



MARMARA UNIVERSITY  
INSTITUTE FOR GRADUATE STUDIES  
IN PURE AND APPLIED SCIENCES



INVESTIGATION OF PALLADIUM RECOVERY THROUGH CEMENTATION  
FROM SPENT AUTOMATIVE INDUSTRY PLATING SOLUTIONS

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**MASTER THESIS**

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# MARMARA ÜNİVERSİTESİ

## FEN BİLİMLERİ ENSTİTÜSÜ

Marmara Üniversitesi Fen Bilimleri Enstitüsü Yüksek Lisans Öğrencisi Neslinur Çöke'nin "Investigation of palladium recovery through cementation from spent automotive industry plating solutions" başlıklı tez çalışması, 8 Mayıs 2023 tarihinde savunulmuş ve jüri üyeleri tarafından başarılı bulunmuştur.

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### 3. ÖZET

#### **Kullanılmış Otomotiv sektörü kaplama çözeltilerinden sementasyon ile paladyum geri kazanımının araştırılması**

Bu çalışmada, atık kaplama çözeltilerinden paladyum sementasyonunda metalik çinko ve kalay tozlarının kullanımı ve performanslarının karşılaştırılması incelenmiştir. Sementatör – çinko ve kalay miktarı, reaksiyon sıcaklığı ve reaksiyon süresinin paladyum çökmesi (yüzde) üzerindeki etkileri derinlemesine incelenmiştir. Ayrıca, her bir sementatör için paladyum sementasyon kinetiği araştırılmış ve aktivasyon enerjilerinin Zn ve Sn için sırasıyla 4.2 kJ/mol ve 12.6 kJ/mol olarak bulunması reaksiyonun difüzyon kontrollü olduğunu göstermektedir. Kalaydan paladyum geri kazanımı, 200 mg kalay tozu kullanıldığında bile %100'e ulaşmazken, 40 dakikada paladyumun tam sementasyonu için 30 mg çinko yeterliydi. Çinko miktarı 100 mg'a ulaştığında 10 dakikada sementasyon tamamlandı. Ancak paladyumun kalay ile sementasyonu, 1 saat sonunda 200 mg kalay ile %100 değil, sadece %80'in üzerine çıkmıştır.

**Anahtar kelimeler:** Sementasyon, Pd, atık kaplama solüsyonu, geri kazanım.

#### 4. ABSTRACT

##### **Investigation of palladium recovery through cementation from spent automotive industry plating solutions**

The use of metallic zinc and tin powders to cement palladium from waste plating solutions and the comparison of their performance were examined in this study. The effects of cementator –zinc and tin-quantity, reaction temperature, and reaction time on palladium precipitation (percent) were studied in depth. Furthermore, the palladium cementation kinetics were investigated to every different cementator, and it was discovered that the activation energies are 4.2 kJ/mol and 12.6 kJ/mol for Zn and Sn, respectively, indicative of the fact that the reaction is regulated by diffusion. The palladium recovery from tin did not reach 100% even when using 200 mg of tin powder, while 30 mg zinc was enough for the complete cementation of palladium at 40 min. When the quantity of zinc reached to 100 mg, the cementation was completed after 10 min. However, the cementation of palladium by tin did not attain to 100 % but only to over 80 % using 200 mg tin at the end of 1 h.

**Key words:** Cementation, Pd, waste plating solution, recovery.

## 5. SYMBOLS

**C<sub>0</sub>**: Concentration of Pd<sup>2+</sup> in the solution;

**C<sub>t</sub>**: Concentration of Pd<sup>2+</sup> ions in solution after cementation for time t;

**t**: Cementation time (min);

**F**: Faraday constant;

**n**: Number of electrons transferred in the oxidation-reduction reaction;

**E°**: Standard potential of the chemical reaction; K

**e<sub>q</sub>**: Equilibrium constant;

**k**: Rate constant;

**A**: Frequency factor (L mol<sup>-1</sup> s<sup>-1</sup>);

**E<sub>a</sub>**: Activation energy of the reaction (kJ mol<sup>-1</sup>);

**R**: Universal gas constant (8.314 J mol<sup>-1</sup> K<sup>-1</sup>);

**T**: Absolute temperature (K);

**X**: Fraction of cemented palladium

## 6. ABBREVIATIONS

**ppm:** Particles per million

**PGM:** Platinum group metals

**Pt:** Platinum

**Pd:** Palladium

**Rh:** Rhodium

**PGE:** Platinum group elements

**DOC:** Diesel oxidation catalysis

**AAS:** Atomic absorption spectrometer

**DMF:** Dimethyl formamide

**SHE:** Standard hydrogen electrode

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## 1. INTRODUCTION

Platinum group metals (PGMs) have a high economic value PGM has been recognized as important raw materials [1]. The scarcity of PGMs in the earth's crust, their utilization in a variety of using (catalysis and electronics, fuel cells) the difficult replacement of PGMs, as well as the high supply risks associated with them, are factors that make PGMs critical raw materials [2]. On the other hand, today, the reserves of platinum group metals in the world have decreased due to the consumption of high-grade resources (PGM), and in low-grade reserves, the base metal is generally sulfide matrix. The use of these low-grade reserves is not an environmentally viable choice due to the narrow local market for waste sulfuric acid and gas emission regulations. Therefore, hydrometallurgical methods are an alternative to traditional pyrometallurgical deposits, especially for low-grade and palladium-rich deposits [3]. Due to these problems experienced in the supply process of the platinum group elements, it was urgent to increase the benefit gained by converting a material that was previously thought to be disposable, into a renewable resource through recycling processes. In recent years, there has been a breakthrough in research and development for PGM recovery from secondary sources. These secondary sources include spent automotive catalysts, electronics, electronic circuits, electronic scrap, industrial catalysts, spent nuclear fuel, military equipment, jewelry, dental alloys, more recently in cancer treatment and even residues from ore processing plants for deposits containing noble metals [4-7]. As the catalysis is very critical for main industrial applications especially in petrochemistry, Pt, Pd and Rh in the PGM once considered “industrial”, are nowadays taking parts of jewelry and consumer applications. The automotive catalysts affected the demand and mining activities since early 80s. For instance, the increment in the price of Pd in the 90s may be credited to the development of Pd-based catalysts systems and its replacement for the classical European three-way catalytic converters. Similarly, the price of Pt reached to the top of late 20 years in 200, thus caused a drop of the worth of Pd in the markets. Therefore, the main reasons of the fluctuation in the PGM prices may be attributed to several factors such as technological development including catalysis which effect the demand of the PGM, the world-wide supply of the PGM and the production costs [8]. Since 1987, the mostly increasing trend of Pd prices shown in Fig. 1 [9] is the main reason of this current study.

To achieve the goal of “Responsible consumption and production” of the sustainable development [10], the reduction of the use of the natural resources and thus the use of the secondary sources from the recovery to satisfy the increasing demand of PGM, precious and rare earth metals is the key element in this process. Generally, the secondary production of Pd covers the metal recovery of acid leachates [11]. Amongst refinery methods, adsorption, ion exchange, solvent extraction (SX) (also known as liquid-liquid extraction), cementation, evaporation, chemical precipitation, electrochemical and sorption methods have been used to recover PGMs from aqueous solutions over the past few years: [6, 7, 11-14]. Recovery of precious metals from wastewater is also very important for the protection of the environment and the protection of resources [15].



Figure 1. 1 Interactive chart of historical daily palladium prices back to 1987.

The price shown is in U.S. Dollars per troy ounce.

The current price of palladium as of May 04, 2023 is \$1,374.00 per ounce.

The goal of one article was to determine the best parameters necessary for the effective and uncontaminated dissolving of palladium using the least amount of damage to the alumina carrier. When coupled with an oxidizing agent, palladium has the potential to form a wide variety of soluble chloro complexes. These complexes have the ability to speed up the dissolving process. A little amount of hydrogen peroxide might considerably increase palladium dissolving in weak hydrochloric acid while keeping the alumina support untouched. Leaching with a solution containing 5% H<sub>2</sub>O<sub>2</sub> and 7% HCl at 60°C for 2 hours with a liquid/solid ratio of 10/1 resulted in complete palladium dissolution. The leach fluid contained 0.5 percent aluminum and 0.04 percent palladium, with a pure aluminum-rich residue in the filtered solids. By reducing the leach fluid with formic acid, palladium might be extracted. The efficiency of palladium reduction was improved by heating the solution, it resulted in palladium particles that were big enough to be filtered out individually. Palladium powder with a purity of 98 percent and a recovery efficiency of >99% was created. [16].

Palladium-catalyzed C-C or C-heteroatom bonding in organic synthesis is a widely used method in both academic study and industrial production, according to another article. The recent decade has seen an increase in the usage of palladium catalysts for fine chemical, pharmaceutical intermediate and active ingredient synthesis. It is imperative to find cost-effective ways to remove palladium impurities from the final product because of the problem of residual palladium. The shortage of palladium necessitates the need for a cost-effective recovery technology. Palladium was recovered from an aqueous sodium bisulfite solution at high temperature in the form of a sodium palladium tetra sulfite dihydrate complex, Na<sub>6</sub>Pd(SO<sub>3</sub>)<sub>4</sub>·2H<sub>2</sub>O [17].

The extraction of Pt<sup>4+</sup> and Pd<sup>2+</sup> using LIX 84 I in HCl medium was studied in one of the studies based on the solvent extraction. LIX 84 I was successful for Pt<sup>2+</sup> in HCl medium. However, for Pt<sup>4+</sup> extraction, the ammoniacal solutions-based media showed much more efficiency [18].

The financial aspect of the precious metals recovery present in exhausted diesel oxidation catalysis (DOC) is very critical as the world is driven on automobiles. As the diesel-driven vehicles have been preferred by the drivers worldwide for decades, a huge amount of waste

diesel oxidation catalyst containing Pd and Pt (about 0.1 % of total) needed to be recycled. In one study, the exhausted DOC was leached by hydrochloric acid, then Pt and Pd present in the structure were selectively precipitated using ammonium chloride forming  $(\text{NH}_4)_2\text{PtCl}_6$  and  $(\text{NH}_4)_2\text{PdCl}_6$ , respectively [19].

In another study, palladium was deposited in a magnesium disk using Mg powder from 0.01 M  $\text{PdCl}_2$  in DMF solution at 323-333K. High adhesion of nano- and micro- Pd particles on the magnesium surface was determined [20].

In one study, Pd values were recovered from the spent catalysts, firstly by leaching with a mixture of hydrochloric acid and hydrogen peroxide at about 90°C for 3 h, then by precipitation using sodium borohydride solution of concentration of 10 % at 100°C at optimal conditions from  $\text{H}_2\text{PdCl}_4$  precursors [21].

In a more recent study, as a more environmentally friendly and effective approach of Pd recovery was employed by adsorption on dry hydrated alumina (alumina hydroxide). It was found that the maximum adsorption capacity of HA was 2.19 mg  $\text{Pd}^{2+}$  per gram of adsorbent metal [22]

Cementation is the process of removing metals from a solution based on the electrochemical reaction between the cementing metal and the precipitated metal ion [23].

In another study, the samples of commercial petroleum catalysts containing 0.45 mass % Pt, 0.24 mass % Pt and 0.25 mass % Pd, respectively were primarily dissolved using the sulfuric acid solutions of 6.0 M at 100°C for 2-4 h for Pt and of 8.0 M at 100°C for 18 h, then cemented using Al powder of 53-104  $\mu\text{m}$  [24].

In literature several studies associated with the cementation of noble metals by different cementators such as zinc powder was used to aid in the cementation of Rh from used washing solutions [25], recovery of Ru using zinc metal in the presence of accelerator [26], or the cementation of silver from radiographic films using iron and zinc [27] are found. Rh-containing waste washing water can be recovered in an efficiency range of more than 99% if excessive levels of zinc are used, as free acid consumes zinc and Rh forms a chemical complex [25]. The recovery of Ru ions present in the spent plating baths is very important

due to the market value of this metal which is currently higher than Pt in 2022. In this recent study [26], the cementation of the Ru by zinc was investigated taking account of several parameters such as amount of cementator metal, time, temperature, agitation and the addition of NaCl in the sulfuric acid medium. The recovery of Ru with a yield of more than 99 % was attained. In another study [27], the silver present in the waste radiographic films is recovered via a chemical process comprised of the dissolution of the films by nitric acid, then the cementation with iron and zinc separately in just one step comparing to the precipitation by sodium hydroxide. Electronical wastes including printed circuit boards, contain not only copper but also precious metals such silver, gold and palladium as an urban mining resource. In one study in order to extract these metals, some leaching steps were applied to dissolve firstly copper and some of silver using oxidative sulfuric acid (1.2-2 M at 80°C, adding Fe<sup>3+</sup>, O<sub>2</sub> and H<sub>2</sub>O<sub>2</sub> as oxidizing agents), then Pd and Cu using oxidative chloride solution (NaCl of 2 M, HCl of 1.4 and 2 M adding HNO<sub>3</sub> and H<sub>2</sub>O<sub>2</sub> as oxidizing agents) followed by cyanidation (cyanide solution of 0.1 M stabilized pH at 9-11 at 20°C using O<sub>2</sub> as oxidizing agent) to recover Au, Ag, Pd, and Cu. In place of cyanidation as an option, an investigation of the thiourea solution was carried out, however the results were disappointing. The cementation process was performed at 60°C in sulfuric acid solution at 1 h for Cu and 30 min for Al and Zn. For chloride leaching solution, the treatment was performed at 70°C for 30 min with Cu and Al powder. The yield of cementation was above 98 % in case of Al and the adding increasing amount of Al did not affect the efficiency of the process [28].

