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ABSTRACT

This study introduces a contribution of using the El Minia carbonate filler pigment for paper making. El Minia limestone samples were grind to very fine powder ranging from 2 to 10 μm, for utilization in paper filler/coating industry, with using testing techniques; X-ray fluorescence (XRF), X-ray diffraction (XRD), Scanning electron microscopy (SEM). The limestone assessment includes more examinations to confirm the suitability of studied samples for alkaline paper manufacture such as, chemical analysis and physical properties, brightness, refractive index, oil & water absorption, moisture content, water soluble, surface area and soundness tests as per paper industry standards.

1. Introduction

Calcium carbonate "CaCO3", is one of the most important and useful materials in many industries. It is extremely common and found throughout the world in sedimentary rocks. It comprises more than 4% of the earth's crust. Calcium carbonates natural forms are chalk and limestone, produced by the sedimentation of the shells of small fossilized snails, shellfish, and coral over millions of years. Although all three forms are identical in chemical terms, they differ in many other respects, including purity, whiteness, thickness and homogeneity.

The paper industry uses limestone-based product to manufacture fillers and coating pigments. Calcium carbonate pigment is used for filling and coating, for example in making of printing papers and board. CaCO3 valued worldwide for high brightness and light scattering characteristics, as well as it is used as an inexpensive filler to make bright opaque paper. Also it helps to produce papers with high whiteness and gloss and good printing properties.

In 2008, world production of paper and paperboard was 380 million tons according to Food and Agriculture Organization (FAO). Over 90% of paper and paperboard is produced in Asia, Europe and North America. Asia is the biggest producer with 34% of all production and Europe and North America are trailing with 30% and 29% respectively.

There are different grades of paper used for many purposes, for example: coated, uncoated, bond, note book, offset, index, newsprint, computer, copier, gloss, picture and inkjet papers.

The main types of mineral filler for acid papers are talc, hydrous kaolin, calcined kaolin, precipitated silica's /silicates (PSS), and titanium dioxide. For neutral/alkaline papers, talc, hydrous kaolin, calcined kaolin, PSS, titanium dioxide, ground calcium carbonate (GCC), and precipitate calcium carbonate (PCC) are used. The estimated productions of some types of paper and paperboard in 2008 were illustrated in (Fig. 1).

Kaolin, calcium carbonate (GCC and PCC), and talc are the most widely used mineral fillers, with regional variations depending on local resources available (Fig. 2). Filler pigments must have a high degree of whiteness, a high index of refraction, small particle size, low solubility in water, and low specific gravity. It is also important that the filler be chemically inert to avoid reactions with other components in the sheet and in the papermaking system. The filler should contain a minimum of impurities, and the grit content must be low to avoid excessive wear of the wire and other processing equipment such as cutting blades. Furthermore, unless the filler has very unusual properties, it must be inexpensive [1–6]

The annual Egyptian production of paper in Egypt about 150,000 tons while the domestic consumption about 650,000 tons, to compensate the difference between production and consumption, there is a large import quantities cost a lot of hard currencies. The percentage of filler used to produce different types of paper products are indicated in Table 1.

There are many Egyptian companies for paper making, the most important production companies rankled as annual production is

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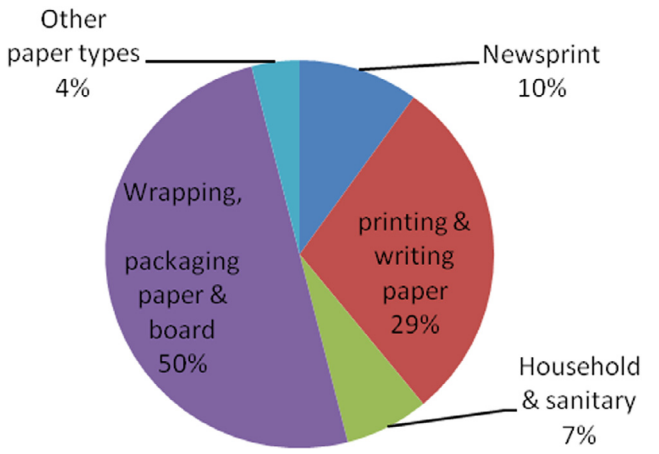

Fig. 1. Global production of paper and paperboard grades in 2008 (Finnish forest Industries 2009).

