



Improvement of Low-Grade Rutile Using Chemical and Physical Processes

A.A. El-Shennawy

Nuclear Materials Authority, Cairo, Egypt

Received 25th Dec. 2017
Accepted 11th Mar.
2018

Rutile is a very important mineral for several industrial applications. In the present work, the physical and chemical methods used to upgrade low grade rutile will be discussed. A sample of 10 Kg was collected from Abu Khashaba beach area at the Mediterranean coast, Egypt. The leaching process for rutile mineral whereby iron coatings around rutile particles are removed using sulphuric acid of (20 wt% concentration) at 160°C. The after leaching sample is sent for physical separation processes which include up-current classifiers, gravimetric separation, hydraulic separation and magnetic separation. Stereo microscope and XRF analyses were used to study the heavy and light mineral fractions. Identification of the treated rutile sample is established and the results reveal that, at optimum conditions, a high grade rutile can be produced containing 95.8% Ti with 0.8% Fe, 1.8% Zr and 0.80% Nb.

Keywords: Rutile, Upgrading, Chemical treatment, Physical beneficiation

Introduction

The Egyptian black sands are the end products of the disintegrated materials from the igneous and metamorphic rocks, and its deposits extend along the Mediterranean coast from Abu Qir in the west to Rafah in the east [2, 3]. These deposits occur as beach sediments and coastal sand dunes Fig (1). The east Rosetta area contains relatively enriched beach black sands. The rutile content of the Rosetta ranges from 0.05 wt% in the uppermost meter to 1.5 wt% in the highly concentrated surficial beach black sands (maximum depth of 20 cm) in the eroded areas. Rutile is among the minerals having the highest refractive indices at visible wavelengths of any known crystal. It also exhibits particularly large birefringence and high dispersion. Owing to these properties, it is useful for the manufacture of certain optical elements, especially polarization optics, for longer visible and infrared, wavelengths up to about 4.5 μm . Rutile is valued for its opacity

strength (commonly called hiding power) and brightness. Other important features of titanium dioxide pigments have excellent resistance to chemical attack, good thermal stability and resistance to UV degradation. Rutile pigment is more resistant to UV light than anatase, and is preferred for paint, inks, plastics, especially those exposed to outdoor conditions. The major consumer industries for titanium dioxide pigments are mature sectors in high-resources countries where they are used for surface coatings, paper, paperboard and plastics. Therefore, consumption of titanium dioxide tends to parallel general economic trends. Paint and coating applications have the largest global use, while plastics and paper account for most of the remainder. The total world consumption of titanium dioxide in 2001 was: coatings 55%, plastics and rubber 24%, paper 12%, printing inks 3% and others: 6%. In 2005, the world consumption was as follows: coatings 58%,

plastics and rubber 23%, paper 11% and others 8% (Figure 2). Some other uses of titanium dioxide include catalysts, ceramics, coated fabrics and textiles, floor coverings and roofing granules [4]. The annual world production of titanium dioxide is 5.1 million tons, where the production of Europe, US and China are 1.4, 1.4 and 1.7 million tons respectively. Much smaller amounts of titanium dioxide are used as semi-

conductors and to catalyze the photodecomposition of water into hydrogen and oxygen. It also has a high dielectric constant and a high resistance; hence, it is used in capacitor manufacture. The strong bonding between titanium and oxygen gives great thermal stability, so its melting is 2100 K, it is thus used as a ceramic material and also used to increase the acid resistance of vitreous enamels.

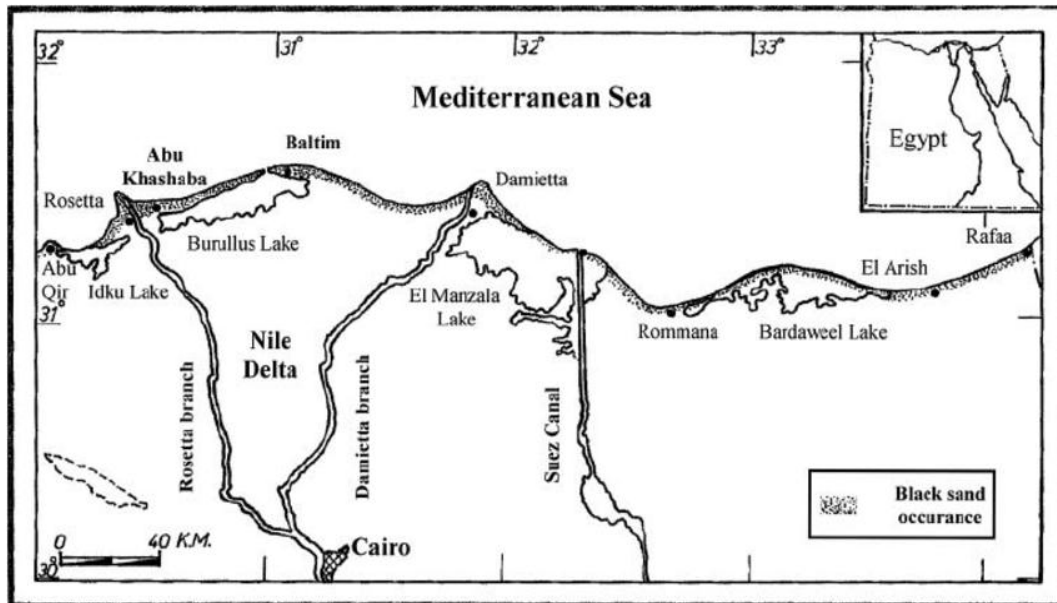


Figure (1): Distribution of the black sand deposits in Egypt

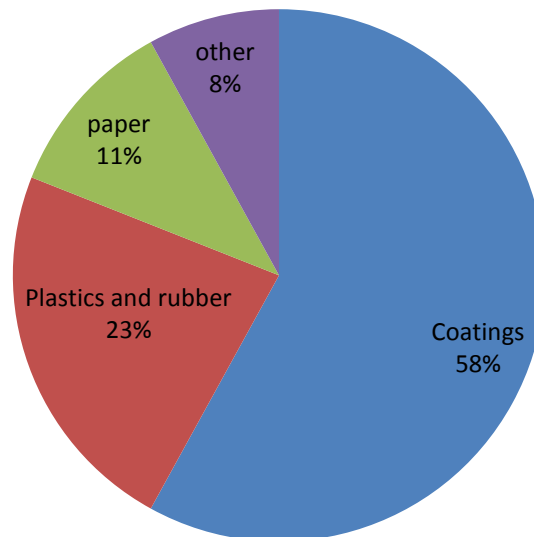


Figure (2): Uses of titanium dioxide

Iron coatings around rutile particles are the most detrimental impurities and can be reduced through the leaching process via the addition of sulphuric acid to rutile mineral at 160°C whereby iron is removed. After, the leaching process, treated rutile was subjected to further physical processing which is to be adopted for the effective removal of the detrimental impurities that may be in intimate association with the mineral quite often superficially

Physical process is used to achieve the aims of this investigation are separation by up-current classifiers (act on the differences in size and density of mineral particles), gravimetric separation (depends on the difference of specific gravity between the important minerals and the gangue.), hydraulic separation (may be defined as the separation of solid particles into two or more products according to their velocities when falling through a fluid medium generally water is used as fluid medium.) and magnetic separation (this machine is used for the continuous separation of small magnetic particles from certain minerals to produce mineral purification). The results of this study led to achieve the desired product of high grade rutile which is imperative to meeting market requirements, that customers demand for using in coatings, plastics, rubber, paper and printing inks.

