An Innovative Method for Egyptian Monazite Mineral Digestion by Sulfuric Acid

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Abstract: *The present work deals with a study of an innovative method for Egyptian monazite mineral digestion by 98%sulfuric acidin hydrothermal autoclaves, where the digtion of monazite take place.The aim of this work is to obtain the optimal condition of monazite digestion using sulfuricacid so that all elements contained in the monazite that are U, Th, RE, PO_4 dissolved as much as possible.The parameters are sulfuricacid consumption (weight ratio of monazite ore: sulfuricacid), digestion temperature and digestion time.The results showed that the optimal conditions of digestion are 1: 1.6 of weight ratio of monazite ore: sulfuricacid, 170°C of digestion temperature, 8 hours of digestion time with 78.6% recovery on 85%monazite mineralpurity without pre-treatment or grinding for the mineral (most pronounced advantages of the acid process) which equal to 92.5% of pure monazite mineral.Such findings were also supported by X-ray diffraction and scanning electron microscopy analyses.*

Keywords: Monazite mineral, Digestion

1. Introduction

As monazite is chemically and thermally stable concentrate in the form of crystalline phosphate mineral, it is difficult to dissolve such material in acids or alkali. It requires a suitable condition to leach out the complex materials/metals present in the monazite using acidic or alkaline solutions.

Monazite is distributed throughout many countries around the world, most notably in heavy sand deposits. These heavy sand deposits also hold other minerals of economic importance, namely ilmenite, zircon, and rutile. Because the sand deposits are of so much importance, monazite extraction methods may need to be developed and improved upon quickly. Monazite is made up of approximately 20–30% Ce, 10–40% La, and appreciable amounts of heavy REEs, with REE oxides all-together accounting for approximately 70% of monazite's weight **(1).**

Different authors studied the direct leaching of monazite sand using acidic solutions of sulfuric, hydrochloric and nitric acids under the different experimental conditions.The sulfuric acid has been usedmost extensively for the leaching of monazite, where the sulfate ($SO4^{2-}$) ion of H_2SO_4 acts as a ligand which reacts with RE at high temperature.Fernelius et al. in1946 as well as Kim and Osseo Asarein 2012 used 98% sulfuric acid to leach out monazite at 200–230°C which was subsequently neutralized to separate REEs and Th.**(2)**

General processing methods have been developed for these well-known REE minerals: acid baking (mostly by sulfuric acid) followed by water-leaching can be applied to treat them **(3).**In the previous research, the effects of two different chemical decomposition methods, namely sulfuric acid baking and caustic digestion, to enhance the REE recovery from a refractory ore were investigated. The REE-containing particles were scattered throughout the ore, and some of them were even trapped in other minerals such as Fe oxide, although the total REE concentration was relatively high at 3.4% TREO. From the preliminary leaching tests using nitric acid, the maximum REE recovery only reached 61–73%; thus, a significant amount of REEs was still left in the residue.

Using sulfuric acid baking–water-leaching, the REE recovery was improved to 97–100% after theore was baked at 2.0 acid/solid ratio and 200 °C for 2 h. The REE recovery reduced with increasing leaching temperature because of the CSD solid formation at elevated temperatures and the accompanying REE co-precipitation.

The REE ores in Chuktukon deposits from Russia showed similarmineralogical properties as the Araxá ores and direct chemical processing was also considered, i.e., nitric acid-leaching in an autoclave**. (4)**

The sulfation reaction of monazite with acid was virtually complete after baking at 250 °C for 2 h, resulting in >90% solubilization of rare earth elements, thorium and phosphate. After baking at 300 °C, a thorium phosphate type precipitate was formed during leaching, leading to a sharp decrease in extraction of thorium and phosphate, but the leaching of rare earth elements reached nearly 100%. As the bake temperature was further increased to 400–500 °C, extraction of thorium, phosphorus and the rare earth elements decreased due to formation of insoluble thorium-rare earth polyphosphates. The formation of these polyphosphates is thought to be related to dehydration of orthophosphoric acid produced in the initial reaction of monazite with sulfuric acid. Between 650 and 800 °C, monazite was partially re-formed, leading to a further decrease in rare earth extraction to 55%. The re-forming of monazite appeared to be due to a reaction between the thorium-rare earth polyphosphates and rare earth sulfates. **(5).**

The sands are ground to 95 per cent minus 65 mesh, end then digested in 93 percent sulfuric acid for four hours at 210°C. The acid to sand weight ratio, based on 100 per cent sulfuric acid, is 1.56. This digestion produces a rubber-like dough material which is quite soluble in cold water. Ten pounds of cold water per pound of sand are added to solubilize the monazite sulfates **(6).**

Monazite digesting approximately as 25 g of monazite in 75 ml of 98 % sulphuric acid at 200 °C for 3 hours as digestion time using the glass beakers on the stirring hot plate. Then, the mixture was cooled to room temperature, adding 200 mL water to dissolve the metal sulphates, and filtering to produce a clear solution.(7)

The concentrate of monazite was baked at 250°C for 4 h with a sulphuric acid to concentrate (S/C) weight ratio of 4:1. Temperature (180–250°C) had little effect on the extraction of REEs, but greatly affected the extraction of thorium and uranium. In general, the extraction of thorium and uranium decreased with an increase in temperature (8).