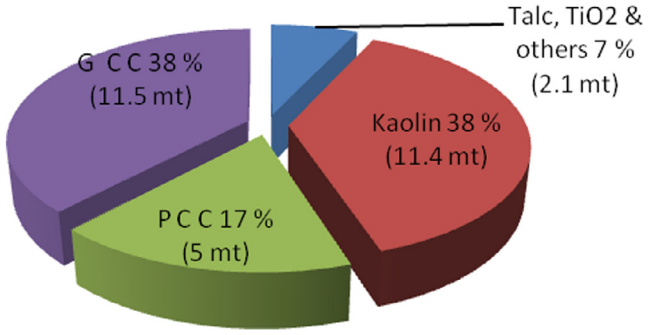

Fig. 2. Breakdown of filler pigment used for paper making at 2002 (Harris 2004).

Table 1
Paper product and filler contents.

0–15%	Newsprint
20–32%	SC gravure paper
6–10%	LWC base paper
8–15%	Wallpaper
5–10%	Mechanical catalogue
5–20%	Wrapping base paper
10–25%	Wood free printing paper
10–25%	Wood free writing paper
2–10%	Corrugated board
2–10%	wallpaper board

Qena company with annually production about 120,000 tons, Al Ahlya (EMAC) with annual production 60,000 tons, and Rakta company produces 30,000 tons [7]

This article aims to contribute the utilization of El Mina huge quantities of high grade calcium carbonate and its suitability for making of filler/coating of paper and paperboard and stop the loss of hard currency used for importing the same ore.

2. Geological setting

El Minia-Maghagha area has a rectangular shape and lies on the Eastern side of the Nile River. It is located between latitude 28 ° and 28 °40′N and longitudes 30° 50′ and 31° 30′ E.

The exposed carbonate rocks of El Minia-Maghagha areas includes five units of Middle Eocene age. These units are composed mainly of limestone [8,9]. The oldest exposed unit is El Minia Formation which is composed of white, hard, and fossiliferous limestone, this unit is conformably overlain by snow white, soft, fossiliferous limestone of Samalut Formation. Samalut Formation overlain by creamy white, mictritic, marly limestone of the Maghagha Formation. This unit is conformably overlain by brownish yellow, sandy, fossiliferous limestone of Qarara Formation. The top most part of Qarara Formation includes nodular, chalky, limestone of Fashn Formation. The studied sample was collected from El Minia and Samalut formations for laboratory examinations (Fig. 3).

3. Materials and methods

Thirty samples were collected from different localities along the area in between El Minia city and Beni Khalid to represent the studied limestone, the representative samples were ground to very fine particles for measuring the physical properties, chemical analysis, and X-ray diffraction, and SEM studies.

Carbonate samples were subjected to specific tests and evaluation compare with the international specification and standard to determine their suitability for alkaline paper and paperboard filler/coating manufacture.

The assessment of ground calcium carbonate characterizations were conducted according to the following standards: Specific gravity ASTM D 153, Oil absorption ASTM D 234 and ASTM D 281, Water absorption, Moisture content ASTM D 280, Particle size, Particle shape, ASTM E 70 of Hydrogen ion concentration, ASTM D 2196 for Matter soluble in water: max 1%, Hardness, Appearance & Color of powder, Brightness, purity as CaCO3: 95%, Refractive index, SEM, chemical analysis, XRD, and soundness test. Standard properties of ground, precipitated and kaolin ores utilized in paper making are listed in Table 2 as a references for studied sample.

4. Results and discussions

The physical and chemical assessment tests were accomplished for El Minia carbonate samples as follows:

Calcium carbonate filler pigment represent a considerable part of paper manufacture, the amount of filler vary from 5% to 30% of the whole finish. Several reasons why fillers are used in papermaking, the main reasons are their low cost compared to fibers "The price of bleached chemical fiber is roughly five to seven times as much as filler prices" and their ability to improve optical properties in the final product. Fillers can also improve surface properties of paper and by that have a positive effect on the printability of the final product [10,11].

Also fillers can improve the surface properties of paper or paperboard as well as have positive effects on the opacity, brightness and colour. Opacity is increased because of filler particles scatter light very well [12].

Fillers also have a smoothening effect on the paper surface, because small filler particles settle in between of fibers they together form a smooth paper surface, which is required in rotogravure printing. Although fillers are needed for good printing image, excessive amount of filler will compromise the paper surface strength.

