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Research Paper / Makale

Recovering of Disposed Nickel – Titanium Rotary Endodontic Files via Sulfuric Acid Leaching Treatments

Muhammed İhsan ÖZGÜN[1a*], Arslan TERLEMEZ[2b], Mahmut Ercan ACMA[3c], Yasin Ramazan EKER[1d], Ahmet Burçin BATIBAY[1e]

[1]Department of Metallurgical and Materials Engineering, Faculty of Engineering and Architecture, Necmettin Erbakan University, Konya, Turkey
[2]Department of Endodontics, Faculty of Dentistry, Necmettin Erbakan University, Konya, Turkey
[3]Department of Metallurgical and Materials Engineering, Faculty of Chemical and Metallurgical, İstanbul Technical University, Istanbul, Turkey.

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Abstract: Nickel - titanium based alloys are widely used as a root canal file in dental canal treatment in endodontics. According to the Turkish Ministry of Health, approximately, two million root canal treatments were applied yearly in Turkey. Ni-Ti rotary files have been used for 80 % of these endodontic root canal treatments. Rotary files contain 55-60 wt.% nickel and 40-45 wt.% titanium. Ni-Ti endodontic files can be recovered by hydrometallurgy, which is an economical way, instead of treating them as medical waste. The aim of this study is to provide economical hydrometallurgical recycling of metallic wastes that cannot be recovered by direct melting. Nickel and titanium based endodontic rotary files were recovered via using different leaching techniques in high corrosive environments such as dissolution in concentrated acid, baking in sulfuric acid and hydrothermal treatment in concentrated sulfuric acid. The acid concentration, temperature and time parameters were optimized for concentrated sulfuric acid leaching in autoclave. The acid baking method is a simple system more efficient than the pure dissolution in acid. At the end of the hydroxide structures dehydration, TiO_2 (anatase) and NiO powders were obtained. Moreover, under pressure within non-stirring autoclave the rotary file is completely dissolved with a cost-effective two-step process. Thus, an efficient recycling process has been created for waste Ni-Ti alloy tooth files.

Keywords: endodontics Ni-Ti files, recycling, hydrometallurgy, root canal treatment

Endodontide Kullanılan Nikel-Titanyum Atık Eğelerin Sülfürik Asit Liçi İşlemleri ile Geri Kazanımı

Öz: Nikel-titanyum esaslı alaşımlar endodontide dental kanal tedavisinde kök kanal eğesi olarak kullanılmaktadır. T.C. Sağlık Bakanlığı'na göre, Türkiye'de yılda yaklaşık iki milyon kök kanal tedavisi uygulanmakta ve bunların %80'inde Ni-Ti eğeler kullanılmaktadır. Eğeler ağırlıkça %55-60 nikel ve ağırlıkça %40-45 titanyum içerir. Ni-Ti endodontik eğeler tıbbi atık olarak değerlendirilmesinden, ekonomik bir yol olan hidrometalurji yöntemleri ile geri kazanılabilir. Nikel ve titanyum esaslı endodontik eğeler, konsantre asitte çözünme, sülfürik asitte pişirme ve konsantre sülfürik asitte hidrotermal işleme gibi yüksek korozif ortamlarda farklı liç teknikleri kullanılarak geri kazanılmıştır. Bu çalışmanın amacı, hidrometalurjik yöntemle doğrudan eritme ile geri kazanılamayan metalik atıkların ekonomik geri dönüşümünü sağlamaktır. Asit konsantrasyonu, sıcaklık ve zaman parametreleri otoklavda konsantre sülfürik asit liçi için optimize edilmiştir. Asitte pişirme yöntemi, asit çözeltisi liçinden daha verimli basit bir sistemdir. Hidrotermal işlemin sonunda ise meydana gelen hidroksit yapılarının dehidrasyonu sonucu TiO_2 (anataz) ve NiO tozları elde edilmiştir. İlave maliyeti olmayan, otoklav içinde basınç altında ve karıştırılmaksızın eğeler tamamen çözülmüştür. Böylece kullanılmış atık Ni-Ti alaşımlı diş eğeleri için bir geri kazanım işlemi ortaya konulmuştur.