In some other studies [29-30], the leaching solutions of the waste of printed circuit boards are rich in some precious and critical raw materials. In case of sulfuric acid usage in the leaching process of these boards, the dissolution of some precious metals including silver was feasible. Following the leaching with sulfuric acid, the cementation of silver by metallic Cu, Al and zinc was applied in one study [29]. The concentration of silver of the synthetic leaching solution was 20 mg/L as the WPCB sample was analyzed to contain 694 g/t of silver. The most promising and the effective cementation yield was obtained using zinc. Another work of the same group [30] on the downstream processing of WPCB chloride leach solutions for recovery of base and precious metals was carried out using a chemical reaction involving adsorption and precipitation. The tests used a man-made leach solution resembling

the chemical make-up of the expectant leach solution acquired in the first investigation (1 M HCl, 116.5 g/L Cl<sup>-</sup>, 30 g/L Cu<sup>2+</sup>, 2.5 g/L Fe<sup>3+</sup>, 5 mg/L Au<sup>3+</sup>, 10 mg/L Ag<sup>+</sup>, and 20 mg/L Pd<sup>2+</sup>). The leach solution was first initially exposed activated carbon (AC) adsorption (20 g/L AC, 80°C), where gold was preferentially recovered over silver and palladium, achieving 88 percent Au recovery at 0.5 h (92 % at 3.5 h) compared to only 3-6 % for Ag/Pd. Metallic copper was added to the gold-barren solution after the adsorption and filtering stages to allow Cu<sup>2+</sup> to be reduced to Cu<sup>+</sup> and Pd to be cemented on metallic copper. 93 % of the Pd was recovered throughout the mixing period (1 hour), however only 1.4 % of silver was cemented onto metallic copper.

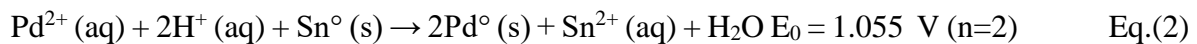
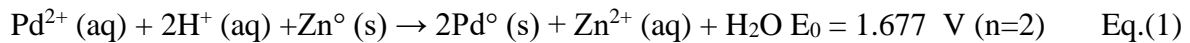
Another investigation looked at the Merrill–Crowe cementation process, specifically high temperature eluates from carbon adsorption and desorption operations to see how well it worked for simultaneously extracting platinum, palladium, and gold from cyanide solutions using this approach. As well as the Merrill–Crowe method, platinum and palladium recovery in the presence of gold, copper and nickel is also mentioned. Optimal experimental circumstances at 60°C resulted in a solution with 150 ppm free cyanide, a reaction time of 90 minutes, 175 ppm base metal, and 880 ppm precious metal in it. There were 91, 54, and 19 % cementation yields at these circumstances for Au, Pd, and Pt. Under industrial-like conditions, we added 1.5 times the stoichiometric amount of Zn to the low-level cementation mixture and 0.68 times less to the high-level cementation mixture to track the competitive characteristics of cementation over time. No matter how much zinc powder (0.15 g Zn) was added to the mono ionic Pd and Pt solutions, their cementation failed to complete, resulting in just 48% and 36% of the Pd and Pt being dissolved, respectively [31].

Pd (II) ions in plating solutions used in the automotive plastics industry by metallic zinc and tin are being investigated for their influence on recovery conditions in this study. Conventional oxidation/reduction potentials for Zn, Sn, and Pd are tabulated in Table 1.1.

Table 1. 1 The standard oxidation / reduction potentials of zinc, tin, and palladium

Redox Half Reaction	Potential vs. Standard hydrogen electrode (SHE), E°(V)
$Zn^{\circ} \rightarrow Zn^{2+} + 2e^{-}$	+ 0.762
$Sn^{\circ} \rightarrow Sn^{2+} + 2e^{-}$	+ 0.14
$Pd^{2+} + 2e^{-} \rightarrow Pd^{\circ}$	+ 0.915

Sn has a potential difference of 1.055 V, while Zn has a difference of 1.677 V [32]. Zinc and tin, on the other hand, might cement palladium out of the solution. As a result, the cathodic process reduces Pd ions.  $E_0$  (reduction) –  $E_0$  (oxidation) is used to compute the cell potentials of reactions. General reactions were given in Eq. (1) and (2):



Thus,

At equilibrium,  $E = 0$  and  $Q = K_{eq}$ . By applying  $T=298.15 \text{ K}$ ,  $R=8.314 \text{ J/mol.K}$ , and ln-log conversion, the following is obtained:

$$E^{\circ} = (0.0592/n)\log K_{eq}$$

**For Eq. 1:**

$$1.677 = 0.0592/2 \log [Zn]/[Pd][H]^2$$

$$-56.66 = \log [PdO][H]^2/[Zn] = \log [PdO]/[Zn] - 2pH$$

If the pH and molarity of ZnI are considered to be 1, the Pd concentration of the solution is calculated as [Pd], resulting in  $10^{-56.66}$ , which is practically zero.

**For Eq. 2:**

$$1.055 = 0.0592/2 \log [\text{Sn}]/[\text{PdO}][\text{H}]^2$$

$$-35.64 = \log [\text{Pd}][\text{H}]^2/[\text{Sn}] = \log [\text{PdO}]/[\text{Sn}] - 2\text{pH}$$

If the pH and molarity of SnI are considered to be 1, the Pd concentration of the solution is calculated as [Pd], resulting in  $10^{-35.64}$ , which is also practically zero.

$$\Delta G^\circ = -nFE^\circ \quad (3)$$

According to equation 4, all reactions have a negative standard free energy change (-323.61 kJ/mol for Eq. 1 and -203.58 kJ/mol for Eq. 2). The number of transported electrons is n, and the Faraday constant is F (96,485 C/mol e<sup>-</sup>). This indicates that under normal circumstances, all reactions are spontaneous.

The Nernst equation can be used to determine the concentration of Pd in the solution once the cementation process has been completed:

$$E = E^\circ - (RT/nF) \ln Q \quad (4)$$

Palladium cementation reactions described in Eqs. 1-2 clearly proceed in the direction suggested by these values, making a reversible process virtually implausible (33). Adding cementator to an acidic solution containing metal ions can diminish the metal's thermodynamic reduction potential. This is the case with palladium. Pd<sup>2+</sup> ions are neutralized and precipitate as a result of the difference in standard electrode potentials between palladium and cementator. Having a low concentration ratio indicates that the solution has an extremely low concentration of palladium. It is therefore possible to extract palladium using zinc or tin powders [34].

The aim of this study is to examine the cementation performance of zinc and tin for Pd recovery, moreover, to define the thermodynamic parameters of activation by temperature-controlled shaking. In order to attain these goals, the cementation processes using different amounts of zinc and tin and, at different temperatures and durations were performed.

## 2. MATERIALS AND METHODS

### 2.1 Preparation of the Solution

The plating waste solution from the automobile industry, which contains palladium (II) chloride and a dispersion reagent, is chosen as the initial solution. First of all, the dispersant present in the solution is removed using hydrogen peroxide. By the atomic absorption spectrometer, the palladium content was found to be 634 ppm after being measured using an Analytic Jena Atomic Absorption Spectrophotometer and for the experimental studies three stock solutions Pd (II) with a pH of 0.87 as initial solution. Distilled water is used for the wet chemical analyses. Metallic zinc and tin powders of analytical grade is used for the cementation process. Fig 2.1. shows that spent automotive industry plating solutions.



Figure 2. 1. Spent automotive industry plating solutions

## 2.2.Process Design for Experiments

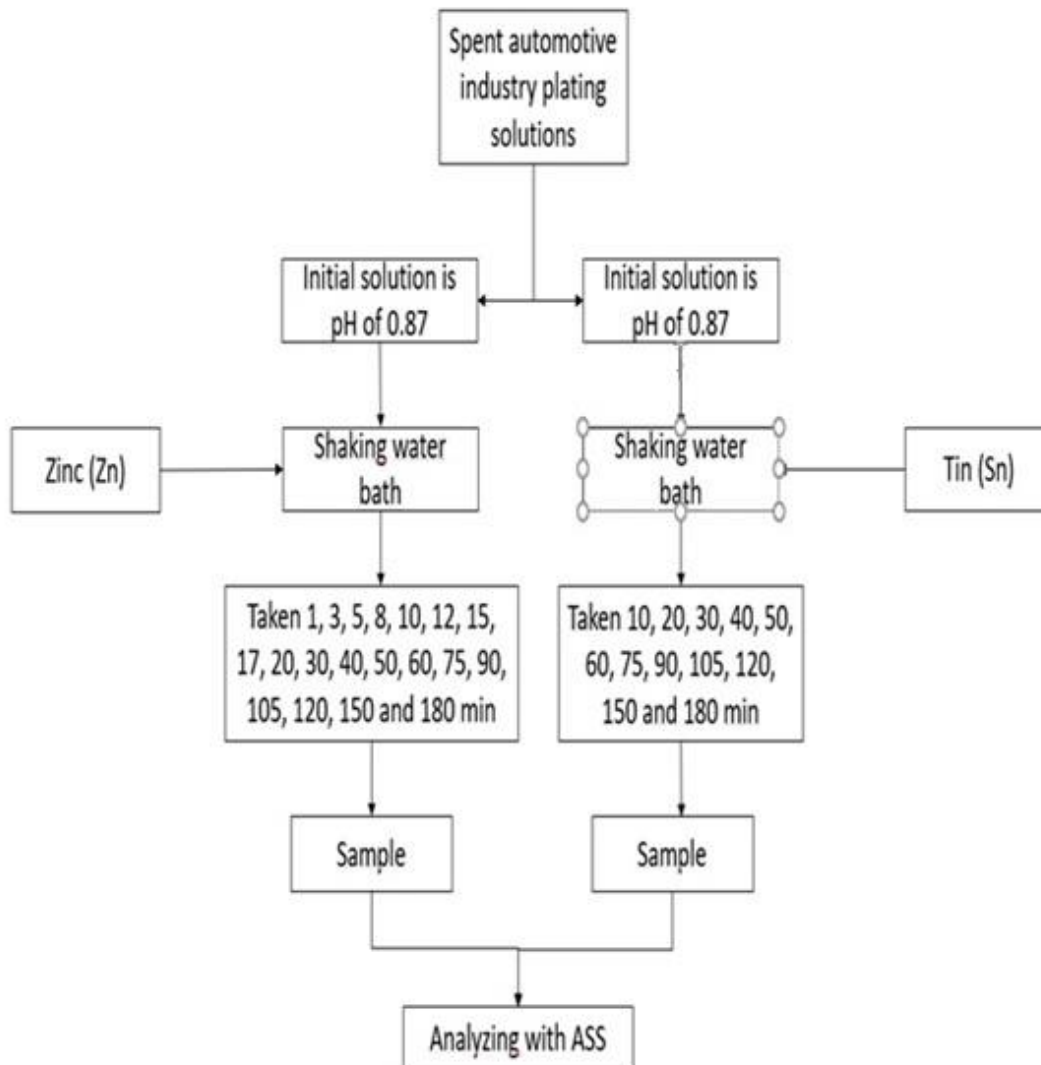


Figure 2. 2. The flow chart of the experimental procedure

Figure 2.2 depicts the study's flowsheet in all of its stages. All weighing procedures were performed using laboratory precision analytical balances in order to guarantee the correctness and dependability of the results.

### 2.2.1. Experimental Procedure

Palladium (II) chloride waste solution obtained following plating process in the automotive industry containing dispersant reagent was selected as the starting solution. First of all, the dispersant present in the solution was removed using hydrogen peroxide. By the atomic absorption spectrometer, By the atomic absorption spectrometer, the palladium content was found to be 634 ppm after being measured using an Analytic Jena Atomic Absorption Spectrophotometer and a stock solution of Pd (II) with 0.87 pH as initial solution for the experimental studies was prepared. Fig 2.3. shows that initial solution is pH of 0.87. The composition of the starting Pd (II) solution is given in Table 2.1. For the wet chemical analyses, distilled water was used. Metallic zinc powder (particle size 45  $\mu\text{m}$ ; Emsure®, CAS No: 7440-66-6, Merck) and tin powders (powder, 45  $\mu\text{m}$  particle size, 99.8 % trace metals basis; CAS No:7440-31-5, Merck) were used for analysis.

In this experiment, only high-quality, analytical substances were employed. Optimizations were made to the cementation parameters of time, temperature, and the amount of metallic powders of zinc and tin used. Solution pH was measured using a HANNA wireless pH electrode with HI2002-01edge® Dedicated pH/ORP Meter. The TSB-28C Shaking Water Bath was utilized to provide the necessary shaking. The Shaking Water Bath is depicted in Fig. 2.4. After each cementation trial, we used filter paper to separate the solids from the liquids (Blue band, Sartorius). After cementation, the AAS Analytic Jena Atomic Absorption Spectrophotometer detects the concentration of zinc and tin ions in the solution.

This atomic absorption spectrometer is depicted in Fig. 2.5.



Figure 2. 3. Initial solution is pH of 0.87



Figure 2. 4. Shaking Water Bath



Figure 2. 5. The atomic absorption spectrometer (Analytic Jena)

The Pd ions in the solution were precipitated using zinc and tin metallic powders at concentrations that were stoichiometric multiples of the amount of palladium used in each experiment. Each time, zinc/tin powder was added to increase the amount of a 7 mL stock Pd solution to a 15 mL centrifuge tube. The precision analytical balance used in the lab is displayed in Fig. 2.6. 7 mL of stock Pd solution and zinc/tin powder were added to a 15 mL centrifuge tube, as shown in Fig. 2.7. (falcon tube). The experimental study was executed using a temperature-controlled water bath for the purposes of temperature control, uniform temperature distribution, and uniform heat convection. The centrifuge tube is seen in a shaking water bath in Fig. 2.8. Study design details are presented in Table 2.2. This process was carried out three times, one with each possible arbitration specimen.