For the opening of raw mineral materials, NaOH of the "chemically pure" qualification was used. Monazite concentrate powder of a certain fraction and known mass was placed in an autoclave, and NaOH solution of a given concentration and volume was introduced.

The most important factors affecting the completeness of alkaline opening of monazite concentrate are contact time, temperature, and degree of fineness of the initial material; on the contrary, a change in the alkali content in the solution and the solid-to-liquid ratio affect it to a lesser extent. The optimal conditions for the mentioned process were found to be: a degree of fineness of particles from 0.05 to 0.125 mm at [NaOH] = 19 mol/L, a solid-to-liquid ratio = 1:4 and a contact time of 3 h at 160 °C. The maximum process yield reaches 96 ± 2% **(9).**

This study was conducted to investigate anddevelop possible alternatemethod for monazite digestion by sulfuric acid to avoid all the dangerous which produce through the normal digestion method also through the dissolution process.

2. Experimental

The experiments that form the basis of this study were conducted employing the monazite concentrate (85%) occurs as a brittle mineral, with a hardness index of 5–6 on Moh's scale and a specific gravity which varies from 4.6–5.5, depending on the thorium content.

2.1. Chemicals and reagents

The monazite mineral used in this work was obtained from nuclear materials authority (black sand project), Egypt. Sulfuric acid 98% and the dissolution were by distilled water.

2.2. The structural flexibility of monazite

The monazite-type compounds crystallize in a monoclinic structure with space group $P21/n$ (Z=4). The structural arrangement is based on the nine-fold coordination of the metallic cation and is usually described as an equatorial pentagon interpenetrated by tetrahedron formed by the oxygen atoms coming from the phosphate groups (**Figure 1**) 65, 73, 74. The structure is described as a chain, along the c axis ([001] direction), formed by an alternation of LnO_9 polyhedra and phosphate tetrahedra (so-called polyhedron-tetrahedron chains). In the monazite structure, two distinct Ln-P distances exist along the chains which induce a distortion of the LnO9 polyhedron, and a set of nine distinct bond distances between lanthanide and oxygen atoms.
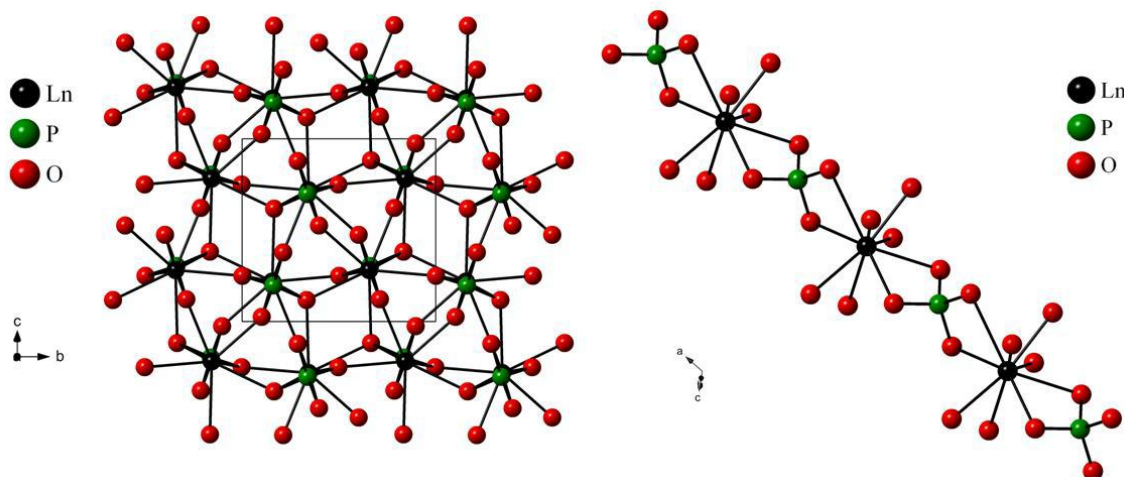