Anahtar Kelimeler: Endodontik Ni-Ti eğeler, geri kazanım, hidrometalurji, kök kanal tedavisi

Bu makaleye atıf yapmak için
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ORCID ID: [a]0000-0003-0048-3439, [b]0000-0002-6092-4817, [c]0000-0003-1315-2030, [d]0000-0001-7395-4364, [e]0000-0002-2606-5115

1. Introduction

According to the statistics of the Turkish Ministry of Health, in 2014 approximately 2 million endodontic canal treatments were performed. Ni-Ti alloy files were preferred in 80 % of all treatments [1]. The recovery of scrap metal is more economical than the metal extraction from ores. Therefore, the recycling can be considered as the new generation of material engineering. Furthermore, the recovery must be safe, eco-friendly and adapted to the starting waste material. The biocompatible Ni-Ti based endodontic files have been extensively used for tooth root canal treatment since the report published by Walia et al. [2]. Ni-Ti alloy is capable of wearing due to greater hardness than the dentin channels around, besides it may take the channel bend profile. Nickel - titanium alloys' surface is coated by a compact $NiTiO_3$ oxide layer inducing a bioinert surface which resists to abrasion and corrosive body fluids or solutions used during surgical interventions [3]. Although there are single-use and sterile multi-use commercial forms of Ni-Ti alloy files in endodontic treatment, fracture risk increases due to metal fatigue in repeated use and sterilization processes [4].

Ni-Ti based alloys are made from very pure raw materials produced by casting and powder metallurgy. Vacuum Arc Melting (VAR), Vacuum Induction Melting (VIM) or Electron Ray Melting (EBM) casting methods are widely used in the production of Ni-Ti alloys, but the most homogeneous chemical composition and microstructure can be obtained via powder metallurgy [5]. The compact $NiTiO_3$ oxide layer of Ni-Ti file, is negatively affected the Ni-Ti rotary files melting and caused material losses. In addition, due to the existing oxygen, the brittle $Ti_4Ni_2O_x$ ($0<x<1$) type oxide may form during the powder metallurgy process. In particular, at casting temperature, the oxygen affinity of Ni-Ti phase is very important [6]. However, the oxide film formed by thermal oxidation treatment of titanium castings if 800°C are formed on is known passivation layer may be more rigid and brittle [7]. When impurities and oxides are not eliminated, elemental accumulation can be changed in comparison to the waste Ni-Ti rotary files. Due to the structure of the impurity and differences in chemical composition, the mechanical properties cannot satisfy the desired quality [8]. That's why waste Ni-Ti rotary files cannot be re-melted and re-casted or re-pulverized for new production. Currently the metallic waste containing nickel or titanium is used as alloying additives in the production of stainless steel [9]. However, while the use of pure nickel in stainless steel is 65 %, the use of nickel-containing scrap does not exceed 14 % [10]. Moreover, more than half of the titanium scrap goes into ferro-titanium production. This causes a reduction in the recovery rate of pure titanium [9].

In literature, since titanium or nickel ores were industrially leached with sulfuric acid [11], trials of Ni-Ti recovery has been done with strong acid environments (H_2SO_4, HNO_3, HF) [12]. However, due to the passivation surface and the pitting corrosion, the dissolution was restricted [13]. Acid baking (addition of water in hot acid) and hydrothermal leaching process under pressure (autoclave) were known as highly efficient leaching processes for metal extraction from ore or metal recovery from recycling materials, but none of them have been used for Ni-Ti recovery in the literature. In fact, with acid baking method the vanadium recovery from shale mineral has been increased from 50.7% to 90.1% just by increasing the process temperature from 140^oC to 200^oC and the cooking time from 10 to 90 minutes [14]. On the other side, increasing the temperature of concentrated acid (98%) from 100^oC to 300^oC leads to increased the leaching efficiency of lithium-ion battery wastes from by 16% [15]. Concerning the autoclave leaching process, the extraction of rare earth elements from monazite concentrate (Tomtor -Russian City- Deposit) have been 98.0 - 98.5% with process at 120^oC and 2 hours duration time [16]. Besides, almost 100% of metals present in printed circuit boards have been leached within 6M sulfuric acid and 15% H_2O_2 mixture via hydrothermal process at 90^oC [17].

Both methods are improving the metal leaching within acidic media where temperature plays an important role. The acid baking is a two-step process to attack directly the metal by reducing the formation time of the surface passivating layer. The hydrothermal leaching is a one-step process which force the metal oxidation although the surface passivizing layer. Both methods have not been applied previously for the recovery of Ni-Ti alloy files. The essential point of this study, that the effects of both methods have been investigated for the recovery of Ni-Ti files. The results obtained show that the leaching process with autoclave can be a working process for recovery.