Materials and Method

Materials

In this work, a sample of 10 Kg low grade rutile separated from black sands of Abu Khashaba beach area at the Mediterranean coast is used. After characterization of the raw material by X-ray fluorescence and stereo microscope, it was subjected to leaching and physical processes.

Methods

The techniques used for beneficiation the low grade of rutile sample involves:

- Leaching process for the rutile sample through chemical treatment using sulphuric acid to eliminate most of impurities from the rutile surface mainly iron
- Physical processes of ore dressing for further beneficiation using separation techniques of up-current classifiers, gravimetric separation

hydraulic separation and magnetic separation that depend on the physical properties of the constituents

The following methods were applied in the present work:

1-UP – Current classifiers

Just enough water was injected through perforated spray pipes, providing a rising up – current of water. Mineral feed entering the top of the classifier meets the rising current and a mechanical stirrer of 1 HP and stirring speed 200 rpm. The interaction of the rising current and the settling solids creates a fluidized bed of particles that causes fine and low density mineral grains to rise over the over flow weir together with the process water [1]. Coarse and higher density grains pass through the fluidized bed to the lower tapered dewatering section Figure (3). Up current classifiers are used for mechanically eliminating impurities stuck on the surfaces of the rutile particles, in addition to clean and remove all the slimes and fine quartz from the rutile particles to get a rutile sample containing all mineral grains free from slimes. Then, the cleaned sample was transferred to the leaching process and the tailing (slimes and low density mineral grains) was filtered, dried, weight and bagged for analysis.

2-Leaching process

Acid leaching for the rutile sample was carried out using a glass reactor provided with a mechanical agitator of teflon – coated stirring rod. Sulphuric acid of 20wt% concentration was poured in the reactor then heated to 160°C and after a certain time (30 minutes)[5,6,8,11,13] the suspension of the reaction products was immediately filtered, dried, weighted and bagged for analysis and the treatment rutile sample was transferred to the hydraulic separation

3-Hydraulic separation

After various trials, it was possible to design a hydraulic classifier to get a higher quality of mineral grains. The hydraulic classifier is a device characterized by the use of water additional to that contained in the feed pulp, and introduced so that its direction of flow opposes that of the settling particles.

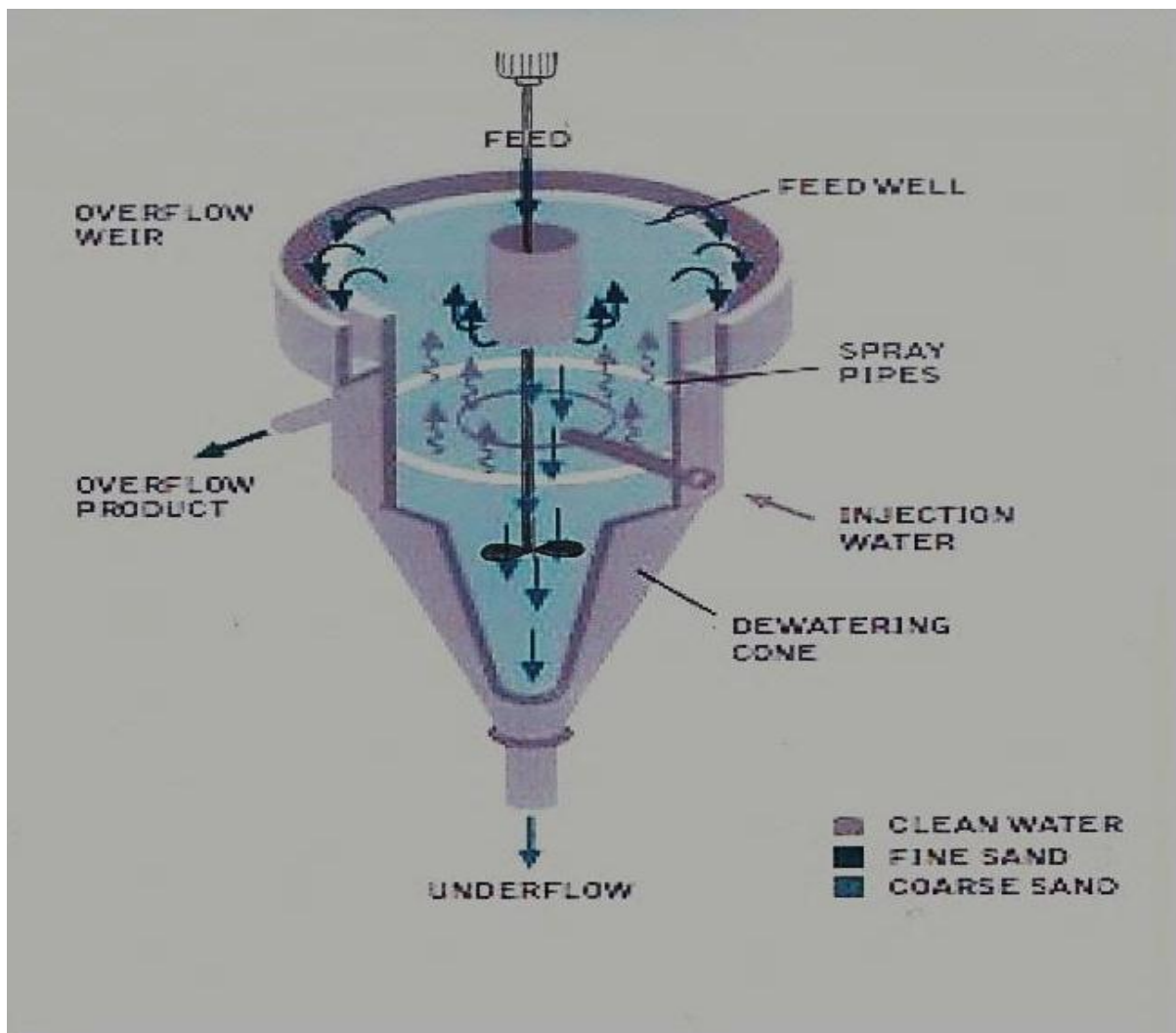


Figure (3): Longitudinal section of up-current classifiers

Description of the device

This device consists of several conical glass units connected to each other by a glass connection which connects the top of the first glass unit with the bottom of the second glass unit, and the top of the second glass unit with the bottom of the third glass unit, etc. These units are mounted on a chassis of ascending heights in a way that the ascending distance between these units is the equal to finally take a ladder form as shown in Figure (4.a) and Figure (4.b). Each one of these glass units is connected to an independent water source. The intensity of each water source can be controlled by a special lock that pushes the water stream through this unit from the bottom up. There is also, beside each lock of the water-pushing locks, another lock that pulls the materials

being separated and concentrated in each one of these glass units. Also, at the end of each conical glass, there is a small side lock through which the deposits layers above each other can be separated by controlling the opening of the side lock through which the first deposited layer can be withdrawn then the second deposited layer. This lock is additionally used to wash these glass units by opening the lock responsible for pushing the water stream from bottom up then emptying this stream through the side lock that is attached to each conical glass.