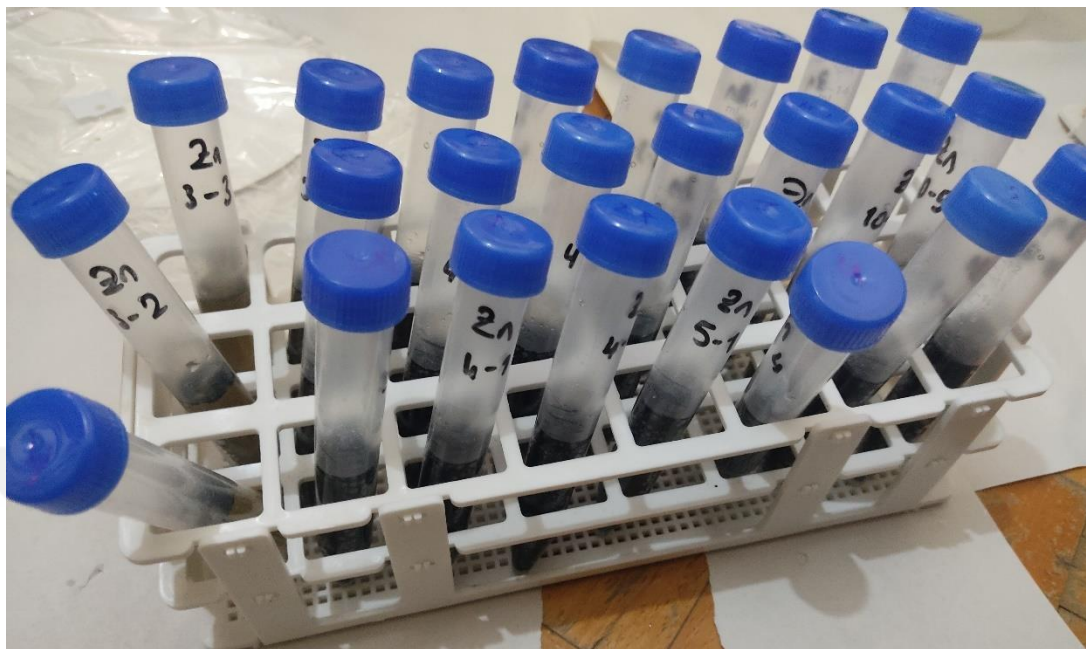
Figure 2. 6. Laboratory Precision Analytical Balance

Table 2. 1. The composition of the starting Pd (II) solution

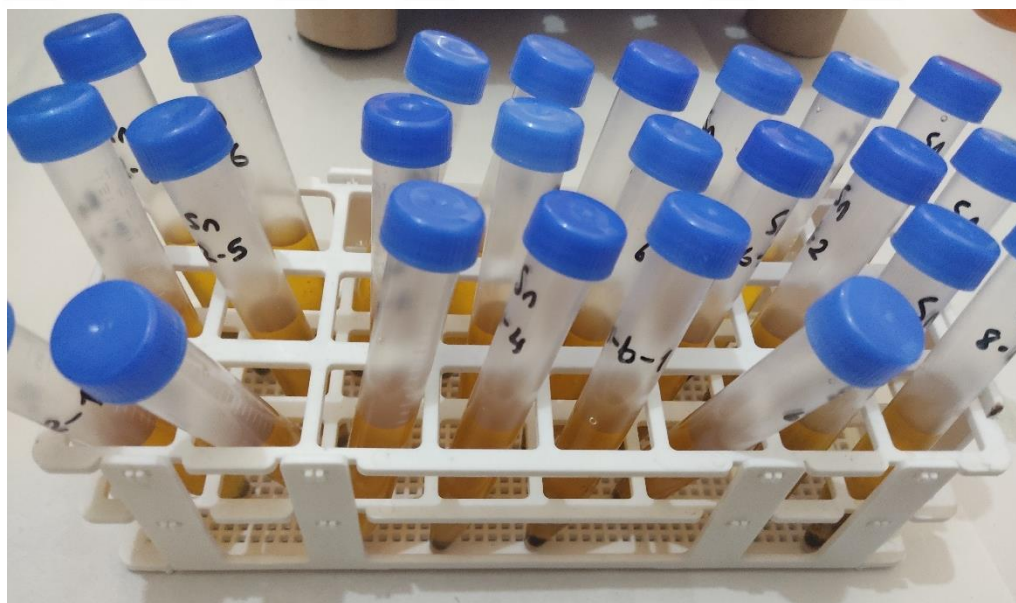
Element	Concentration (ppm)
Pd	634
Sn	3.84
Zn	7.31

Table 2. 2. Experimental conditions.

Parameters	Type of cementators	Ranges
	Zinc	10-100 mg
	Tin	20-200 mg
Temperature		25-55°C
Time		1-180 min

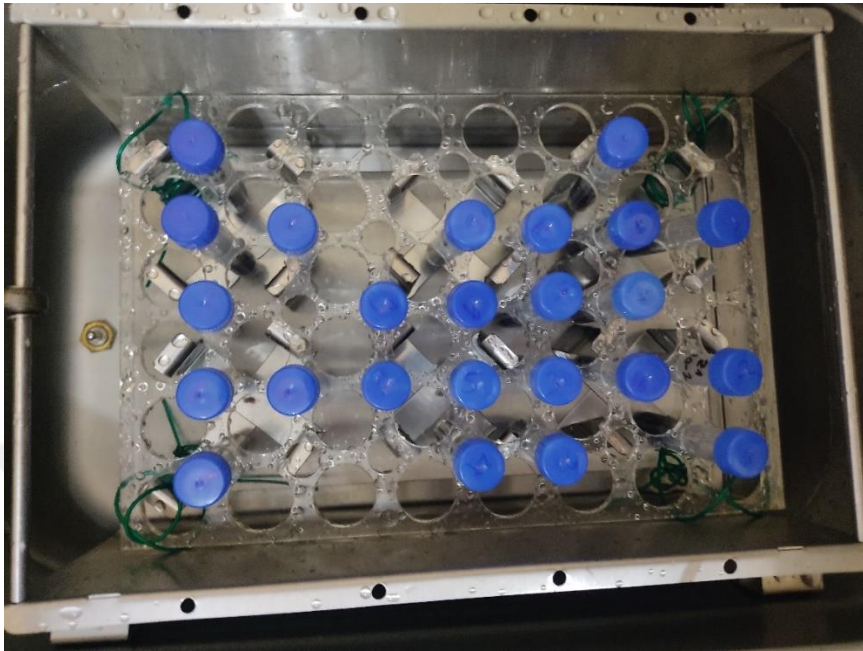


(a)

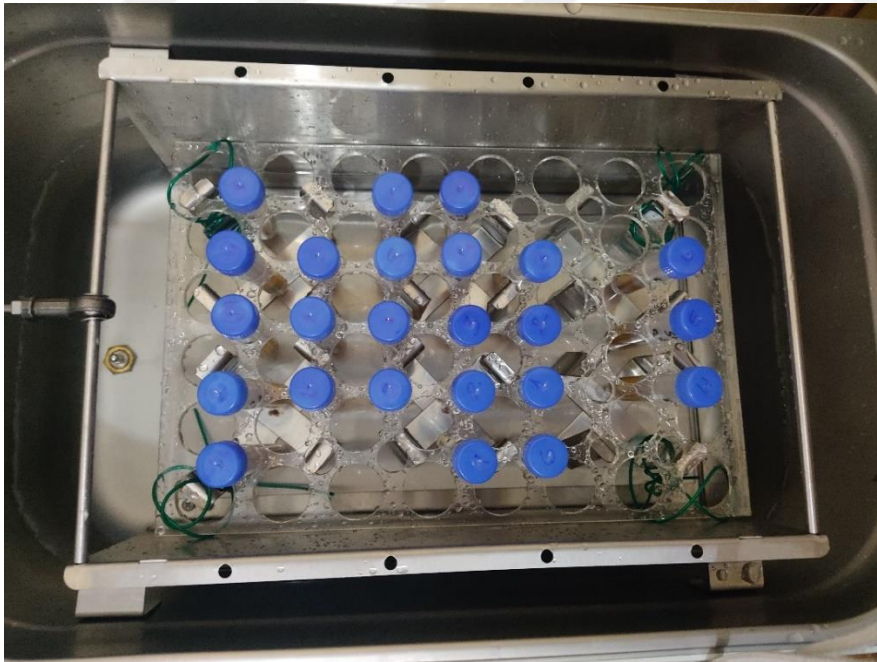


(b)

Figure 2. 7. 7 mL of stock Pd solution and zinc/tin powder were added in 15 mL volume centrifuge tube. (a) zinc and (b) tin



(a)



(b)

Figure 2. 8. Centrifuge tube in shaking water bath. (a) zinc and (b) tin

In order to remove any lingering cementator, Pd powder was subjected to a treatment that included 0.1 M HCl with a pH of 0.87, distilled water, and acetone. In order to get rid of any remaining cementator, this was done. After being mixed into a powder form, the ingredients were dried in a vacuum oven at 80°C for an hour. Finally, the fine powder was loaded into the instrument's receptacle. Figure 2.9 depicts the steps involved in getting ready for character analysis. Scanning electron microscopy with energy-dispersive X-ray analysis (SEM-EDX) and secondary-element X-ray spectroscopy (SEM-EDS) was.

The following formula was used to calculate palladium's cementation % during the process:

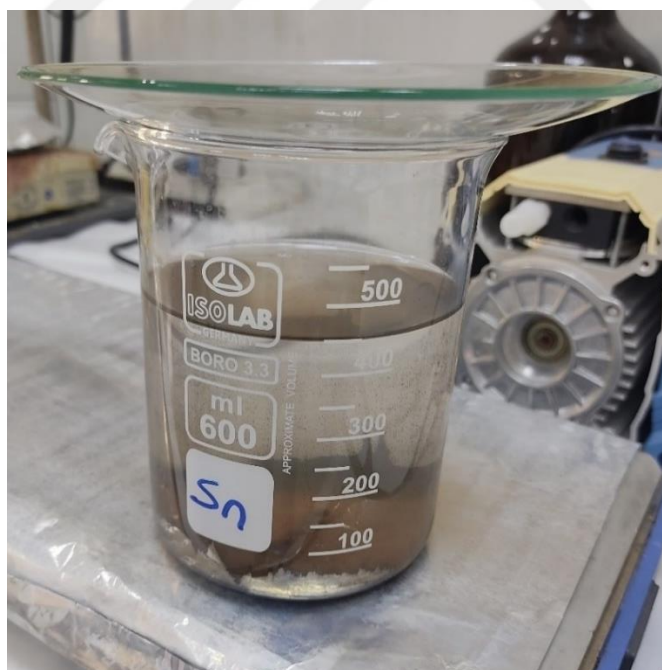
$$\text{Cementation (\%)} = \left( \frac{[\text{Pd}^{2+}]_o - [\text{Pd}^{2+}]_f}{[\text{Pd}^{2+}]_o} \right) \times 100 \quad (5)$$

where  $[\text{Pd}^{2+}]_o$  is the palladium concentration at the start of the experiment (634 ppm) and  $[\text{Pd}^{2+}]_f$  is the palladium concentration at the end of the experiment (in ppm).

A kinetic investigation was carried out so that the behavior of palladium cementation from the waste solution could be investigated.



(a)



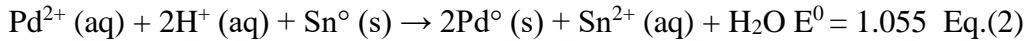
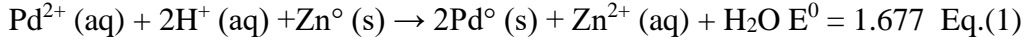
(b)

Figure 2. 9. Preparing to characterization analyzes. (a) zinc and (b) tin

### 3. RESULTS AND DISCUSSION

#### 3.1. Effect of Cementator Quantity and Type

When the Nernst equation is applied to a basic electrochemical cell like the Pd/Zn or Pd/Sn cell, how the cell voltage changes as the reaction occurs and as the concentrations of the dissolved ions change may be seen [35]



Thus  $Q = [\text{Zn}^{2+}]/[\text{Pd}^{2+}]$  is the reaction quotient. Assume that the cell has 1.0 M  $\text{Pd}^{2+}$  and  $1.0 \times 10^{-3}$  M  $\text{Zn}^{2+}$  in it at the beginning. Eq. 3 can then be used to determine the cell's starting voltage.

Similarly, for the case of  $\text{Zn}^{2+}$ ;

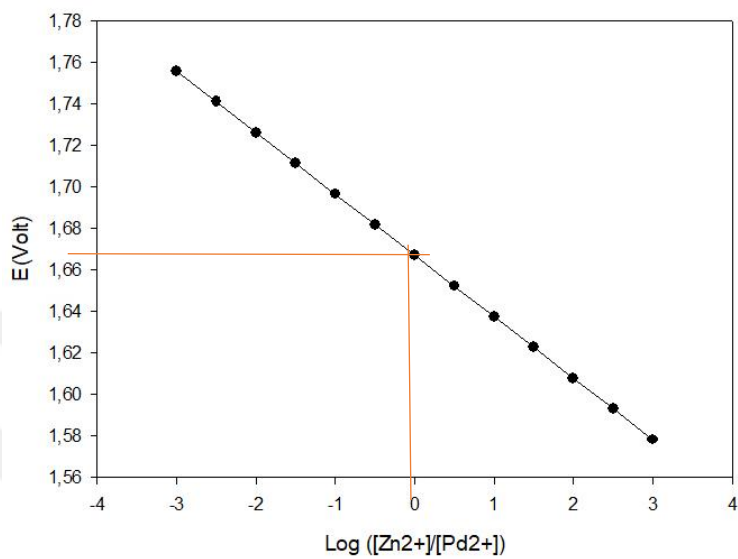
$$\begin{aligned} E_{\text{cell}} &= E_{\text{cell}}^{\circ} - \left( \frac{0.0591 \text{ V}}{n} \right) \log \frac{[\text{Zn}^{2+}]}{[\text{Pd}^{2+}]} && \text{Eq. (3)} \\ &= 1.677 - \left( \frac{0.0591 \text{ V}}{2} \right) \log \frac{1 \times 10^{-3}}{1.0} = 1.77 \text{ V} \end{aligned}$$

Similarly, for the case of  $\text{Sn}^{2+}$ ;

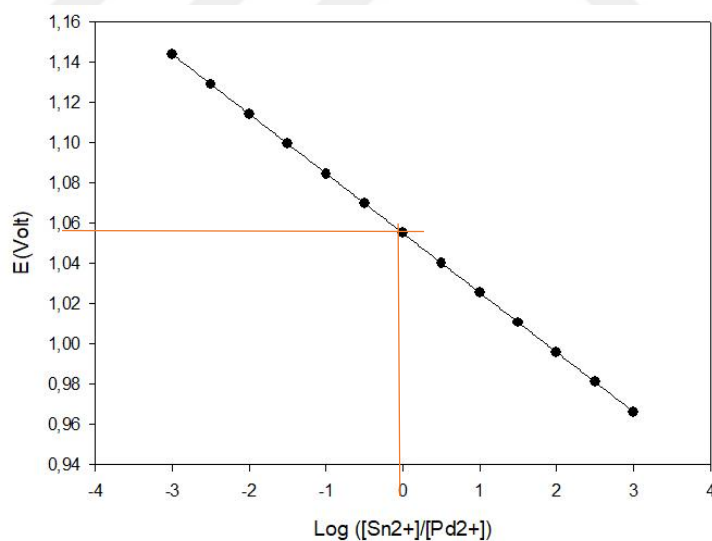
$$\begin{aligned} E_{\text{cell}} &= E_{\text{cell}}^{\circ} - \left( \frac{0.0591 \text{ V}}{n} \right) \log \frac{[\text{Sn}^{2+}]}{[\text{Pd}^{2+}]} && \text{Eq. (4)} \\ &= 1.055 - \left( \frac{0.0591 \text{ V}}{2} \right) \log \frac{1 \times 10^{-3}}{1.0} = 1.144 \text{ V} \end{aligned}$$

