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Silver recovery from dental amalgam wastes

Abstract

Alloys produced with mercury and other metals are called amalgam. Dental amalgams are important alloys and contain 40-50% mercury with the addition of silver (22-39%), tin (12-18%) and copper (2-18%). Therefore, these amalgams have high economic value and need to be evaluated. This experimental study deals with recovering their metal contents by physical and chemical separation techniques. Within the framework of this study, distilled non-contact dental amalgam wastes were subjected to size reduction, leaching with nitric acid and cementation with copper. Leach liquor was filtered and both solution and leach residue were characterized. Results have shown that, leaching efficiency was above 99.8% and leach solution contained 16 g/L Ag^{+}, and 8.5 g/L Cu^{2+} ions. Later, silver was recovered from solution by cementation with copper. The basic parameters in the cementation experiments, such as cementator quantity, stirring speed, pH, and temperature were examined. Cementation efficiency reached above 99.9% and chemical analysis has shown that silver concentration of solution decreased from 16g/L to 1.7 mg/L.

Keywords: dental amalgam, silver, acid leaching, cementation

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Introduction

Alloys made with mercury and other metals are known as amalgam. Dental amalgams are important alloys having mercury (Hg≈40-50%) as a main component and include silver (≈22-39%), tin (≈12-18%) and copper (≈2-18%). Considering the content of dental amalgams, due to the combination of silver, tin and copper in the structure, they have high economic value.[1,2] The mixing of silver and other elements and mercury is known as amalgamation. During this process, metallic powders are dissolved in the mercury along the surfaces, and this process leads to the formation of new phases in the structure. These new solid phases result in the plastic state of amalgam. At the end of amalgamation, resulting phases are rigid. The metallurgical phases that are occurred as a result of these reactions are shown in detail in Table 1.[3] The metallurgical properties belonging to these phases are complex and the final phase varies according to the content of the starting alloy. In case of Ag-Sn alloy containing copper below 4%, amalgam become harder and stronger but more brittle. In contrast, if the alloy contains copper about 4-5%, separate Cu_3Sn phases form in the structure. These phases increase the workability of amalgam and decrease the fragility.[3] Basic reactions which occur during amalgamation are as follows:

$$Ag_3Sn + Hg \rightarrow Ag_2Hg_3 + Sn_{7-8}Hg \quad (1)$$

Table 1 Resulting phases of dental amalgams[3]

Phase	Chemical formula
γ	Ag_3Sn
γ_1	Ag_2Hg_3
γ_2	$Sn_{7-8}Hg$
ε	Cu_3Sn
η	Cu_6Sn_5
Silver-Copper Eutectic	Ag-Cu

Resulting alloy may also contain large amounts of unreacted γ-Ag_3Sn phase in the structure. Modern amalgam compositions can contain copper up to 30%. In this case the following reactions take place in the next step;

$$Sn_{7-8}Hg + Cu \rightarrow Cu_3Sn + Hg \quad (2)$$

$$Sn_{7-8}Hg + Cu \rightarrow Cu_6Sn_5 + Hg \quad (3)$$

Elemental form of mercury occurs as a result of the reactions (2) and (3), in a subsequent step it reacts with the Ag-Sn alloy and consequently the desired γ_1-Ag_2Hg_3 phase is formed in the structure. Occurrence of these reactions offers many advantages in terms of performance of the material. The developing structure arising from the reactions (2) and (3) is more resistant to creep and corrosion. Having been eliminated of corrosion is a significant advantage, especially if mercury were released from the filling; it directly enters the gastrointestinal tract of the user. Moreover, the material produced as a result of these reactions compared to other traditional amalgams access rapidly to the high strength values.[3,4] Dental amalgam is one of the most commonly used permanent filling materials in restorative dentistry. Its physical and mechanical properties, stability, ease of use, and relatively low cost have made amalgam the preferred choice in many clinical situations when compared with other direct restorative materials such as composites and glass ionomers.[5] However, one of its major components is mercury which is of particular concern due to its potential adverse effects on humans and the environment. There are different types of amalgam wastes produced in dentist offices such as:[6]

I. Non-contact amalgam (scrap) is excess mix leftover at the end of a dental procedure. Many recyclers will buy this clean scrap.

II. Contact amalgam is amalgam that has been in contact with the patient. Examples are extracted teeth with amalgam restorations, carving scrap collected at chair side, and amalgam captured by chair side traps, filters, or screens.