How this device works

The sample to be separated and the contained materials in it that have high economic value to be

concentrated is put in the first glass unit which is mounted in the lower level. This is done after filling a part of this unit with water so that the level of both, the water and the sample, in this unit is lower than the level of the glass connection that connects the first unit to the second unit. Then, the lock that controls pushing the water stream from bottom top is adjusted through this unit so that the stream stirs the sample lightly. This stream will carry the materials with the lower specific density from the first glass unit and transfer it to the second glass unit so that the running water stream from bottom top inside the glass unit stirs the transferred materials from the first unit and that is after adjusting the rate of water stream burst. This stream will carry the lower density materials and transfer it to the third glass unit to repeat what happened in the first and second units, etc. This process is repeated until reaching the last glass unit so that the water stream getting out of this unit is received in a container to precipitate what it contains if the water stream is still loaded with some slimes. There are several factors that must be taken into account when operating this device in order to accomplish the desired purpose of it, and they are:

- Adjusting the rate of water stream burst from bottom to top inside each one of the units of the hydraulic separation device. This depends on the study of the natural characteristics of the materials desired to be separated and concentrated.
- Adjusting the amount water put in the first glass unit of the device so that the level of both the water and the sample in this unit is lower than the level of the glass connection that connects the first unit with the second unit. This allows the running water stream from bottom to top to stir the sample thoroughly and also allowing the particles of the material to be separated to be arranged inside this unit before it is transferred to the second stage.
- Increasing the number of the constituent glass units of the device because this helps in the process of separating various materials that are desired to be separated and reaching high levels of concentration



Figure (4.a): Hydraulic separation device

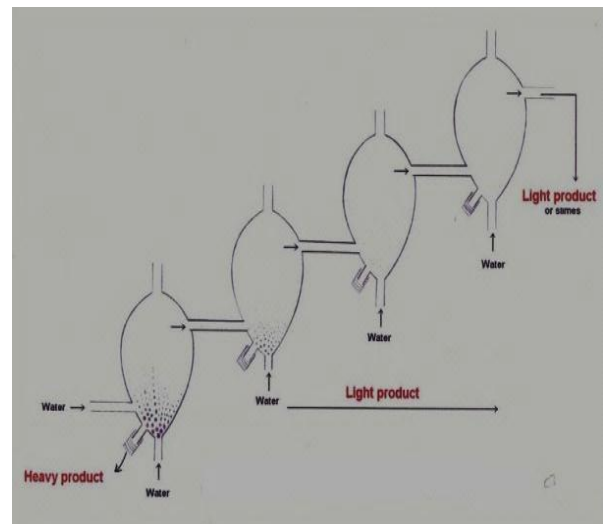


Figure (4.b): Principle of hydraulic classifier

4-Gravimetric separation

This was achieved by the shaking table concentrator which consists of a sloping deck with ariffled surface. A motor drives a small arm that shakes the table along its length, parallel to the rifle and rifle pattern. The riffles are arranged in such a manner that heavy material is tapped and conveyed parallel to the direction of the oscillation Figure (5). Water is added on the top of table perpendicular to the table motion. The heaviest and coarsest particles move to one end of the table while the lightest and to the finest particles tend to wash over the riffles and to bottom edge [7,9,12,14–16]. Intermediate points between these extremes provides recovery of the middling (

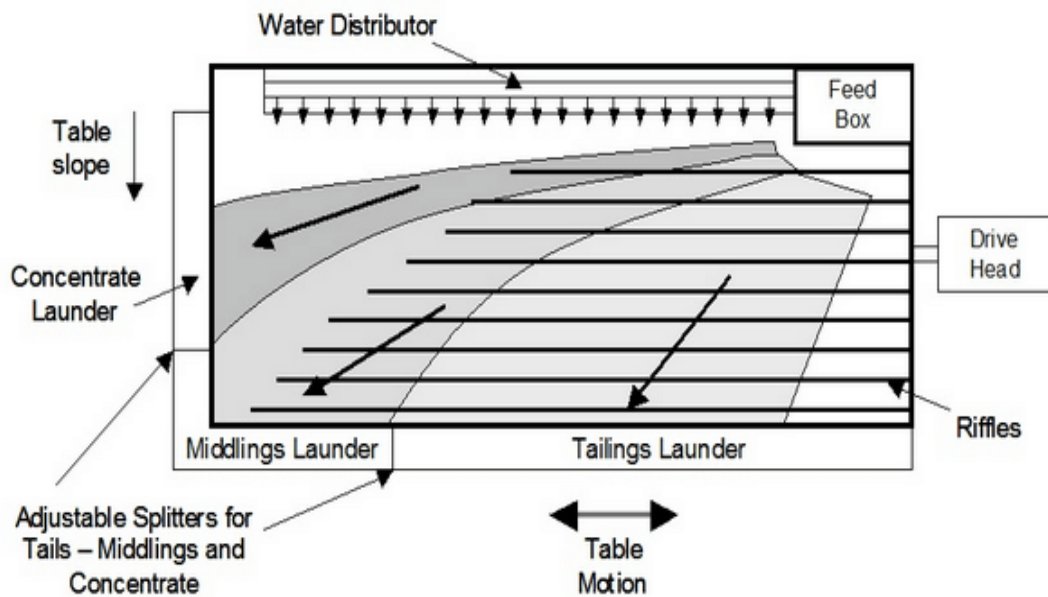


Figure (5): Distribution of shaking table

intermediate size and density) particles. The leached sample was prepared washing water. Both the stroke speed(70rpm), table slope (2 degree) and water flow rate(1.3L/min)are adjustable.

5. Magnetic separation

The concentrated rutile sample, coming from the previous step, was dried and conducted by dry magnetic separation using the Induced Roll Separator at magnetic intensity of 1.5 Tesla (15000 Gauss). The rutile (grade B) being treated is fed from a hopper or vibratory feeder at a controlled rate on to a high intensity magnetic. The magnetic material attaches itself onto the roll face or is deflected towards the roll. The non-magnetic material is thrown off the face at a normal trajectory. The magnetic material is discharged off the roll face at a point of lower magnetic intensity

aided by a brush. A splitter plat is interposed between the two product streams [10,15,16].As a result, magnetic materials are separated from the concentrate rutile that affects the quality of the upgraded final rutile concentrate. Both the magnetics(impurities) and non – magnetic (product rutile)materials were weighted and bagged for analysis.

Based on the laboratory processing studies conducted on the raw rutile sample for beneficiation of low-grade rutile sample, a beneficiation flow sheet is suggested as follows Figure (6).