As a result, the starting voltage is higher than  $E^{\circ}$ , due to reaction quotient (Q). There is an increase in  $[\text{Sn}^{2+}]$  or  $[\text{Zn}^{2+}]$  in the solution due to dissolution of the tin or zinc metal powders, whereas the  $[\text{Pd}^{2+}]$  concentration drops in the solution due to cementation reaction. Since the ratio of  $\text{Sn}^{2+}/\text{Pd}^{2+}$  or  $\text{Zn}^{2+}/\text{Pd}^{2+}$  is continually increasing, the cell voltage is steadily decreasing during this process. When  $[\text{Sn}^{2+}]$  or  $[\text{Zn}^{2+}]$  equals  $[\text{Pd}^{2+}]$ , then  $Q = 1$  and  $E_{\text{cell}} = E_{\text{cell}}^{\circ}$ . Beyond this point,  $[\text{Al}^{3+}]$  or  $[\text{Zn}^{2+}]$  in the solution will continue to rise –i.e. to dissolve in the solution–, whereas  $[\text{Pd}^{2+}]$  in the solution will continue to fall. As a result, the value of Q will continue to rise, resulting in a further drop in  $E_{\text{cell}}$ . The cell potential drops to 1.58 V when the amounts of  $\text{Zn}^{2+}$  and  $\text{Sn}^{2+}$  (and 0.97 V the amounts of  $\text{Sn}^{2+}$  and  $\text{Pd}^{2+}$ ) as the concentration of the

cementator and cementated metal in the solution are reversed (i.e., 1.0 M  $Zn^{2+}$  and  $10^{-3}$  M  $Pd^{2+}$ ). Fig. 3.1 shows theoretical E values based on log molar ratios.



(a)



(b)

Figure 3. 1. Calculated values of E as a logarithmic function of the molar ratio. a) Zn (b) Sn

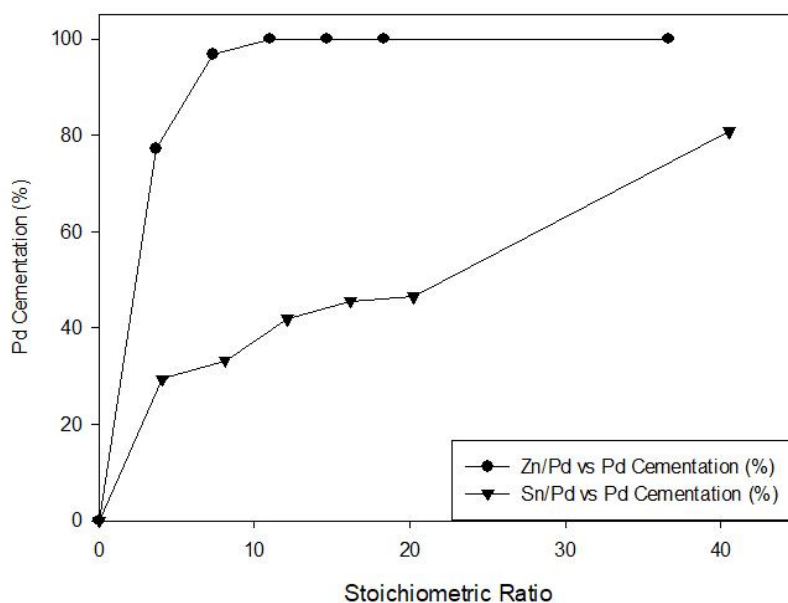
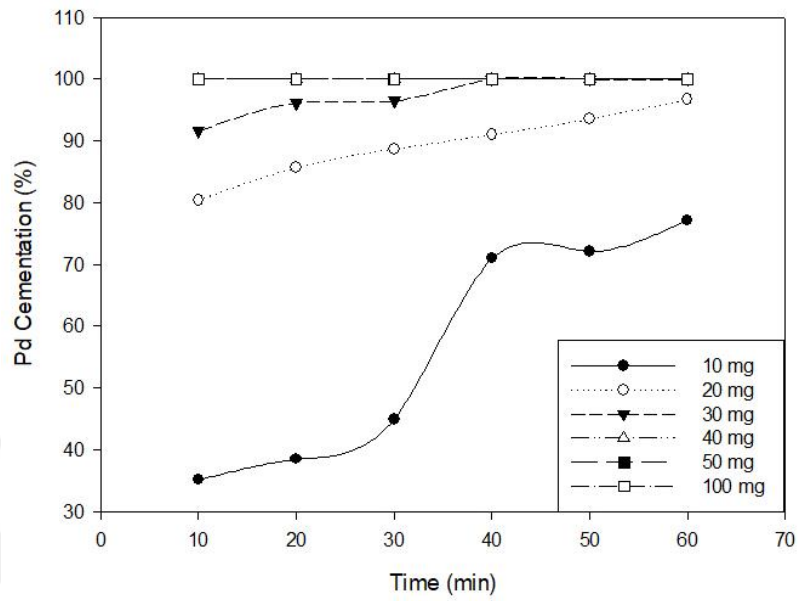


Figure 3. 2. Changes in palladium cementation (percent) (a) with Zn/Pd stoichiometry (25 °C, 200 rpm, 1 h and 7 mL of 634 ppm Pd<sup>2+</sup>). (b) with the stoichiometric ratio of Sn/Pd (25 °C, 200 rpm, 1 h and 7 mL of 634 ppm Pd<sup>2+</sup>).

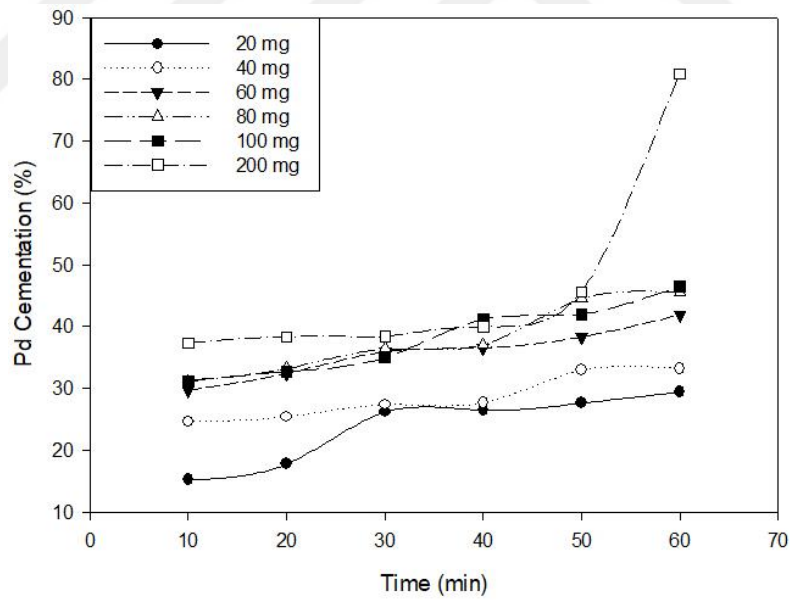
The influence of the type of cementator and the amount of palladium recovered were studied. Experiments were conducted using 634 ppm Pd<sup>2+</sup> with 200 rpm stirring for 1 h at 25°C in a temperature-controlled environment. Palladium recovery (in percentage) varies with cementator type and quantity, as seen in Figures 3.1-3. Palladium can be recovered from both metal powders, as illustrated in the image.

The amount of palladium recovered varies changing according to the type and amount of cementator. The palladium recovery from tin did not reach 100% even when using 200 mg of tin powder, while 30 mg zinc was observed to be enough for the complete cementation of palladium after 40 min. When the quantity of zinc reached to 100 mg, the cementation was completed at 10 min. However, the cementation of palladium by tin did not attain to 100 % but only to over 80 % using 200 mg tin at the end of 1 h.

A greater rate of metallic palladium recovery was attained by increasing the surface area during contact through an increase in the proportion of active metal, zinc, and tin present in each Pd<sup>2+</sup> ion. [25-27].



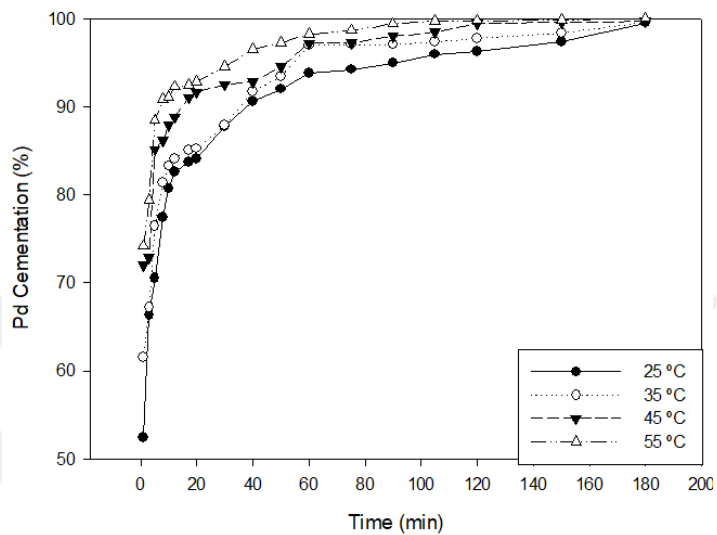
(a)



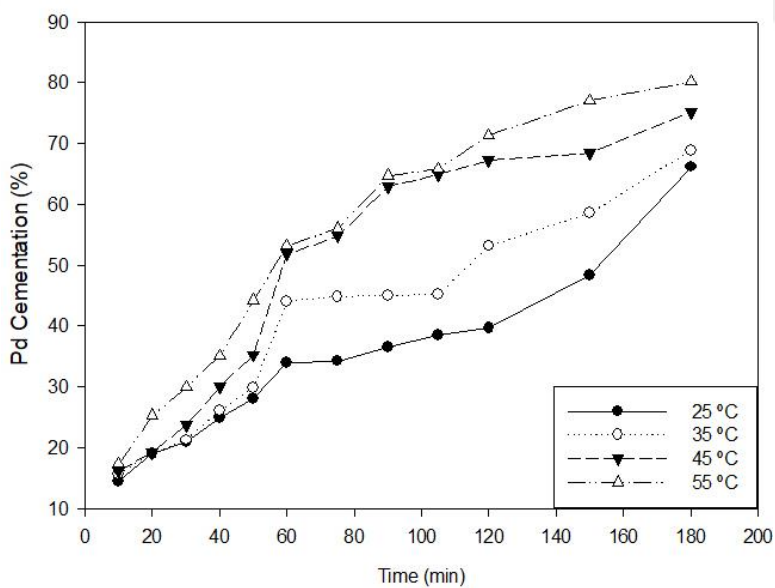
(b)

Figure 3.3. Variation in solution palladium cementation (%) over time (25 °C, 200 rpm, 7 mL of 634 ppm Pd<sup>2+</sup>). (a) Zn (b) Sn

### 3.2. Effects of Temperature and Time



(a)



(b)

Figure 3. 4. Changes in palladium cementation (percent) with time and temperature for 180 min (a) Zn (20 mg zinc, 200 rpm, 7 mL of 634 ppm Pd<sup>2+</sup>). (b) Sn (100 mg tin, 200 rpm, 7 mL of 634 ppm Pd<sup>2+</sup>).

Using 7 mL of Pd<sup>2+</sup> at 634 ppm and 20 mg Zn and 100 mg Sn for 180 minutes at 200 rpm at a variety of temperatures (25°C, 35°C, 45°C, and 55°C), the impacts of time and temperature were investigated through a series of experiments. Like in previous studies [25-27], the temperature and duration had a significant effect in cementation, as can be seen in Figures 3.4, and 3.5. The reaction between palladium ions and the active metal particles happened due of the increment in temperature. When the temperature was adjusted from 25°C to 55°C, palladium recovery improved considerably. Over 50% efficiency was achieved using zinc particles in just 1 minute at 25°C, whereas at 55°C, efficiency was already about 75%. Over 90% zinc efficiency was reached after 120 minutes of operation. However, even at the end of 180 min, the maximum efficiency in the case of tin was only about 80 % at 55°C, and the minimum yield was only 60 % at 25°C, thus an approximately 33% improvement in palladium recovery by cementation was observed.

### 3.3.Cementation Kinetics

The integrated rate law can be used to calculate the kinetic model from the reaction order. These values were obtained by extrapolating from Figures 3.6. and 3.7, which show the cementation kinetics of the Pd cementation process employing Zn and Sn. Several kinetic models and equations –from one dimensional to Erofeev equations- are studied.

In this case, the palladium cementation results were best explained by the one-dimensional diffusion of zinc and tin (Fig. 3.7). The strong coefficient of correlation found when fitting experimental data suggests that the process is diffusion-controlled. Because of this, the equations from Fig. 3.7 were used to construct Arrhenius plots as shown.