Figure 1: Representation of the crystal structure of LnPO$_4$monazite **(10).**

2.3. Ore Characteristics

The ore used in this study was monazite mineral; Figure2 shows an X-ray diffraction (XRD) analysis of the mineralwith microscope photo picture.Monazite-containing particles were observed through a scanning electron microscopy (SEM) analysis, as displayed in Figure 3. In the subsequent energy-dispersive X-ray (EDX) analysis (Figure 4), monazite grains were observed with zircon, ilmenite and rutile minerals.
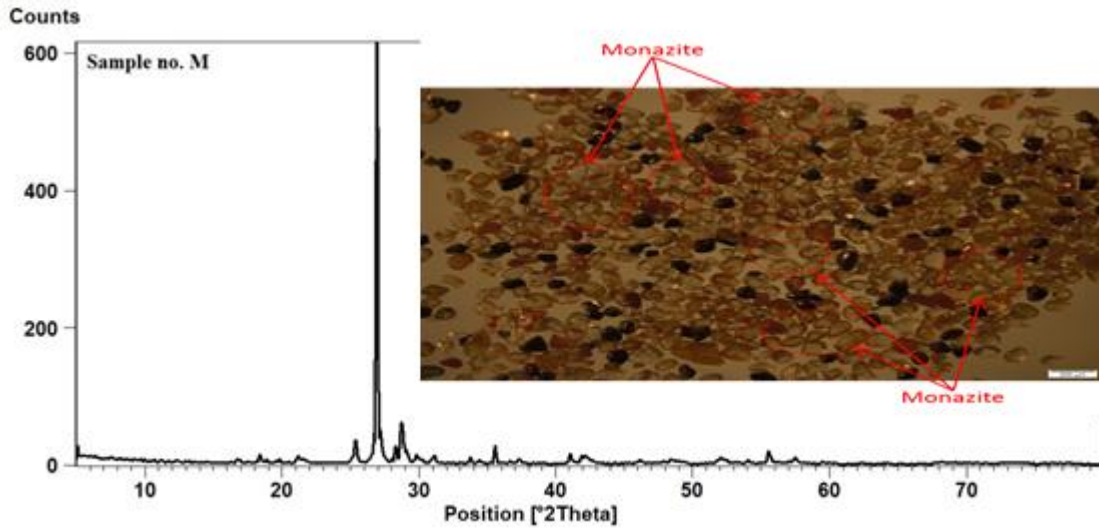
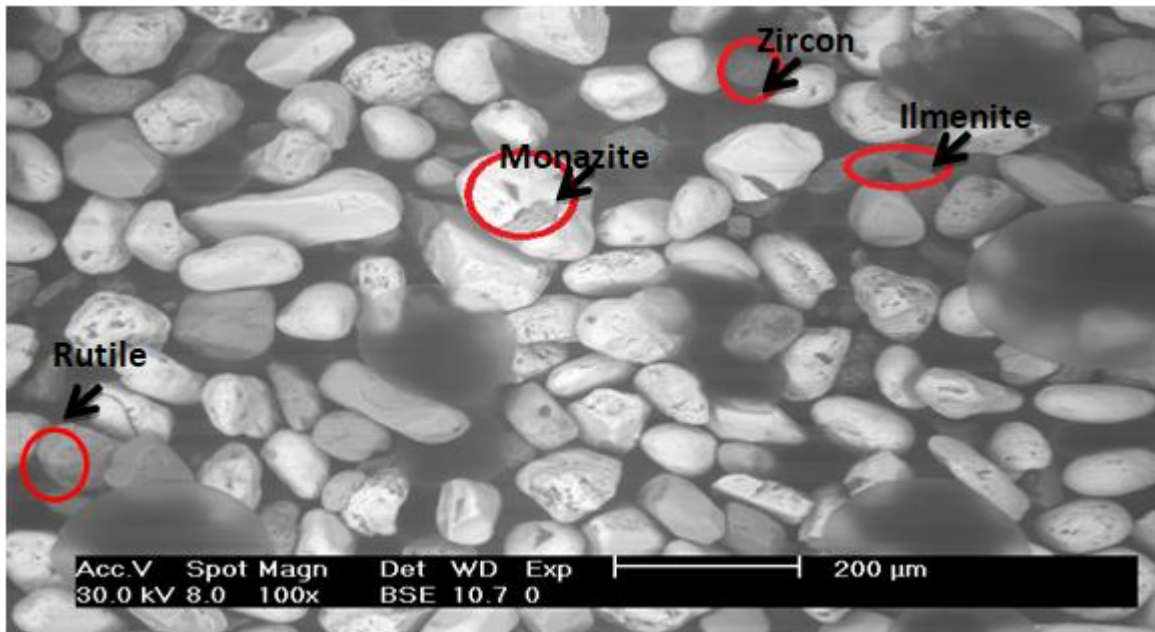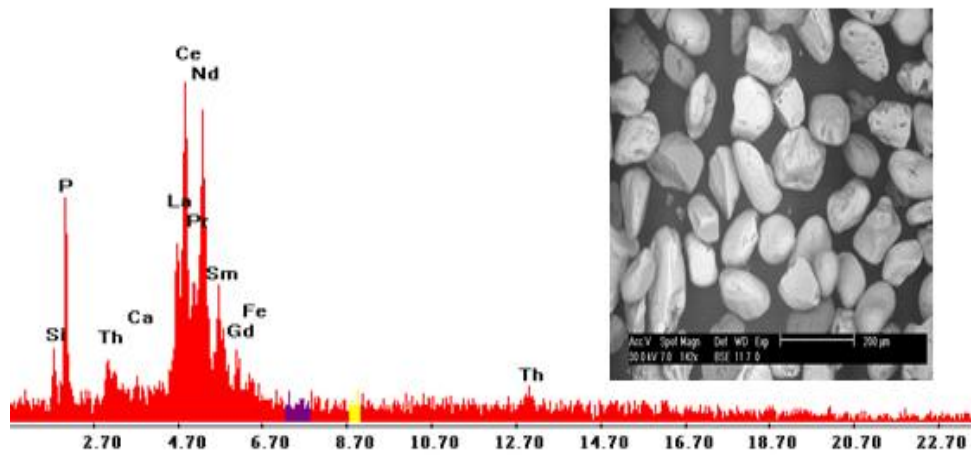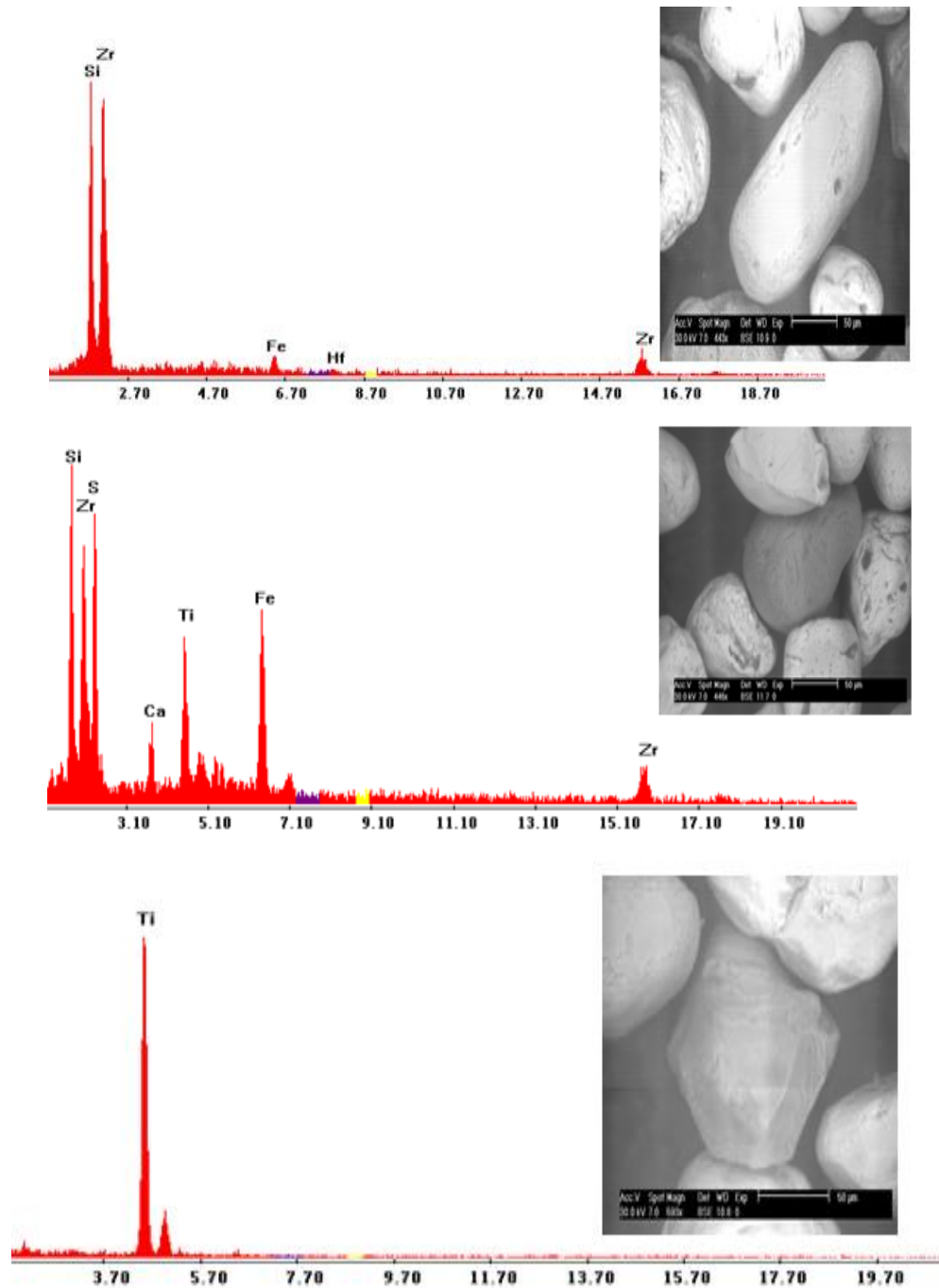**Figure 2:** XRD pattern of the monazite mineral