About 1000 grams of chemically stable Ni-Ti waste files are generated monthly from the clinics of Necmettin Erbakan University Faculty of Dentistry. In this work, the preliminary study shows the highest leaching efficiency of endodontic Ni-Ti files have been obtained within sulphuric acids solutions. In order to optimize the recovery, three different hydrometallurgical methods have been used (i) acid baking, (ii) heating the file within the solution under atmosphere and (iii) heating within the solution under pressurized environment. After the determination of the most effective dissolution process, the metallic ions have been separated by precipitation giving the opportunity to use the final products in new applications.

2. Experimental Methods

2.1. Sample Preparation and Characterization

The endodontic files consist of a holding part, a protective polymer piece and the Ni-Ti tip. All these parts have been separated using forceps to warranty the product purity at the end of the recovery process (Fig.1). Thus, the holding part and the polymer can be recovered with further appropriate methods.

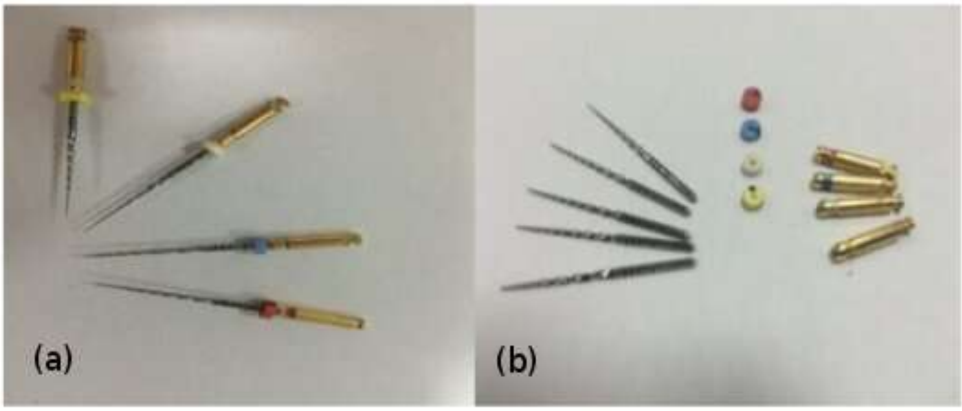

Figure 1. Disposal endodontic Ni-Ti files and physically separated parts of Ni-Ti file

The chemical composition of Ni-Ti endodontic files was determined by using X-ray fluorescence spectrometer (Rigaku^{TM}, NEX–CG Energy Dispersive). The results show that Ni and Ti are the major elements, however minor elements are also present (Table 1XRF results was showed that the type of the files is the alloy specified as NiTi-60, containing 60 wt% nickel and 40 wt% titanium [18].

Table 1. XRF analysis results of the recovered Ni - Ti files' tip

Component	Concentration (wt%)
Ni	58.72
Ti	40.07
Other (Si, V, Al, Mg)	1.21

The morphology as well as the elemental distribution on the surface of the Ni-Ti files has been characterized via Scanning Electron Microscope–Energy Dispersive Spectroscopy (HITACHI^{TM}, SU1510). Ni and Ti are homogeneously distributed on the sharped surface of the rotary files which contains corrosion pitting (Fig.2). The elemental mapping and the EDS rate calculation show a high presence of oxygen which take place of the surface nickel since 48.39 wt% Ni and 12.39 wt% O are calculated on the surface (Fig.3). The basic component metallic values must be obtained using hydrometallurgical leaching processes to create a clean substance cycle [19]