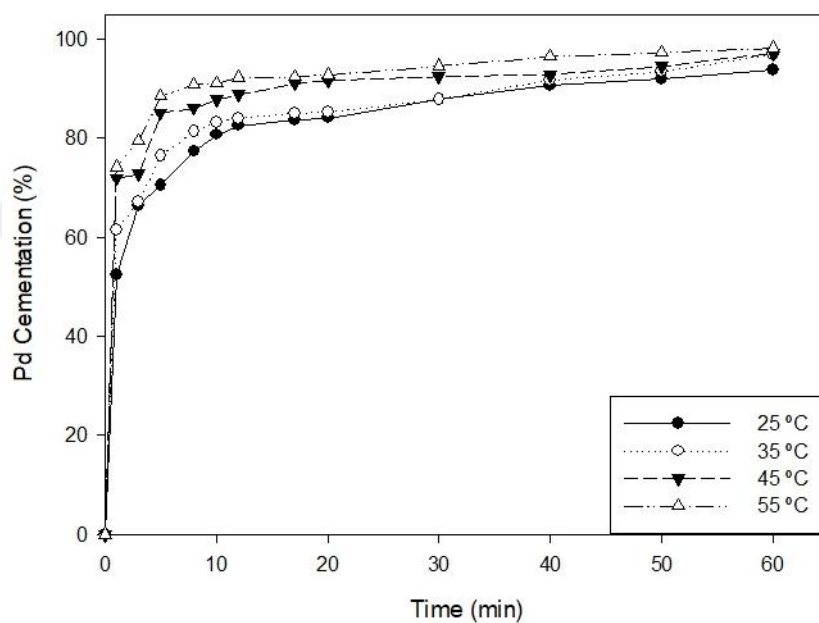
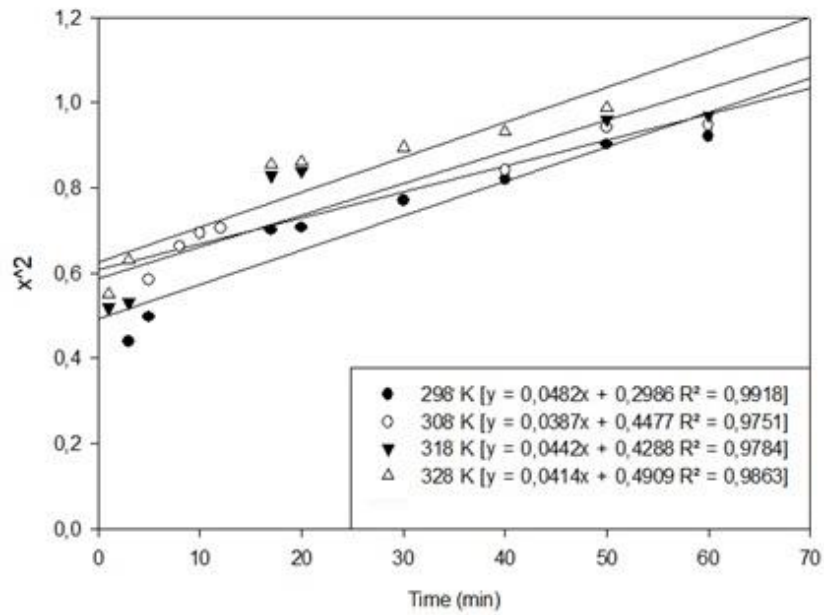
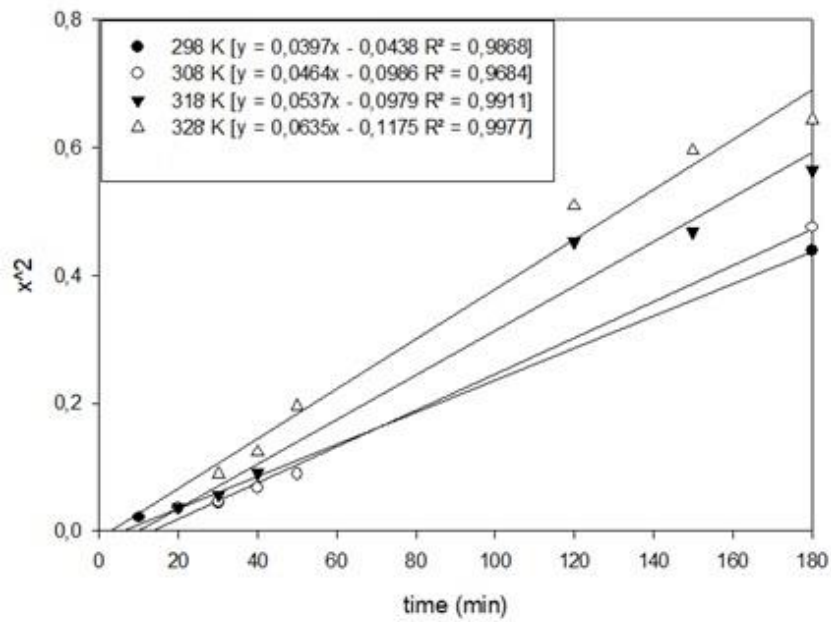


Figure 3. 5. Changes in palladium cementation (percent) with time and temperature for 60 min (a) Zn (20 mg zinc, 200 rpm, 7 mL of 634 ppm Pd<sup>2+</sup>).

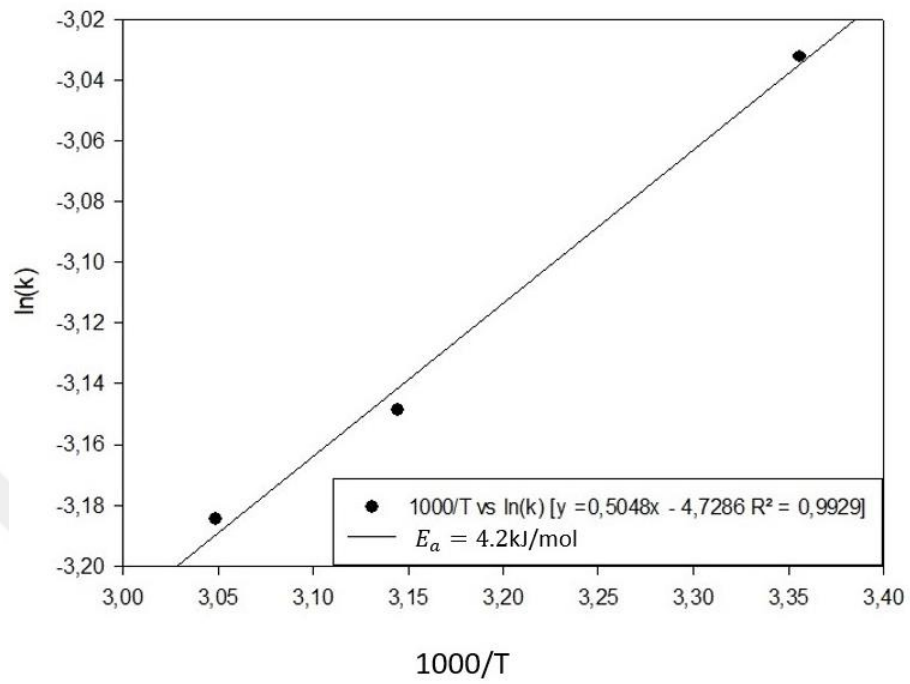


(a)

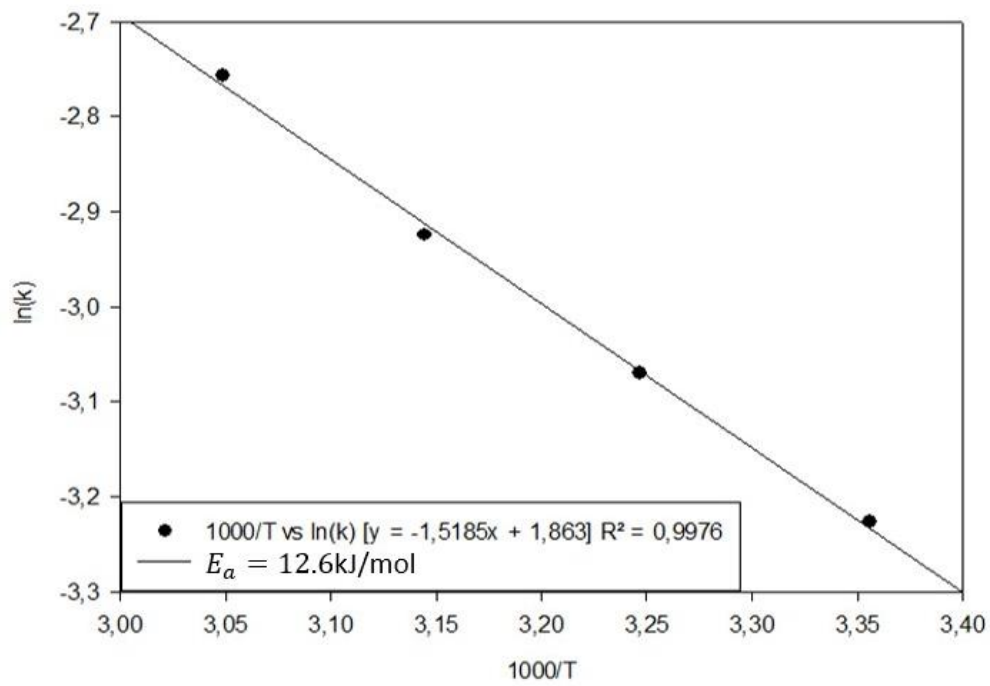


(b)

Figure 3. 6. Time-temperature graph showing the relationship between a)  $[(X^2)]$  for zinc, and b)  $[(X^2)]$  for tin



(a)



(b)

Figure 3. 7. Arrhenius plot using related kinetic models for a) zinc, and b) tin

Activation energies ( $E_a$ ) were determined from the plots shown in Fig. 3.7, which were made possible by the Arrhenius equation in Eq. 6.

Rate constant ( $k$ ), activation energy ( $E_a$ , in J/mol), gas constant ( $R$ , in J mol<sup>-1</sup> K<sup>-1</sup>), and temperature ( $T$ , in K, Kelvin) are all variables in the equation:

$$k = \ln A - E_a/R * 1/T \quad (6)$$

Units of frequency factor  $A$  are expressed as L mol<sup>-1</sup> s<sup>-1</sup>. It accounts for the likelihood of the right molecular orientation and the rate at which reactions occur. The activation energy of the process can be calculated by multiplying the slope of the line in the negative direction by the gas constant  $R$ . The activation energy is the end consequence.

Therefore:

$E_a = 4.2$  kJ/mol for Zn cementation

Calculated activation energy ( $E_a$ ) for Sn cementation: 12.6 kJ/mol

### 3.4. Characterization of the Produced Powders After Cementation

To get rid of any remaining water in the metal powder, acetone and distilled water were used. During one hour at 80°C, the powders were vacuum-dried. As shown in Figure 3.8-10, agate mortar-ground agglomerated particles were subjected to a SEM-EDS examination.

Even after impurities were eliminated, a palladium concentration of 95.72 % was found (i.e. HCl treatment), in the case of zinc-based cementation. Figures 3.9 and 3.10 show SEM images of Pd metallic powder after cementation with Zn and Sn. They show the failure of the complete elimination of the impurities.

Despite the absence of hydrochloric acid leaching, Figure 3.a and b show that some unreacted Zn and Sn and cementation by-products coexist with palladium metal. This conclusion is supported by the EDS data depicted in Figs. 3.9 and 3.10. A single-phase palladium powder may be obtained following hydrochloric acid leaching.

SEM images (Figs. 3.8. and 3.10) indicate that the powder has a typical cemented powder structure, with submicron particles making up the porosity structure. Figures 3.12-14 show XRF results that are in agreement with this conclusion.

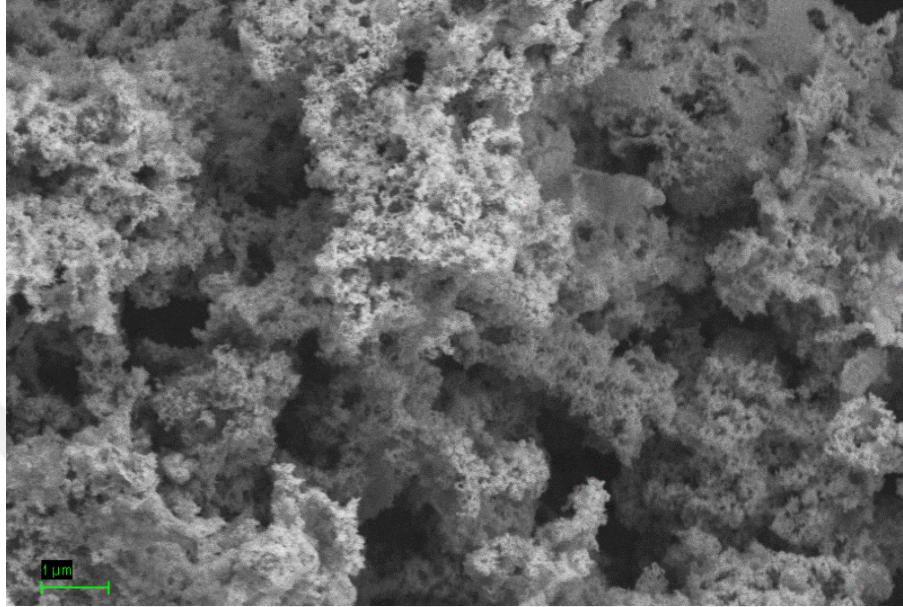
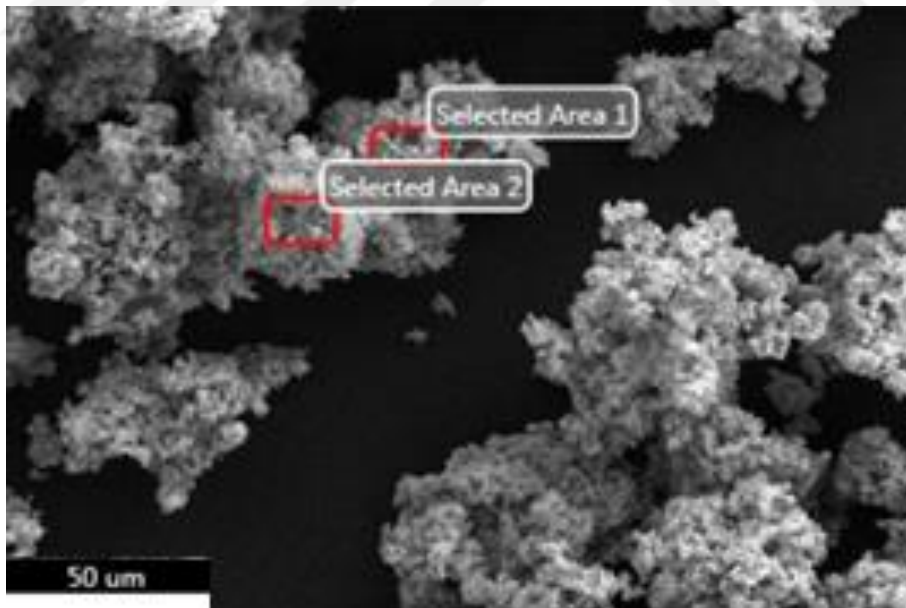
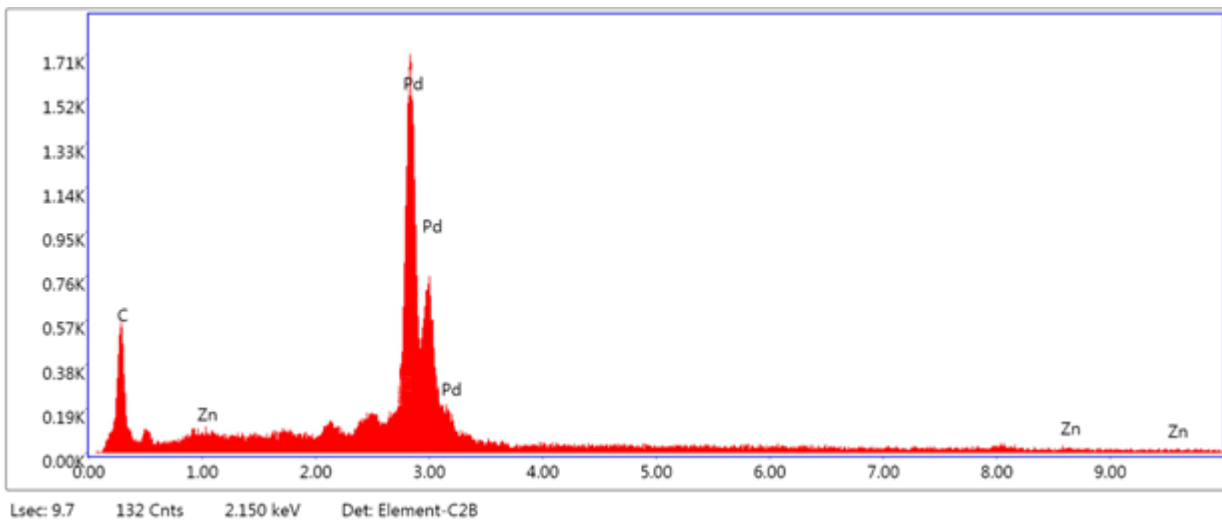