III. Chair side traps capture amalgam waste during amalgam placement or removal procedures (traps from dental units dedicated strictly to hygiene may be placed in the regular garbage).

IV. Vacuum pump filters or traps contain amalgam sludge and

water. Some recyclers will accept whole filters, while others will require special handling of this material.

V. Amalgam sludge is the mixture of liquid and solid material collected within vacuum pump filters or other amalgam capture devices.

VI. Empty amalgam capsules are the individually dosed containers left over after mixing precapsulated dental amalgam. There are four possible harmful effects of dental amalgam –oral galvanism, toxicity, allergenicity, and ecological grievances.

Steps for recycling amalgam waste are listed as:[6]

a) Stock amalgam capsules in a variety of sizes to minimize the amount of amalgam waste generated.

b) Amalgam waste may be mixed with body fluids, such as saliva, or other potentially infectious material, so use personal protective equipment such as utility gloves, masks, and protective eyewear when handling it.

c) Contact an amalgam waste recycler about any special requirements that may exist in your area for collecting, storing and transporting amalgam waste.

d) Store amalgam waste in a covered plastic container labeled "Amalgam for Recycling" or as directed by your recycler. Consider keeping different types (e.g., contact and non-contact) of amalgam wastes in separate container talk to your recycler about any advantages in doing so.

Dental amalgams are criticized with being associated with many diseases such as multiple sclerosis, and mental disorders. In the blood of people using amalgam fillings on their teeth, mercury concentrations are found higher than other people. On the other hand, in 1994, it is indicated on an article that, although dentists and their employees have higher mercury in their bodies than normal people, they do not get any disease with high rates.[7] At all scientific studies are focused on the assumption that the mercury in amalgam fillings does not interact with biological organisms. However, Stone and his colleagues[8] revealed that waste water samples from different scale dental hospitals, methyl-mercury content was found much higher than that of in nature. In this study, it is indicated that methyl-mercury can be found on waste waters of a first time made dental restoration hospital and draw attention to the importance of waste management at the amalgam restoration hospitals.[8,9] Drummond and his colleagues[10] identified that approximately 421 mg/day non-contact and 64 mg/day contact amalgam wastes produced for per dentist. As a result of this statistical study, in the State of Illinois that has a population of 12.500.000 and 6455 dentists working within the boundaries, they calculated the quantity of mercury, connected to non-contact amalgam as 947 kg/year. Similarly, they calculated the quantity of mercury, connected to contact amalgam waste as 144 kg/year.[10,11] Iano et al.[12] for mercury recovery have used high temperatures through exposure to direct flame (650°C) by an electrical mantle long processing time, and hazardous reagents as potassium cyanide and Sadiseva et al.[5] focused on extracting mercury from dental amalgam scrap to limit ecological grievances by using vacuum distillation method at 398°C.

As can be seen clearly, dental amalgam waste is not only threat to society, but also a part of a waste of precious group. While contained mercury makes recycling of this waste group mandatory, silver makes this waste group precious. There are important studies made on silver recovery from dental amalgam waste. Lee & Fung[13] offered to recycle silver in distilled dental amalgam wastes in two different ways. Dissolved silver was precipitated with NaCl after HNO_3 leaching. In the first method, the resulting AgCl is dissolved with 25% NH_3 and silver was recovered with the yield of 89.9±2.5% and with the purity of 99.99%±0.17 via electrolysis process. Another method they used is the reduction of AgCl with glucose. Glucose was added after AgCl suspension was heated in a solution of NaOH for a while and so silver is recovered. Precipitating process after the washing process, silver is recovered with the yield of 92.4%±2.5 and with the purity of 99.5%±1.1.[13]

Pereira and her colleagues[14] followed a similar process as Fung and Lee's study of reduction with glucose. However, they used l-ascorbic acid and sucrose as reducing agent. In the study where sucrose was used, silver was recovered with the yield of 71.9% and the purity of 87.1%. On the other hand, in the study where l-ascorbic acid was used, silver was recovered with the yield of 84.4% and the purity of 91.1%.[14] Cementation that will be used in this experimental study has been used to recover noble metals or heavy metal ions from solutions since 16th century.[15] Cementation is based on a redox reaction between noble metal ion and relatively base metal. Cementation is an easy process to recover metal ions from solutions. Also, because of low cost, high efficiency and ease of applicability, it is a preferable method in hydrometallurgy. Metallic copper is commonly used for cementation of silver. The cementation reaction of silver with copper occurs as follows:

$$2Ag^{+} + Cu^{0} \rightarrow 2Ag^{0} + Cu^{2+} \quad (4)$$

The parameters that affect cementation reaction are temperature, pH, ion concentrations, stirring speed, oxygen content of solutions, specific surface area of cementator, and presence of other ions in the solution. The aim of this experimental study was to investigate the possibilities of recovering silver from dental amalgam wastes by hydrometallurgical processes. For his purpose, nitric acid (HNO_3) was used in the leaching and copper powder was used in the cementation experiments.