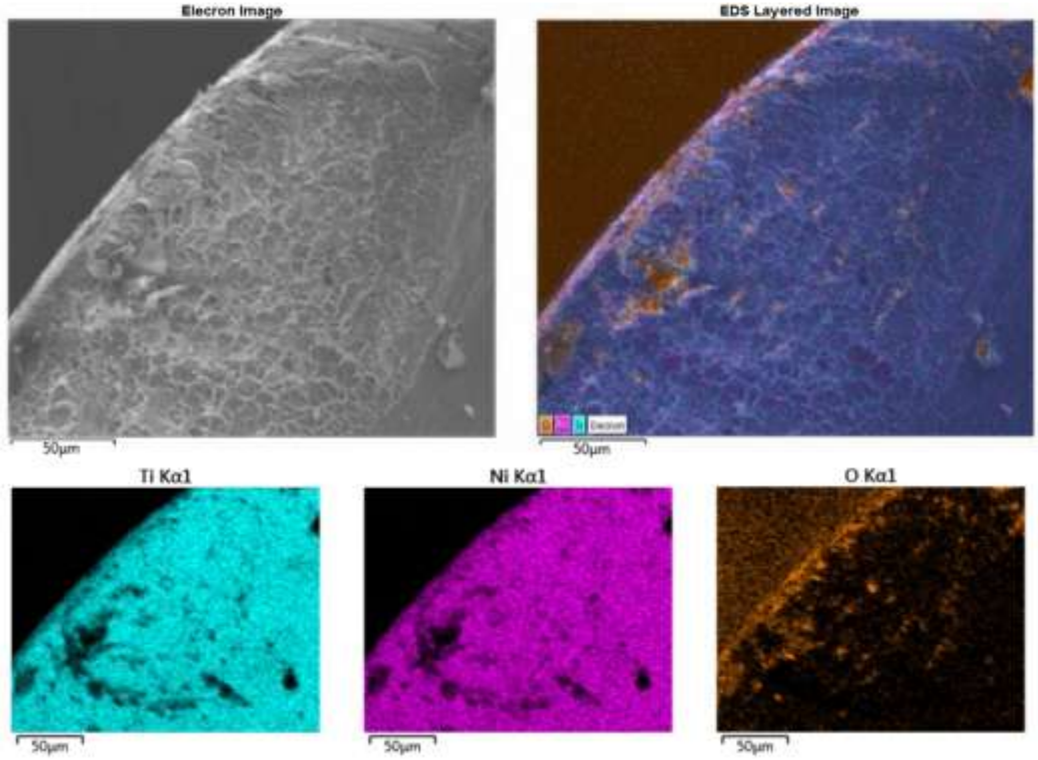

Figure 2. SEM image and EDX element distribution of the cross-sectional surface of waste Ni-Ti files

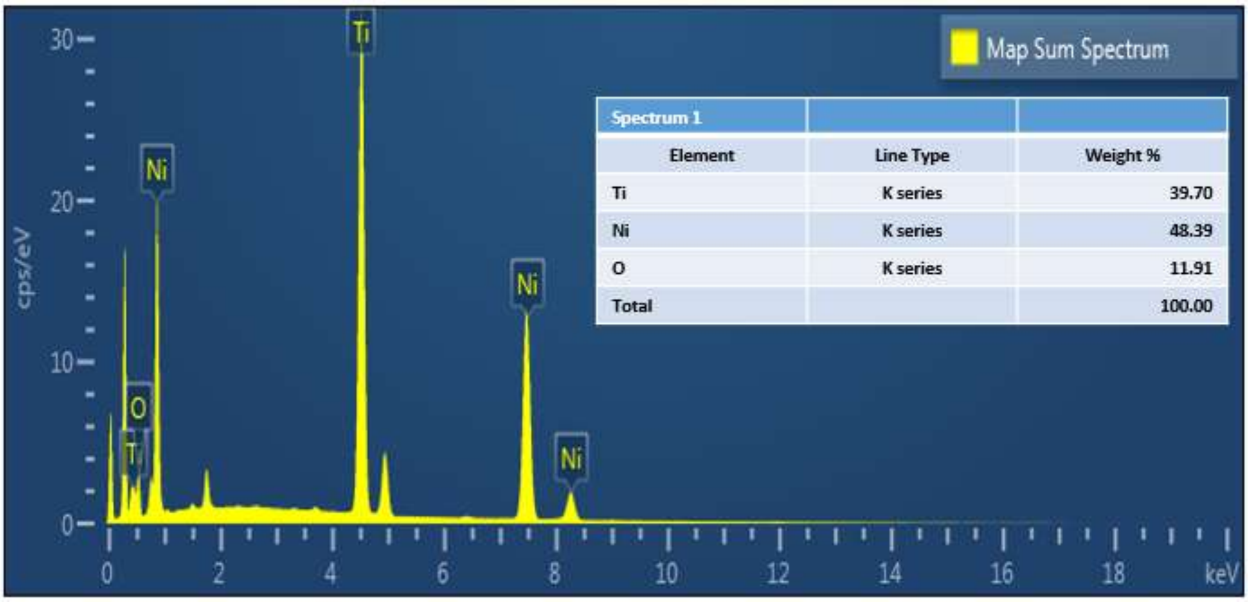

Figure 3. EDX element mapping spectrum of the cross-sectional surface of waste Ni-Ti files