Figure 3. 8. Microstructure of metallic Pd powder cemented using Zn (Magnification x 20.85 K)

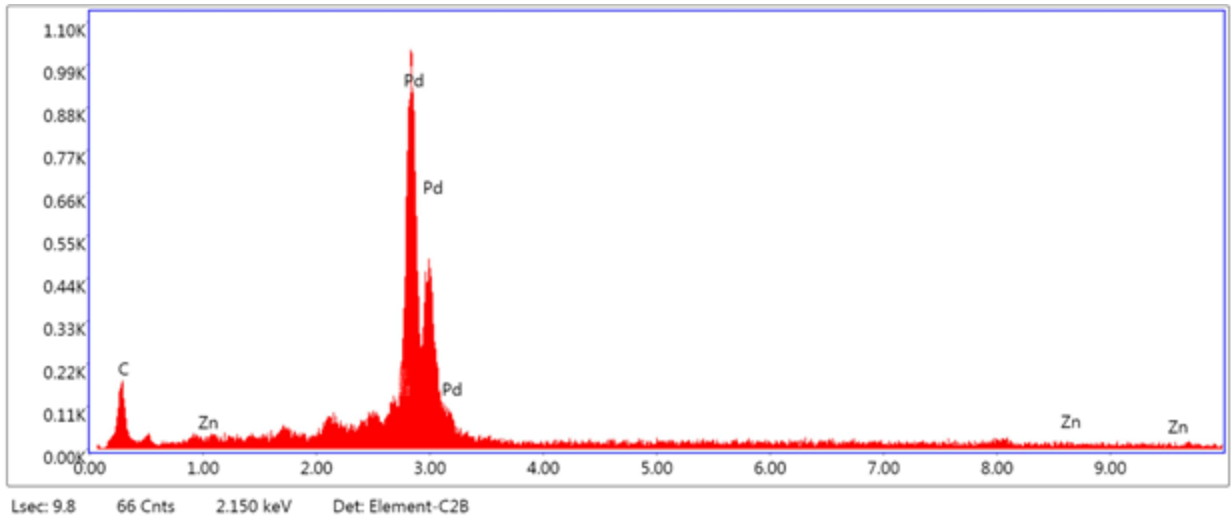




**eZAF Smart Quant Results**

Element	Weight %	Atomic %
C-K	0.00	0.02
Pd-L	95.72	93.21
Zn-K	4.28	6.77

(a)



**eZAF Smart Quant Results**

Element	Weight %	Atomic %
C-K	0.01	0.04
Pd-L	85.72	78.70
Zn-K	14.27	21.26

**(b)**

Figure 3. 9. EDS analysis result of the metallic Pd powder cemented by zinc at the selected areas 1 (a) and 2 (b).

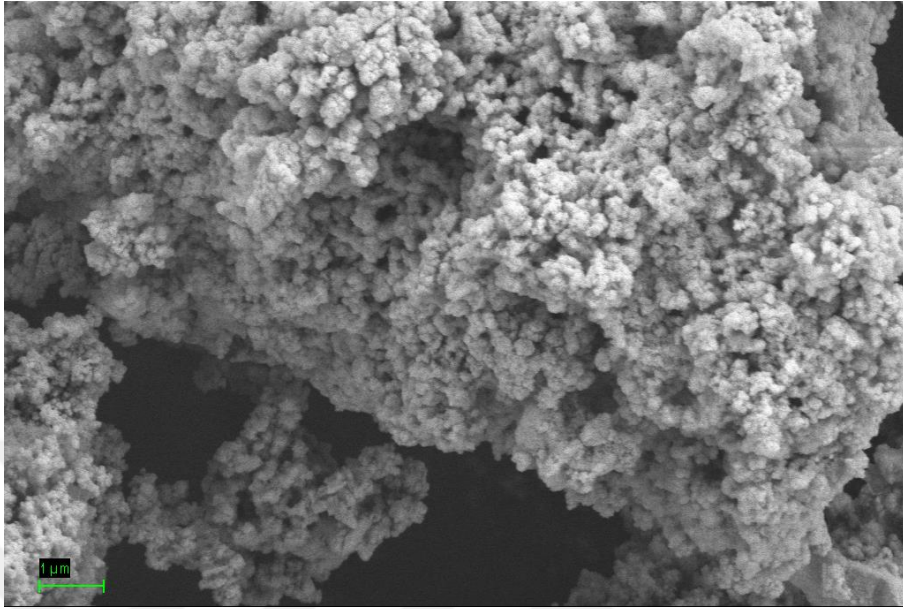
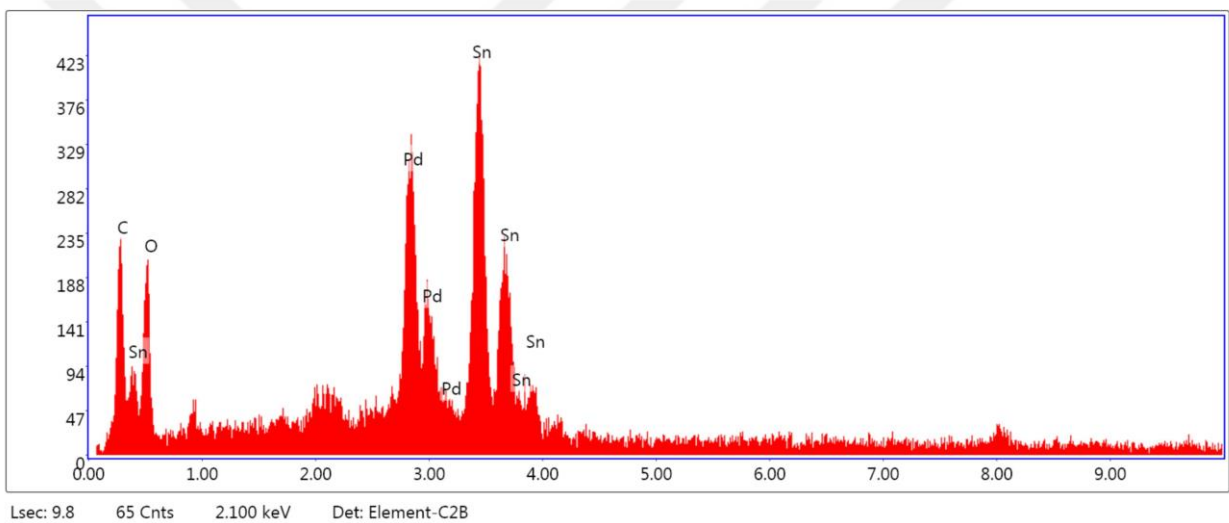
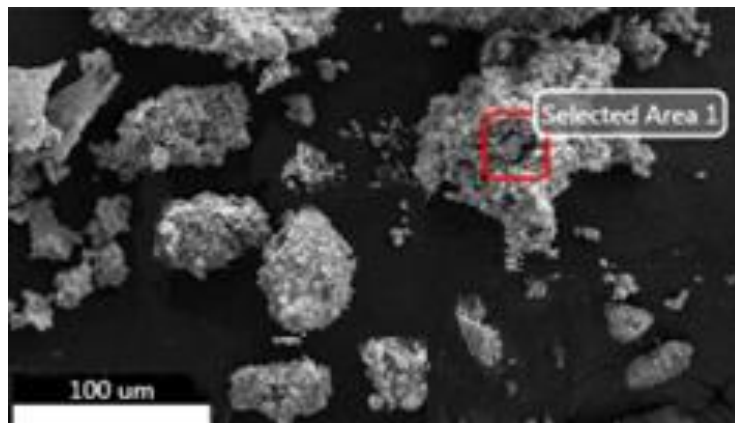


Figure 3. 10. Microstructure of metallic Pd powder cemented using Sn (Magnification x 20.00 K)



### eZAF Smart Quant Results

Element	Weight %	Atomic %
C K	2.30	12.12
O K	9.99	39.44
PdL	28.75	17.07
SnL	58.95	31.37

(a)

Figure 3. 11. EDS analysis result of the metallic Pd powder cemented by tin at the selected area 1 (a).

#### 4. CONCLUSION

To obtain platinum group elements, it was necessary to increase the profit from recycling a material previously deemed unusable. PGM recovery from secondary sources is a new research and development breakthrough. Secondary sources include used automobile catalysts, electronics, and even ore processing plant residue. Technical advancements, particularly catalysis, affect PGM consumption, worldwide supply, and manufacturing costs. Over the last few years, a variety of approaches have been used to recover PGM's from aqueous solutions: In addition to environmental and resource preservation, precious metal recovery from wastewater is critical.

For redox reactions, it is critical to know the cementation parameters. The palladium precipitated effectively by the two competing cementators, as demonstrated. The fundamental objective of this work is to propose a simple and practical method for obtaining high palladium recovery efficiency under natural atmospheric circumstances.

It was shown that at 25 °C, using 100 mg of tin did not result in a complete recovery of palladium, but that using 100 mg of zinc powder virtually completely eliminated all palladium ions. The recovery rate of palladium improved from 25 °C to 55 °C. Increasing the response time does not require any more heating to get a higher percentage of Pd recovery. These noteworthy findings demonstrated the additive impact of temperature and time on the process.

Due to the low degree of interfacial interaction in aqueous solutions, the activation energies of the individual cementators involved in diffusion-controlled processes are hardly affected by using the stoichiometric amount of cementators.

## 5. REFERENCES

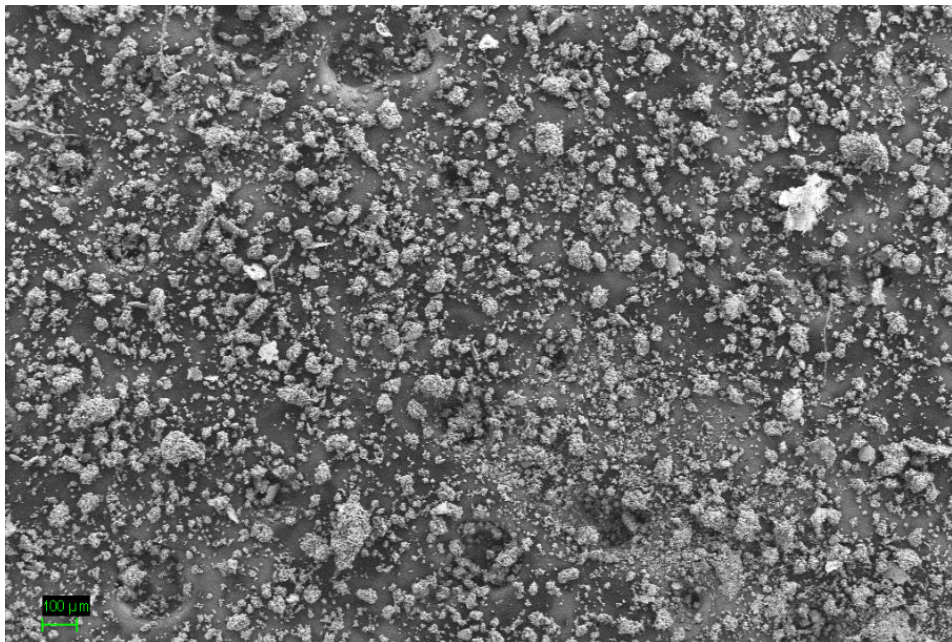
- [1] L. Erdmann, T.E. Graedel, Criticality of non-fuel minerals: a review of major approaches and analyses, *Environ. Sci. Technol.* 45 (2011) 7620–7630, <http://dx.doi.org/10.1021/es200563g>.
- [2] M. Saurat, S. Bringezu, Platinum group metal flows of Europe, Part 1 – global supply, use in industry, and shifting of environmental impacts, *J. Ind. Ecol.* 12 (2008) 754–768, <http://dx.doi.org/10.1111/j.1530-9290.2008.00087.x>.
- [3] J. Kielhorn, C. Melber, D. Keller, I. Mangelsdorf, Palladium – a review of exposure and effects to human health, *Int. J. Hyg. Environ. Heal.* 205 (2002) 417–432, <http://dx.doi.org/10.1078/1438-4639-00180>.
- [4] C. Melber, D. Keller, I. Mangelsdorf, Palladium: Environmental Health Criteria, World Health Organization, Geneva, 2002.
- [5] K. Ravindra, L. Bencs, R. Van Grieken, Platinum group elements in the environment and their health risk, *Sci. Total Environ.* 318 (2004) 1–43, [http://dx.doi.org/10.1016/S0048-9697\(03\)00372-3](http://dx.doi.org/10.1016/S0048-9697(03)00372-3).
- [6] M.A. Barakat, New trends in removing heavy metals from industrial wastewater – review article, *Arab. J. Chem.* 4 (2011) 361–377, <http://dx.doi.org/10.1016/j.arabjc.2010.07.019>.
- [7] J.A. Dean, Lange’s Handbook of Chemistry, 12th ed., McGraw-Hill Inc., New York, 1979.
- [8] C. Hagelüken, “Markets for the Catalyst Metals Platinum, Palladium and Rhodium”, *Metall* 60, p.31- 42, January 1-2 2006
- [9] <https://www.macrotrends.net/2542/palladium-prices-historical-chart-data>
- [10] <https://www1.undp.org/content/oslo-governance-centre/en/home/sustainable-development-goals.html>