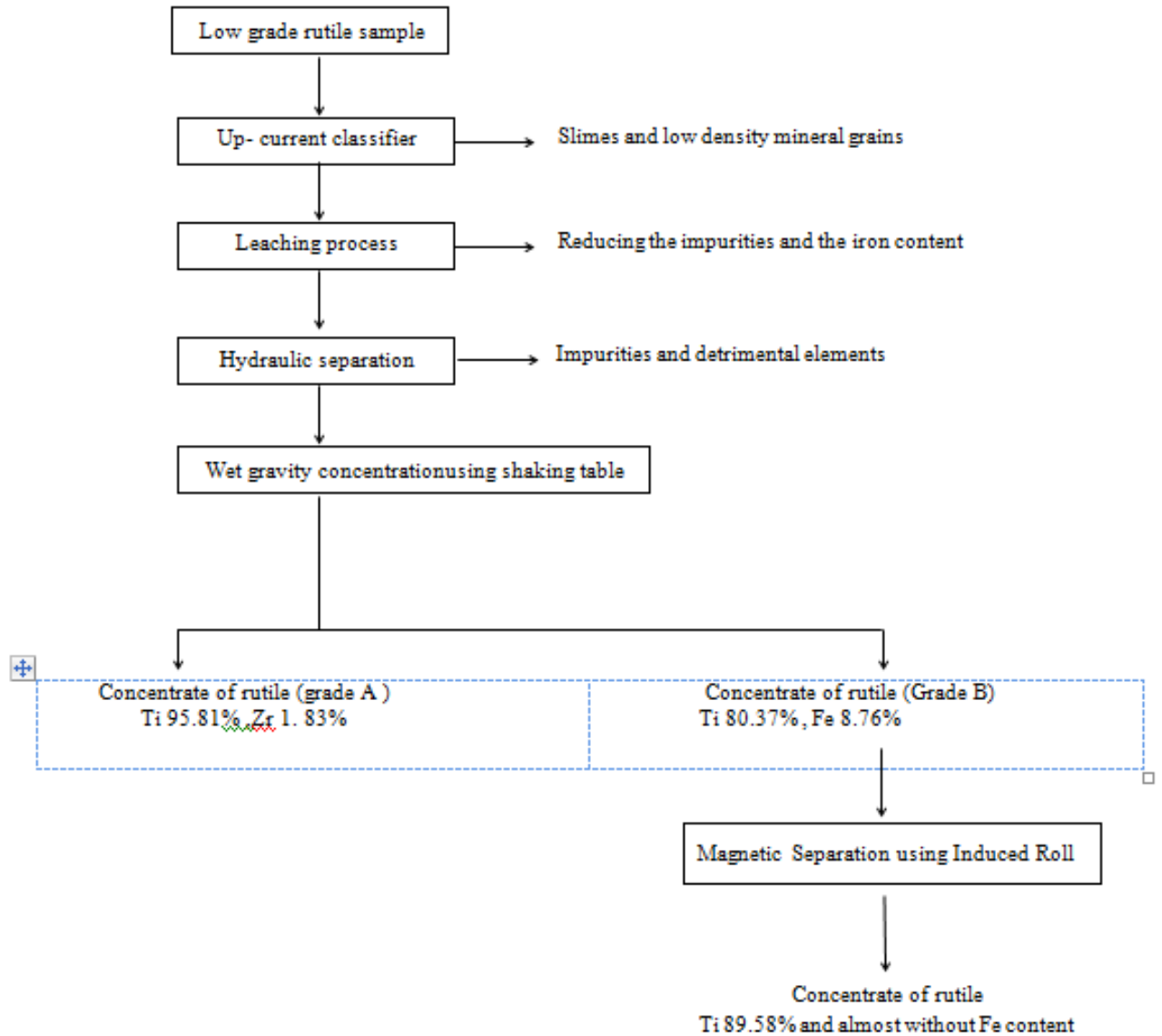


Figure (6): A simplified flow sheet showing the various concentration and separation steps for obtaining the high-grade rutile concentrate

Results and Discussion

Before investigating the physical and chemical processes for beneficiation of low-grade rutile sample, it is reasonable to throw the light on the composition of rutile sample. The results of chemical analysis of the sample under investigation by means of X-ray fluorescence is illustrated in Figure (7). It shows that rutile sample

contains Ti(62.96%), Zr(10.43%), Fe(12.32%), Si(4.36%), Zn (1.167%), Ca (1.69%), Cr(1.69%), Pb (1.65%), V (1.06 %), Mn(0.98%) and Nb(0.60%). Characterization showed that sample cannot directly be used for any value added industrial applications.

The rutile sample was first subjected to mechanical elimination of the impurities stuck on the rutile particles surfaces by mean of up current classifier. The collected tailing (slimes and low density mineral grains) were filtered and dried for analysis by XRF. The results are shown in Figure (8) which

it appears that the eliminated impurities from the raw rutile sample such as Si(33.06%),Ca(17.71 %),Fe(17.84 %), Al (11.19%), Zr(3.71%), K (1.79 %), Mn(1.40 %),Zn(1.34%), Nb(0.10%) and Pb(0.50%).