The chemical analysis of samples collected from El Minia areas were examined to ensure that the limestone samples used as a pigment are inert, stable and not contain detrimental impurities. The chemical analysis results revealed that the major elements is CaO, accordingly the CaCO3 content ranging from 99.30 to 99.65%. The physical and chemical analysis was conducted at the Egyptian Petroleum Research Institute and Egyptian Mineral resources Authority "Central laboratories Sector", and the results obtained are illustrated in Tables 4 and 5.

These testing for calcium carbonate powder were carried out according the following techniques and testing:

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a- Outcrop of limestone

b- Quarry of chalky limestone

c- Cutting of limestone building blocks

d- location of limestone quarry's

Fig. 3. Field photos showing outcrop and quarry of pure limestone at El Minia East Nile Valley.

Table 2
Properties standard limits of Kaolin, PCC and GCC fillers used in paper manufacture.

Property	Kaolin	PCC	GCC
Brightness	80 85%	90–97%	> 90–96%
Particle size	2 μm	Manufacture fine	Required grinding
Opacity	Excellent	high at high load	Moderate at high load
Loading level	20–30%	Limited to 20%	20–30%
Sheet strength	Good	Moderate	Excellent
Bulking	Moderate	Good	Good
Absorption	Low	High	Low
Chemical reactivity	Inert	Unstable in acid	Unstable in acid
Flexibility	Filler/Coating	Mainly filler	Alkaline - filler/coating
Processing	Extensive	Energy extensive	Grinding/sizing
Availability	Restricted	Satellite plants	Geologically plentiful
Price	Low (N. America)	Based on cost	Low (Europe)

Table 3
Brightness of El Minia calcium carbonate.

Limestone samples	Brightness (z-direction)
Sample 1	91
Sample 2	93.5
Sample 3	90.5
Sample 4	91.5

4.1. Specific gravity

The representative samples of limestone measured according to [13] and the results are ranging from 2.6 to 2.7 g/cm^3 as indicated in Table 4. , as per standard the low specific gravity is preferred for paper manufacture.

4.2. Oil absorption

The test were carried out using linseed oil mixed with carbonate powder and the specific paste obtained at the ratio of oil quantity is ranging from 32 to 36 g/100 g (g of oil/g of powder), as per [14,15].

4.3. Moisture content

The moisture content of limestone powder was determined at 105 °C and the results ranging from 0.05 to 0.07% and considered low percentage moisture according to [16].

4.4. Particle size

Calcium carbonate pigments for paper making occurs in the form of a fine powder or lumps by using crushing equipment's was ground to very fine grains. The recommended size of limestone powder pigment shall be in limit of 2–10 μm as shown in (Fig. 4). The vast majority of particles are much smaller in size than 10 μm; there is some evidence that a mixture of particle sizes is desirable for increased durability, reduced absorption and reduced permeability of the film, also the particle size distribution graph (Fig. 5), showing that the 80% of analyzed sample is less than 10 μm in size.

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Table 4
Physical properties of limestone filler pigment.

Ore Type	Physical Properties					
	Sp. Sp. gravity g/cm^3	oil absorp. %	Moisture %	pH	Acid soluble	hardness water soluble
Limestone sample 1	2.70	33	0.05	8.5	99.0	3.0 0.96
Limestone sample 2	2.69	32	0.06	9	99.0	3.0 0.86
Limestone sample 3	2.72	36	0.05	8	98.0	3.0 0.95
Limestone sample 4	2.70	34	0.07	9	98.5	3.0 0.93

Table 5
Chemical compositions of limestone at some localities of El Minia.

Ore Type	Chemical composition					
	CaO	Al2O3	Fe2O3	MgO	H20	L.O.I
Limestone sample 1	55.61	0.11	0.12	0.07	0.20	43.80
Limestone sample 2	55.70	0.14	0.16	0.11	0.11	43.70
Limestone sample 3	55.56	0.10	0.07	0.13	0.10	43.75
Limestone sample 4	55.67	0.11	0.13	0.11	0.10	43.80

Fig. 4. (a) Grinding machine of limestone (b) Final product of grind limestone.

