well as making electrolyte cleaning unnecessary.

The technical result is achieved in reducing the consumption of reagents for previously used cleaning operations, reducing the one-time demand for selective ion-exchange resin due to its regeneratability, increasing the productivity of the refining, reducing the cycle time for the refining of silver, palladium, while simultaneously high purity of the resulting product.

The ion-exchange skid is located at the Krastsvetmet premises in Krasnoyarsk city, Russia. The skid is placed beside the silver electrorefining facilities.

FIGURE 1 - Simplified flowsheet of silver electrorefining with integrated palladium removal ion-exchange skid.
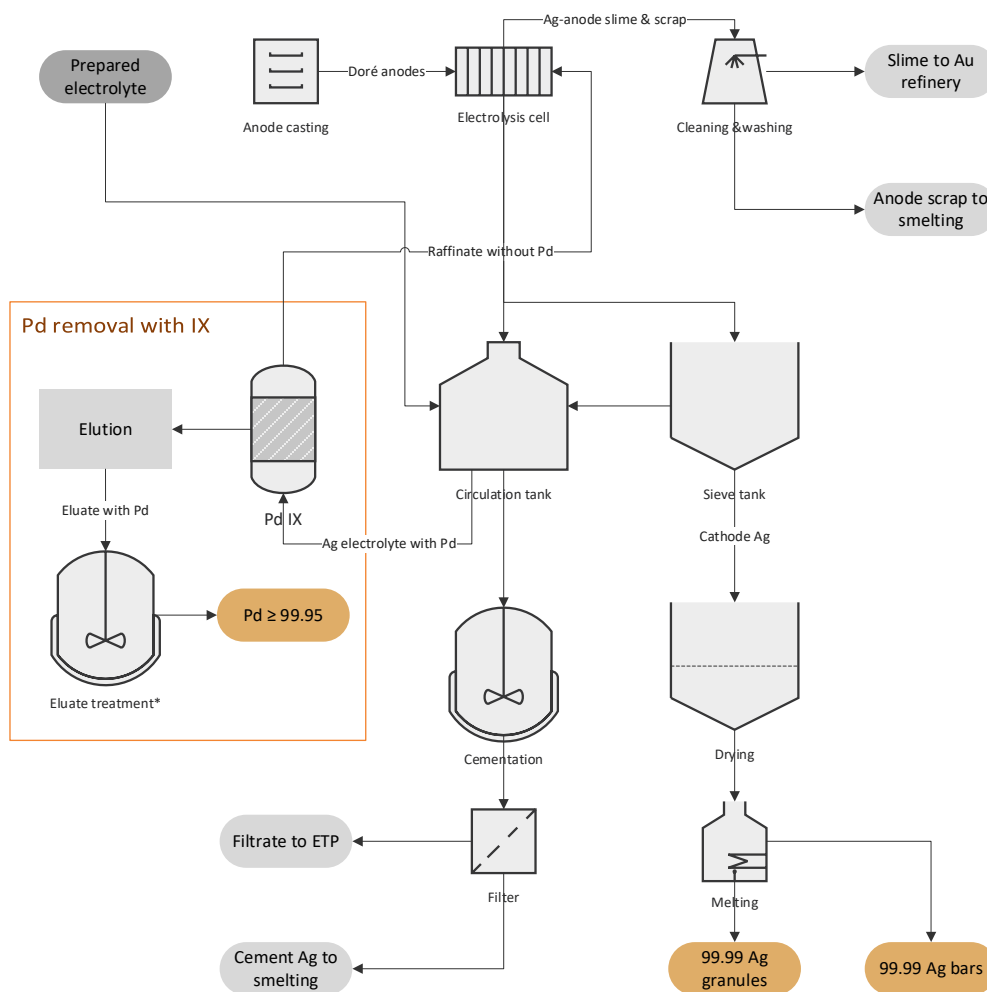
The implemented flowsheet is given in Figure 1. The flowsheet shows the integration of ion-exchange skid into the existing silver electrorefining line. Ion-exchange columns get silver electrolyte from the circulation tank. When passing through the column, palladium is captured by the resin from the electrolyte, and palladium-free electrolyte goes back to electrorefining line. When the resin gets saturated with palladium, palladium is eluted from the resin. Eluate treatment allows obtaining fine palladium with a purity of ≥99.95%.

RESULTS

FIGURE 2 - Pd content in anodes vs time.
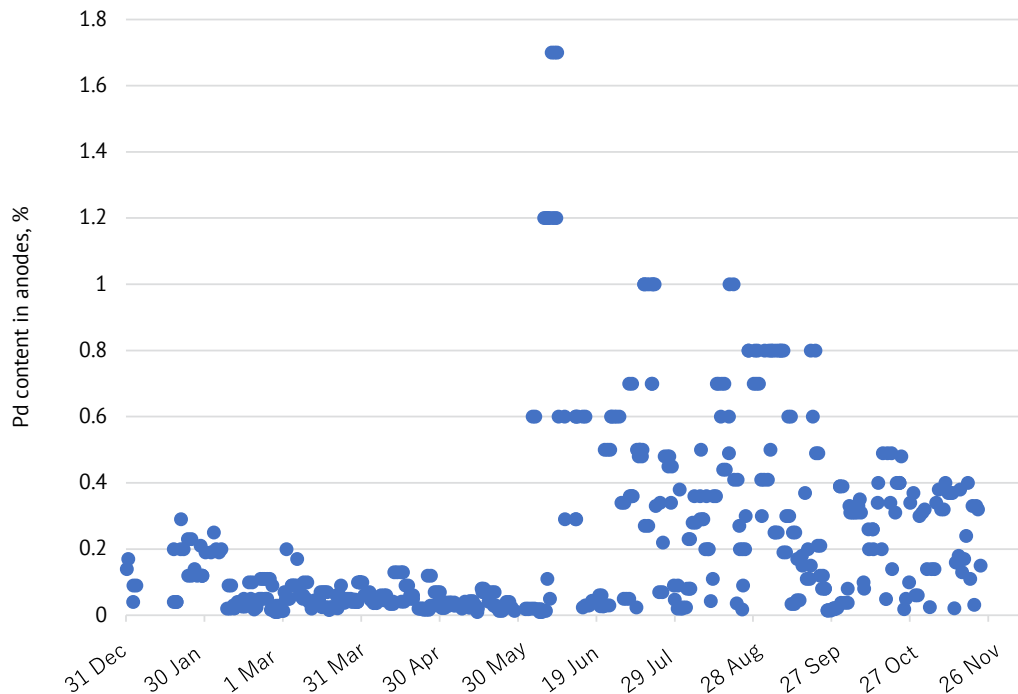
For this data set (Figure 2), ion-exchange was installed on the production line in May. This graph shows the palladium content of the incoming anodes.

Before ion-exchange, it was important to keep palladium content below 0,2% to have minimum carry-over. Once the ion-exchange was installed, it was no longer needed and as a result anode with palladium concentrations, up to 1,3% were treated. This presents an important time saving before electrorefining.

Figure 3 shows a load of electrolysis on lines 1 & 2 and lines 3 & 4. Since ion-exchange was installed on lines 1 & 2 in June, they were able to treat an increasing amount of anodes. As a result, lines 3 & 4 were used less and less.

FIGURE 3 - Silver electrorefining units load vs time.
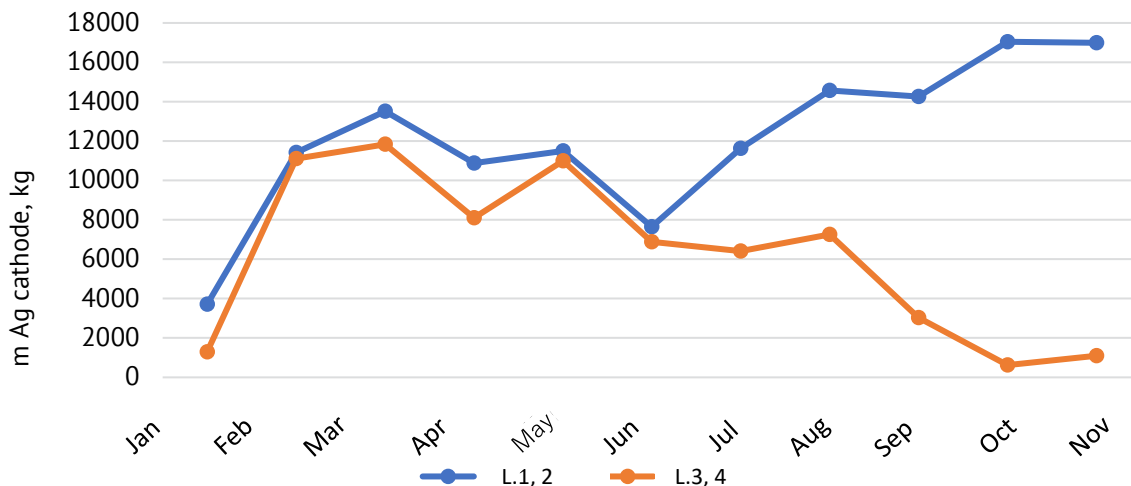
Figure 4 shows the current strength in lines 1 & 2. With the introduction of ion-exchange, it was possible to run electrorefining at much higher current strength. This explains the increase in productivity seen in the other data.

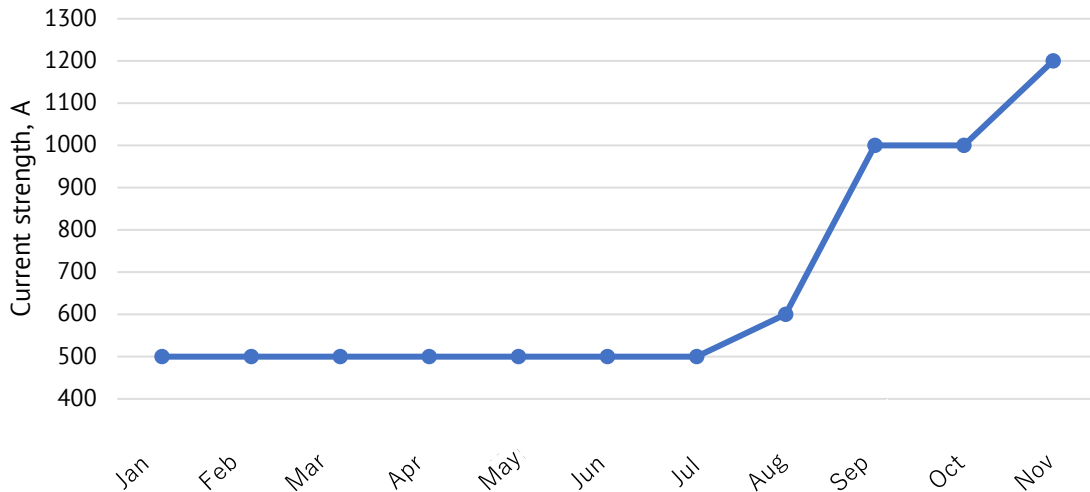**FIGURE 4** - Silver electrorefining current strength vs time.

Table 1 shows the decrease in lead time in lines 5 & 6. As the ion-exchange is installed, lead time decreases even as throughput nearly doubled. This represents an important cost-saving.

TABLE 1 - Electrorefining (ER) lead time in hh:mm.

ER unit	Jan	Feb	Mar	Apr	May	Jun	Jul	Aug	Sep	Oct	Nov
#5	76:30	53:57	49:25	58:42	50:54	52:12	57:50	51:28	48:25	38:22	36:51
#6	64:50	53:35	50:10	57:13	52:00	57:00	55:30	53:02	44:06	39:56	36:57

Exothermic reaction between resin and electrolyte are not present. Other resins are known to react (violently) with nitrate solutions. From experience, it is known that this is not the case for AXION, as seen in the cooling curves (Figure 5).

FIGURE 5 - Cooling curves.
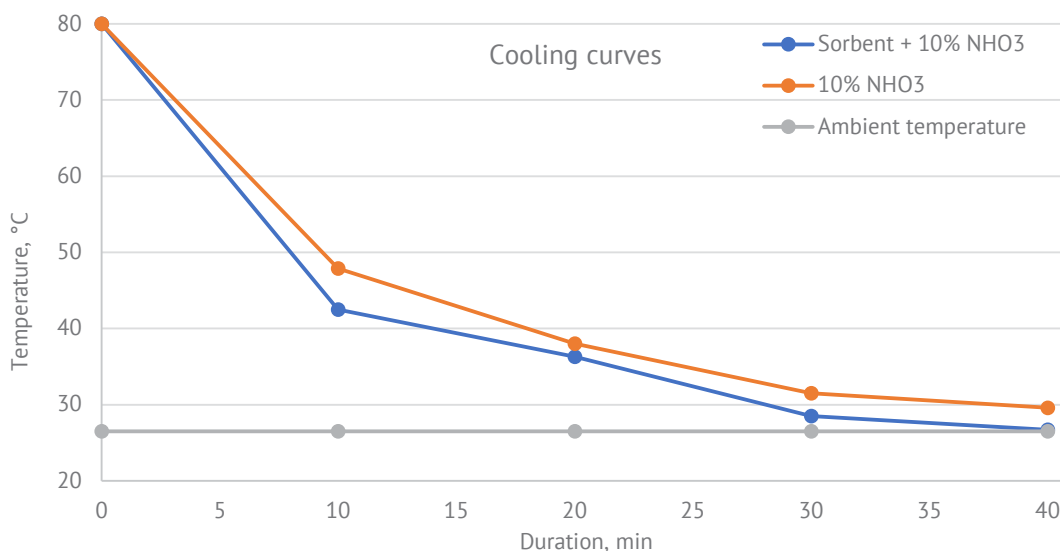
Also, Pd IX for Ag-ER is AgN3 free system. According to research carried out on azide formation, silver azide (AgN3) forms only when NaN3 is present in the system. As such;

1. Solonina [7] obtained AgN3 in the form of a very fine powder in the interaction of an aqueous solution of pure NaN3 with a solution of AgNO3.

2. In 1911, AgN3 was obtained by electrolysis of a 3% NaN3 solution with Ag anode [8], in 1919, by electrolysis with Ag anode of NH4N3 (which is also forming with the presence of NaN3) solution.

3. Taylor and Rinkenbach [9], when developing a method for producing AgN3, avoided the preparation of large crystals easily formed from dilute solutions, and concentrated solutions of NaN3 and AgNO3 were recommended for the precipitation of AgN3.

Since NaN3 is not used and is not formed in the offered Pd IX for Ag-ER, this system is AgN3 free that was also checked by Krastsvetmet's analytical support.

CONCLUSIONS

The palladium ion-exchange skid at Krastsvetmet silver electrorefining lines located in Krasnoyarsk, Russia, demonstrated successful operation of the palladium capture process from the silver electrolyte. The results indicate that, on average, residual palladium content in the electrolyte after ion-exchange is ≤ 3 mg/l and, subsequently, palladium concentration in the rich fraction of eluate is ≥15,000 mg/l. The eluate is successfully treated to fine Pd with ≥99.95% purity.

The ion-exchange skid operation lasted 5 months to obtain sufficient data to be analysed and continues its operation as a part of electrorefining lines.

The results from the ion-exchange skid operation will be used for design and scale up to a customized commercial skid applied as an option to existing lines of electrorefining and electrowinning.

ACKNOWLEDGEMENT

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The Electrochemistry and Electrokinetics of Alkaline Sulfide Gold Leaching

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ABSTRACT

Gold has been known to readily dissolve in alkaline sulfide systems for some time. However, the system has received little attention because of the complex electrochemistry occurring. Also, research specific to the system has been conducted to account for the formation of elemental sulfur during the partial oxidation of sulfide ores. Sulfur formation makes it difficult for cyanide to penetrate and lixiviate the gold. Thus, this research began as proposed method to effectively leach gold after partial sulfide oxidation. Now it has evolved beyond this initial application. Hence, during February 2002 and June-August 2004 a Rotating Electrochemical Quartz Crystal Microbalance (REQCM) was used to better understand the fundamental electrochemical and electrokinetic principals of the Alkaline Sulfide Gold Leaching System (ASGLS). The alkaline sulfide system is a viable alternative to traditional cyanide based processing.

The variables that were investigated in the system included:

- The effect of sulfide concentration $[S^{2-}]$;
- The effect of hydrosulfide $[H^{S-}]$;
- The effect of polysulfide concentration $[S_x^{2-}]$;
- The effect of NaOH concentration;
- The effect of temperature; and,
- The effect of gold purity.