Material & method

Dental amalgam waste subjected to this experimental study was supplied from Istanbul Technical University Medical Health Center. Dental amalgam wastes were characterized by PANalytical X'PERT PRO XRD as shown in Figure 1. It shows that the phase analysis of the amalgam waste that are similar to the ones given in the literature. Furthermore, existence of $Ag_2Hg_{3.02}$, Cu_6Sn_5 and $Cu_{3.02}Sn_{0.98}$ phases as main components in the amalgam structure shows that the material is a high copper amalgam. After distillation process, mercury free dental amalgams produced were used in experimental study shown in Figure 2. Experimental procedure included grinding, leaching, and cementation steps. Distilled dental amalgam samples were wet ground with SPEXTM Mixer Mill for 90 minutes. Grinding media/material ratio was selected as 5/1. Wet milling was performed by using ethanol. Ground material was sieved below 315µm and dried in oven at 200°C for six hours. Dried powder was leached in 50% HNO_3 at a solid/liquid ratio of 1/5 for four hours. After leaching and solid/liquid separation, both solid residue and leach liquor were analyzed by X-Ray Fluorescence (XRF) Spectrometer and Atomic Absorption Spectrometer (AAS), respectively. Later, cementation experiments were carried out at different pH values and different stirring speeds. Cementation was carried out with copper powder. Particle size analysis of copper powder, carried out by Malvern Mastersizer 2000, is shown in Figure 3. Results showed that the average particle size (d_{50}) was determined as 313.17 µm. SEM image of copper particles is shown in Figure 4.

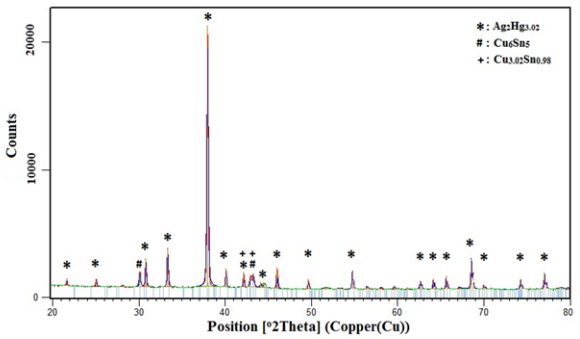

Figure 1 XRD pattern of dental amalgam wastes used in the experiments.

Figure 2 Mercury-free distilled amalgam used in the experiments.

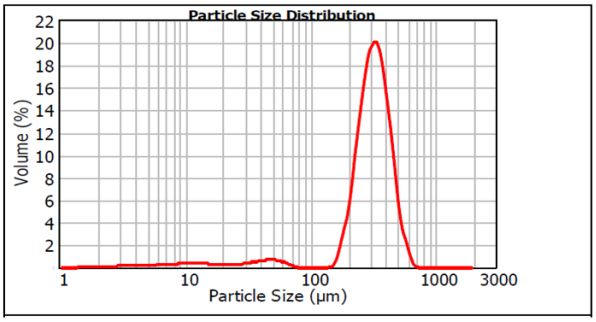

Figure 3 Particle size distribution of copper powder.

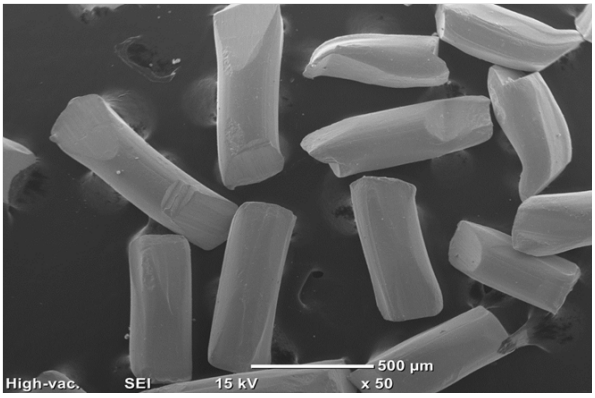

Figure 4 SEM images of copper particles.