Figure 3.SEM image of the monazite mineral

Figure 4: SEM/EDX spectra of monazite mineral-containing grainswith zircon, ilmenite and rutile minerals

2.4. Sulfuric Acid digestion

The main objective of the laboratory studies; first, to study the digestion of monazite sand in order to lower the acid requirements and to determine the conditions necessary to make a pilot plant digestion; secondly, to remove all the pollution of fumes produced from the normal digestion.

To decompose the ore to a more soluble form, sulfuric acid digestion was applied to the ore treatment. Various solid /acid ratios (w/w) were tested, i.e., 1:4.5, 1:2.25, 1:1.8, 1:1.62, 1:1.5, 1:1.4 and 1:0.9, and the ore and acid mixture was digested in autoclave at different temperatures (100, 150 and 170 °C) for different hours (3, 4, 5, 6, 7 and 8 h). The digested ore was subsequently introduced to the water-solubilization step. The metal contents in the solid phase before and after digestion were measured by the scanning electron microscopy (SEM), energy-dispersive X-ray (EDX) and XRD diffraction analysis.

3. Result and discussion

3.1. Sulfuric Acid digestion

During the sulfuric acid digestion method, monazite is reacted with concentrated sulfuric acid for known time. During the reaction, the REE, uranium and thorium phosphates are reacted with the sulfuric acid to form a deep-grey mud containing rare earth, uranium and thorium sulfates is carried out according to the general equations:

$$2REPO_4 + 3H_2SO_4 \rightarrow (RE)_2(SO_4)_3 + 2H_3PO_4 \qquad (1)$$

$$Th_3(PO_4)_4 + 6H_2SO_4 \rightarrow 3Th(SO_4)_2 + 4H_3PO_4 \qquad (2)$$

$$U_3(PO_4)_4 + 6H_2SO_4 \rightarrow 3U(SO_4)_2 + 4H_3PO_4 \qquad (3)$$

In this regard, according to the above scheme for the complete conversion of monazite concentrate to their components, it was necessary to determine the optimal conditions for the quantitative amounts of the ore and acid ofthe autoclave processing.

Traditional methods of digestion for natural water samples include fusion, dry ashing, perchloric acid, sulphuric acid–nitric acid and boiling on a hot plate, with more recent methods generally using autoclaving, UV photo-oxidation and microwave heating (11).

Hydrothermal autoclaving methods are generally straightforward, givereproducible results and use sealed vessels that are lessprone to contamination.

The velocity of the reaction and the degree of the decomposition of monazite mineral depends upon the acid to the sand ratio and the temperature of the reaction.

3.1.1. Effect of temperature

The effect of temperature on the digestion process was examined for the ore treated with a**solid /acid ratio (w/w) of 1: 4.5 for 3hours**, as shown in Figure 5.The monazite digestion percents increased with increasing temperature from 100 to 170 °C. At 100°C, the digestion percents was 7% which increased to 15% at 150 °C and reach to 25% at 170 °C which consider the best percent of digestion.
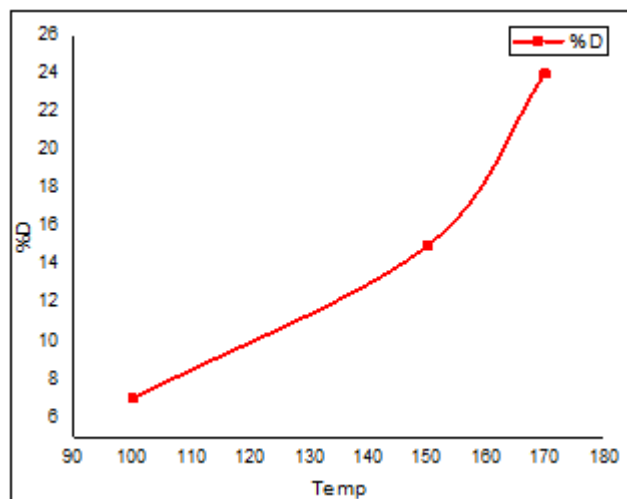

Figure 5: The digestion percents at different temperatures with a solid /acid ratio (w/w) of 1: 4.5.

3.1.2. The effect of different digestion time with different solid / acid ratio

The liquid to solid (L/S) ratio affects the viscosity of the solution with the solvent agent. Higher L/Sratio provides a sufficiently low viscosity for the leachate solution to circulate freely, hence better leaching. Several studies have been done on the effect of L/S ratio for the extraction of rare earth elements, thorium and uranium from monazite concentrate. The study was carried out using 98% of H_2SO_4 and the L/S ratio tested varied at 1:4.5, 1:2.25, 1:1.8, 1:1.62, 1:1.5, 1:1.4 and 1:0.9 for digestion process. The higher L/S

ratio has the possibility of more effective contact between the solid and liquidspresent in the liquid phase in mixing digestion removes the solid products formed on the particles in the normal digestion. According to the autoclave process the previous fact was changed according to the following experiments.

- The effect of digestion time was examined for the ore treated with the first**solid /acid ratio (w/w) of 1: 2.25atdifferent times (3, 4 and 5hours) at 170** °C which was the best temperature for digestion percent. As shown in Figure 6, the monazite digestion percents increased with increasing of the digestion time from 3 to 5hours. At 3 hours the digestion percents was 30% which increase to 48 then to 54.5 % at 4 and 5 hours respectively.
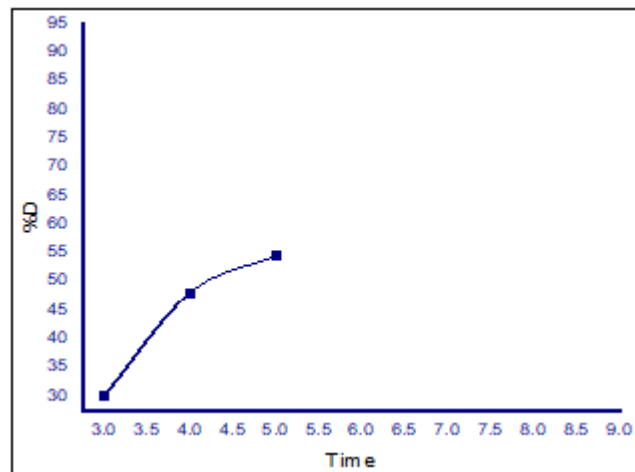

Figure 6: The monazite digestion percents at different time with solid /acid ratio 1: 2.25