TECHNOLOGY BACKGROUND

Electrochemical research on the Alkaline Sulfide Gold Leaching System (ASGLS) has been done at Monash University in Melbourne, Australia. (A bibliography supporting previous work done in this hydrometallurgical system may be found at the end of this article). In this fundamental study, it was determined that polysulfide is the oxidant and sulfide acts as the system lixiviant. To achieve the best leaching rates a ratio of sulfur : sulfide ratio of 1-1.5 : 1 should be used. When hydrosulfide rather than sulfide was added to sulfur leach rates were slowed; it can be implied that leaching in caustic solutions, where sulfide is more stable than hydrosulfide, is beneficial to leaching. Also, silver impurities in the gold increased leach rates. By measuring the leach rate as a function of temperature it was found that activation energy for leaching was 75 kJ/mole. From this value it is assumed that the reaction is chemically controlled since diffusion controlled reactions typically have activation energies less than 25 kJ/mole.

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In two papers found from Xian Institute of Metallurgy and Construction Engineering Research a system called Lime-Sulfur-Synthetic-Solution (LSSS) was tested for its ability to leach gold. In Part I, gold is described to be oxidized with polysulfide and lixiviated by either polysulfide or thiosulfate. During the experimental work different oxidizing chemicals were added to the LSSS solution to test their effectiveness. For a high sulfur and gold/silver bearing ore precious metal dissolutions of over 90% were measured after just ten hours in solution at room temperature.

In Part II, more ores were leached with +90% gold dissolution is achieved in less than three hours for several ores. The different chemical additions are analyzed on effectiveness per amount added basis. According to the paper to maximize gold dissolution kinetics: sodium sulfite should be added at 0.2 molar; oxidizer 'G' should be added at least to 0.10 molar; NH_3H_2O should be added at 0.60 molar; and Cu^{2+} should be added at 0.045 molar.

Although the results found in this paper are very positive, the exact methods for achieving such high gold dissolution at room temperatures were poorly explained. Some of the tests were recently recreated and each test had very poor results.. However, the results in these papers are compelling enough that more work should be done in applying oxidizers to assist gold leaching.

There has also been a lot of research done in areas associated with the ASGLS. A substantial amount of information was found on the hydrosulfide (H2S & HS-) leaching of gold at near-natural pH. Major hydrosulfide areas covered include the following: high temperature thermodynamic research; high pressure leaching; effect of pH and solution potential; and the effect of sulfur concentration.

Also, much of the research has been done to find a way of processing ores that are high in arsenic minerals that consume cyanide. Most of these papers pertain to the pressure oxidation of the sulfide minerals and possible ways to treat the ores.

In addition to these papers there were two noted that pertain to the production of polysulfide for the paper & pulp industries. These papers offer a good background to polysulfide chemistry while not pertaining directly to gold.

The main leaching component in the ASGLS is sulfur. Sulfur varies widely in oxidation state; a combination of sulfide (S^{2-}) and elemental sulfur (S^0) are needed to make for sufficient leaching kinetics in the ASGLS. Both sulfur chemistry and leaching chemistry will be discussed in further detail below.

For the ASGLS, the critical solution ingredient is sulfur. Dissolved sulfur can have an oxidation state ranging from $^-2$ (sulfide) to $^+6$ (sulfate) depending on potential of the system. As sulfide begins to oxidize towards sulfur it will pass through the metastable polysulfide range. A polysulfide molecule is formed when a chain of sulfur atoms is formed. As shown in Table 1, each chain can be up to 5 atoms in length; however, for each polysulfide molecule the charge is constant at $^-2$.

TABLE 1. Oxidation States of Sulfur Species.

Specie	Charge	Name	Oxidation State of Sulfur
SO_4	-2	Sulfate	(+6)
SO_3	-2	Sulfite	(+4)
S_2O_3	-2	Thiosulfate	(+2)
S	0	Sulfur	0
S_5	-2	Polysulfide	(-0.4)
S_4	-2	Polysulfide	(-0.5)
S_3	-2	Polysulfide	(-2/3)
S_2	-2	Polysulfide	(-1)
S	-2	Sulfide	(-2)

Polysulfides can be generated by the additions of sulfur and sulfide to a solution according to the following equation. Relative molar additions of each ingredient will determine the average polysulfide chain length. Also, sulfide can be generated by adding hydroxide to elemental sulfur.

$$S + (x-1)\ S^{-2} \rightarrow S_x^{-2} \tag{1}$$

$$S + 6OH^- \rightarrow 2S^{-2} + S_2O_3^{2-} + 3H_2O \tag{2}$$

Once the polysulfide solution has been used it will need to be treated for waste. By oxidizing sulfur in solution to the +6 state, or to sulfate, the solution can be disposed of easily. The equations below represent the primary anodic reactions; they provide the cathodic reaction with sufficient electrons.

$$4OH^- \rightarrow 4e^- + 2H_2O + O_2 \tag{3}$$

$$S^{-2} \rightarrow 2e^- + S \tag{4}$$
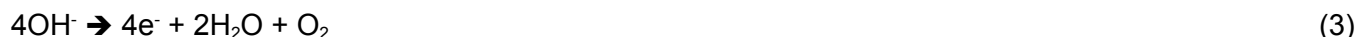
The equations below represents the reduction of polysulfides to sulfate. Note that oxygen is the oxidant in the reaction; during laboratory test work oxygen is provided to help drive the equation to the right.

$$S_x^{2-} + (2x)\ O_2 + 2(x-1)\ e^- \rightarrow xSO_4^{2-} \tag{5}$$

Although there are two gold-sulfur complexes that are responsible for gold dissolution, the dominant lixiviant has been determined to be sulfide. In Table 2 below, stability constants are shown for the two prominent ligands; sulfide and bisulfide. Note that the stability constant for the formation of AuS^- has a much larger magnitude than $Au(HS)_2^-$; therefore, it is determined to be the dominant gold-sulfur form.

TABLE 2. Dominant Gold Reaction Stability Constants.

Ligand	Specie	Reaction	Stability Constant (β)
Sulfide	AuS^-	$AuS^- + e^- \rightarrow AuS^{2-}$	$2 * 10^{36}$
Bisulfide	$Au(HS)_2^-$	$Au(HS)2^- + e^- \rightarrow Au + 2HS^-$	$1.3 * 10^{30}$

According to research done at Monash University suggests that a combination of sulfides and polysulfides are required for leaching to proceed. When solutions of sulfide (S_2^{2-}, 50 g/L), bisulfide (HS^-, 50 g/L), and polysulfide (S_x^{2-}, 50 g/L) were tested for gold leaching capabilities, neither solution showed any measurable gold dissolution. However, leaching does occur when sulfide and polysulfide are combined. Since polysulfides exist at a higher oxidation state than sulfide, polysulfide is theorized to be the oxidizer in the system. In other words, gold is oxidized (Au ➜ Au+) because of polysulfide reduction (S_3^{2-} ➜ S_2^{2-}).

Experiments were completed at Monash University to understand what the dominant lixiviant in the system is. Potential scans of solutions containing just polysulfide showed relatively small, calculated currents at leaching potentials. Purely sulfide solutions, on the other hand, exhibited high calculated currents at leaching potentials. The conclusion is that sulfide is the active lixiviant in the ASGLS. The proposed gold lixiviation chemical equation can be seen below:

$$Au + S^{2-} ➜ AuS^- + e^- \tag{6}$$

Remember that gold leaching did not occur in solutions of just sulfide. Leaching can occur when there is a simultaneous polysulfide reduction to sulfide reaction:

$$S_x^{2-} + 2(x-1)\ e^- ➜ xS^{2-} \tag{7}$$

Variable 'x' can range from 2 – 5. Anderson In the case where x = 2 the polysulfide reaction is as follows:

$$S_2^{2-} + 2e^- ➜ 2S^{2-} \tag{8}$$

Combining the polysulfide reduction (gold oxidation) reaction with the sulfide lixiviant reaction yields the overall reaction. The final ASGLS reaction with the polysulfide molecule as a two atom chain is:

$$2Au + S_2^{2-} + 2S^{2-} ➜ 2AuS^- + 2S^{2-} \tag{9}$$

The important aspect of the ASGLS chemistry is to remember that the system oxidant and the system lixiviant are not the same chemicals. Both sulfide and polysulfide must be present in the system if leaching is going to occur.

REQCM BACKGROUND

The REQCM can read both electrical and mass changes taking place on the metal surface. To make the working electrode, a thin, disc shaped quartz crystal has a platinum film sputtered onto it. Platinum is sputtered on to enable both current to pass through the electrode and so that metal can be deposited onto the surface prior to an experiment. Two wires are connected to the crystal; the first simply provides a path for electrical current to flow, the second sends a signal to a frequency reading device that can read what the resonant frequency of the crystal is, usually about 10MHz. As the mass of the quartz crystal increases, the resonant frequency in the crystal decreases.

During an experiment, mass (gold, silver, or alloy) is first deposited onto the platinum and then it is leached off. As mass is deposited the resonant frequency will go down; correspondingly, as mass is leached off the surface the resonant frequency will go up. Resonant frequency changes can be related to changes in mass on the surface of the crystal. Mass changes in the range of ±1 nanogram (10^{-9} grams) can be accurately measured.

EXPERIMENTAL PROCEDURE

During experimentation with the REQCM, the solid to be leached is electrically deposited onto the platinum surface until a desired solid mass has been plated, usually about 150μg. All electrodes were plated with the same procedure; however, depending on the type of metal that was to be studied, different plating solutions are required. Plating solutions for Au/Ag will have the concentrations found in Table I. Naturally, a pure Au solution will have no silver nitrate added.

TABLE 3. Gold/Silver Alloy Solution

Chemical	Name	Concentration
KAuCN	Potassium Dicyanoarate	0.02M
K$_2$CO$_3$	Potassium Carbonate	0.086M
KCN	Potassium Cyanide	0.23M
AgNO$_3$	Silver Nitrate	*

* (Silver nitrate is added depending on %-Ag desired in alloy.
For example, a 5% silver alloy will need .5mM silver nitrate.)

Once the electrode is plugged in to the holder, the software will start to transfer resonant frequencies into mass. Because each crystal has a unique mass it is important to note the starting mass so that the counsel can be turned off once there has been about 150μg of metal plated. All plating is done while the electrode is spinning. Gold is plated onto the platinum flag at 25A/m^2. The resulting gold surface is uniform and smooth. After 150μg have been plated the current and rotator are turned off and the electrode can be removed from the holder.

The freshly gold plated electrode will have gold plating solution on it after it is removed. All the solution is washed off and the electrode is dried off with compressed air. Now the dry, gold-plated working electrode is ready to be plugged back into the holder for experiments.

A software package within the REQCM is called has been set up to calculate the mass on the crystal with inputs of frequency. For the alkaline sulfide system experimentation, two different types of plots were obtained with the software: leach tests and potential scans.

During a leach test the electrode is simply submerged into the solution and the rate at which metal leaves the surface is recorded along with the Mixed Potential (E$_m$), the potential at which leaching occurs. A typical leach test plot can be seen in Figure 1.
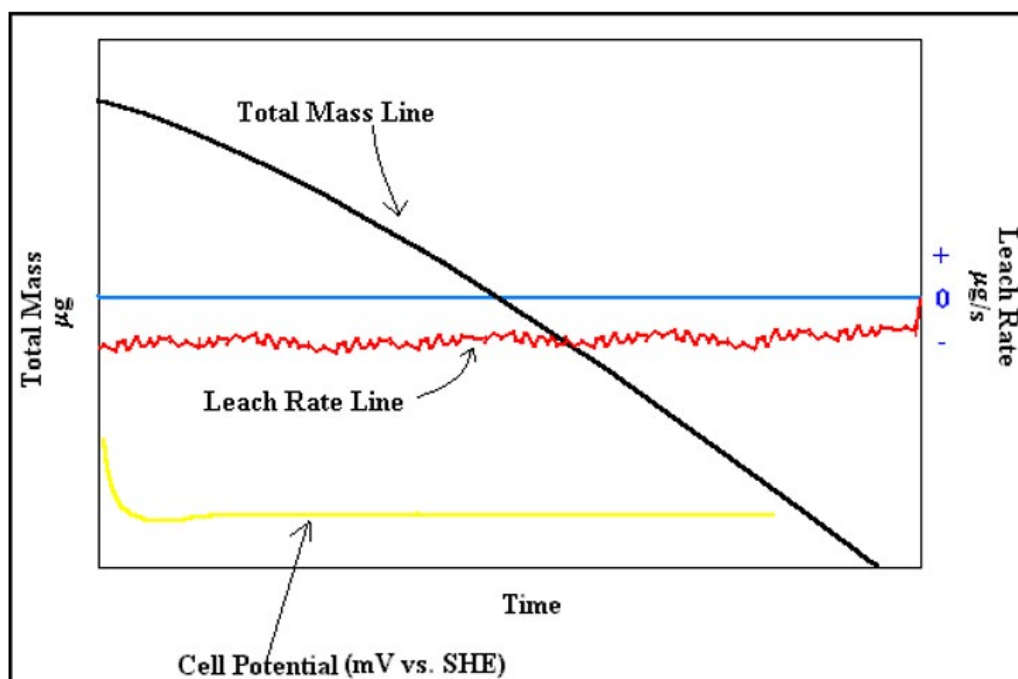
FIGURE 1. Typical Leach REQCM Plot.

It is noted that after the system reaches equilibrium the cell potential (E_m) will level off. Also note the noise in the leach rate line. Even though it is relatively noisy, (± 5 nanograms of the average leach rate) the overall mass loss line is smooth because with a properly working electrode the noise will average out to zero over time. Over a short time, the total mass line will fall into a constant slope. The leach rate will be a negative value because mass is being lost off the crystal.

During a potential scan with the REQCM, the cell potential is adjusted during the entire length of the experiment. Total current, leach rate, and cell potential are measured continuously during the scan. Before a scan is started the sell potential should be set at about 10mV below the E_m so that the exact point where the total current goes from negative (reducing) to positive (oxidizing) can be seen on the graph.

Once the potential scan (i.e., the forward scan) has reached a potential deemed high enough for the experiment the scan is reversed, and potentials are allowed to return (i.e., the back scan) to the starting point of the scan. Ideally the forward and back scans should be identical, but surface phenomena such as passivity often make the two scans different. Surface phenomena cause problems with potential scan reliability, so they should be avoided.

To avoid some of these surface phenomena on the forward scan, a leach test can be run first. If no leach test needs to be done, the electrode should sit in solution for about 5 minutes before starting the scan. For the sulfur/sulfide leaching system, passivity on the back scan can be avoided by reversing the scan before sulfide can be oxidized to sulfur on the electrode surface.

THE EFFECT OF SULFIDE (S^{2-}) CONCENTRATION

Four potential scans were run varying sulfide concentration solutions. No leach tests were run on the sulfide solutions because leach rates are effectively too slow to measure, even at the test temperature of 50°C. From the graph in Figure 2, increases in sulfide concentration enhance gold oxidation. Also, gold oxidation occurs at lower potentials as sulfide concentration increases.
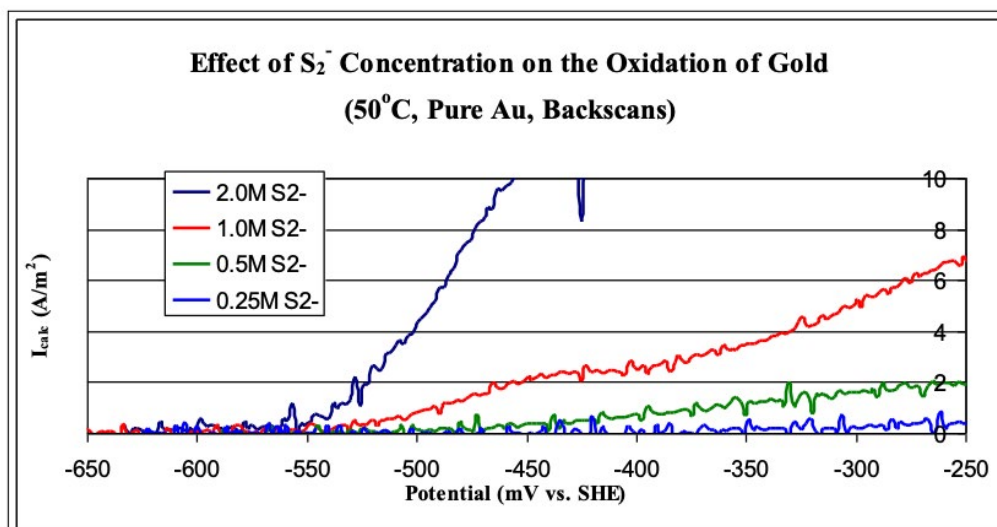
FIGURE 2. Effect of Sulfide Concentration on Pure Gold Potential REQCM Scans.