Results & discussion

Results are summarized in two parts as leaching and cementation. Possible reactions which occur during leaching with HNO_3 are as follows;

$$3Ag(s) + 4HNO_3 \rightarrow 3AgNO_3(aq) + 2H_2O + NO \quad (5)$$

$$3Cu(s) + 8HNO_3 \rightarrow 3Cu(NO_3)_2(aq) + 2H_2O + NO \quad (6)$$

Leaching experiments were carried out at 50% HNO_3 concentration, S/L ratio of 1/5, leaching time of 4 hours, and room temperature. Results showed that, silver leaching efficiency was above 99.8% and leach solution contained 16 g/L Ag^+ and 8.5 g/L Cu^{2+} ions. Leach residue was characterized by XRF and contained 0.397% Cu and 0.113% Ag. In the cementation experiments the effects of cementator quantity (times x 1.0-1.5 stoichiometric ratio), stirring speed (no stirring, 120, 240, and 360rpm), pH (0.5, 1.0, 1.75) and temperature (25, 45, 65°C) on Ag cementation were investigated and the results are summarized below. Experiments of determining the optimum cementator amount were performed at pH 1.75 for four hours. The results are shown in Figure 5. Results have shown that a cementation yield of 99.5% was obtained in case of using 1.2 times the stoichiometrically required copper as a cementator. The resulting cement silvers were characterized by XRF and the results are shown in Figure 6. Silver recovery values seemed to be stable at around 99.5% when using more than 1.2 times the stoichiometrically required copper. On the other hand, gradually decreasing purities were observed with increasing cementator amounts. As a result of the experiments, the optimum cementator amount was determined to be 1.2 times of the stoichiometric ratio. Experiments were performed at room temperature and pH 1.75 to investigate the effect of stirring speed, which was chosen as 0, 120, 240, and 360rpm in the series of experiments where 1.2 times the stoichiometrically required amount of cementator was used. Dendritic silver crystals obtained in the experiment with no stirring are shown in Figure 7 and results are illustrated in Figure 8. Tests for determining the optimum pH were performed at room temperature and at 240rpm constant stirring speed. The results are shown in Figure 9. Effect of pH on cementation rate was dominant at the beginning of experiment and it didn't chance much after 30 minutes of cementation. Effect of temperature on silver cementation is shown in Figure 10. Increasing temperature resulted in decreasing effect on cementation up to 60 minutes of time where they all reached to the same value.

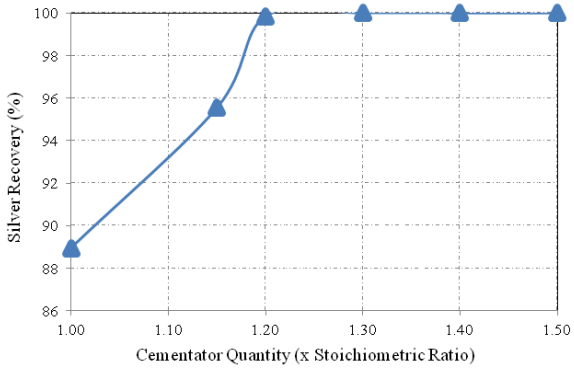

Figure 5 Silver recovery-cementator quantity relation.

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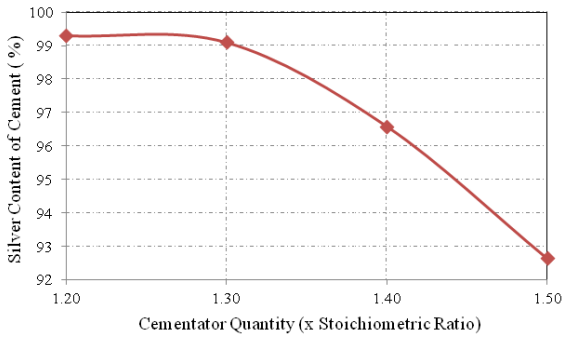

Figure 6 Silver content of cement and cementator quantity relation.