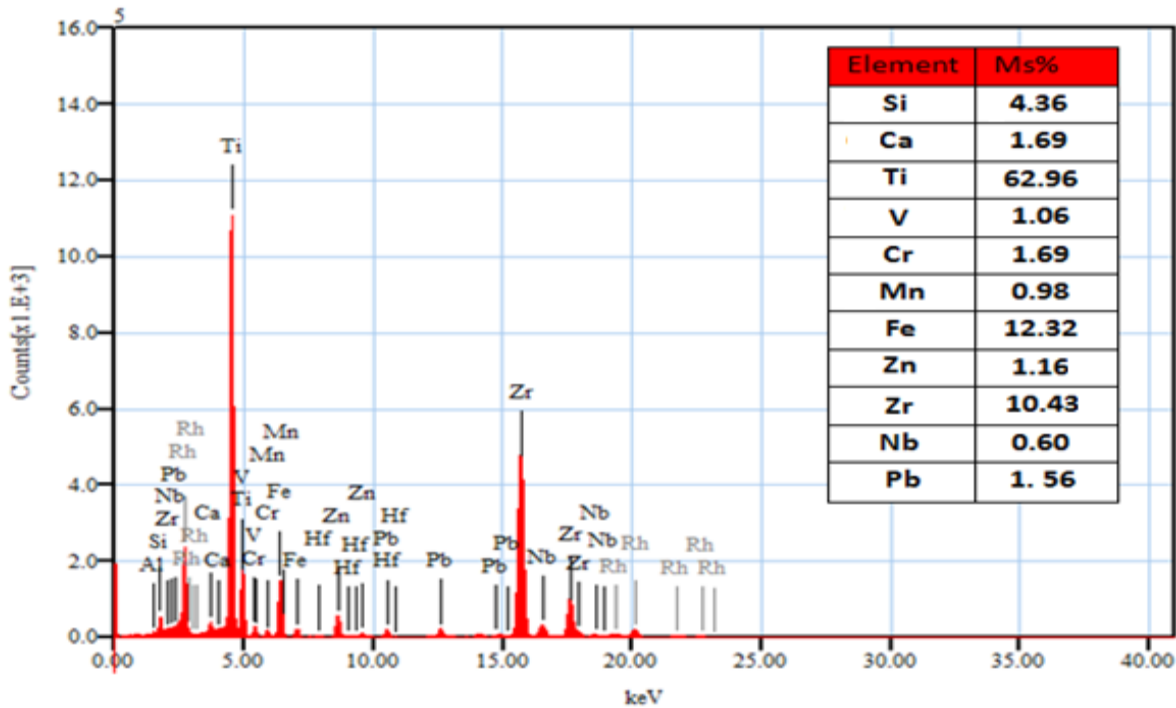


Figure (7): XRF pattern of the original rutile sample

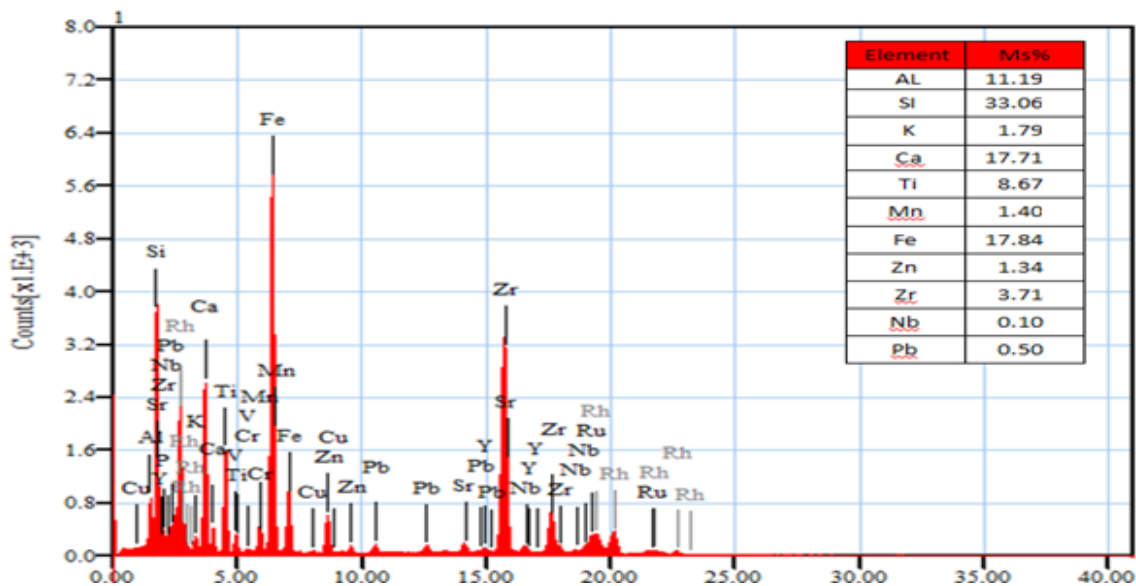


Figure (8): XRF pattern of the collected tailing from the up-current classifier

Leaching of iron and calcium oxides coating rutile particles with sulphuric acid 20wt% at 160°C has been done for reducing them from the rutile sample and formation iron sulphate $Fe_2(SO_4)_3$. The collected impurities were filtered and dried for analysis by XRF. The results of XRF Fig.(9) indicates that the leaching process iron content 22.20% and calcium 2.15% and improves the low-grade rutile sample.

The rutile sample, after iron leaching, was further concentrated by a hydraulic classifier as the upgrading of the rutile sample requires partial removal of impurities and other elements which are detrimental to its end use. The collected impurities and detrimental elements were filtered and dried for analysis by XRF. The XRF results are presented in Fig.(10) which it appears that Fe(26.31%), Si(37.30%), Ca(9.78%), Al(6.35%) and Zn(5.34%), being the most detrimental impurities. Also, a smaller amount of Pb(2.24%), K(1.32%), Mn(1.84%), Zr(0.33%), V(0.27%),

Cr(0.75%) and Sr (0.23%) were liberated and removed from the rutile sample using hydraulic classifier.

The rutile sample taken from the hydraulic classifier was then concentrated by means of a shaking table using different inclinations and flow rates. The best results were obtained at a flow rate of 1.3L/min and an inclination of 2.0 degree. As a result of using the shaking table, two grades of rutile were separated grade A and B where they are dried for analysis by XRF. The obtained results in Figs. (11 and 12) indicate that using the shaking table technique improves Ti content from 62.96% to 95.81% for the grade “A” and to 80.37% for grade “B”. On the other hand iron content was reduced from 12.32% to almost zero%, Si from 4.36% to almost zero%, Zr from 10.43% to 1.83% for the grade “A”. It, also, reduces the iron content from 12.32% to 8.76%, Si from 4.36% to 1.63%, Zr from 10.43% to 6.98%, V from 1.06% to 0.40% and Cr from 1.69% to 0.32%.

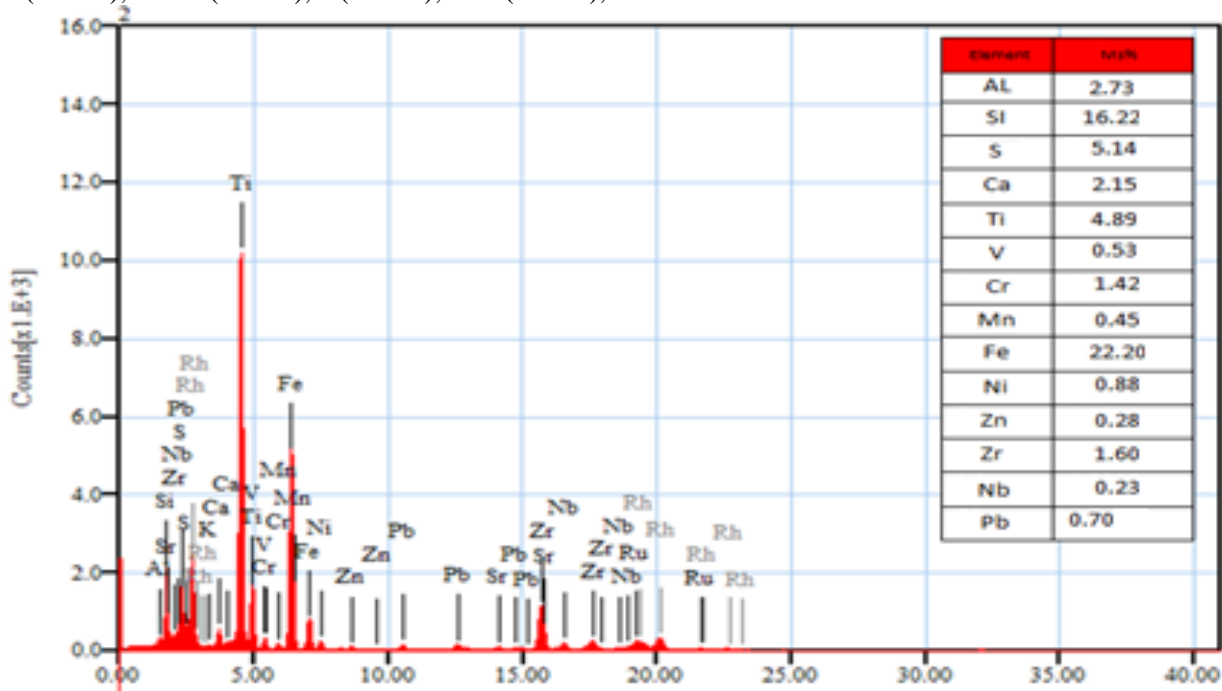


Fig.(9): XRF pattern of the collected impurities from the leaching process

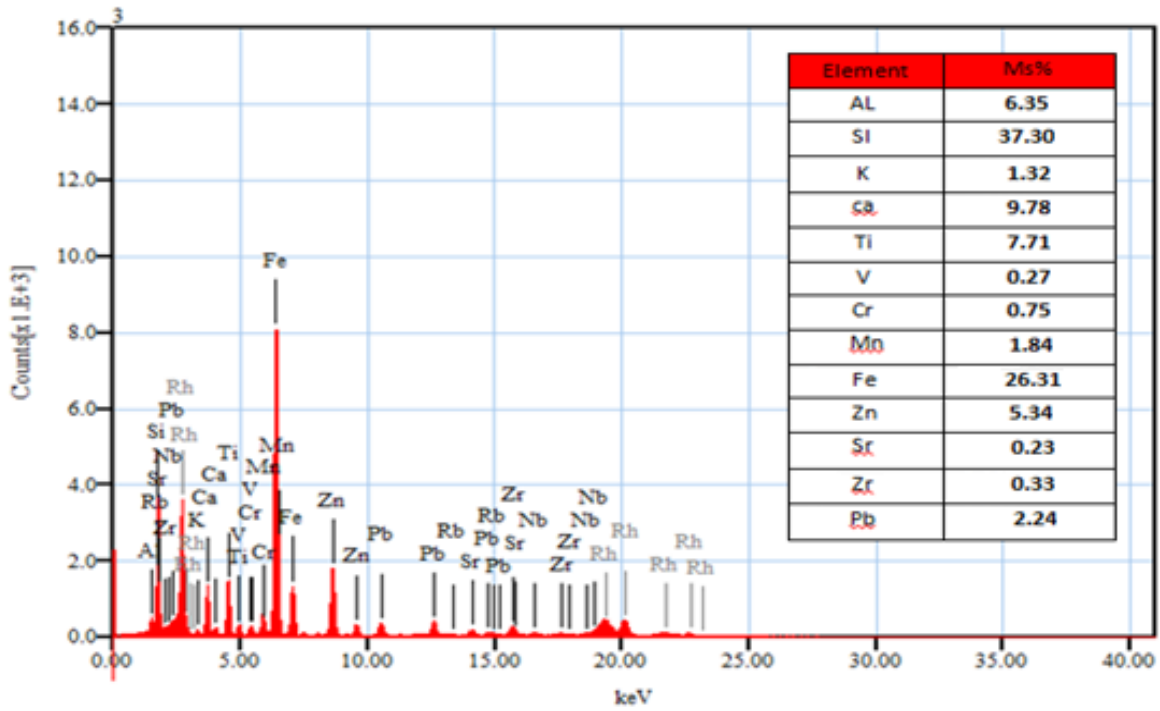


Figure (10): XRF pattern of the collected impurities and detrimental elements from the hydraulic classifier