THE EFFECT OF HYDROSULFIDE (HS⁻) CONCENTRATION

Tests were done to see if adding hydrosulfide rather than sulfide influenced the oxidation of gold. From Figure 3, it is shown that hydrosulfide has a negative impact on gold oxidation at higher potentials when compared to sulfide. However, it is important to note that by adding hydrosulfide, the E_m is raised.
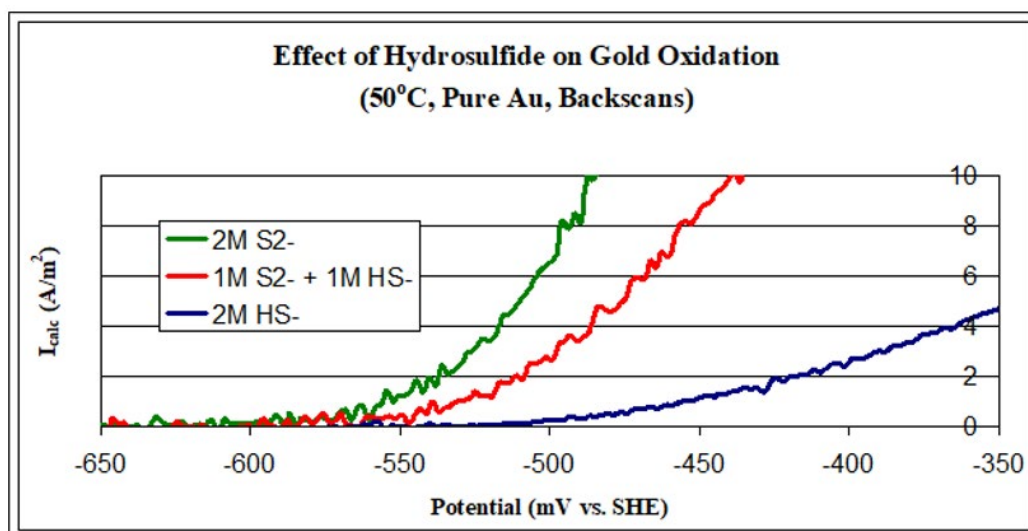

FIGURE 3. Effect of Hydrosulfide on Gold Potential REQCM Scans.

THE EFFECT OF POLYSULFIDE CONCENTRATION

To better understand the effects of polysulfide on gold oxidation two different tests were completed. In the first test the total sulfide concentration was held at 2 molar while the sulfur concentration was increased from 0-3 molar. During the second test the total sulfur (sulfide + sulfur) concentration was held at 2 molar and the mole-% sulfur in the 2 molar solution was varied from 0-30 mole-%.

Figure 4 displays what happens with increasing sulfur concentration when sulfide concentration is held at 2 Molar. Notice there is little difference when potentials are lower than –400 mV vs. SHE; however, E_m continues to get higher as sulfur concentration is increased. The effect of E_m increasing can be seen in the leach tests in Figure 5.
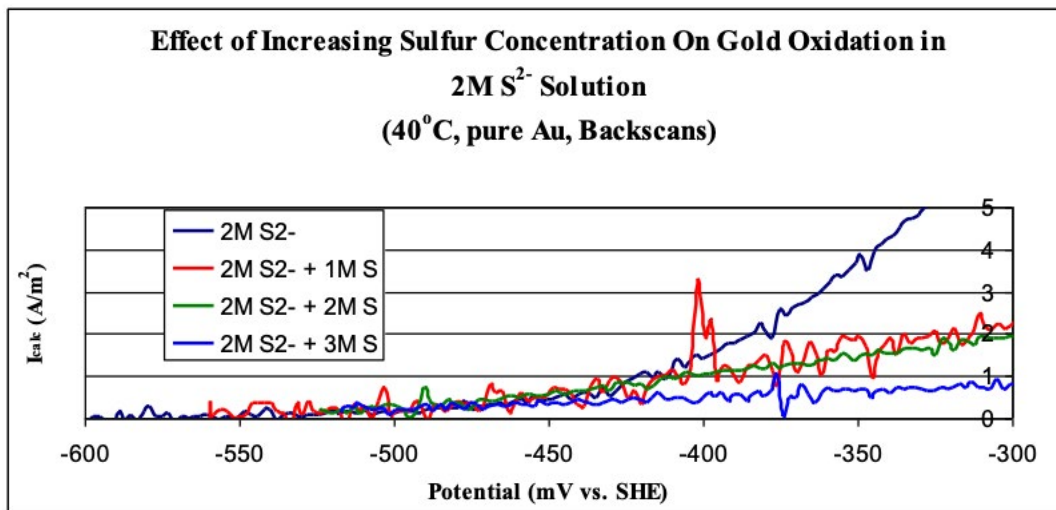
FIGURE 4. Effect of Increasing Sulfur Concentration on Gold Potential REQCM Scans.

As seen, solutions of 2M S^{2-} essentially did not leach; in other words, the current flow due to the oxidation of gold is essentially zero at the solution potential (Em). As sulfur concentration increases, the leach rate also increases. Leach rates increased from 0.2 to 6.5, 7.2, and 8.3 nanograms/second respectively for 0, 1, 2, and 3 molar sulfur additions to 2M S^{2-}.
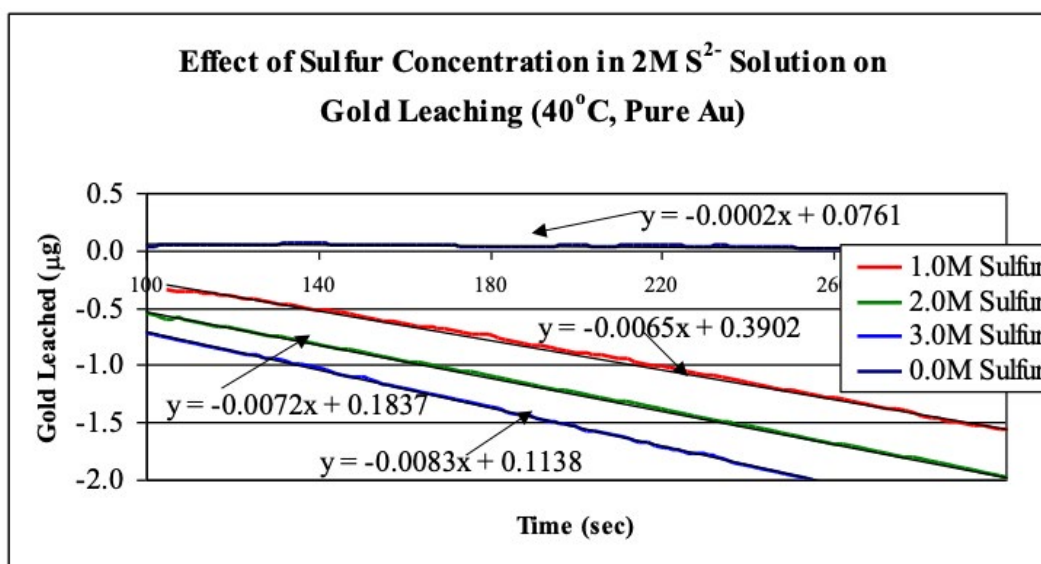
FIGURE 5. Corresponding Leach Tests With Solutions Shown in Figure 6.

Holding the total sulfur concentration at 2 molar produced some informative results as to why leaching is difficult under these conditions. Even though the sulfur and sulfide concentrations are changing, there is still no real leaching occurring because E_m potentials are occurring where gold oxidation is essentially zero as seen in Figure 6. A small amount of leaching can be expected as sulfur concentration goes toward 100 mole-% (E_m increases to gold oxidation regions); however, the leach rates would most likely be insignificant.
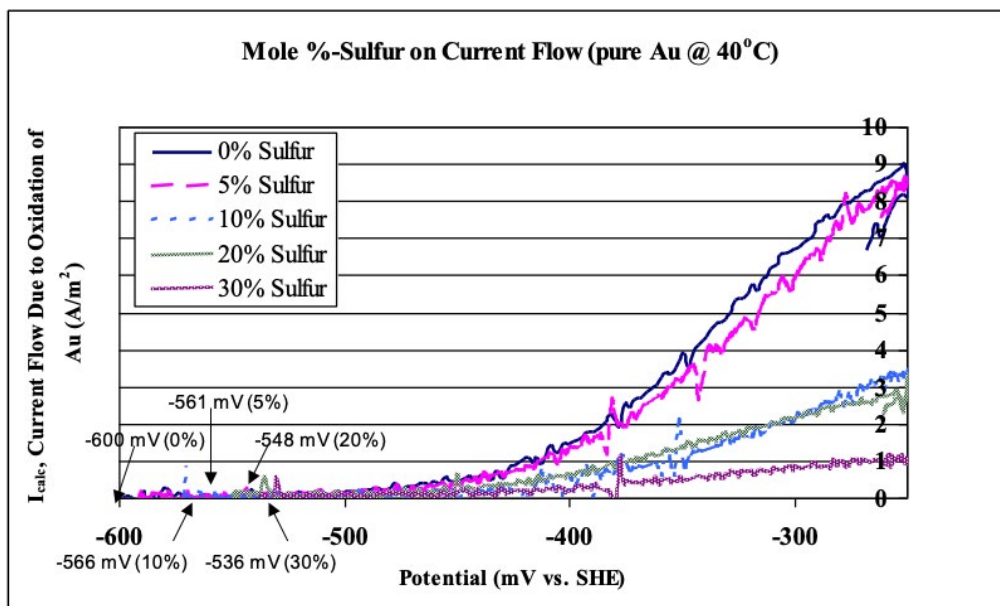
FIGURE 6. 2M Total Sulfur Pure Gold Potential REQCM Scans.

THE EFFECT OF HYDROXIDE ADDITION

Adding NaOH to the leaching system was tested to see the effect it had on gold oxidation. The first test that was run was done with 2M S^{2-} with concentrations of hydroxide ranging from 0-3 molar (See Figure 7.) From Figure 7 it is shown that the addition of hydroxide increases the oxidation of gold to lower potentials.
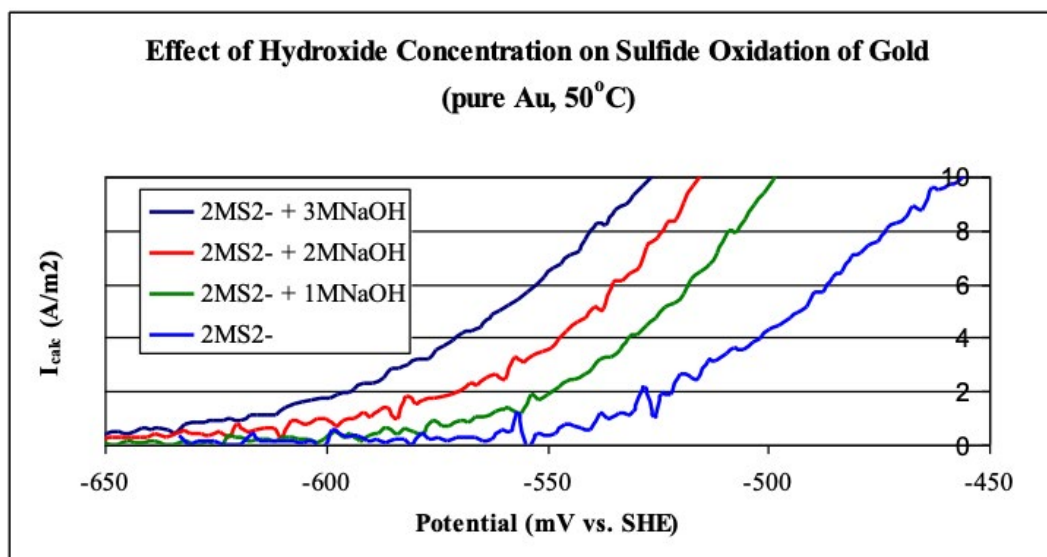
FIGURE 7. Effect of Increasing Hydroxide Concentration in 2M S^{2-} Solution.

Tests were also run to see effects of adding hydroxide to a polysulfide solution. Two different polysulfide solutions were prepared, one had 2M S^{2-} with 2M S while the second had 2M S^{2-} with 3M S. To each of these solutions, one had hydroxide added and one did not. This is shown in Figure 8.
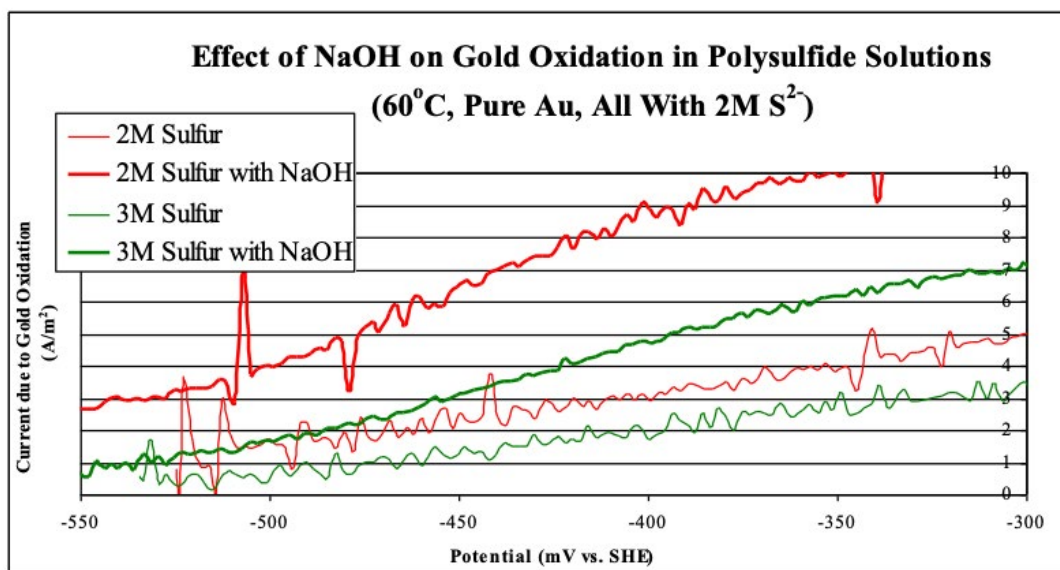

FIGURE 8. Effect of Hydroxide Addition on Gold Oxidation in Polysulfide.

From Figure 8 it is seen that gold oxidizes more readily at lower potentials in solutions where hydroxide is added. To see the effect on gold oxidation at Em, see Figure 9 below. For both solutions, by adding hydroxide the leach rate at 60°C is increased 20-25 ng/s.
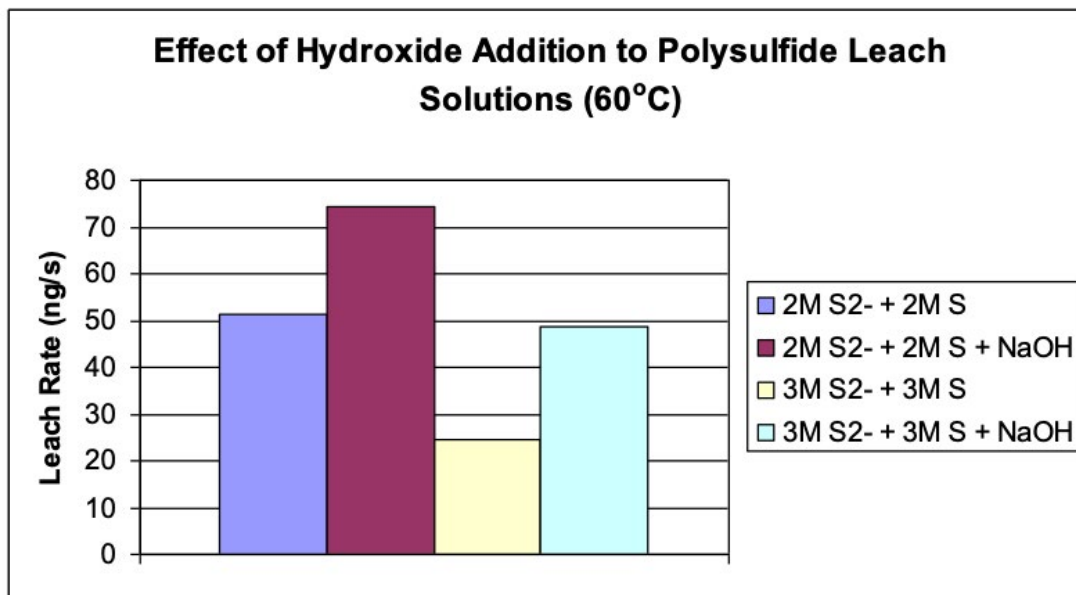
FIGURE 9. Effect of Hydroxide Addition on Gold Leach Kinetics.

THE EFFECT OF TEMPERATURE

In most cases, increasing the temperature of the solution will increase the reaction kinetics. Tests were run to understand how 2M S^{2-} solutions and 2M S^{2-} + 1M S polysulfide solutions were affected by temperature.