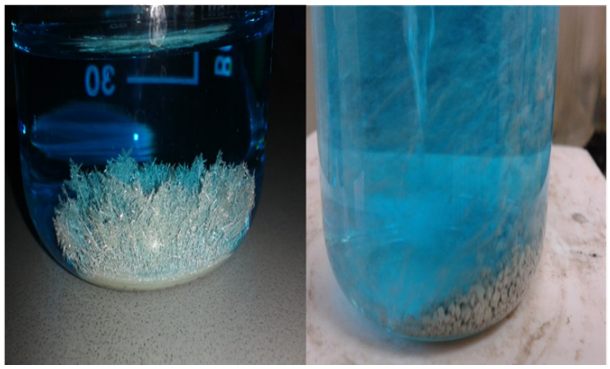

Figure 7 Cement silvers produced (left) with no stirring (dendritic silver crystals) (right) with stirring (240 rpm) at pH 1.75.

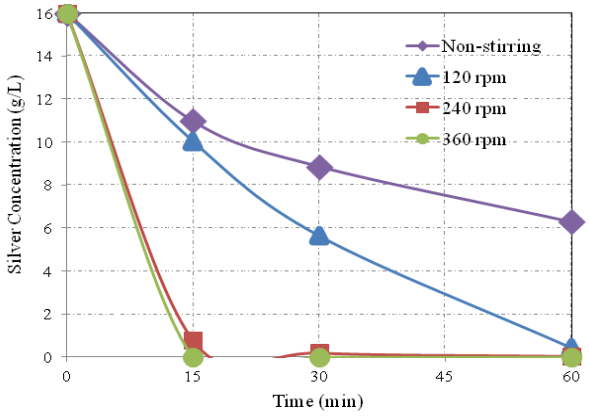

Figure 8 Stirring speed vs cementation time.

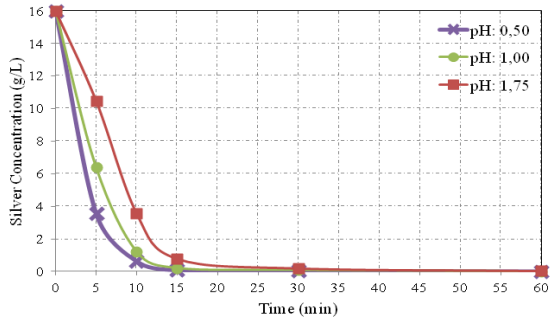

Figure 9 Effect of pH on cementation.

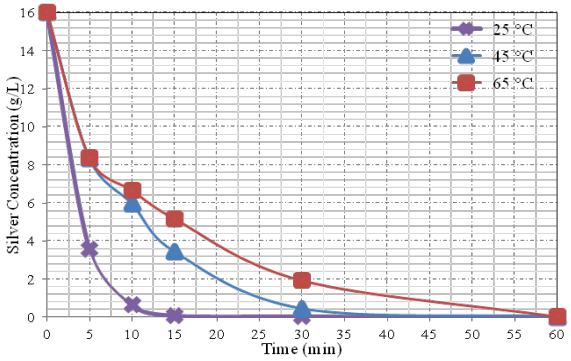

Figure 10 Temperature and cementation relation (at 240 rpm, pH 0.5).

Conclusion

The following conclusions are made as a result of this experimental study on recovery of silver from dental amalgam wastes by using hydrometallurgical processes as leaching and cementation:

i. Leaching was applied to distilled dental amalgam with –315µm in size by using nitric acid and results have shown that leaching efficiency was above 99.8%. The resulting solution contains 16 g/L Ag^{+} and 8.5 g/L Cu^{2+}.

ii. Experiments show that optimum cementator quantity is found as 1.2 times the stoichiometric ratio at pH 1.75 and 240rpm stirring speed. Cementation yield was determined to be above 99.5%.

iii. The cementation rate increased with increasing stirring speed; the optimum of which was found as 240rpm.

iv. Effect of pH on cementation rate was dominant at the beginning of experiment and it did not change much after 30 minutes of cementation.

v. Increasing temperature had decreasing effect on cementation and room temperature gave the best results with time.

vi. As a result of this experimental research, the optimum cementation conditions are determined as pH 0.5, 240 rpm stirring speed, room temperature, cementator amount about 1.2 times the stoichiometric ratio, and 60-minute duration. Silver cementation yield was 99.9% under these conditions meaning that silver from dental amalgam wastes can be recovered successfully.

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Conflicts of interest

Authors declare that there is no conflict of interest.

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