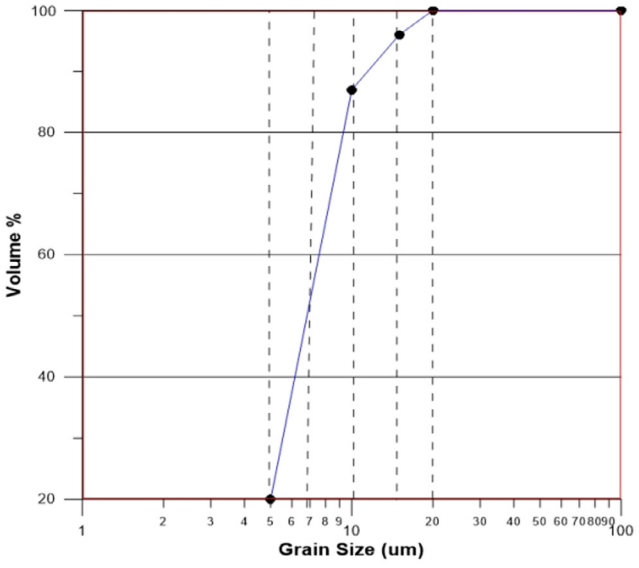

Fig. 5. Particle Size Distribution.

4.5. Particle shape

Particle shape and size influence on the properties of carbonate powder pigment such as consistency, oil absorption, hiding power of paper coating and filler, the carbonate examined grain shape is rounded and sub round.

4.6. Hydrogen ion concentration (pH value)

The pH test carried out to collected sample as per [17] to measure the value of alkaline or acidity of carbonate powder and the results shows that pH is 8.5%, it means the pH range is alkaline.

4.7. Matter soluble in water

The carbonate powder pigment shall be insoluble in water, except traces of soluble salt. The test result indicates that the amount of soluble matter is 0.4%, meanwhile the standard limit as per [18], shall be not exceed than 1% as shown in Table 4.

4.8. Moh's hardness

The hardness of carbonate powder utilized in paper filler and coating is most important for the paper product and production equipment (wear on wire, doctor and slitter wearing), the limestone studied samples hardness is 3 as per Moh's scale (1: talc to 10: diamond).

4.9. Appearance & Color of powder

The color of ore powder is useful in identify the pigment into white or colored pigment, however the history of mineral formation. The visual inspection of limestone sample is milky white to white due to high purity of calcium carbonate content.

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Fig. 6. Brightness of El Minia carbonates.

4.10. Brightness of El Minia calcium carbonate

In paper industry the high dry brightness is preferred to produce the high quality paper. The limestone were crushed to very fine size and tested using Dr. Lange equipment (Fig. 6), and the results achieved the requirements of paper making brightness value ranging from 91 to 93.5% as shown in Table 3.

4.11. Purity as CaCO3: 95%

The CaCO3 content in studied samples are ranging from 99.30 to 99.65%, which called high purity limestone as per [19].

4.12. Refractive index

Refractive Index is the difference between the speed of light in a vacuum and the speed of light in the gemstone. As light passes through a gemstone, it slows down because a gemstone is denser than air. The angle of refraction in the gemstone determines its RI [20]. The RI is easily measured using a refractometer. Limestone fillers are mainly composed of strongly birefringent calcite mineral with refractive indices ranging from 1.49 to 1.65.

4.13. Specific surface area

Specific surface area is measured by the nitrogen adsorption method (BET: Brunauer, Emmet, Teller). The particle fineness, the particle size distribution, and the particle morphology are, depending on the structure, indirectly reflected in the specific surface area of the filler. Finer, non-structured fillers exhibit a higher specific surface than coarser ones. There is, a direct correlation between the specific surface area of filler and, the internal sizing agent demand. An internal sizing agent is applied to the wet end in order to make the paper more hydrophobic. The specific surface area of regular paper fillers ranges between 2.5 and 14 m^2/g^{-1}, while fiber fines show specific surface areas of 6–8 m^2/g^{-1}. The surface area

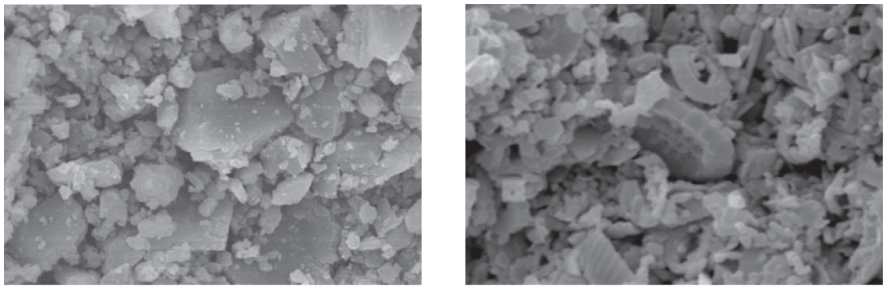

Fig. 7. (a) SEM for El Minia limestone (b) SEM for el Minia Chalk.