 Figure 10 shows the results for potential scans in 2M S^{2-} solutions at temperatures from 30-60°C. As temperature increases, gold oxidizes more readily at lower potentials. Notice the large jump in gold oxidation as the temperature goes from 50°C to 60°C.
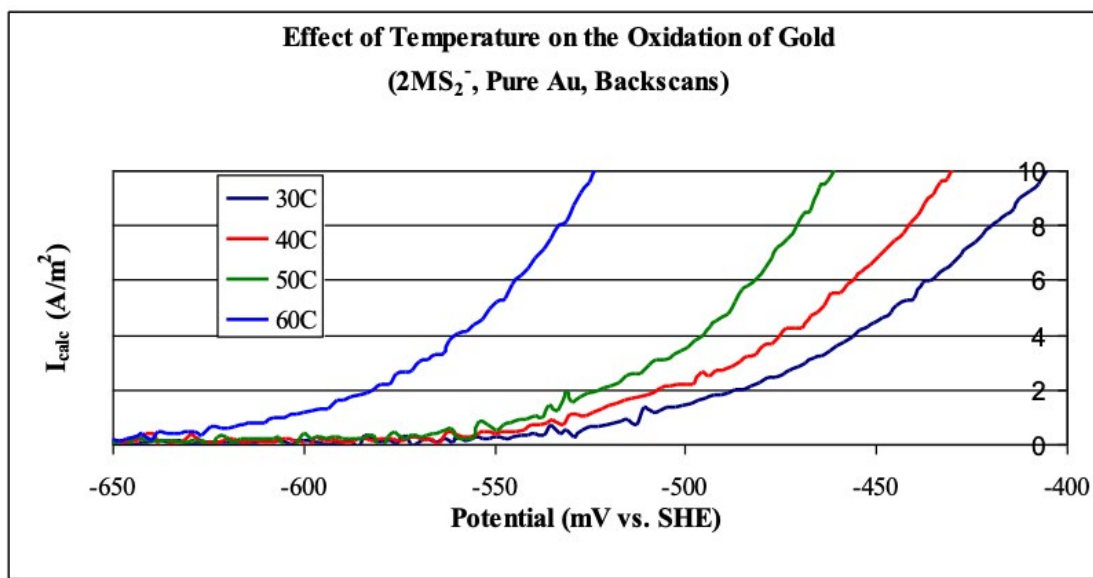
FIGURE 10. Temperature Effects on Gold Oxidation Potential REQCM Scans.

In Figure 11, the effect of temperature on gold oxidation in polysulfide solutions is shown. Again, as temperature increases, gold will oxidize more readily at lower potentials. As with the 2M S^{2-} solution above, there is a large jump as the temperature goes from 40°C to 50°C.
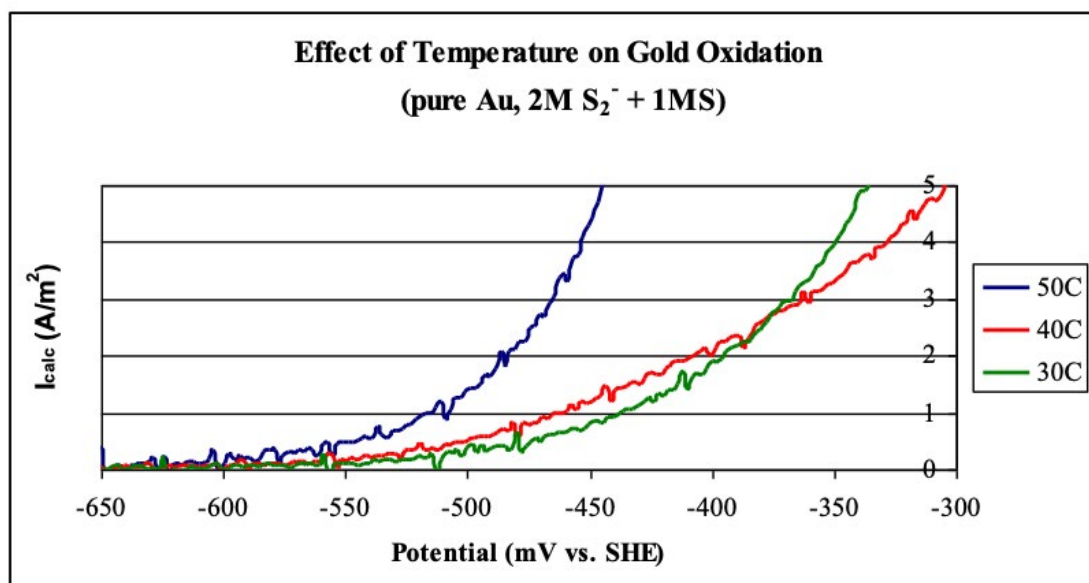
FIGURE 11. Effect of Temperature on Gold Oxidation in Polysulfide Solutions.

Leach tests were further performed on the solutions found in Figure 11; they can be found in Figure 12. The same jump in oxidation kinetics from 40°C to 50°C can be seen in these leach tests. From 30°C to 40°C there is only a 0.5 ng/s rate increase while from 40°C to 50°C there is a 5.7 ng/s rate increase.
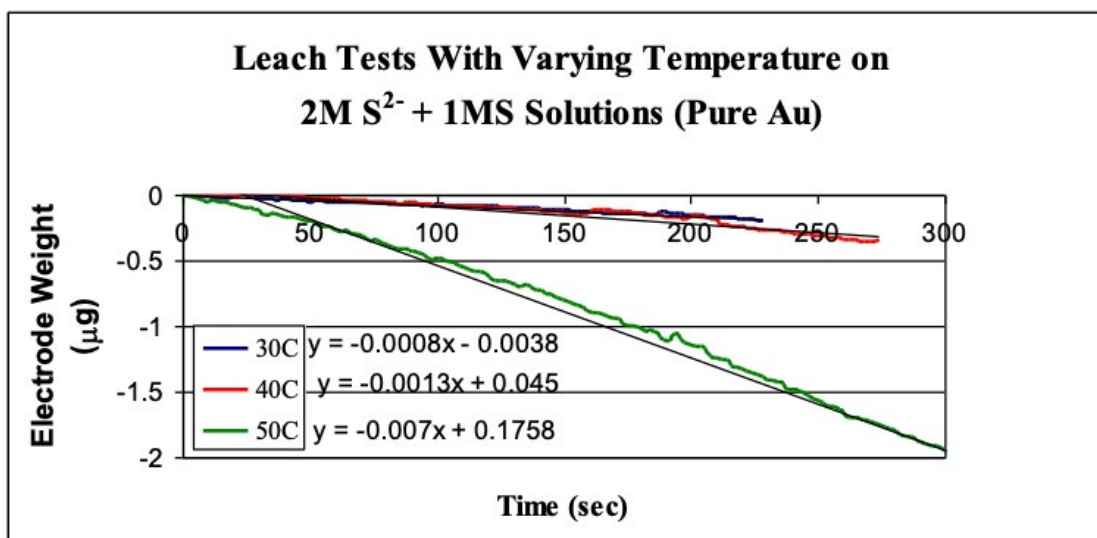

FIGURE 12. Leach Test Varying Temperature in Polysulfide Solutions.

THE EFFECT OF GOLD PURITY

Gold purity is a variable that needs to be studied because most natural gold deposits have at least 5% Ag in them (Hurlbut and Klein, 1977). Two identical leach tests were run for three different solutions. The two tests contained one pure gold plate and one 5% silver plate (see Figure 13.) In the 2M S^{2-} + 1M S solution, the 5% silver alloy leached slightly slower than its pure gold counterpart. However, for the more concentrated solutions (2 and 3 MS), the 5% enhanced the leach rate almost 100%.
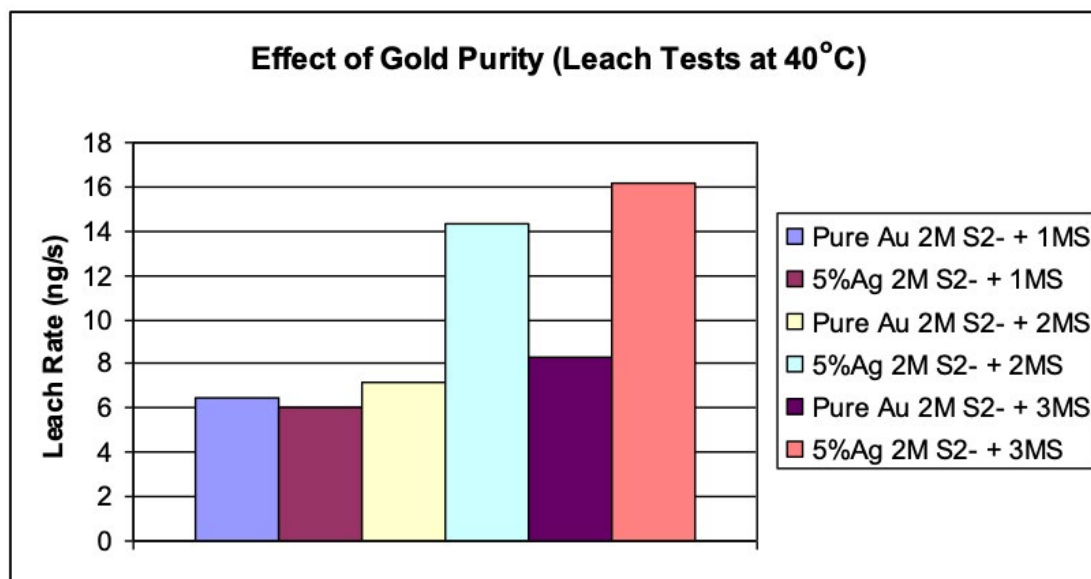

FIGURE 13. Effect of Gold Purity on Leach Rate.

CONCLUSIONS

The first variable studied, effect of sulfide concentration, showed that increases in sulfide concentration help to speed the oxidation of gold at lower potentials. Hydrosulfide had two major effects on the system: 1) adding hydrosulfide slows gold leaching kinetics at a given potentials; and 2) hydrosulfide additions raise the solution E_m. By adding sulfur to the system, the polysulfide concentration was increased. Higher polysulfide concentrations generally increased leach rates; however, more sulfur both slowed leach kinetics at given potentials and raised the E_m. Eventually the addition of more sulfur will slow the leach reaction. Hydroxide additions up to 3 molar were shown to increase leach kinetics at lower potentials in sulfide solutions. Also, hydroxide additions increased leach kinetics in polysulfide solutions. As expected, temperature increased leach kinetics; more importantly, there looks to be a large jump in leach kinetics around the 50-60°C temperature range. The purity of the gold effected leach kinetics positively for concentrated polysulfide solutions above 2M S^{2-} + 1M S.

ACKNOWLEDGEMENTS

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The Role of Pyrometallurgy in the Recovery of Precious Metals from Secondary Materials

Permission granted by the author at time of submission to Precious Metals 1982.

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SYNOPSIS

The increasingly sparing use of precious metals, particularly in association with base materials which inhibit recovery by direct aqueous chemical attack, has made the aggressive solvents and concentration techniques found in pyrometallurgical processes more attractive to the precious metals recovery industry. This paper considers the process metallurgical principles involved in smelting and fire — refining of precious metal bearing waste materials and compares the types of plant available for such operations. Attention is paid to the operational problems encountered and particularly that of atmospheric pollution. Finally, some recent pyrometallurgical developments are discussed in the relation to their potential applicability in the precious metals recovery industry.

INTRODUCTION

It has become a commonplace observation that the increasingly sparing use of precious metals in association with a diverse range of base materials has made modern precious metal reclamation a challengingly difficult task. The high degree of dispersal of the precious metals plus the often intractable nature of the base materials has rendered conventional hydrometallurgical techniques ineffective in extracting all the precious metals into solution. As a result many hydrometallurgical circuits produce residues that are too valuable to be discarded but are resistant to further aqueous treatment. In the face of such materials the aggressive solvents encountered in pyrometallurgical systems are attractive. Indeed, the question is being asked whether, in view of the poor performance of aqueous chemical processes and the high state of development of some pyro-techniques, would it not be more practical in the case of, for example some alumina based materials, to eliminate the aqueous chemical step entirely and go directly to pyrometallurgy for the initial extraction step.

Pyrometallurgy also has other advantages for the precious metal refiner; namely:

- high specific throughputs which promote minimum metal holdings and faster metal returns,
- good process economics inspite of the high temperatures involved,
- gaseous effluents are more readily disposed of than the massive volumes of liquid effluent from aqueous circuits,
- possibility of simple and rapid upgrading to give concentrated feeds to refining circuits.

Although pyrometallurgy appears to be enjoying or about to enjoy something of a renaissance, many of the processes in current use are to quote an Engelhard colleague, Dr. Eric Stern in connection with aqueous refining at the 1981 IPMI symposium 'the reactions employed... have undergone little change over a considerable period of time". [1] The most vivid example of this being the continued use of cupellation in a form that is probably pre-Christian in origin. However, as we shall see later, new processes and practices are intruding into an ancient picture.

PRINCIPLES

Unlike primary metal extraction systems, the metals to be recovered are not major components of the recovery system. The major metallic component in a secondary precious metal recovery process is in fact a base metal phase in which the precious metals collect. The choice of collector phase therefore will govern much of the basic metallurgical chemistry of the system. On the other hand, the choice of slag will depend on the chemical character of the non-precious metal or gangue part of the feedstock. The total system can be likened to solvent extraction at high temperature where the precious metal containing furnace feed is equivalent to the aqueous feed, the collector metal to the organic phase, the resulting collector — precious metal alloy to the loaded organic and the slag to the raffinate (Figure I). The separation of the precious metal from the collector metal is analogous to the solvent extraction stripping stage. The recycled collector metal obviously equates to the regenerated organic and, as in solvent extraction plants, there may be a final cleaning/settling stage to recover in the case of solvent extraction the valuable organic but in the pyrometallurgical case to recover the precious metal rather than the collector metal, although the collector metal is inevitably partially recovered as well.

FIGURE I. The Solvent Extraction Analogy
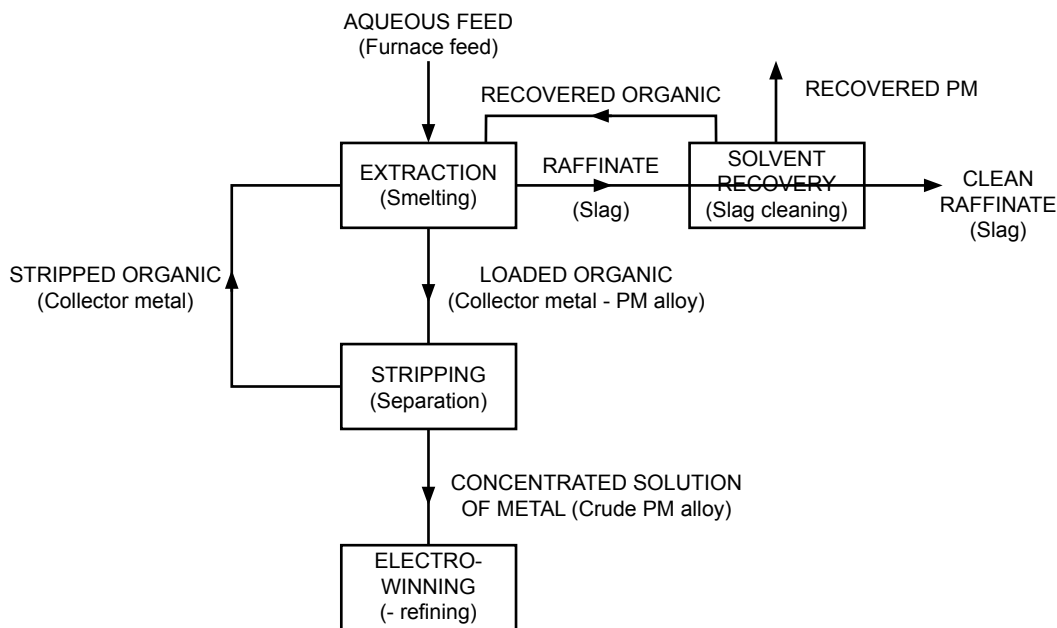
SELECTION OF COLLECTOR PHASE

Continuing the solvent extraction analogy, the selection of the collector metal (organic phase) is made bearing in mind the points tabulated in Table I. The analogy breaks down with selectivity as complete immiscibility in the liquid alloys of interest here is comparatively rare. The loss of collector metal to slag is closely related to the more important parameter of loss of precious metal to slag, as will be shown later. Some common and some possible collectors are outlined in Table II.