2.2. Rotary Files Leaching

The mechanically separated Ni-Ti rotary files have been firstly leached with different concentrated strong acids (HCl, HNO_3, and H_2SO_4) in order to determine the most efficient one. During this first tests, 0.11 gram Ni-Ti file has been kept within hot (80^{o}C) concentrated acid during 5 days under reflux with continuous stirring (100 rpm). Once the most corrosive acid has been chosen, two other leaching processes were proceeded.

The second leaching process is the acid baking where Ni-Ti files were kept at 200^{o}C for 2 hours in 50 ml 98% H_2SO_4 (boiling point 337^{o}C). Different file/acid weight ratio has been selected (1/3, 1/5, 1/7 and 1/9). At the end of the heat treatment, 10 ml of water was added drop by drop within the hot mixture. The obtained slurry is mixed at 100 rpm and 100^{o}C during 1 hour in order to release the possible cations that can be precipitated with SO_4^{2-}.

The third process is realized within autoclave with different H_2SO_4 concentrations (1M, 3M, 5M), different process times (30, 60, 90 and 120 minutes) and at different temperatures (150, 175, 200, 225 and 250^{o}C). Since water is boiled above 100^{o}C, the pressure inside the autoclave is increasing with the temperature. For all processes, the cation concentrations in acidic solutions have been determined by atomic absorption spectrometer (Perkin Elmer^{TM} Analyst 700). Acid baking and autoclave leaching methods were not applied to Ni-Ti alloys prior to this study. These methods do not require high investment costs.

2.3. Cations Precipitation and Dehydration

At the end of leaching processes, Ti^{4+} and Ni^{2+} ions are simultaneously present in acidic solution. By adjusting the solution pH with 1M NaOH under continuous stirring at 400 rpm, both cations have been consecutively precipitated at pH = 1 for Ti^{4+} and pH = 10 for Ni^{2+}. Following each precipitation $Ti(OH)_4$ and $Ni(OH)_2$ solid residues have been separated, washed with distilled water and dried at 300^{o}C during 2 hours. Chemical content of the dehydrated oxides was determined by X-Ray Florescence (Rigaku^{TM}, NEX - CG, Energy Dispersive) and their crystallographic structures by X-Ray Diffraction (GNR^{TM}, APD 2000 Pro) methods.

3. Results

Strong mineral acids are completely dissociated in aqueous solution resulting in high corrosion ability especially towards metals. However, the leaching behavior is depending to the affinity between acid anions and metallic cations. That’s why preliminary leaching processes have been performed during 5 days at different temperature and with concentration of HNO_3, HCl and H_2SO_4 in order to determine the most efficient acid (Fig.4). Whatever the temperature and the concentration the most effective acid to leach Ni-Ti rotary files is H_2SO_4. In fact, within the most corrosive conditions (5M concentration at 80^{o}C) more than 14% Ni-Ti files have been dissolved within 5M sulfuric acid while less than 10% has been dissolved in HCl and less than 5% in HNO_3. This result can be partly explained by the low boiling points of both HCl (109^{o}C) and HNO_3 (121^{o}C) comparing to H_2SO_4 (337^{o}C) and the anions oxidation degree (Cl^-, NO_3^- and SO_4^{2-}). Due to its higher boiling point and anion oxidation degree, highly reactive hydronium ions H_3O^+ are released and kept within the leaching medium.

The acid baking process has been developed to increase suddenly the concentration of H_3O^+ with high mobility. In fact, the introduction of some water drops within the hot strong acid accelerates the formation and the release of H_3O^+.