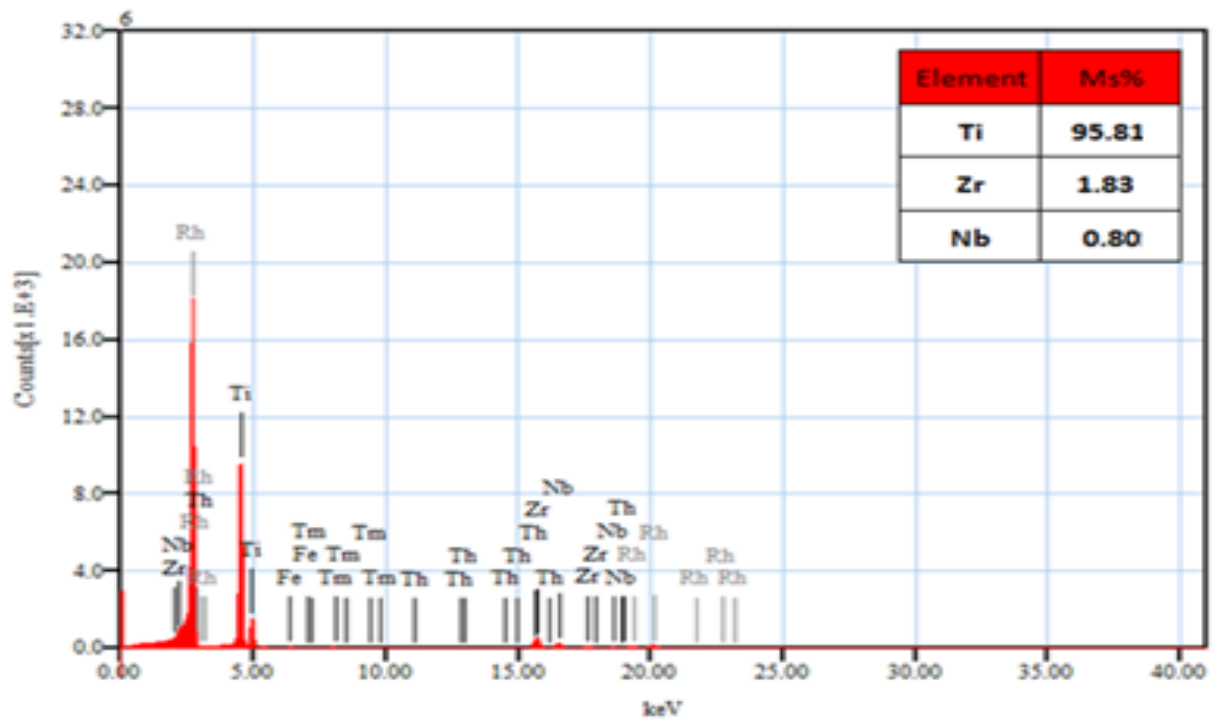


Figure (11): XRF pattern of concentrate (A) from the shaking table

Grade “B” from shaking table was also subjected to magnetic separation, using an induced roll separator. The results are shown in Figure (13). The comparison between Figs.(12 and 13) indicate that

magnetic separation improves Ti content of grade “B” from 80.37 % to 89.58% and reduces the iron content from 8.76% to almost zero%.