TABLE I: THE SOLVENT EXTRACTION ANALOGY:
THE SELECTION OF ORGANIC SOLVENT/COLLECTOR METAL

SOLVENT EXTRACTION	PM - PYROMETALLURGY
1. Low organic loss to the Aqueous Phase.	Low Collector Metal (PM) Loss to the Slag Phase.
2. Ease of Formation of the Organo-metallic Complex.	Ease of Solution of the PM.
3. Ease of Regeneration of Organic Phase (Stripping).	Ease of Separation of PM/Collector Metal.
4. Cost.	Cost.
5. Selectivity.	Selectivity.

TABLE II: POSSIBLE COLLECTOR PHASES FOR PRECIOUS METALS

COLLECTOR	AFFINITY FOR PM's								SLAG LOSSES % PM	COST ¢ / LB	OPERATIONAL TEMPERATURE RANGE °C	SEPARATION AND RECYCLE
	Ag	Au	Pt	Pd	Rh	Ir	Rh	Os				
Lead*	x	x	x	x	x	x	x	x	<0.05	28	900-1200	Separation and recycle as PbO well established method.
Copper*	x	x	x	x	x	x	x	x	<0.01	75	1200-1300	Separation well established, recycle problem.
Iron		x	x	x	x	x	x	x	?	10	ca. 1500	Separation techniques available, recycle probably unnecessary.
Nickel		x	x	x	x	x	x	x	?	320	ca. 1500	Separation techniques available, recycle problem.
Aluminum	x	x	x	x	x	x	x	x	0.1-0.2	76	up to ~2000	Separation techniques available, recycle not considered.
Mattes*	x	x	x	x	x	x	x	x	<0.01	ca. 40	1000-1200	Separation techniques difficult, recycle not practiced.
Speiss*	x	x	x	x	x	x	x	x	Very low	ca. 130	ca. 1000	Removal of As and Sb difficult and hazardous.

*Known Industrial Use.

Lead Collection

Because of the extensive solubility in lead (ca. SO wt%) of all the precious metals at low temperatures (1000°C), the ready separation of Pb by pyrometallurgical means (cupellation) and the low operational temperatures required (ca. 1100°C), lead is the traditional collector metal. It is in current use in all of the major secondary precious metal smelters. The main drawbacks to its use are the need for rigorous environmental controls and unsatisfactory recoveries of Ir, Ru and Os at the cupellation stage.

Copper Collection

Silver and gold are completely miscible with copper above 1100°C. The platinum group metals, certainly platinum, palladium and rhodium, show good solubility (30-50%) at 1200°C. The main disadvantage of copper is separation and recycling. Unless the precious metal concentration is low enough to permit electrolysis — as is

the case where precious metal recovery is a by-product of a secondary copper smelter then the separation and particularly the recycle of copper involves a further multi-stage process. The problem of copper recycle both from the point of view of cost (copper is 2-3 times more expensive than lead) and precious metal control is a great deterrent to the choice of copper as a collector. The problem of cost does not of course arise when adequate concentrations of copper are inherent, such as in feeds sourced from electronic scrap. The advantage of copper over lead is that under currently projected regulations the environmental controls for copper will be less stringent.

Iron Collection

Iron is cheap and is well known for its great affinity for the platinum group metals. It has a lesser affinity for gold and is immiscible with silver in both the liquid and solid states; its use would therefore be restricted to materials which primarily contain the platinum group metals. Separation would be a relatively straightforward leach operation possibly preceded by upgrading step using preferential oxidation. The main disincentive to the use of this otherwise excellent collector is temperature. Iron-platinum group metal alloys with compositions in the appropriate range — say — 10% platinum group metals have melting points in excess of 1400°C. The melting points could be lowered by the addition of — say — carbon to ca. 1150°C (the iron carbon eutectic) but this would probably lead to process difficulties on separation. If the high temperatures involved in the use of pure iron-platinum group metal alloys can be accommodated (they are just within the range of modern refractories) then the great affinity of iron for the platinum group metals could be utilized.

Nickel Collection

Like iron, nickel is a good solvent of platinum group metals and gold but has very limited solubility for Ag while the melting points of nickel alloys containing ca. 10% precious metals are also above 1400°C. The addition of carbon is not as effective as in the case of iron, the nickel-carbon eutectic forming at ca. 1320°C. The addition of copper which conveniently forms a continuous range of solutions with nickel is a possibility but substantial additions (ca. 80%) would be required to reduce the melting point below 1200°C. The addition of a third element, sulfur, to form a Ni-Cu sulfide is potentially of interest; however, see the section on mattes below. Of even greater cost than copper, nickel also possesses the disadvantage of the necessity of recycle, unless of course the feedstock naturally contains usable quantities of nickel or nickel and copper.

Aluminum Collection

The use of aluminum as a collector for the relatively rich residues emanating from the leaching of matte and lead bullion from primary platinum metal production has recently been patented. [24] The aim is to extract the precious metals into a readily soluble alloy thereby avoiding the conventional multistage hydrometallurgical route. With materials that are very rich and essentially metallic in character melting with aluminum at ca. 1000°C is sufficient but with lower grade materials, non-metallic in character the process involves an alumino-thermic reaction (temperatures in excess of 2000°C). The resulting slags carrying up to 0.2% platinum metals would require cleaning. The potential use of aluminum as a collector preferably would be restricted to small quantities of high grade material.

Matte Collection

These are metal sulfides or mixtures of metal sulfides. That they are good collectors of all the precious metals is proven by the recovery of quantities precious metals from copper and nickel-copper mattes. Additionally, they have low melting point of ca. 1000°C. Most common base metals: copper, nickel, iron, cobalt, lead, tin, zinc, aluminum form sulfides with some degree of stability; therefore the deliberate generation of mattes using precious

metal wastes most of which contain one or more base metals produces mattes of considerable complexity. For this reason, in real systems, the generation of mattes is usually kept to a minimum but as indicated above, simple nickel-copper mattes have some interesting properties. On slow solidification a metallic nickel-copper phase separates into which the precious metals segregate. This phenomenon is used by the South African primary producers to recover platinum group metals. The metallic phase is then recovered by conventional mineral technology. If a reasonably clean precious metal feedstock is available, then the use of nickel-copper mattes appears to be a potential method of recovery. In general, however to extract precious metals mattes require lengthy and complex processes usually involving roasting or converting followed by aqueous leaching. If generated in any quantity they also may lead to the additional problem of sulfurous emissions. Except in special circumstances, mattes are not favored as primary collectors for precious metals.

Speiss Collection

These are base metal arsenides or sometimes antimonides or mixtures of these. Speisses have a marked affinity for platinum group metals, a fact which has been used in the past [2] to collect platinum group metals, particularly Rh, Ir, Ru, and Os. As with mattes, the difficulty with speisses lie not with their properties as collectors, which are good, but with their subsequent treatment, that is the separation and containment of arsenic and antimony. The toxicity of these two elements is an additional reason for their unpopularity and like mattes their generation is avoided wherever possible.

SLAG DESIGN

To obtain the desired distribution of precious metals between collector and slag, the selection of the correct slag system is equally important as the selection of collector. Compared to primary metal practice, the slag to metal ratio tends to be higher, perhaps as high as 2:1. The achievement of low metal losses to the slag is therefore essential for good metal recoveries. In view of this it is surprising that slag design appears to have been a neglected art in the precious metal industry, probably because of the often unknown composition of the feedstocks. However, with good sampling and modern rapid analysis methods this obstacle can be overcome.

Industrial slags are extremely complex but some general comments can be made as to the qualities required of a good slag:

- low viscosity (< 5 poise),
- moderate liquidus temperature (<1200°C),
- rapid formation,
- high (thermodynamic) activity of the collector phase in the slag.

The almost invariable presence of silica (SiO_2) in secondary feedstocks has meant that silicate slags are the norm, in particular slags based in the system $CaO-FeO-SiO_2$. This slag system is also common to many of the non-ferrous primary processes and hence there is a considerable body of relevant data.[3,4] The olivine slags, $2(Fe, Ca) O \cdot SiO_2$, in this system meet the criteria stated above, the liquidus temperatures are < 1200°C and the viscosities are low (<2 poise). (Figure II). The reclamation of alumina based catalysts inevitably means that some residues contain high concentrations of alumina. Olivine slags have a limited capacity to dissolve alumina (ca. 15%) without increasing the liquidus temperature beyond practical limits. Viscosity also increases with alumina content but this is sometimes a physical effect due to the presence of undissolved particles of alumina (that is the slag also does not meet the criterion of rapid formation.) An alternative system for high alumina feeds are slags based on the Na_2O-SiO_2 side of the $Al_2O_3-Na_2O-SiO_2$, system (Figure III). These slags have liquidus temperatures of less than 1200°C for alumina concentrations of up to ca. 25%.

FIGURE II. CaO-FeO-SiO$_2$ system (from "Phase diagrams for Ceramists")
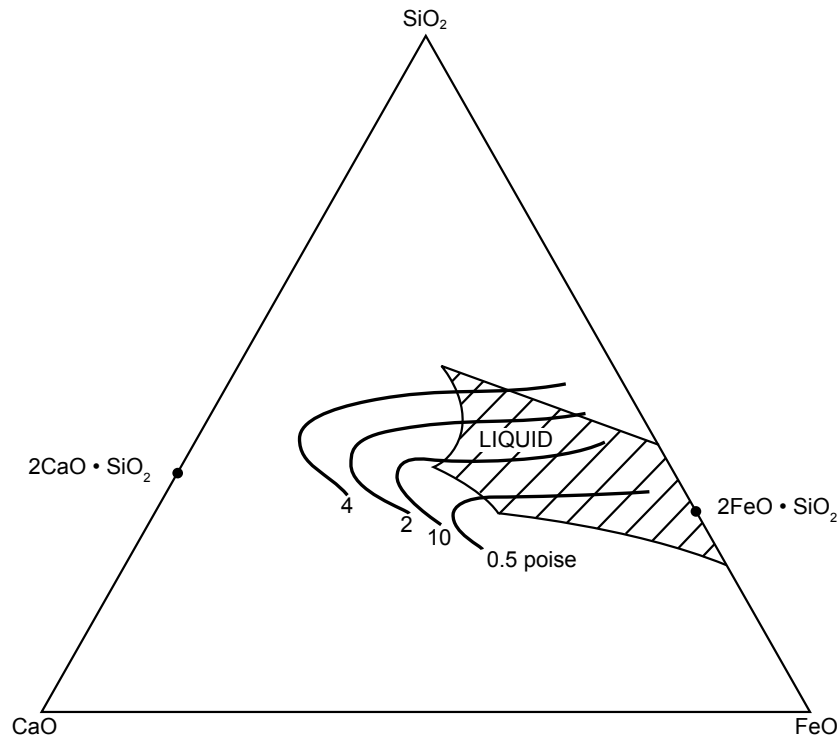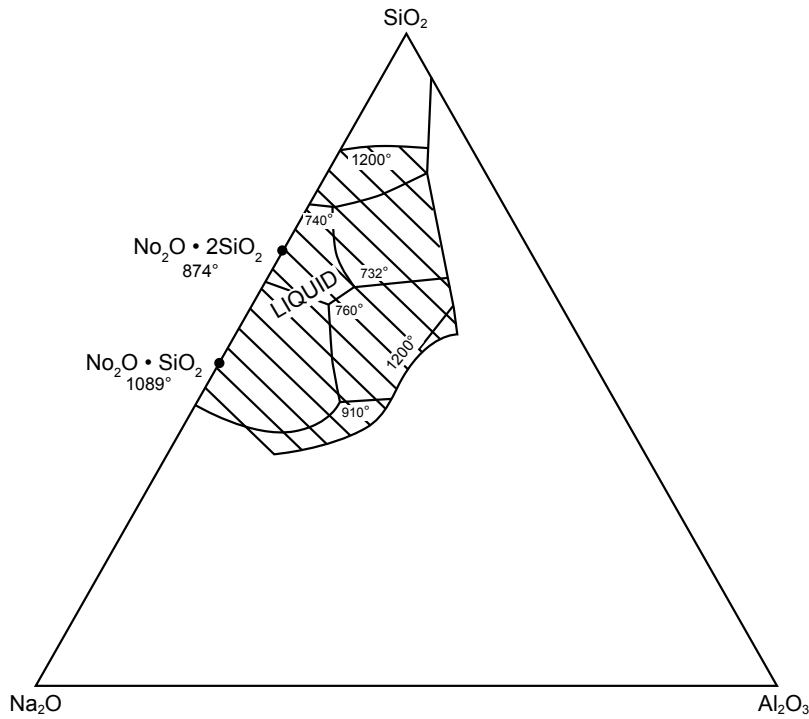Liquid region at 1200 °C   Lines of iso-viscosity at 1400 °C (in poise)

FIGURE III. Na$_2$O-Al$_2$O$_3$-SiO$_2$ system, indicating range of compositions where liquidus temperature <1200°C
(from "Phase Diagrams for Ceramists")

Structurally, liquid silicates are believed to be polymers, the monomer is the tetrahedral $(SiO_4)^{4-}$ ion. Pure, fused silica consists of a random, three-dimensional silicon-oxygen network and it is because of this extensive polymerization that its viscosity is high. The addition of ionic metal oxides such as CaO, Na_2O, FeO destroys (depolymerizes) the network into smaller silicate polyanions separated by metal cations. Ultimately, at the metal oxide to silica mole ratio of 3:1 the network is completely destroyed and only $(SiO_4)^{4-}$ ions exist. At this point the viscosity is at the minimum as is exemplified by simple binary silicates in Figure IV. The polymer structure of liquid silicates leads also to the phenomenon of minimum viscosities not coinciding with minimum liquidus temperatures as illustrated by the CaO-Al_2O_3-SiO_2 system (Figure V). One way around this problem — as every furnaceman knows when faced with a molten but viscous slag and no more temperature — is to add fluorspar (CaF_2). The large fluoride ion is particularly effective in breaking down the silica network. Alternatively, the liquidus temperature can be lowered by adding borax $(Na_2B_4O_7)$. Boric oxide, B_2O_3, like silica is a network former but does so at lower temperatures. The penalties paid for the use of fluxes such as fluorspar and borax are increased reagent cost and refractory wear.