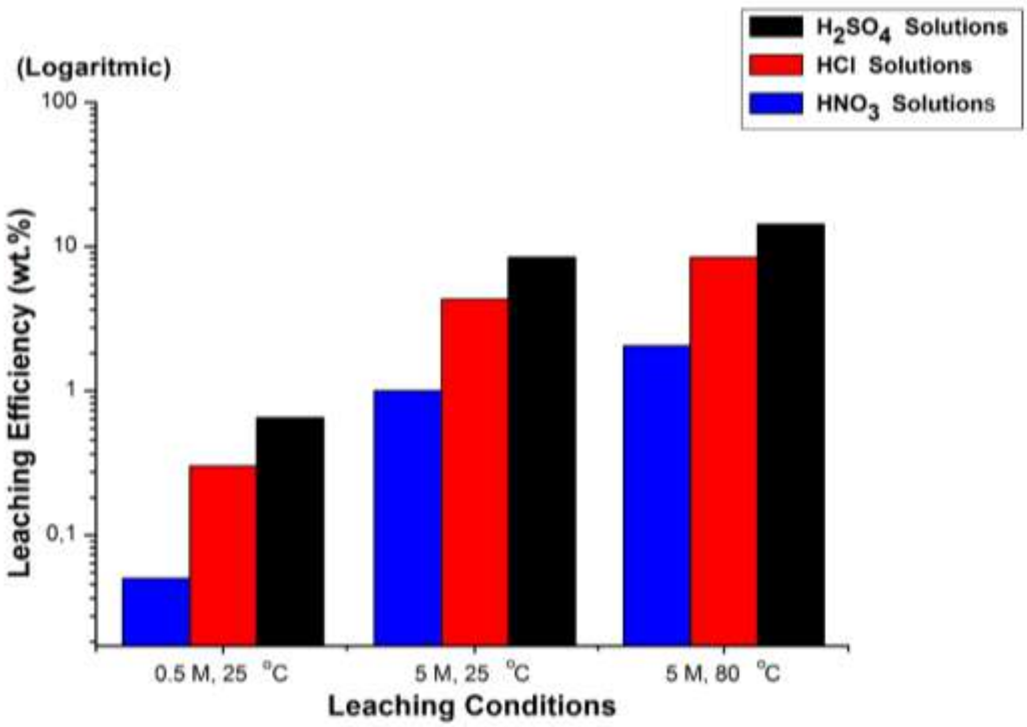

Figure 4. Dissolution efficiency of Ni - Ti files in mineral acids (H_2SO_4, HCl and HNO_3)

In order to optimize the formation of hydronium, different samples / acid ratio have been tested (from 1:3 to 1:9) (Table 2). The dissolution is increasing with the acid rate reaching an upper limit at about 60 % with 1:7 ratio.

Table 2. Sample / acid ratio and dissolution yield of Ni-Ti alloy in acid baking

Sample / Acid Ratio	Dissolving Yield (wt. %)
1/3	35.42
1/5	40.54
1/7	58.81
1/9	60.10

The dissolution of each cation varies with increasing the acid rate; as expected the release of titanium increases, but the one of nickel decreases (Fig. 5). This behavior is attributed to the precipitation of Ni based salt since the metal cannot be evaporated with these conditions. In fact, Ni leaching within H_2SO_4 involved the formation of hydrogen sulfide (H_2S) according to equation 1 [20]. Yet, H_2S spawns the formation of insoluble nickel sulfide (NiS) according to the equation 2 [20].

$$4\,Ni \;+\; 9\,H_2SO_4 \;\rightarrow\; 4\,NiSO_4 \;+\; H_2S \;+\; 4H_3O^+ \;+\; 4\,HSO_4 \qquad (1)$$

$$Ni \;+\; H_2S \;\rightarrow\; NiS \;+\; H_2 \qquad (2)$$

The hydrothermal process suggests a leaching under pressure which is controlled via the heat treatment temperature of the autoclave. The acid concentration and the treatment duration are the other important parameters for this process (Fig. 6). The full dissolution of the Ni-Ti files has been obtained with 5 M acid for the lowest temperature (150°C) during 120 min process.