- The effect of digestion time was examined for the ore treated with a **solid /acid ratio (w/w) of 1: 1.8 at different times (4, 6 and 8hours) at the same temperature (170** °C). As shown in Figure 7,the percent of digestion was increased from 54.5% at 4 hours to 77% for 8 hours.
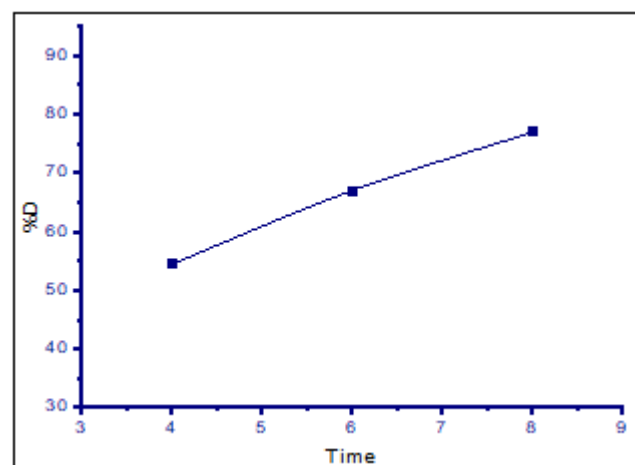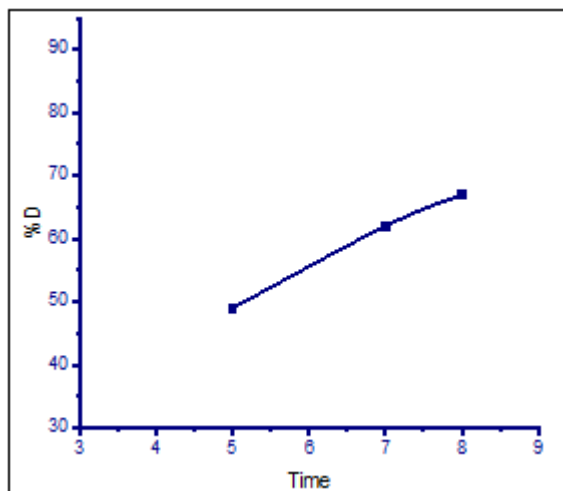

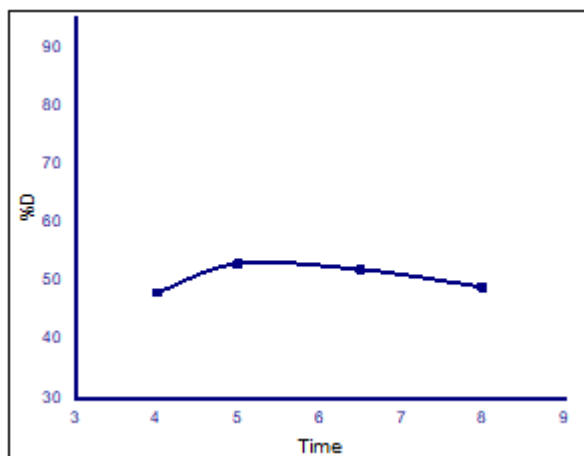**Figure 7:** The monazite digestion percents at different time with solid /acid ratio1:1.8

- The effect of digestion time was examined for the ore treated with a **solid /acid ratio (w/w) of 1: 1.4 at different times (5, 7 and 8hours) at the same temperature (170** °C).

As shown in Figure 8,the percent of digestion was increased from 49% at 4 hours to 67% for 8 hours.
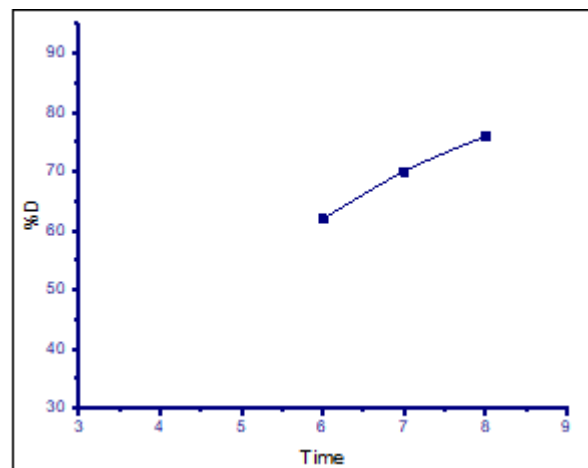

Figure 8: The monazite digestion percents at different time with solid /acid ratio 1:1.4.

• The effect of digestion time was examined for the ore treated with a **solid /acid ratio (w/w) of 1: 0.9 at different times (4, 5, 6.5 and 8hours) at the same temperature (170 °C)**. As shown in Figure 9,the percent of digestion was increased at 5 hours which reach to 53% and decrease with the increase of time which equal 49% at 8 hours.
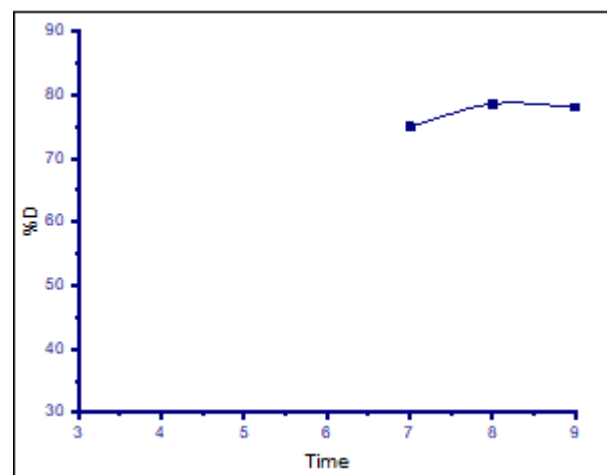

Figure 9: The monazite digestion percents at different time with solid /acid ratio 1:0.9.