FIGURE IV(A). The breakdown or depolymerization of the molten silica network by the addition of a metal oxide such as Ca O. (after Richardson [25])
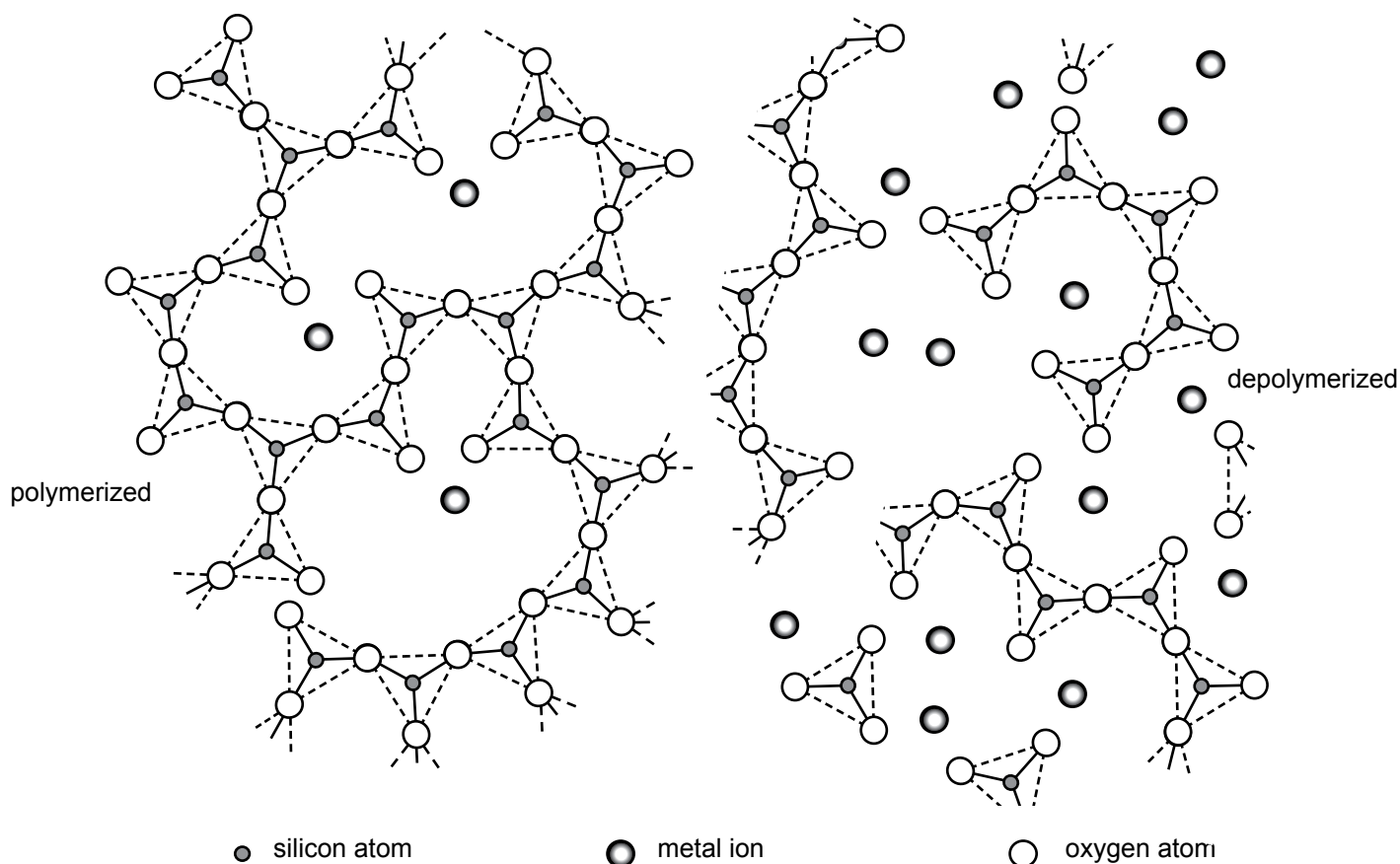
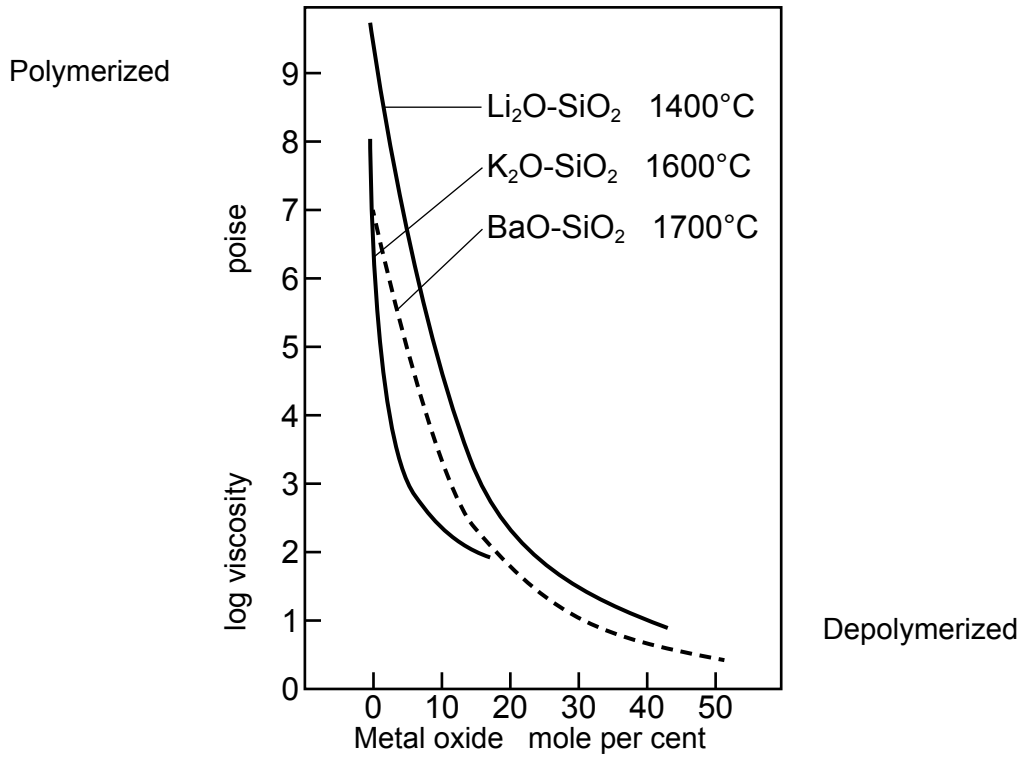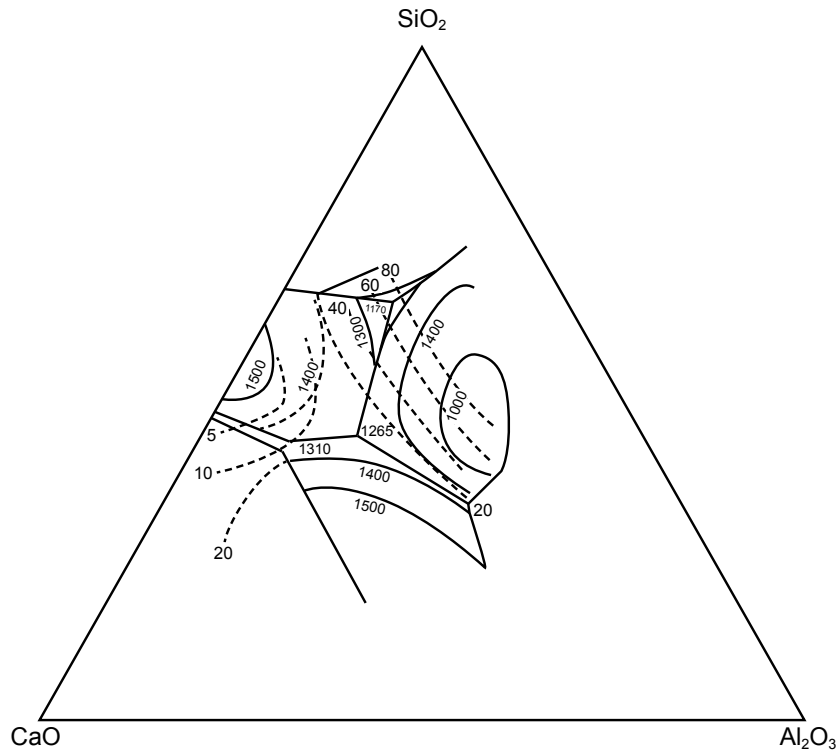**FIGURE IV(b).** The affect of metal oxides on the viscosity of molten silica. (after Mackenzie [26])

**FIGURE V.** CaO-Al$_2$O$_3$-SiO$_2$ system (from "Phase Diagrams for Ceramists") showing part of the liquidus surface. (Temp = deg C) Iso-viscosity lines at 1600°C (in poise)

In principle, the viscosity sensitive silicates may be side stepped by going to systems such as CaO-Al$_2$O$_3$. Unfortunately, although the viscosities are low, the liquidus temperatures rise sharply (Figure VI).

FIGURE VI. SYSTEM CaO-Al$_2$O$_3$ (from "Phase Diagrams for Ceramists") Temp = °C
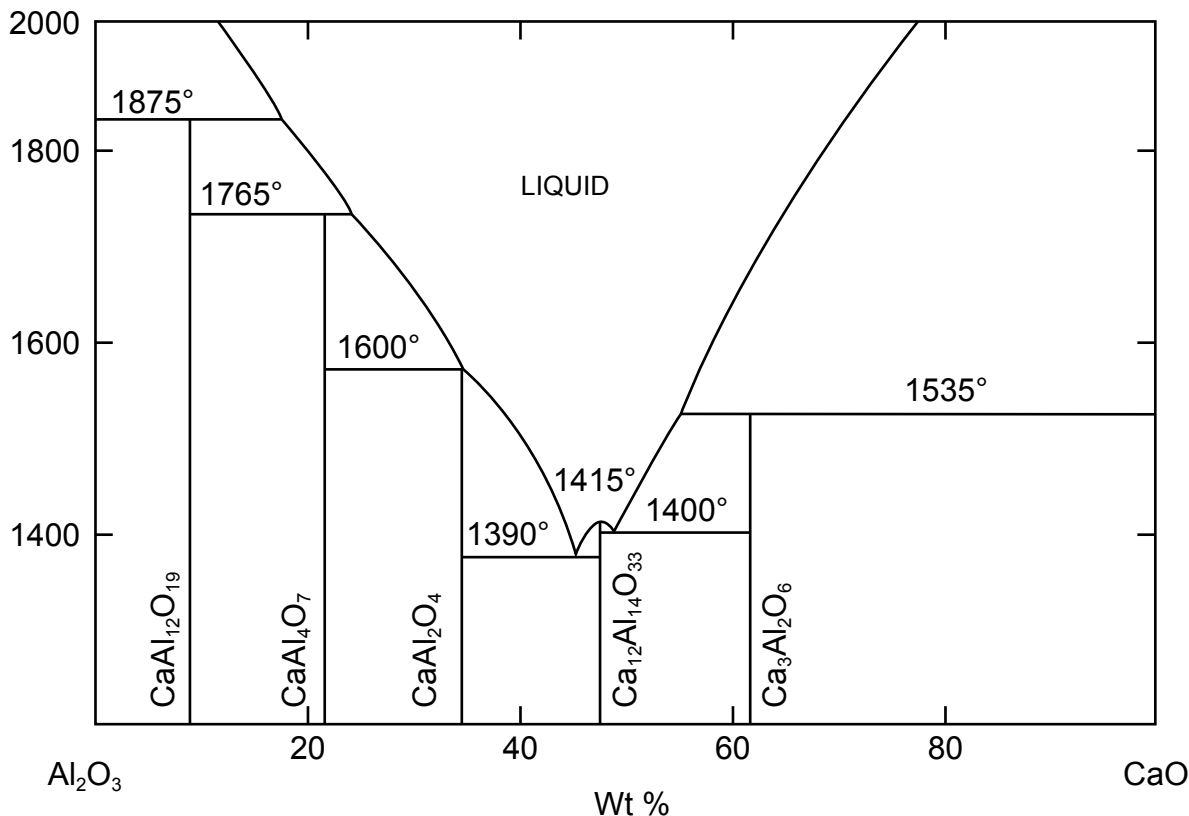
To minimize collector phase losses and hence precious metal losses to the slag it is necessary that the collector phase in its dissolved form has a high thermodynamic activity, that is it is easily displaced from the slag. This is usually achieved by adjusting the slag composition, for example in the case of lead by adding lime to the slag — as can be seen for the a simple CaO-PbO-SiO$_2$ slag (Figure VII) where the addition of lime rapidly increases the activity of lead oxide in the slag.

SEPARATION METHODS

Methods of separating and concentrating the precious metals from their collectors fall into several categories. These are:

- preferential oxidation in the molten state,
- preferential chlorination in the molten state,
- leaching,
- electrolysis or electrowinning.

Only the first two methods fall within the brief for this paper, although leaching is often preceded by calcination or roasting. Preferential chlorination is, of course, the Miller process for the separation of gold from silver and base metals. This process was well reviewed by Attwood at an earlier IPMI meeting [18] and will not be discussed.

FIGURE VII. Iso-activity lines for PbO in PbO-CaO-SiO₂ at 1200 °C (after Richardson)
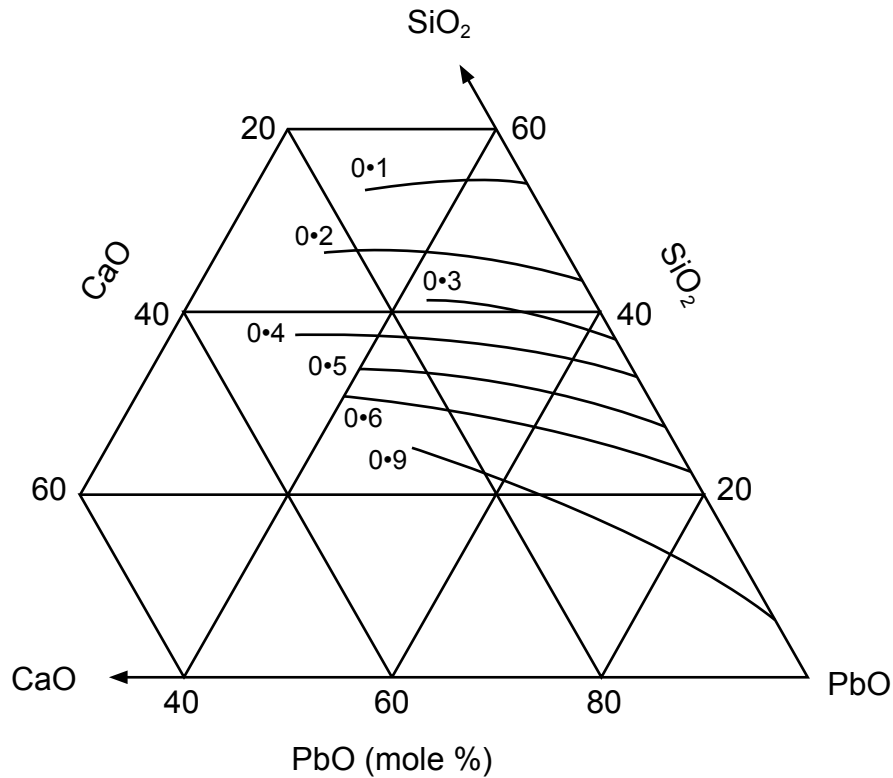
Preferential or selective oxidation is a common and highly developed pyrometallurgical technique, examples are oxygen steelmaking and copper matte converting. The usual example from the precious metal refining industry is cupellation which is the separation of lead from the lead-precious metal alloy which results from lead based smelting. Fundamentally, preferential oxidation depends on the relative stability of metal oxides (in the case of cupellation and oxygen steelmaking) or oxides/sulfides (in the case of matte converting). The well known free energy/temperature diagram illustrates the differences in stability between the oxides of the precious metals and the commonly associated base metals (Figure VIII). The precious metal oxides are less stable, that is, more resistant to oxidation than the base metal oxides. Bismuth and copper lie closer to the precious metals than do the other base metals such as lead, tin, or zinc and this is the reason for the fact that copper is usually the main impurity in silver and also for the difficulty of removing bismuth (which has a deleterious affect on mechanical properties of silver). Gold and the platinum group metals with the exception of osmium and possibly ruthenium and iridium remain largely unaffected at cupellation temperatures (ca. 1000°C). At cupellation temperatures lead oxide or litharge is a fluid liquid and differences in density make its separation an easy task. Litharge, behaving now as a slag, has the capacity to absorb oxides of the other base metals, none of which are liquid at these temperatures. However, the increase in concentration of copper in the litharge as well as increasing the liquidus temperature also appears to stabilize silver oxide relative to lead oxide as is shown by Figure IX. Thus both the chemical loss of silver as well as the physical loss due to entrained prills of metal increases. Interestingly, if iron or nickel were used as a collector, then the separation and concentration of platinum group metals could, in principle, be readily achieved because of the relative stability of wustite (FeO) and its ability to form a low melting slag.