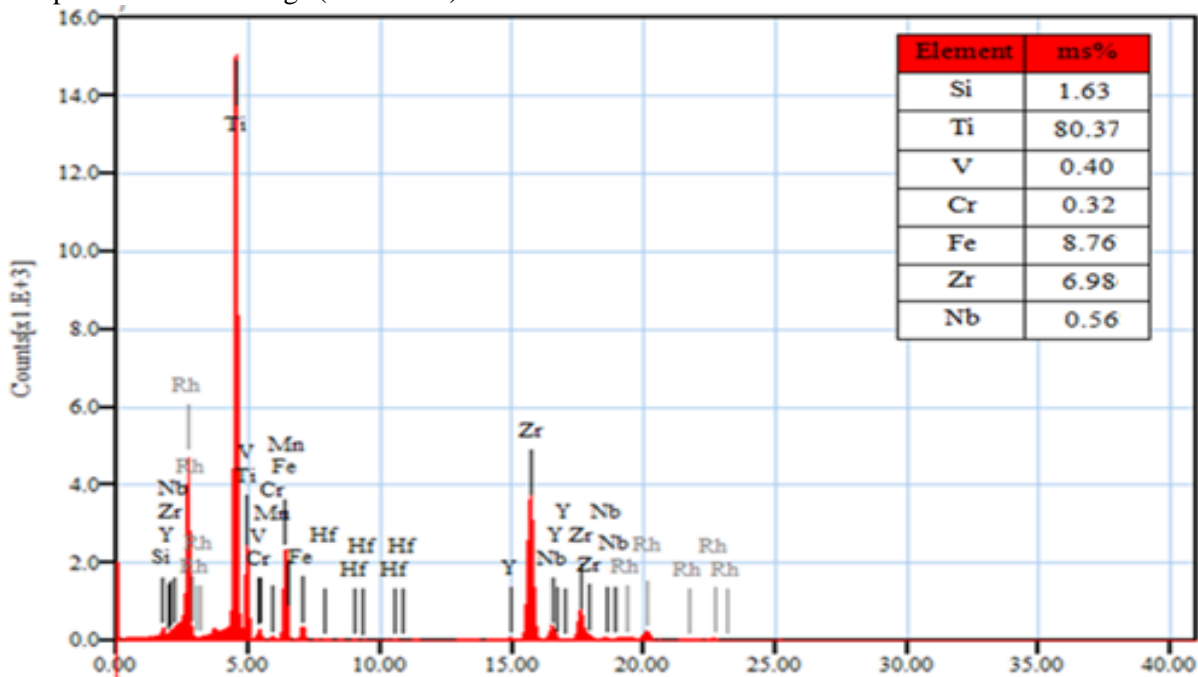


Figure (12): XRF pattern of concentrate (B) from the shaking table

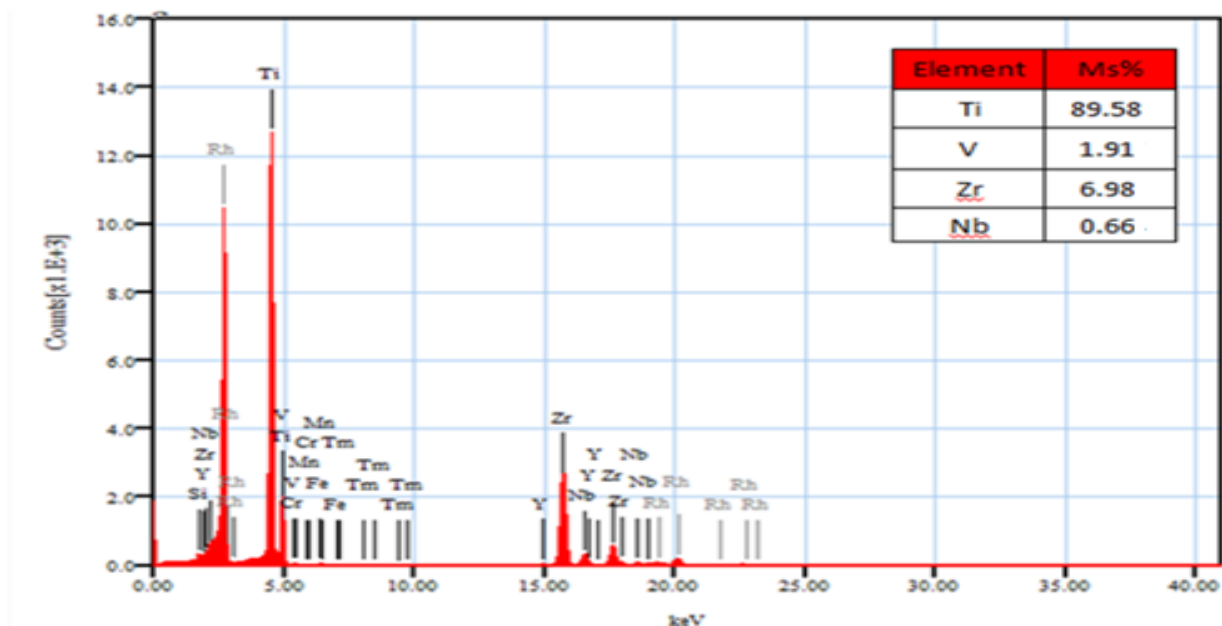


Figure (13): XRF pattern of concentrate (B) after subjected to magnetic separation

Finally, the original rutile and its upgraded samples were investigated as grains spread on a glass slide (10slides for each sample) using the stereomicroscope for making restriction for

number of metal granules existing on each of the slides of these samples. Identification of average purity degree of each of the samples are given in Tables from (1 to 5).

Table (1): Modal analysis of the original rutile sample

sample No.	Rutile	Ilmenite	Leucoxene	Sphen	Zircon	Sec.iron oxid	Epidot	Silica	Hematite
1	143	73	6	58	29	8	4	11	12
2	184	90	10	80	40	10	5	15	7
3	71	28	2	15	12	4	2	3	5
4	113	64	6	49	25	6	6	13	8
5	97	49	10	38	24	5	3	6	4
6	209	103	17	78	42	10	5	10	16
7	58	27	3	26	14	3	6	3	4
8	122	51	5	55	28	6	3	13	9
9	76	38	3	19	15	3	2	2	5
10	119	66	5	48	26	6	4	3	4
Average	119.2	58.9	6.7	46.6	25.5	6.1	4	7.9	7.4

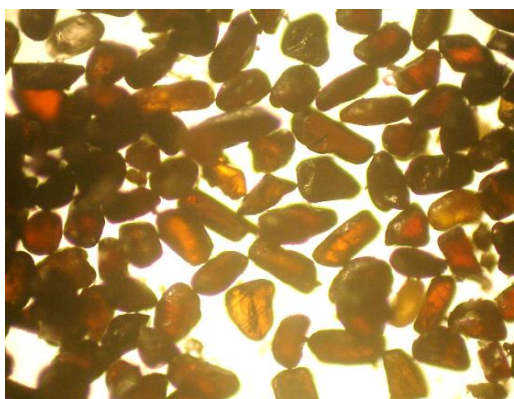


Figure (14): Photomicrograph showing rutile grains of the original rutile sample, (X20)



Figure (15): Photomicrograph showing sphen grains of the original rutile sample, (X20)

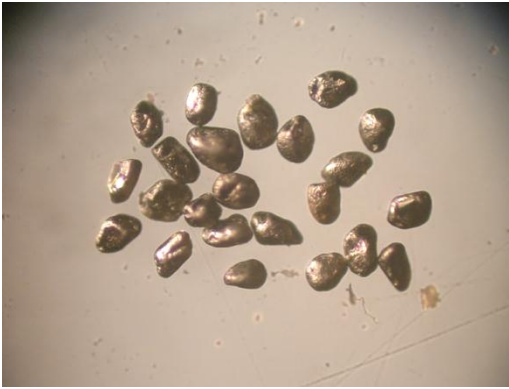


Figure (16): Photomicrograph showing ilmenite grains of the original rutile sample, (X20)



Figure (19): Photomicrograph showing secondary iron oxide grains of the original rutile sample, (X40)



Figure (17): Photomicrograph showing leucoxene grains of the original rutile sample, (X20)

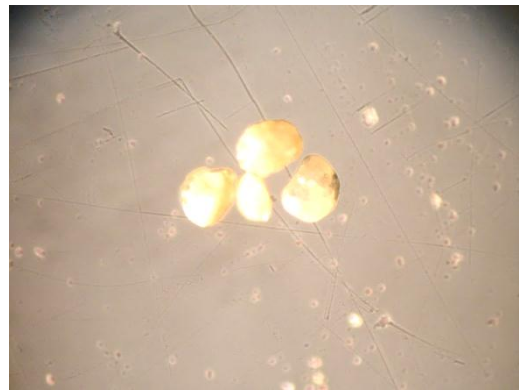


Fig.(20): Photomicrograph showing epidote grains of the original rutile sample, (X20)



Figure (18): Photomicrograph showing zircon grains of the original rutile sample, (X20)



Fig.(21): Photomicrograph showing hematite grains of the original rutile sample, (X20)

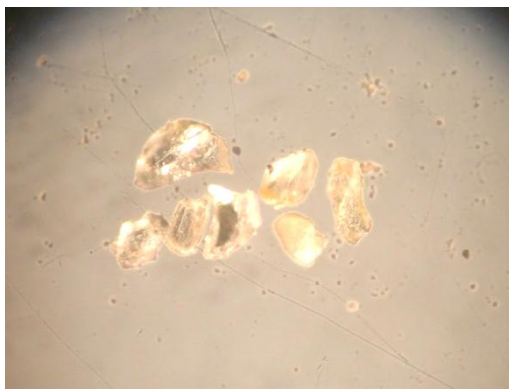


Fig.(22):Photomicrograph showing silica grains of the original rutile sample, (X20)

Table(2): A model analysis of the treatment sample by leaching process

sample No.	Rutile	Sphen	Leucoxene	Ilmenite	Zircon	Epidot	Silica
1	121	60	14	15	17	4	8
2	173	78	24	23	24	6	14
3	141	70	16	17	19	5	10
4	91	37	14	12	11	3	8
5	37	18	4	4	3	1	2
6	67	41	8	9	7	2	6
7	79	39	8	8	6	2	5
8	110	70	17	15	10	5	10
9	121	59	12	12	9	3	7
10	102	38	21	17	7	3	6
Average	104.2	51	13.8	13.2	11.3	3.4	7.6



Figure (23): Photomicrograph showing rutile grains of the treatment sample by leaching process, (X20)



Fig. (24): Photomicrograph showing sphengrains of the treatment sample by leaching process, (X20)



Figure (25): Photomicrograph showing ilmenite grains of the treatment sample by leaching process, (X20)

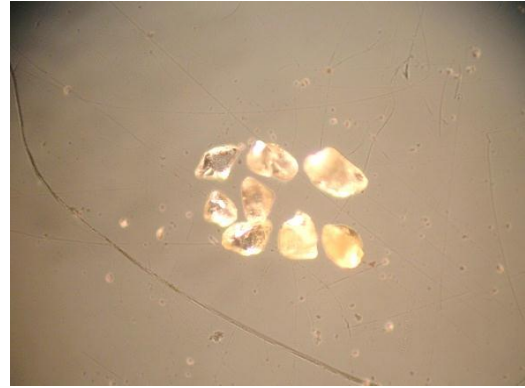


Figure (27): Photomicrograph showing silica grains of the treatment sample by leaching process, (X20)