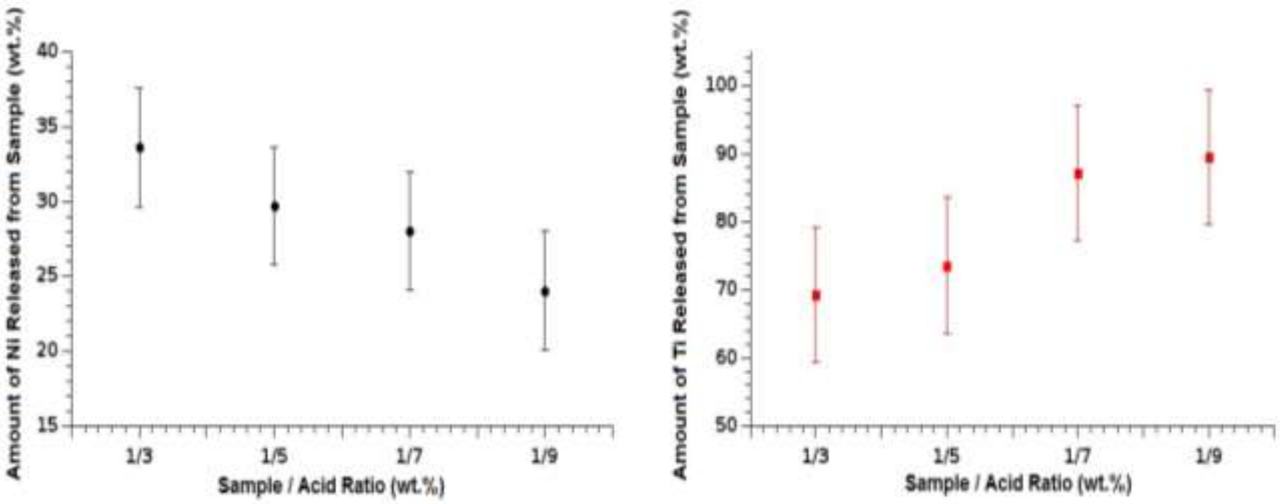

Figure 5. Metal cations releasing from Ni-Ti file via acid baking at different sample/acid ratio

Meanwhile, the same result has been observed at 225°C but for the shortest duration (30 min). This result confirm that sulfuric acid naturally attacks Ni-Ti files and this reaction can be rated with temperature and pressure control.

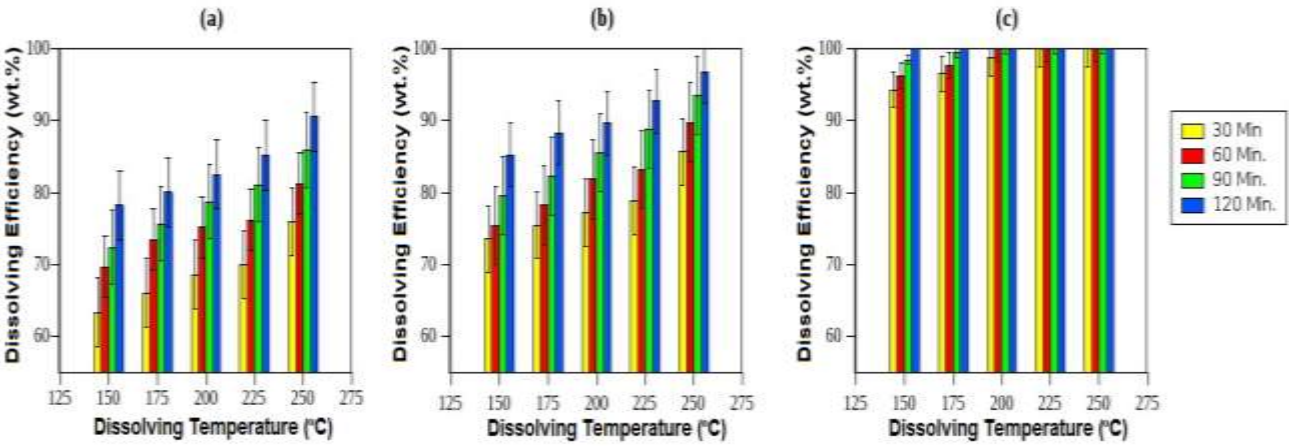

Figure 6. Temperature-time-concentration relationship of dissolution efficiency in autoclave for 10 ml H_2SO_4 solution (a)1 M, (b) 3 M, (c) 5 M

The recovery of both cations from the final acidic solution is possible via their precipitation with increasing the pH. The solid phase obtained at pH 1 almost consists of Ti, while at pH 10 Ni is mostly present (Table 3). The solids separated and dehydrated by filtration at each pH are both oxides (Fig.7). At pH 1, titanium oxide (TiO_2) is under the tetragonal anatase phase [21].

Table 3. XRF analysis results of dehydrated precipitates

Component	Concentration for precipitate at pH 1(wt. %)	Concentration for precipitate at pH 10(wt. %)
Ti	98.88	1.51
Ni	0.39	97.81
Other	0,73	0.68

The metastable anatase crystal turns irreversibly into rutile phase above 450°C involving the loss of its photocatalytic properties [22]. At pH 10, nickel oxide (NiO) is under rock-salt phase [23]. NiO is a p-type anti-ferromagnetic semiconductor which can be also reduced electrochemically [24].