FIGURE VIII. Relative stabilities of metal oxides (after Rosenqvist; Kubaschewski and Alcock)
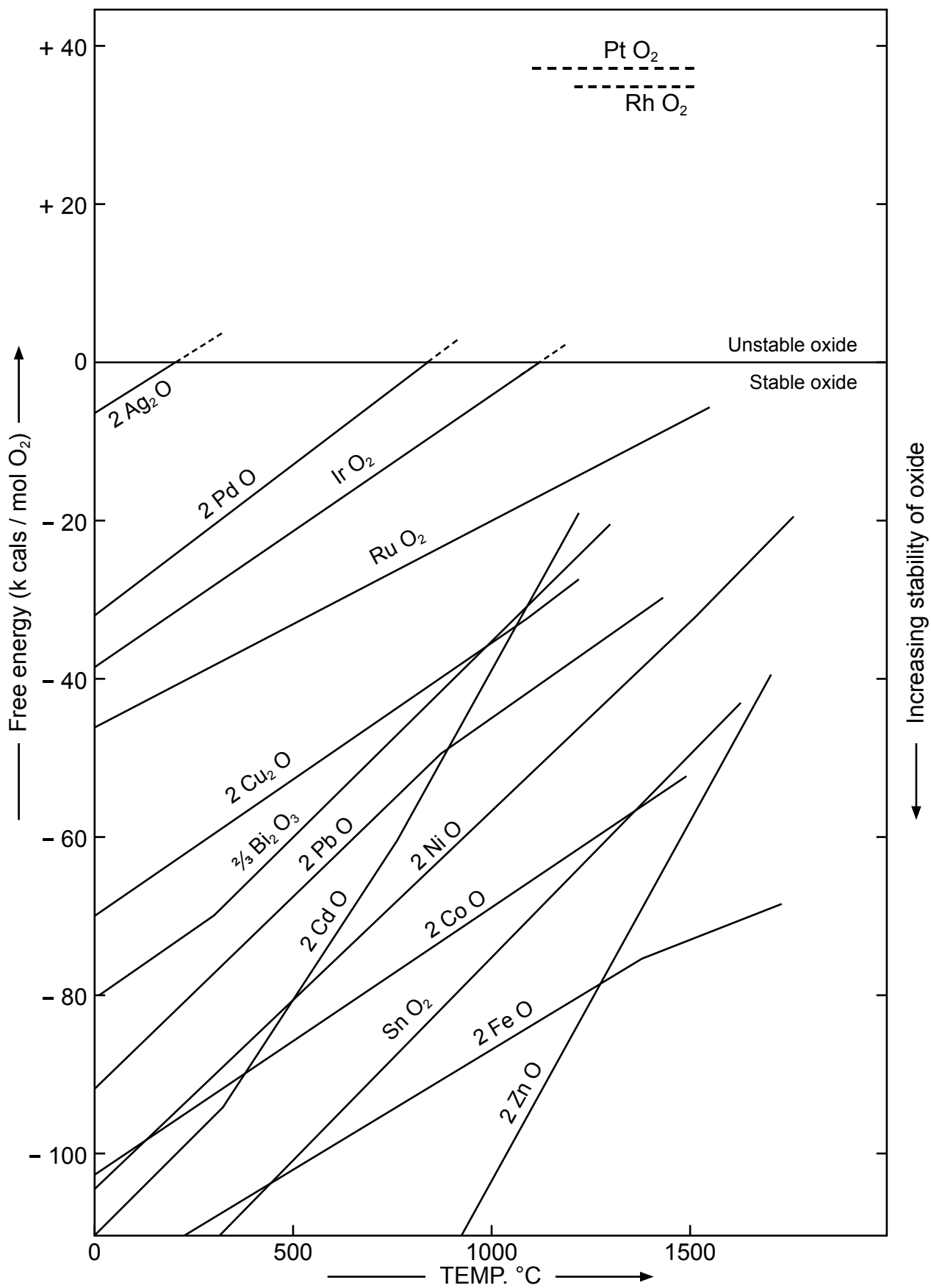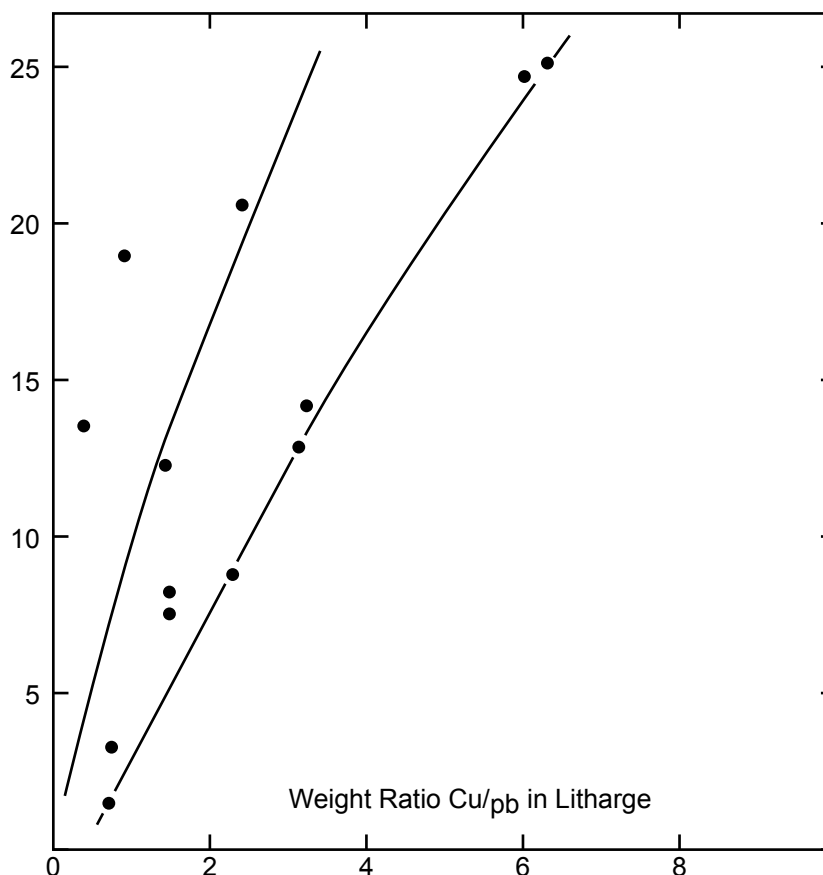
FIGURE IX. Effect of copper concentration on silver losses to litharge during cupellation

Weight Ratio Cu/$_{pb}$ in Litharge

PROCESS ENGINEERING

Over the years the secondary precious metal recovery industry, in the opinion of the writer, has isolated itself from the mainstream of extractive metallurgical thought and development. It is only recently that it has begun to adopt modern process design aimed at implementing metallurgical reactions in an efficient manner. Examples are the top blown rotary converter [5], the electric furnace [6], agglomeration [6,7] and subsurface gas injection. [8,9]

Most pyrometallurgical processes tend to be transport rather than reaction controlled, that is the rates at which reactants and/or products or heat is transferred to or from the reaction site controls the overall rate at which the process proceeds. The small static reverberatory or induction furnaces, with their ill-mixed and poorly agglomerated feeds that are often encountered in the industry must be the least kinetically and thermally efficient reactors available to the pyrometallurgist. By designing reactors which promote good contact between the reacting phases and between the phases and the source of heat, valuable increases in process efficiency can be gained without altering the fundamental chemical reactions. The application of such principles has been the mainstream of pyrometallurgical advance over the last three decades.

Modern reactors enhance transfer processes by increasing the number of heat transfer modes and the degree of agitation (Figure X). To take some of the examples mentioned above, the rotary converter owes its increase in kinetic efficiency to its rotation which causes agitation and its increase in thermal efficiency both to agitation and the increase in the number of heat transfer paths. The electric furnace although having more heat transfer paths than a reverb furnace also gains efficiency from the fact that the convection medium is a liquid with a relatively

high specific heat. The blast furnace owes its survival in process engineering terms to the use of agglomerated feedstocks which greatly enhance gas/solid contact (and also to the fact that it is able to use the carbonaceous material often present in precious metal waste material as fuel.)

FIGURE X. Principle Modes of Heat & Mass Transfer in Furnaces
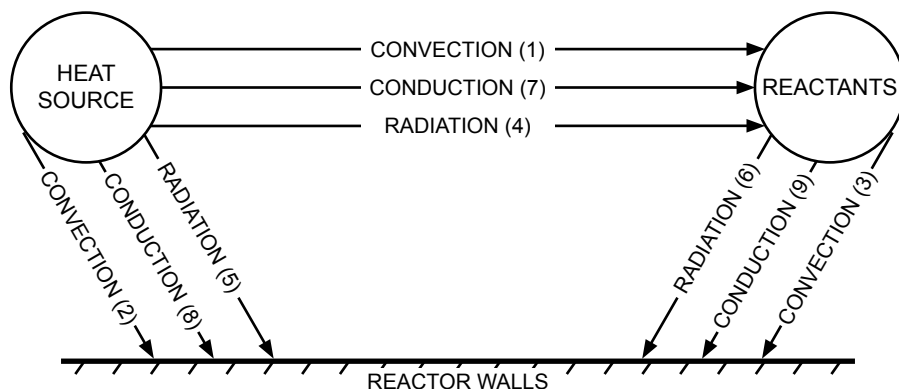
|		HEAT TRANSFER			MASS TRANSFER
	CONVECT^N		RADIAT^N	CONDUCT^N	
FURNACE	1 2 3		4 5 6	7 8 9	
REVERB, STATIC	✔ ✔		✔ ✔		DIFFUSION, MANUAL AGITATION
ROTARY	✔ ✔		✔ ✔	✔	MODERATELY AGITATED
ELECTRIC	✔ ✔			✔ ✔ ✔	MODERATELY AGITATED
BLAST	✔ ✔ ✔		✔ ✔	✔ ✔ ✔	FLUID/SOLID CONTACT

INDUSTRIAL PRACTICE

A typical basic precious metal recovery circuit is shown in Figure XI. There are two types, the first where the primary objective is the recovery of the precious metals and the second where the precious metals are recovered as by-product of the recovery of a major non ferrous metal. The first type is operated mostly by the major precious metal companies and is usually lead based, the second by smelters recovering either copper or lead or both.

In the case of the precious metal smelters, agglomeration is now commonly practiced in one form or another, the smelting unit can be a blast furnace [7,10], an electric furnace [6,20], a static reverb furnace [6,7], or a rotary furnace. If reverb furnaces are used then slag cleaning in an electric or blast furnace is usual. High grade feeds also give an additional reason for secondary slag cleaning. The primary separation process is cupellation from where the lead collector, in the form of litharge, is recycled leaving a crude silver to go forward for the secondary separation process which is silver electrolysis. Gold and the platinum group metals report to the anode slimes.

In the case of the non-ferrous smelters agglomeration is common except where the main feed is metallic scrap. The smelting unit is usually a blast furnace [11,12] and an independent slag cleaning unit is operated by at least one plant [13] to recover both non-ferrous and precious metal values. The primary separation will be a base metal refining process or processes such as converting for a copper plant or lead softening for a lead plant. The secondary separation stage may be electrolysis (for copper) or the Parkes Process (for lead); the former generating the precious metals in the form of anode slimes, the latter as a 'silver crust'.

FIGURE XI. Generalized PM Recovery Circuit
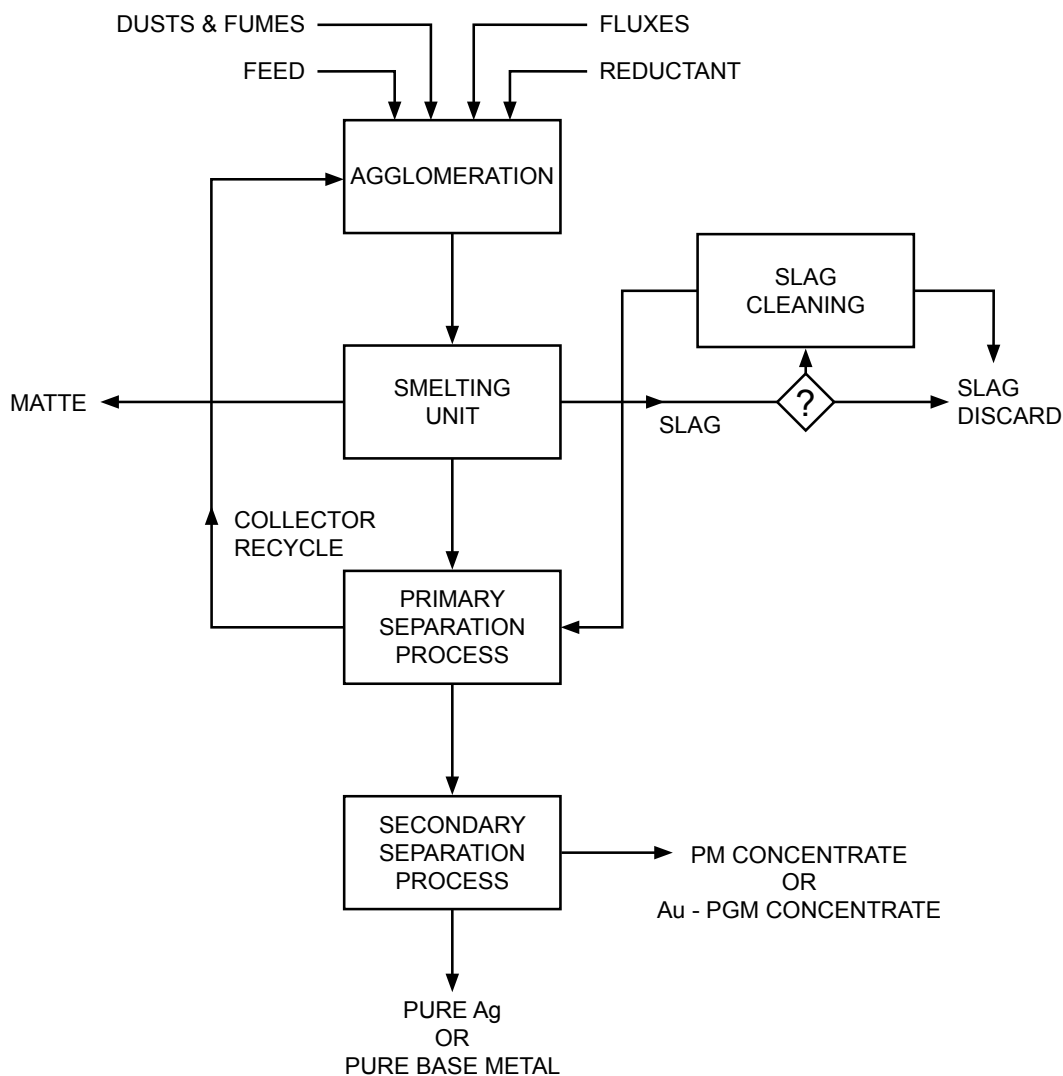
The operational difficulties associated with both these types of plants include:

- variable and complex feeds where the major components are often unknown and undetermined,
- control of reducing conditions,
- metal/matte separation,
- control of metal losses to the slags,
- poor efficiency of the cupellation process (lead based processes),
- dust and fume control at the work place and to the atmosphere.
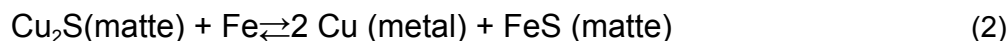
Complex Feeds

The secondary metal producer is constantly faced with the problem of complex feeds. For the precious metal reclaimer, the problem is particularly acute as the metal of value is nearly always the minor and often the only reported constituent. The major constituents which technically dominate the recovery system are often largely unknown. A knowledgeable and astute buying department is a valuable asset but the combination of accurate sampling, real time analysis, automatic mixing and computer stock and process control is the real key to solving this problem.

Reducing Conditions

Control of reducing conditions is crucial to smooth furnace operation. Precious metal bearing wastes often contain carbonaceous material whose reducing power is difficult to assess. If conditions are too reducing, then the risk is run of either reducing undesirable high melting point elements, such as iron and nickel, to the metallic form with the consequent formation of furnace accretions [6], or accumulating unoxidized carbonaceous matter in the slag with consequent increases in viscosity. (One of the few advantages of a static reverb furnace is its toleration for excess carbon). If conditions are too oxidizing then metal losses to the slag become unacceptable.
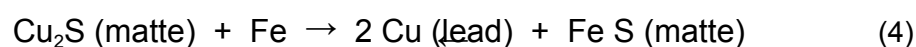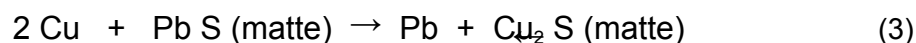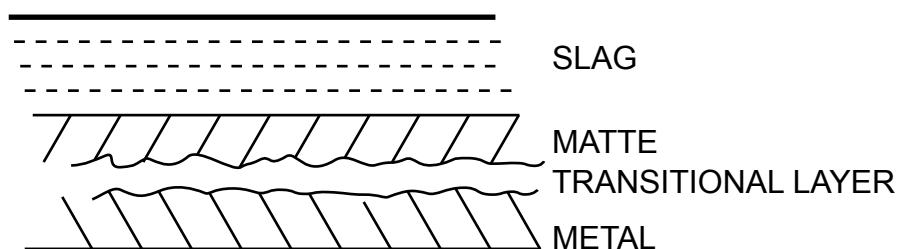
Matte-Metal Separation

The clean separation of metal and matte phases is important both for the control of the precious metal distribution and the contamination of the metal phase with sulfides which could lead to processing problems at subsequent stages. Poor separation takes the form of an imprecise interface between metal and slag phases which appears to be a transitional liquid that is neither metal nor matte (Figure XII). The equilibrium between metal and matte is believed to be controlled by reactions of the type. [14,15]

$$2Cu + PbS(matte) \rightleftarrows Pb + Cu_2S \text{ (matte)} \tag{1}$$

$$Cu_2S(matte) + Fe \rightleftarrows 2 Cu \text{ (metal)} + FeS \text{ (matte)} \tag{2}$$

The equilibria formed by these reactions are very complex, the non-formation of Fe-Pb-Cu-S matte is claimed to be due to low sulfur and oxygen pressures within the furnace. The oxygen pressure can be manipulated within certain limits but whether a sufficiently high sulfur pressure could be attained to promote clean separation without generating an undesirably large volume of matte phase is open to question.