- [11] F. Di Natale, M. Orefice, F. La Motta, A. Erto, A. Lancia (2017) Unveiling the potentialities of activated carbon in recovering palladium from model leaching solutions, *Separation and Purification Technology* 174 (2017) 183–193.
- [12] J. Hoffmann, Recovery of platinum-group metals from gabbroic rocks metals from auto catalysts, *JOM* 40 (1988) 40–44, <http://dx.doi.org/10.1007/BF03258173>.
- [13] Y. Konishi, K. Ohno, N. Saitoh, T. Nomura, S. Nagamine, H. Hishida, Y. Takahashi, T. Uruga, Bioreduction deposition of platinum nanoparticles on the bacterium *Shewanella* algae, *J. Biotechnol.* 128 (2007) 648–653, <http://dx.doi.org/10.1016/j.jbiotec.2006.11.014>.
- [14] M. C. Costa, A. Assunção, R. Almeida, A. M. R. da Costa, Carlos Nogueira, Ana Paula Paiva (2018) “N,N'-dimethyl-N,N'-dicyclohexylsuccinamide: A novel molecule for the separation and recovery of Pd(II) by liquid-liquid extraction”, *Separation and Purification Technology*, 201, 96–105.
- [15] Umeda, H., Sasaki, A., Takahashi, K., Haga, K., Takasaki, Y., & Shibayama, A. (2011). Recovery and concentration of precious metals from strong acidic wastewater. *Materials Transactions*, 52(7), 1462–1470. <https://doi.org/10.2320/matertrans.M2010432>
- [16] Barakat, M. A., Mahmoud, M. H. H., & Mahrous, Y. S. (2006). Recovery and separation of palladium from spent catalyst. *Applied Catalysis A: General*, 301(2), 182–186. <https://doi.org/10.1016/j.apcata.2005.11.028>
- [17] Tu, S., Yusuf, S., Muehlfeld, M., Bauman, R., & Vanchura, B. (2019). The Destiny of Palladium: Development of Efficient Palladium Analysis Techniques in Enhancing Palladium Recovery. *Organic Process Research and Development*, 23(10), 2175–2180. <https://doi.org/10.1021/acs.oprd.9b00204>
- [18] M.V. Rane, V. Venugopal (2006) “Study on the extraction of palladium(II) and platinum(IV) using LIX 84I”, *Hydrometallurgy* 84, 54–59.
- [19] S. Ilyas, R. R. Srivastava, H. Kim, H. A. Cheema (2020) “Hydrometallurgical recycling of palladium and platinum from exhausted diesel oxidation catalysts”, *Separation and Purification Technology* 248, 117029.

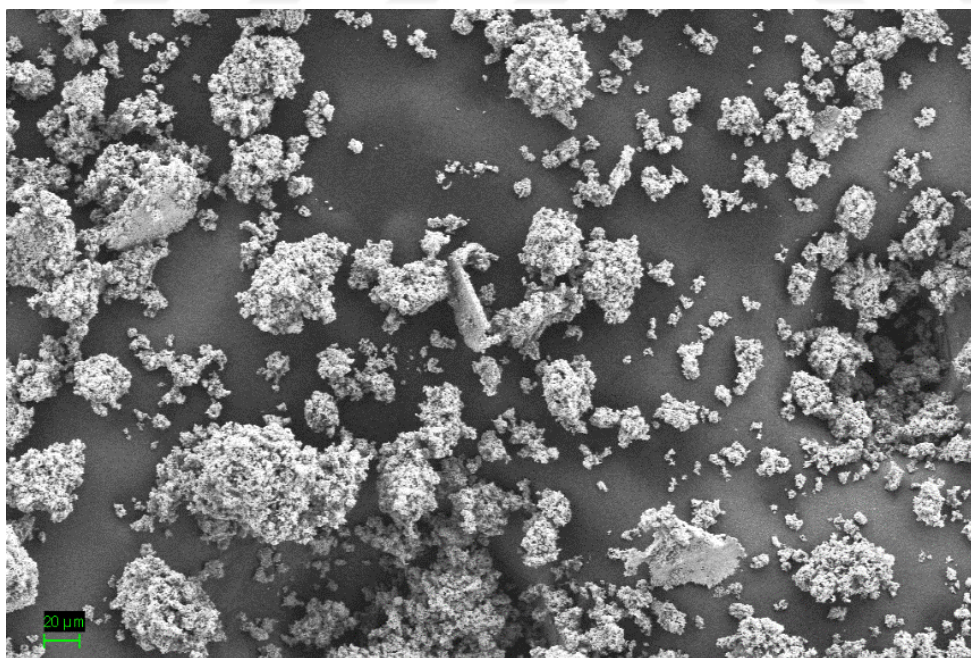
- [20] O. Kuntiyi, O. Dobrovetska, S. Korniy, G. Zozulya, G. Mykhalyna (2014) “Palladium deposition on magnesium in PdCl<sub>2</sub> solutions in DMF”, *Chemistry & Chemical Technology*, Vol. 8, No. 2, 193-196.
- [21] S. Sarioglan (2013) “Recovery of Palladium from Spent Activated Carbon-Supported Palladium Catalysts”, *Platinum Metals Rev.*, 57, (4), 289–296.
- [22] M Ciopec, A. Negrea, N. Duteanu, P. Negrea, N. Nemes, G. Dobra, S. Iliev, L. Cotet, A. Boiangiu, L. Filipescu (2020) “ Palladium recovery by adsorption on aluminum hydroxide”, *U.P.B. Sci. Bull., Series B*, Vol. 82, Iss. 4, 111-124.
- [23] Havlik, T. (2008). Hydrometallurgy. In *Hydrometallurgy*.  
<https://doi.org/10.1533/9781845694616>
- [24] M. Kim, E. Kim, J. Jeong, J. Lee, W. Kim (2010) “Recovery of Platinum and Palladium from the Spent Petroleum Catalysts by Substrate Dissolution in Sulfuric Acid”, *Materials Transactions*, Vol. 51, No. 10, pp. 1927 to 1933.
- [25] Aktas S. (2011) “Rhodium recovery from rhodium-containing waste rinsing water via cementation using zinc powder”, *Hydrometallurgy* 106, 71–75.
- [26] Serdar Aktas S., Morcali M.H., Aksu K., Aksoy B. (2018) "Recovery of Ruthenium Via Zinc in the Presence of Accelerator", *Trans Indian Inst Met* 71(3):697–703.
- [27] S. Aktas, M. H. Morcali & O. Yucel (2010) Silver Recovery from Waste Radiographic Films by Cementation and Reduction, *Canadian Metallurgical Quarterly*, 49:2, 147-153, DOI: 10.1179/cmqr.2010.49.2.147
- [28] P. Quinet, J. Proost, A. Van Lierde (2005) “Recovery of precious metals from electronic scrap by hydrometallurgical processing routes”, *Minerals and Metallurgical Processing (Mining, Metallurgy and Exploration)*, Vol. 22, No:1, pp. 17-22.
- [29] H. Deveci, E.Y. Yazici, A. D. Bas (2016) “Cementation of Silver from Synthetic Leach Solutions of Waste of Printed Circuit Boards (WPCB)” *IMPC 2016: XXVIII International Mineral Processing Congress Proceedings - ISBN: 978-1-926872-29-2*, pp. 1-9.

- [30] E. Yazici, H. Deveci, A. Ehsani (2014) “Recovery of metals from chloride leach solutions of waste of printed circuit boards by adsorption and precipitation”, XXVII International Mineral Processing Congress, 170-179. DOI: 10.13140/2.1.4372.8968
- [31] Mpinga C.N., Bradshaw S.M., Akdogan G., Snyders C.A., Eksteen J.J., (2014) “Evaluation of the Merrill–Crowe process for the simultaneous removal of platinum, palladium and gold from cyanide leach solutions”, *Hydrometallurgy*, 142, 36–46.
- [32]<https://opentextbc.ca/introductorychemistry/back-matter/appendix-standard-reduction-potentials-by-value-2/>. Accessed 20 September 2020.
- [33] Van der Pas V, Dreisinger D (1996) A fundamental study of cobalt cementation by zinc dust in the presence of copper and antimony additives. *Hydrometallurgy* 43:187-205.
- [34] Shamsuddin, M (2016) *Physical Chemistry of Metallurgical Processes*. John Wiley & Sons, Hoboken.
- [35] [https://chem.libretexts.org/Bookshelves/General\\_Chemistry/Map%3A\\_General\\_Chemistry\\_\(Petrucci\\_et\\_al.\)/20%3A\\_Electrochemistry/20.4%3A\\_Cell\\_Potential\\_as\\_a\\_Function\\_of\\_Concentrations#:~:text=Concentration%20Cells,-A%20voltage%20can&text=An%20electrochemical%20cell%20of%20this,decrease%2C%20as%20will%20Ecell.](https://chem.libretexts.org/Bookshelves/General_Chemistry/Map%3A_General_Chemistry_(Petrucci_et_al.)/20%3A_Electrochemistry/20.4%3A_Cell_Potential_as_a_Function_of_Concentrations#:~:text=Concentration%20Cells,-A%20voltage%20can&text=An%20electrochemical%20cell%20of%20this,decrease%2C%20as%20will%20Ecell.) (16/05/2022)
- [36] Aktaş S., Çetiner B.N. (2020) Investigation of Alkaline Leaching Parameters on Stibnite Concentrate, *Mining, Metallurgy & Exploration* (2020) 37:1729–1739.

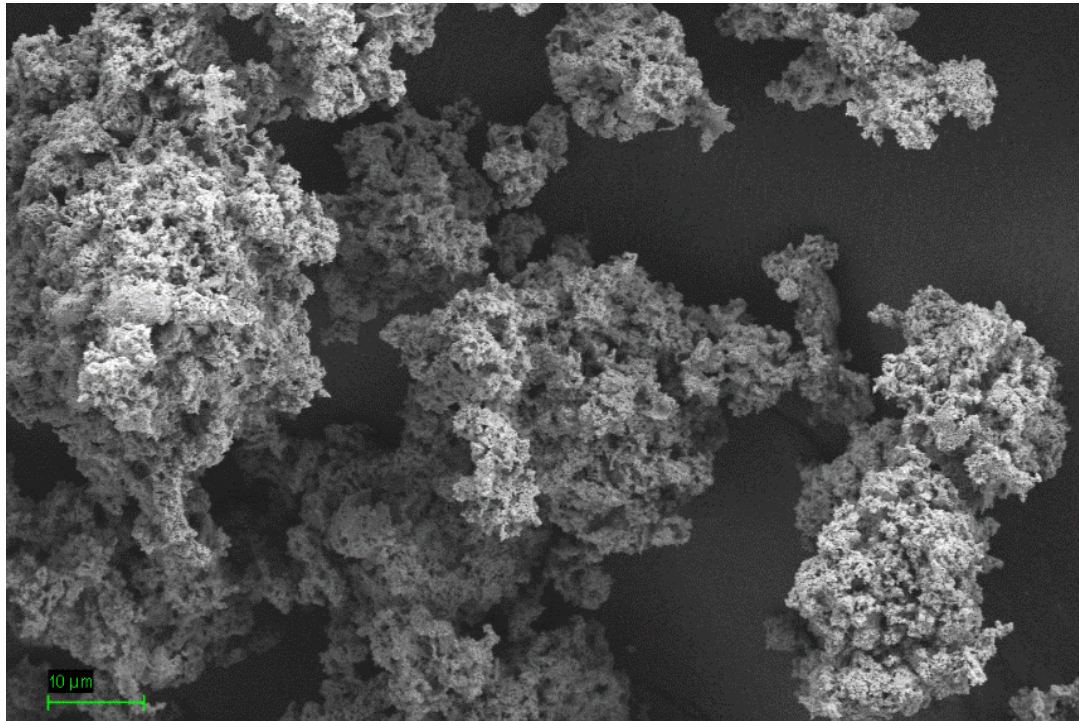
## APPENDIX



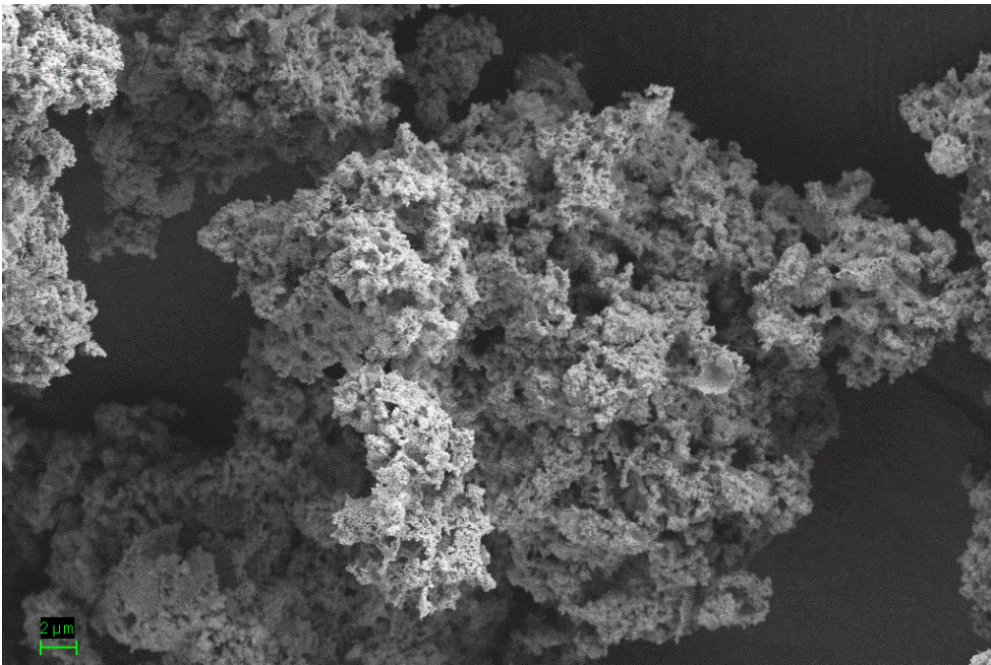
(a)