The effect of digestion time was examined for the ore treated with a **solid /acid ratio (w/w) of 1: 1.5 at different times (6, 7 and 8hours) at the same temperature (170 °C)**. As shown in Figure 10,the percent of digestion was increased at 6 hours which reach to 62% with increasing of time the digestion percent equal 67% at 8 hours.

Figure 10: The monazite digestion percents at different time with solid /acid ratio 1:1.5

The effect of digestion time was examined for the ore treated with a **solid /acid ratio (w/w) of 1: 1.6 at different times (7, 8 and 9hours) at the same temperature (170 °C)**. As shown in Figure 11,digestion percent equals 75% at 7 hours and increase to 78.6% which equal to 92.5 % of digestion to monazite 100% purity at 8 hours the digestion decrease to 78.1% at 9 hours.

Figure 11: The monazite digestion percents at different time with solid /acid ratio 1:1.6

The scanning electron microscopy (SEM), energy-dispersive X-ray (EDX), XRD diffraction analysisand microscope photo picture for the residue after digestion at 8 hours was displayed in Figure12 and 13.
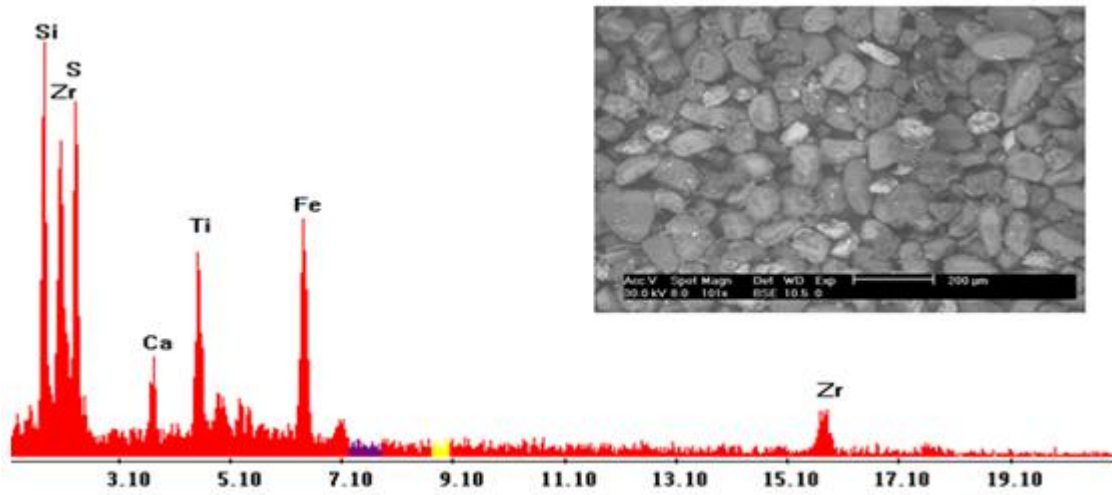
Figure 12: SEM/EDX spectra of the residue after monazite digestion at 8 hours with solid/liquid ratio 1:1.6 at 170° C
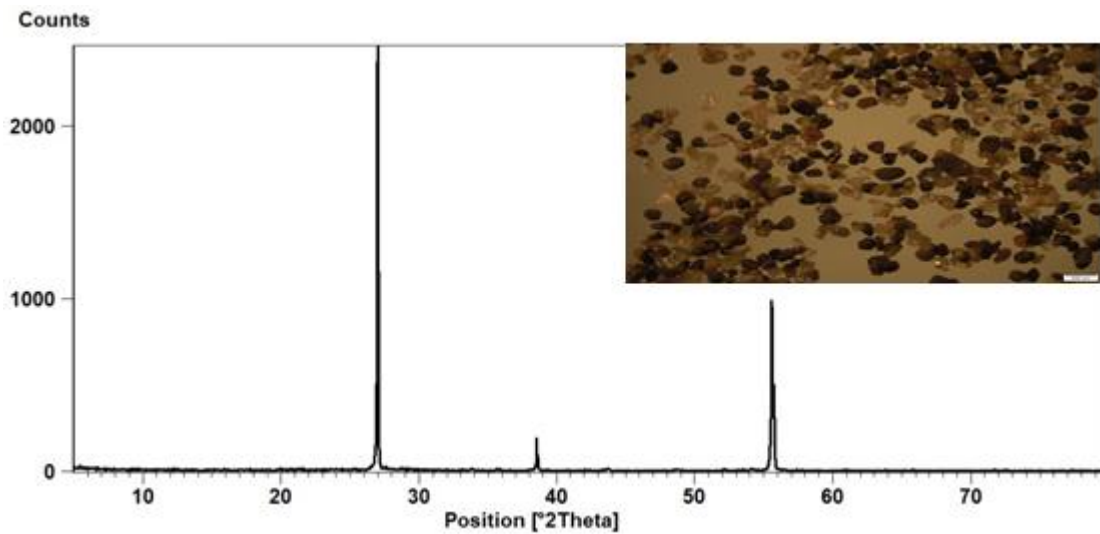