FIGURE XII. Matte - Metal Interface

SLAG

MATTE
TRANSITIONAL LAYER
METAL

$$2 Cu + Pb S \text{ (matte)} \rightarrow Pb + Cu_2 S \text{ (matte)} \tag{3}$$

$$Cu_2S \text{ (matte)} + Fe \rightarrow 2 Cu \text{ (lead)} + Fe S \text{ (matte)} \tag{4}$$

<u>Metal Losses</u>

One of the criteria used in judging the operational success of a smelter is the loss of metal to slag; precious metal smelters are no different. From the meager evidence that is available it appears that dissolved silver and gold and by inference the other precious metals, except perhaps osmium and ruthenium, exist as neutral atoms in slags. [16] This is in addition to the losses in the form of discrete metal droplets. Thus the minimization of slag losses will depend on having:

- a fluid slag,
- high (thermodynamic) activity of the collector phase in the slag,
- formation and agglomeration of metal droplets,
- quiet (non-turbulent) settling conditions.

Slag fluidity has already been discussed. Quiet settling conditions are either inherent in the furnace design or are achieved by the use of a settling forehearth [13,17] and/or adjustments of operating practice. The high activity of the collector phase and the formation/agglomeration of metal droplets are related. The concentration of the collector phase in the slag is usually at least an order of magnitude greater than that of the precious metal(s). Therefore, if the slag can be induced to reject the collector phase, differences in surface free energy will ensure that the greater concentration of collector droplets will then act as agglomeration centers for the precious metal atoms and droplets. This rejection is achieved by adjusting the reducing conditions (oxygen pressure) and ensuring that the slag composition is such that the dissolved collector phase has a high activity, for example as we saw earlier by adding lime to a lead oxide bearing slag. This relationship between low precious metal losses and low collector concentration is well illustrated first by observations on a primary smelter slag where low lead losses equate to low silver losses (Figure XIII) and second, by the very low silver concentrations (<0.005%) achieved after slag cleaning aimed primarily at copper recovery in a secondary copper smelter [13]. The precise assessment of gold platinum group metal losses to slags is problematical because of the low concentrations of these metals in the feedstocks and even lower concentrations in the resulting slags. However, work in the laboratory, particularly in the fire assay field, indicates that low gold and platinum group metal losses are possible (Figure XIV) and appear to be achieved on an industrial scale.

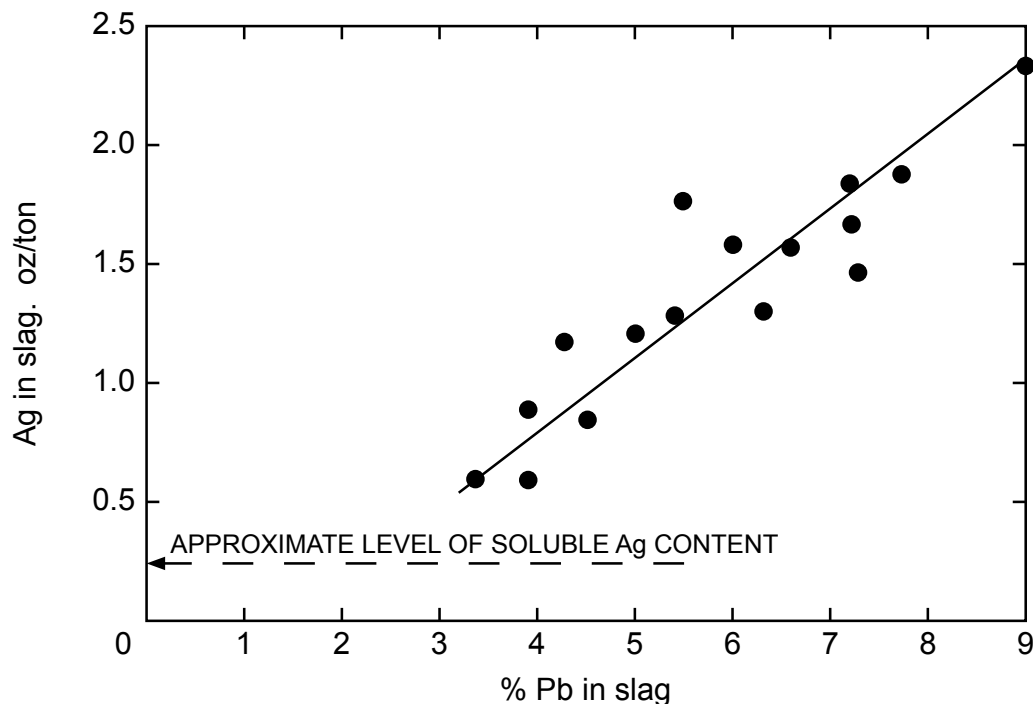**FIGURE XIII.** Relationship between the lead and silver contents of slag. (after Matyas)
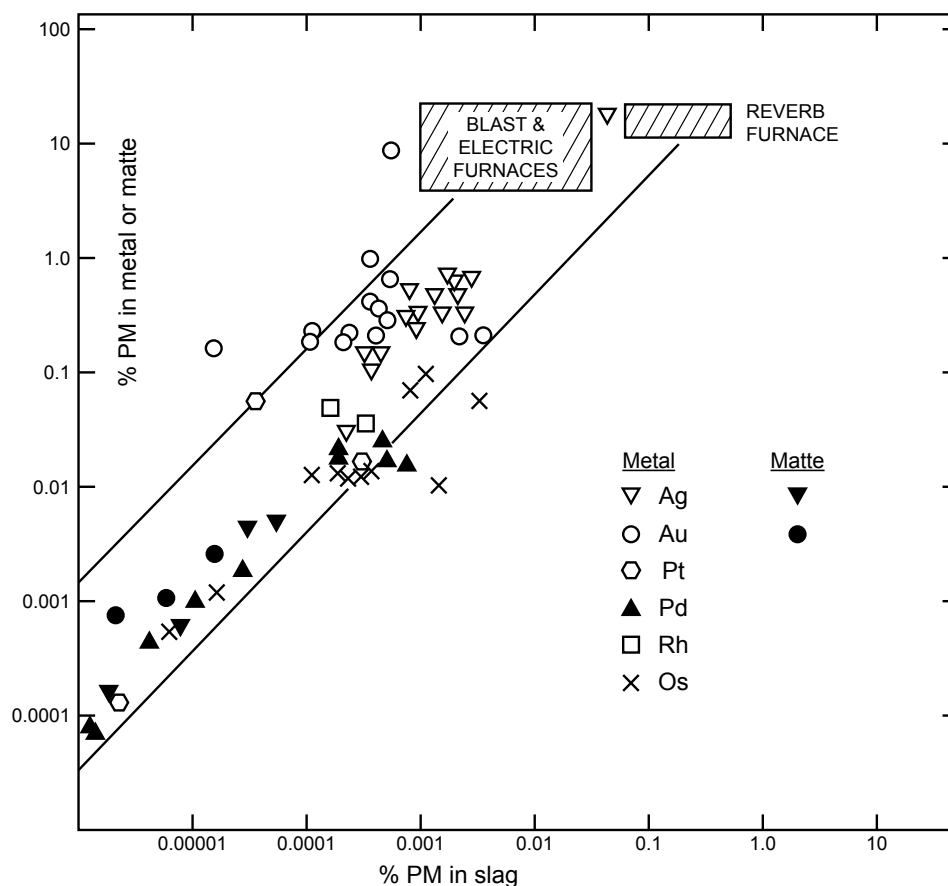
FIGURE XIV. Precious metal distribution between metal or matte and slag (from Ageenkow, Butts, Kershanski, Liddell, Ryan, Tafel, Sinev, and Tseft and Beamish et al.)

Cupellation

Conventional cupellation, where air is blown onto a shallow bath of metal heated by a flame and the resulting litharge manually skimmed off, is a grossly inefficient process. Its limitations and the efforts to remove the limitations have been well described by Attwood.[18] Since this paper was presented, the major development in this area has been the introduction by a European refiners of the top blown rotary converter for cupellation, where the much improved gas/liquid contact also has enabled the cost effective use of oxygen to further improve kinetics and thermal efficiency. The second major drawback to conventional cupellation not entirely solved by improved reactor technology is the loss of platinum group metals particularly osmium and possibly iridium and ruthenium to the litharge when cupellation is taken to its limit of nearly pure silver. This results in a large and unacceptable recirculating load of these metals within the circuit. A practical solution sometimes adopted to avoid this problem is to have a small circuit dedicated to the recovery of platinum group metal rich materials.

Dust and Fume Control

Efficient dust and fume control is nowadays rightly mandatory for pyrometallurgical operations of all kinds. It is particularly rigorous for lead based smelters because of the toxicity of this element, although the provision of adequate control for less toxic dusts is no less onerous and probably similar in cost. A recent design study at Engelhard for a lead based smelter exemplifies the problem (Table III). For every ton of furnace feed almost 200 tons of gas (essentially air) needed to be handled. The actual off-gases from the furnaces comprised only ca. 4% of the total, the hygiene requirements for operating the furnaces comprised a massive 62% while the handling

of solids, that is the furnace feeds and products 34%. In common with other precious metal smelters of this type [19] fabric filters were chosen as the means to reach the particulate emission standards (<10 mg/Nm^3 as lead). Using hard gained in-house experience in this field, the total system was designed with the following in mind:

- Separate hygiene and furnace gas trails. These two trails are basically incompatible because furnace gases are low volume at high temperature and probably acidic; whereas hygiene gases are high volume at low temperature and contain no corrosive components.
- Close control of the inlet gas temperature to the furnace filter.
- Close control of the pressure drop across both filters but particularly the furnace filter-
- Close specifications on air leakage into the filter.
- Insulation and possibly trace heating for the furnace filter.
- An effective method of removing collected dust from the filter hoppers.
- Selection of filters of a design proven to be able to handle metallurgical fume.
- Carrying velocities of 3800-4000 ft/min in the feed preparation and furnace product handling duct systems and 3200-3400 ft/min. for furnace hygiene.
- Careful design of duct runs and hoods and an adequate number of inspection/clean-out ports.

The estimated cost of the pollution control equipment, excluding engineering, was 26% of the total project cost. This compares with the cost of a project for disposing of liquid effluent from an existing aqueous process which was nearly equal to the total cost of the furnace project.

TABLE III: GAS HANDLING REQUIREMENTS FOR A LEAD BASED PM SMELTER

Tons of Gas* Handled per Ton of Furnace Feed

|	Smelting Furnace	Cupellation Furnace	Feed Preparation	Product Handling	Total
Process Gases	5.0	3.1	—	—	8.1
Hygiene Gases	99.5	19.6	31.2	33.8	184.1
					192.2

*essentially air

NEW DEVELOPMENTS

In the opinion of the writer, and has already been indicated, the most significant pyrometallurgical development of recent years in the precious metal refining industry is the application of the oxygen using top blown rotary converter (TBRC). It has already made its mark as a reactor for cupellation and its use as a smelting unit can be foreseen perhaps as a one stage smelting/cupellation unit analogous to the smelting/converting TBRC's in the copper-nickel industry. A small TBRC would be useful for the treatment of the high grade platinum group metal materials referred to as being unsuitable for the larger circuits designed primarily to treat lower grade silver and

gold bearing wastes and ideal for the upgrading of the precious metal alloy from such materials, particularly if the more unusual collector phases such as iron or nickel were used. Indeed, there appears to be a general movement to replace static with rotary furnaces. The short rotary furnace used successfully by the secondary lead industry appears to be particularly well suited to precious metal recovery.[27]

The submerged electrode electric furnace as a replacement for the reverb/blast furnace combination has been pioneered by Engelhard in Europe and is the subject of a paper [6] at this conference. The independence of the electric furnace from fossil fuels, its potentially very high operating temperatures and low volumes of off-gases must extend its application and use.

One of the perennial problems of the precious metals industry is the treatment of cadmium containing silver solders for which Engelhard in the USA has developed a vacuum technique for distilling the cadmium from these alloys. The alloy is inductively melted in a vacuum chamber and maintained at an appropriate temperature and under a moderate vacuum. (Figure XV). The cadmium and some zinc is distilled from the melt and captured in a condenser in the form of a partially agglomerated metal dust. Cadmium levels of 0.1% with silver carry-over of 2-3% are achieved. The essentially cadmium-free silver alloy is suitable for recycling directly to the alloying departments. The cadmium-zinc alloy from the condenser is also suitable for re-use.

FIGURE XV. Distillation of silver - cadmium alloys
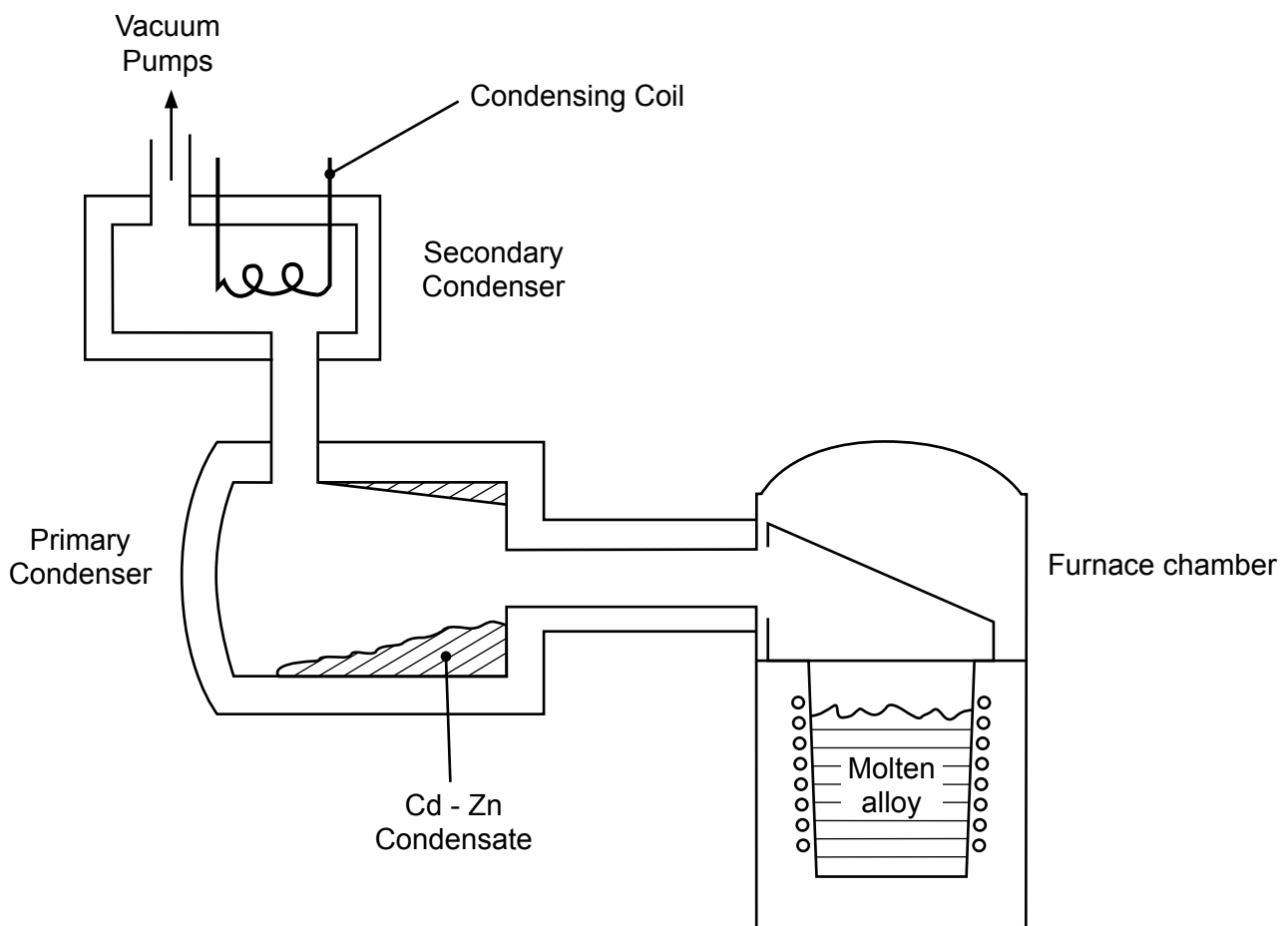
On a more exotic plane plasma systems have been proposed for the direct smelting of alumina based catalysts [21] and platinum group metals concentrates.[22] The high temperatures obtainable with plasma heat sources would, in principle, loosen the restrictions on the liquidus temperatures of slags and collector phase. The engineering of such systems on an industrial scale is a formidable task, though one which is apparently being attempted.[23]

CONCLUSION

The universality of slags as high temperature solvents, the potentially high specific throughputs and the relative ease and moderate cost of pollution abatement have revived interest in pyrometallurgical processes in the secondary precious metal recovery industry. An attempt has been made to show that our understanding of the processes we currently exploit is imperfect and our exploitation of the processes currently available is not extensive. A wider appreciation of the broad spectrum of metallurgical processes plus development work to adapt them to our specific needs is required if we are to meet the challenge of the economic recovery of precious metals in the future.

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