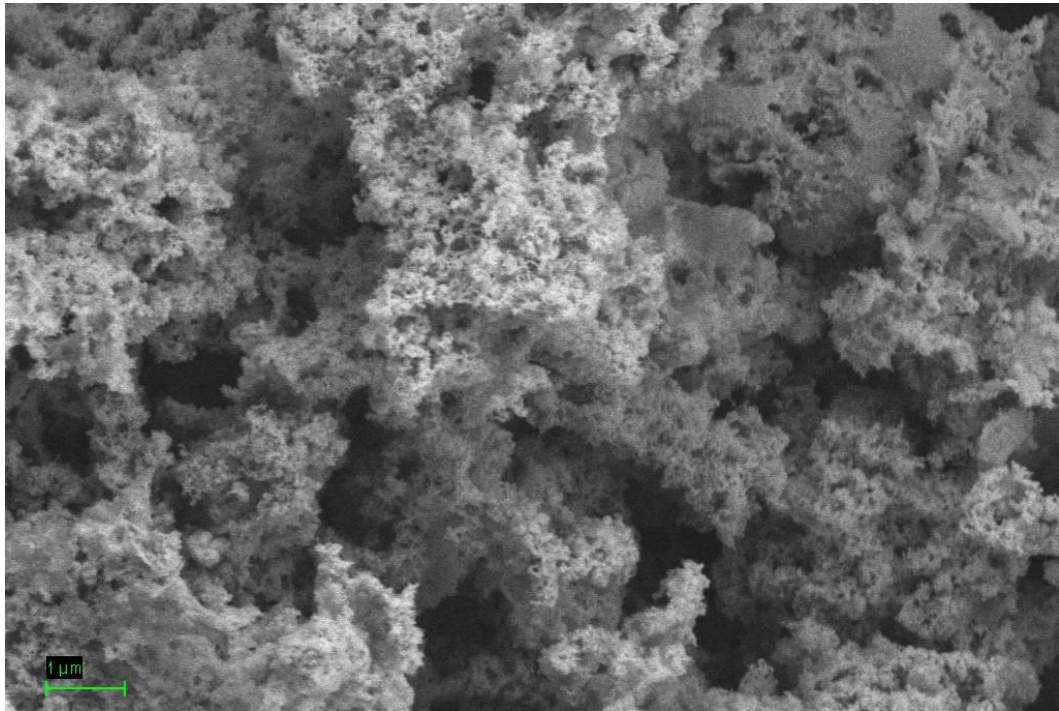
(b)



(c)

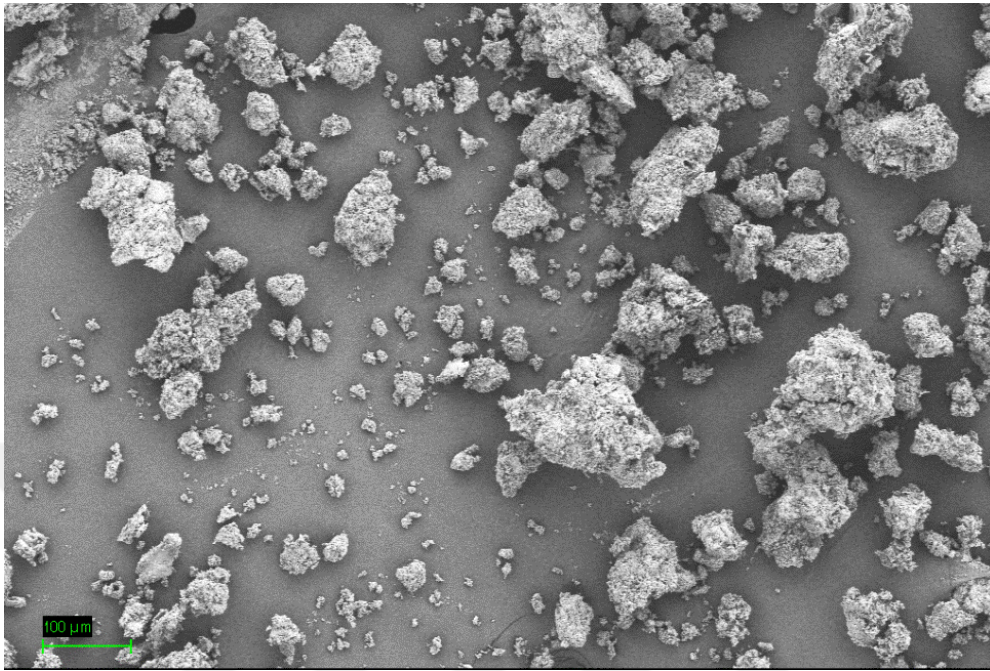


(d)

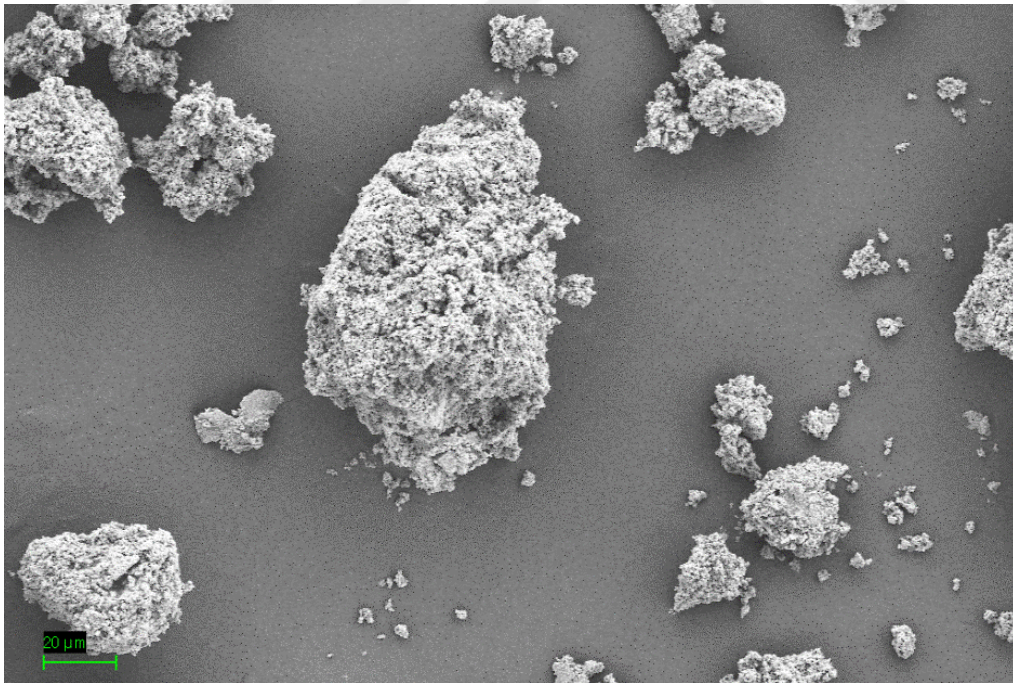


(e)

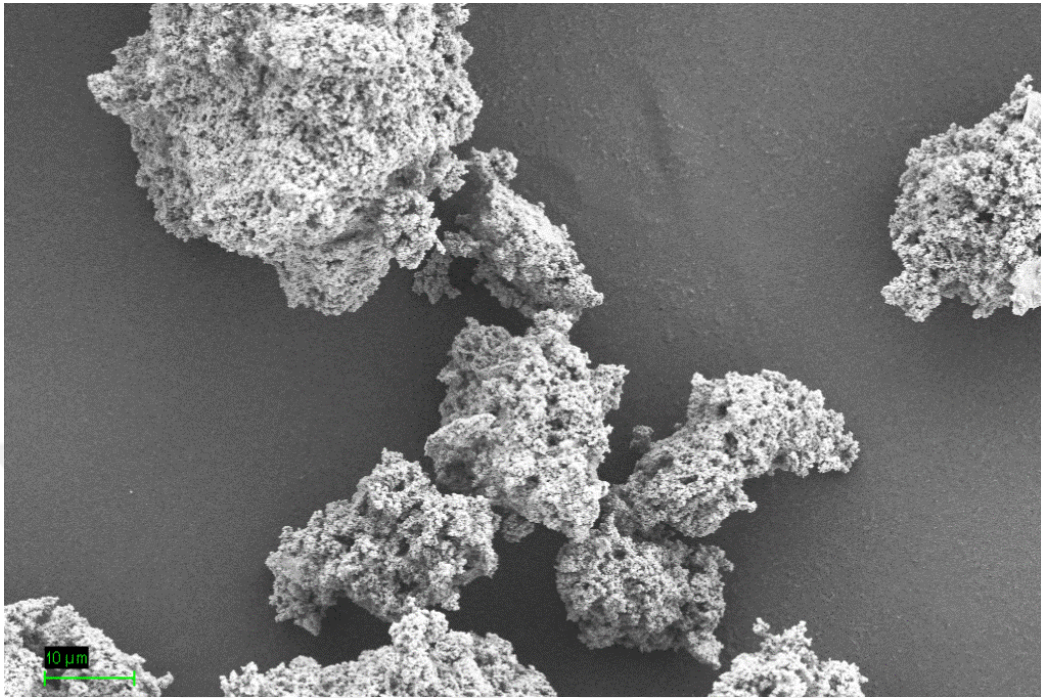
A. 1. Microstructure of metallic Pd powder cemented using Zn (a) 100μm, (b) 20μm, (c) 10μm, (d) 2μm and (e) 1μm



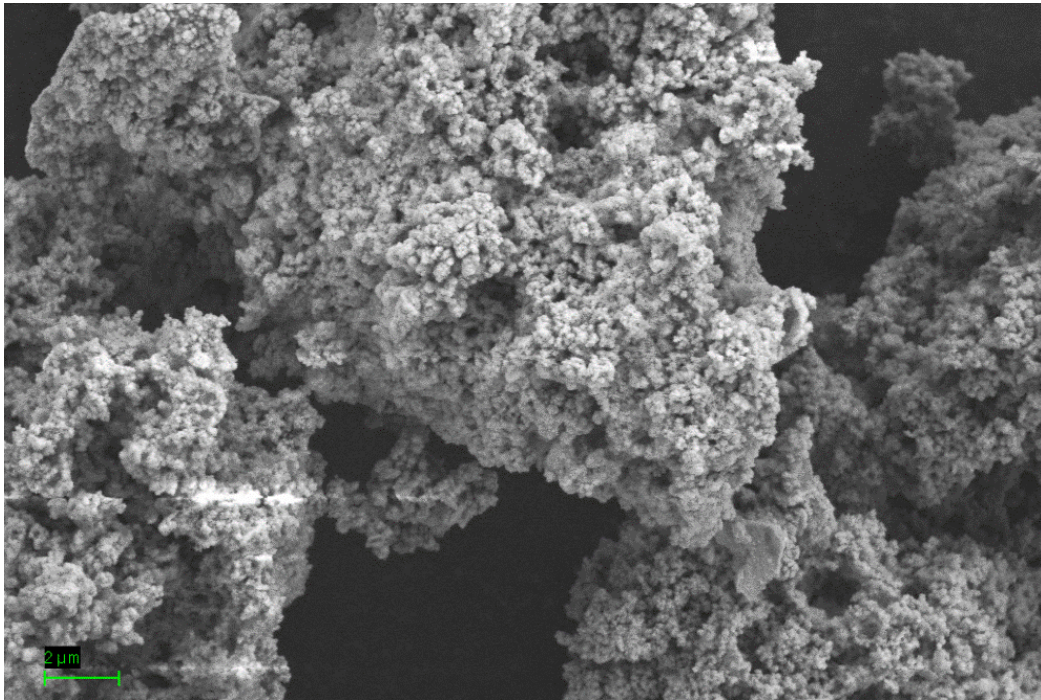
(a)



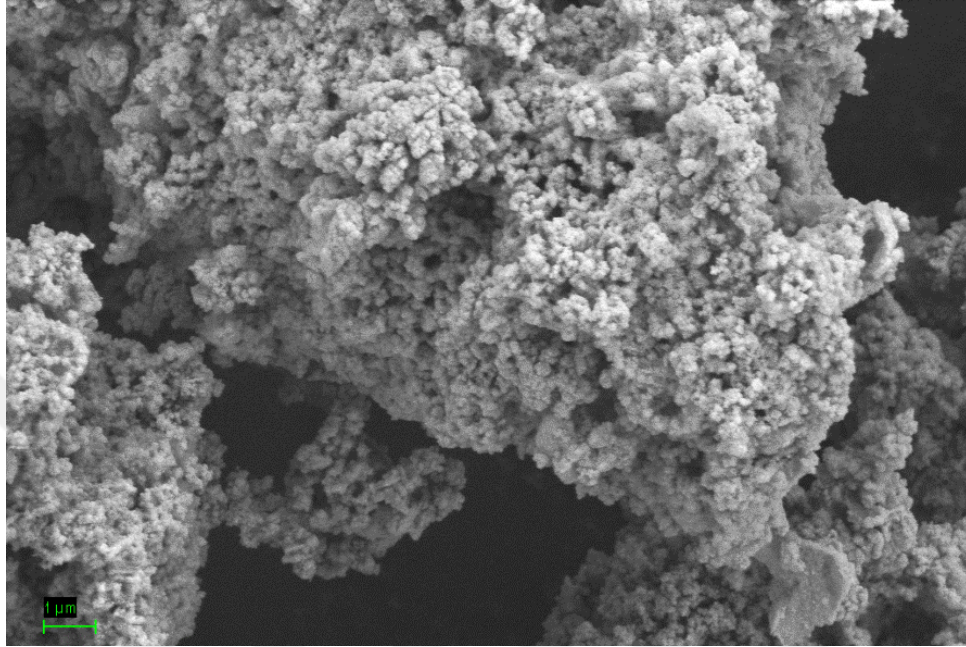
(b)



(c)



(d)



(e)

A. 2. Microstructure of metallic Pd powder cemented using Sn (a) 100μm, (b) 20μm, (c) 10μm, (d) 2μm and (e) 1μm