Figure 13: XRD diffraction analysis and the microscope photo picture of the residue after monazite digestion at 8 hours with solid/liquid ratio 1:1.6 at 170° C

The scanning electron microscopy (SEM), energy-dispersive X-ray (EDX), XRD diffraction analysis and microscope photo picture for the residue after digestion at 8 hours was displayed in Figure14 and 15.
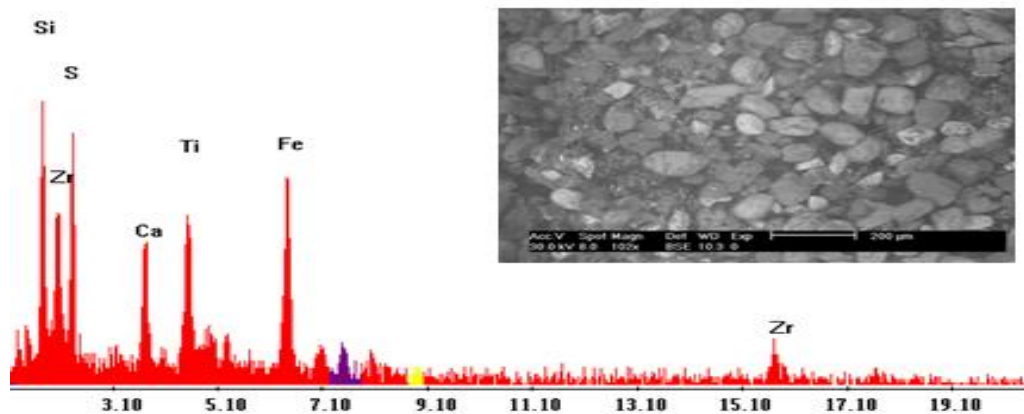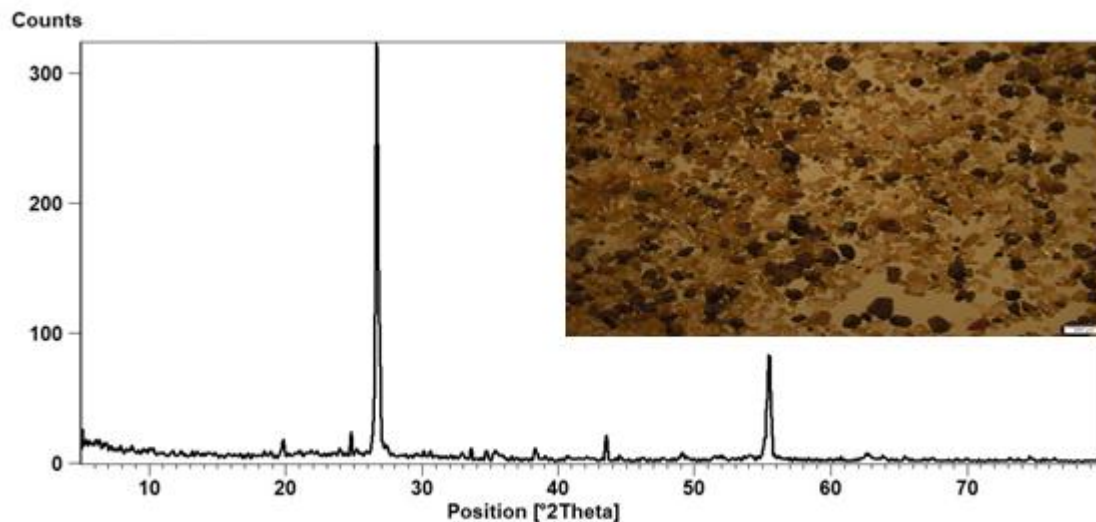

Figure 14: SEM/EDX spectra of the residue after monazite digestion at 9 hours with solid/liquid ratio 1:1.6 at 170° C.

Figure 15: XRD diffraction analysis and the microscope photo picture of the residue after monazite digestion at 9 hours with solid/liquid ratio 1:1.6 at 170° C

Figures 12, 13, 14 and 15 show the SEM/EDX, XRD diffraction analysis and microscope photo pictureof both undigested part at 8 and 9 hours after autoclave digestion. Comparing both SEM images shows that the bright particles are almost missing from the residue after hydrothermal autoclave digestion, compared to the original ore (monazite mineral). It can be argued that SEM/EDX is a localized analysis method; the surface area that was analyzed was large enough to be considered representative for the entire residue. SEM analysis of the mineral before digestions (figure 3) showed a fairly homogeneous spatial distribution of monazite particles with the other minerals of black sands.

4. Conclusion

The results of the current study showed that it was possible to achieve about 92.5% of monazite digestion with concentrated sulfuric acid (98%) after different processes depending on the temperature, solid/liquid ratio and the time of digestion. The effective digtion occurs at 170 °C with solid/liquid ratio 1:1.6for 8 hours in hydrothermal autoclave and offer a more energy efficient alternative to the conventional sulfuric acid process and alkaline conversion process.This indicates that the parameters used in this process are more suitable for more safe, cheaper and easily process of monazite digestion.It was successfully completed by using the chemicals which were easily supplied from local market.

5. Acknowledgment

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