Figure (26): Photomicrograph showing zircon grains of the treatment sample by leaching process, (X20)



Figure (28): Photomicrograph showing the various stages for transformation of ilmenite to leucoxene due to leaching process, (X20)

Table (3): Modal analysis of the separated sample from the gravimetric separation (grade A)

sample No.	Rutile	sphen	Zircon
1	212	106	17
2	134	60	8
3	108	54	9
4	157	72	15
5	137	69	11
6	101	47	9
7	117	59	9
8	225	106	112
9	69	35	5
10	74	37	3
Average	133.4	64.5	19.8



Fig.(29):Photomicrograph showing rutile grains of the separated sample from the gravimetric separation (grade A), (X20)



Fig.(32):Photomicrograph showing rutile grains of the separated sample from the gravimetric separation (grade B), (X10)



Fig.(30):Photomicrograph showing spheñ grains of the separated sample from the gravimetric separation (grade A), (X20)



Fig.(33):Photomicrograph showing ilmenite grains of the separated sample from the gravimetric separation (grade B), (X20)



Fig.(31):Photomicrograph showing zircon grains of the separated sample from the gravimetric separation (grade A), (X20)



Fig.(34):Photomicrograph showing spheñ grains of the separated sample from the gravimetric separation (grade B), (X20)



Fig.(35):Photomicrograph showing zircon grains of the separated sample from the gravimetric separation (grade B),(X20)

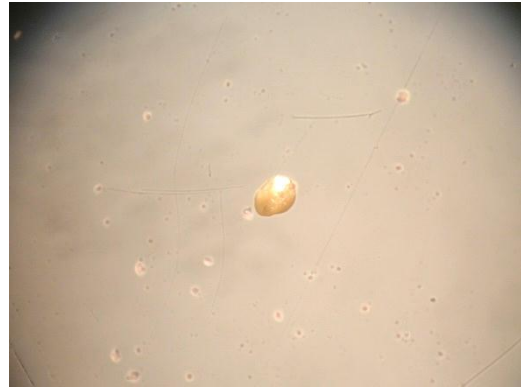


Fig.(36):Photomicrograph showing epidot grains of the separated sample from the gravimetric separation (grade B),(X20)

Table (3): Modal analysis of the separated sample from the gravimetric separation (grade A)

sample No.	Rutile	sphen	Zircon
1	212	106	17
2	134	60	8
3	108	54	9
4	157	72	15
5	137	69	11
6	101	47	9
7	117	59	9
8	225	106	112
9	69	35	5
10	74	37	3
Average	133.4	64.5	19.8

Table (4): A modal analysis of the separated sample from the gravimetric separation (grade B)

sample No.	Rutile	Sphen	Ilmenite	Leucoxene	Zircon	Epidot
1	67	33	11	6	5	3
2	126	57	25	10	11	5
3	187	92	31	16	13	8
4	113	75	21	8	9	4
5	55	27	9	5	4	2
6	97	66	14	7	8	3
7	141	70	23	13	11	6
8	173	93	31	12	13	5
9	43	21	7	4	3	2
10	164	93	25	13	13	7
Average	116.6	62.7	19.7	9.4	9	4.5

Table (5): A modal analysis of the separated rutile sample by magnetic separation

Sample No.	Rutile	Sphen	Zircon	Epidot	Leucoxene
1	53	28	4	2	5
2	98	56	7	1	8
3	116	67	8	3	8
4	76	36	5	1	9
5	180	91	12	4	12
6	161	88	11	3	13
7	81	43	6	2	7
8	66	35	5	3	7
9	131	66	10	4	14
10	49	26	4	2	5
Average	101.1	5.36	7.2	2.5	8.8



Figure (37):Photomicrograph showing rutile grains of the separated sample by magnetic separation, (X10)



Figure (39):Photomicrograph showing zircon grains of the separated sample by magnetic separation, (X20)



Figure (38):Photomicrograph showing sphen grains of the separated sample by magnetic separation, (X10)



Fig(40):Photomicrograph showing leucoxene grains of the separated sample by magnetic separation, (X20)

Table (6): The products that have been attained from low grade rutile sample

Low-grade rutile sample (62.96%)	Products			
	Rutile with purity grade (95.81%)	Rutile with purity grade (89.58%)	Tails	Loss
10 Kg	4.906 Kg	2.454 Kg	1.843 Kg	0.797 Kg

Conclusions

The following conclusions may be drawn from beneficiation of low-grade rutile sample:

- 1- Initial characterization showed that the main impurities in the sample are Fe (12.32%) Zr(10.43 %) and Si (4.36%). Also, smaller amount of Zn(2.16%), Ca(1.69%), Cr(1.69%), V (1.06%), Pb (1.56%), Mn(0.98%) and Nb(0.60%).
- 2- The results of beneficiation studies reveal that while up-current classifiers, leaching process and hydraulic separation removes majority of these contaminating minerals to give an intermediate product rutile, gravimetric separation and magnetic separation are required to upgrade the rutile.
- 3- Based on the laboratory study, beneficiation flow sheets have been suggested for the rutile.

References

- 1-Anon. (1984). Classifiers part 2: Some of the major manufacturers of classification equipment used in mineral processing, *Mining Mag.*, (July)40.
- 2-G.A.Dabbour. (1980) Geological and mineralogical studies on rutile in the black sand deposits from the Egyptian Med.coast. Ph. D. Thesis, Cairo University, Giza.
- 3-G.A.Dabbour. (1995). Estimation of the economic minerals reserves in Rosetta beach sands, *Egyptian minerals*, Vol. 7, PP.1-6.
- 4-Gambogi J. (2005). US geological survey mineral commodity summaries-titanium and titanium dioxide. US. Government printing office Reston, Reston, 178-179.
- 5-Linak E, Inoguchi Y. (2005). Chemical economics handbooks: Titanium dioxide, Menlo Park, CA, CRI consulting.
- 6-Ledgerwood J, Westhuyzen P. (2011). The use of sulphuric acid in the mineral sands industry as a chemical mechanism for iron removal.

- 7-Manser, R.J., et al. (1991). The shaking table concentrator the influence of operating condition and table parameters on mineral separation—the development of a mathematical model for normal operating conditions. *Minerals Engineering* 4 (3/4)369
- 8-Prinsloo, A. (2006). The formation of chemical precipitates in the HAL process and its impact on electrostatic separation of zircon and rutile minerals. Stellenbosch: University of Stellenbosch.
- 9-Sivamohan, R., and Forsberg, E. (1985). Principle of tabling, *Int. J. Min. Proc.* 15, (NOV.)281
- 10-Svoboda, J., (1987). *Magnetic methods for the treatment of minerals*, Elsevier, Amsterdam
- 11-Stoffels, J., (2005). Hal reactor optimization. Namakwa sand.
- 12-Terry, R.L., (1974). Minerals concentration by wet tabling, *minerals processing* 15, (July/Aug.)14.
- 13-Visser, J.D., (2006). Hal temperature and acid dosage optimization. Namakwa sands.
- 14-Wills, B.A., (1981). Laboratory simulation of shaking table performance, *Min. Mag.* (June)489.
- 15-Wills, B.A. (1988). *Mineral processing technology*, 4th ed., Pergamon press.
- 16-Wills, (1992). *Mineral processing technology*, 5th ed., Pergamon, Oxford.