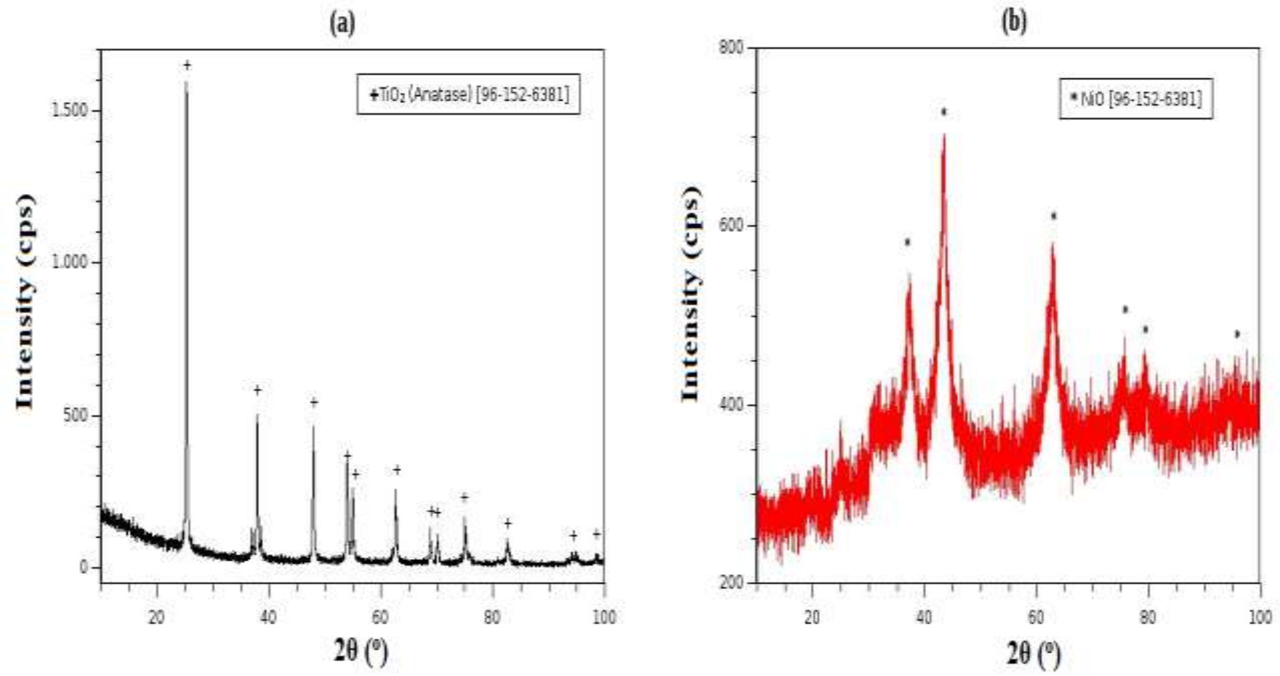

Figure 7. XRD results of dehydrated precipitates (a) precipitation at pH 1 (b) precipitated at pH 10

4. Conclusions

The re-use of waste Ni-Ti file requires a costly process involving melting under vacuum with several steps due to the purity request for advanced engineering or biomedical use [25]. That's why the recovery of this waste for alternative application fields are preferred. The dissolution of metal ions and their separation via precipitation is an effective recovery process but the compact $NiTiO_3$ at the alloy surface restricts the corrosion of Ni-Ti rotary files even after 5 days within concentrated H_2SO_4. Here it has been demonstrated that non-conventional acid baking and hydrothermal leaching processes can improve the dissolution efficiency. Especially in autoclave within tight volume, thanks to the evaporation of solution and the oxygen dissolved the solution the pressure highly increases improving the metal leaching [26]. Furthermore, the leaching time is seriously shortened above 225^{o}C with 5 M acid. Pure anatase is precipitated via increasing of the leaching medium pH up to 1, while highly pure NiO and some impurities precipitate at pH 10 [27]. Both precipitated and separated oxides have an application potential in the industry; NiO can be used as raw material for plating or electronic device applications [28], while TiO_2 can be used as pigment, photocatalytic materials or other nano-scale applications [10].

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