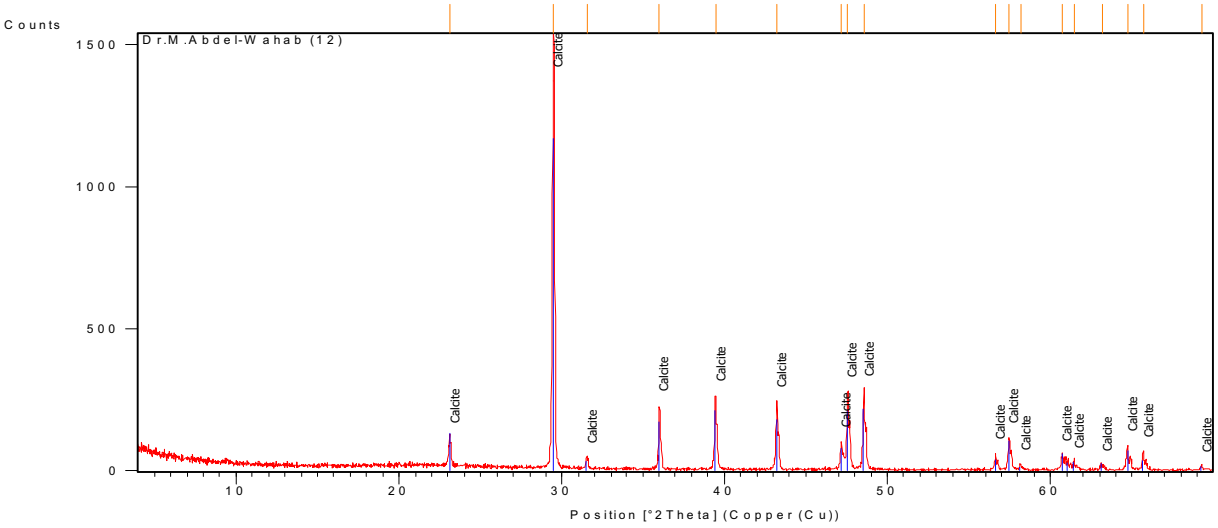

Fig. 8. XRD of Limestone at Samalout area.

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for calcium carbonate powder ranging from 2 to 12 m^2/g^{-1} as per [21].

4.14. Scanning electron microscope (SEM)

The structure of fillers can be observed and characterized best by scanning electron microscopy (SEM). The particle morphology has an influence on light scattering via the number and size of air microvoids in the sheet. For different morphologies, there is a different optimum for light scattering in terms of particle size. The particle morphology has an impact also on the packing of the filler particles in the flocculates usually formed during the papermaking process.

The crystallite habit of natural ground CaCO3 filler is rhombohedral Fig. 7. For high brightness demand, GCC fillers based on limestone and marble are preferred by the paper industry. Lower brightness chalk is used as filler in the production of regular newsprint.

4.15. Chemical analysis

The XRF analysis of collected limestone revealed that the major element is CaO 55.70; accordingly the CaCO3 is 99.65% as indicated in Table 5. These results reflect that the studied ore possess high purity and suitability for industrial proposes and paper making.

4.16. X-Ray diffraction

Four samples were analyzed by XRD and the data of identified minerals of powder samples were plotted in the following diagrams:

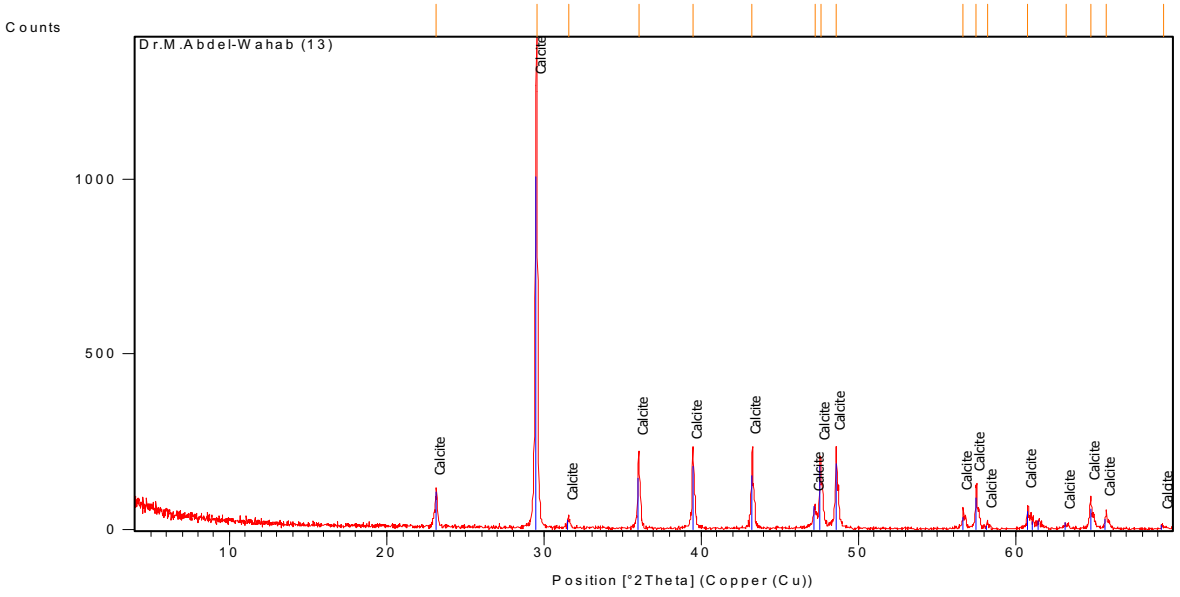

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Fig. 9. XRD of Samalout Limestone.

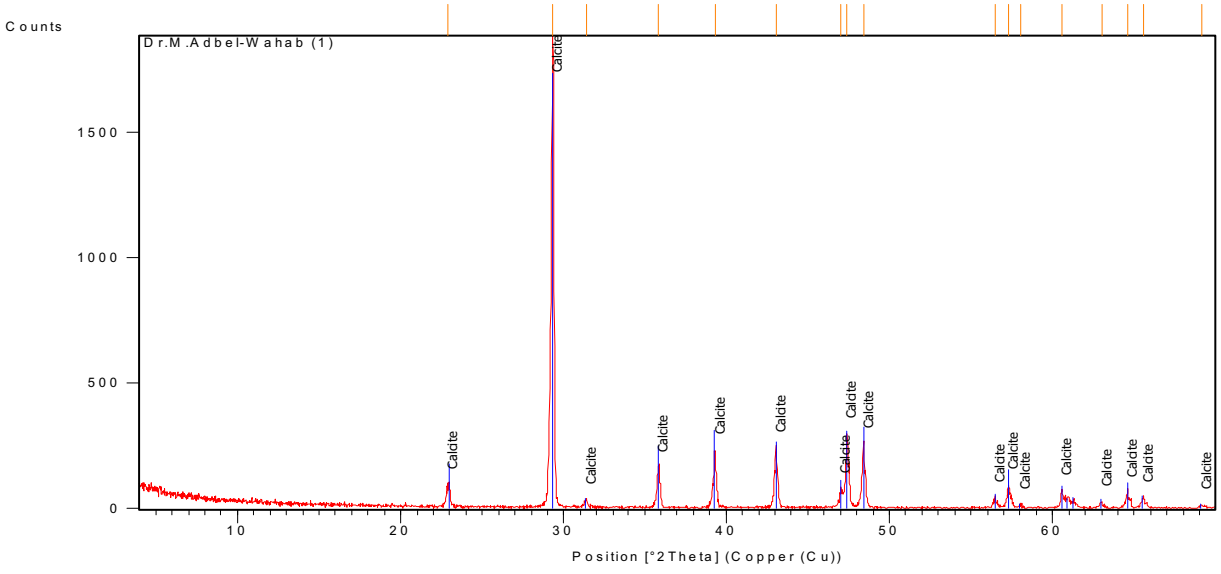

Fig. 10. X-ray diffraction of Beni Khalid carbonate.

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The XRD analysis of studied samples were collected from Samalout areas indicates that the calcite mineral is the most predominant minerals of limestone ore with average ratio 99.5% as shown in (Figs. 8and 9).

The XRD of Beni Khalid limestone (Fig. 10), shows that the samples are composed mainly of calcite, the XRD results complies with chemical composition analysis that the CaCO3 is 99.30%.

4.17. Soundness test

Residues, impurities, contamination, can be coming from origin, processing the industrial mineral, transportation, and from other sources (run-ability in paper machine or coating or calendaring causes streaks and breaks, which are expensive), the test was carried out according to [22], and the obtained results are ranging from 10 to 12% loss of impurities, meanwhile the maximum standard is 15%.

5. Conclusions

This study indicates some positive conclusions:

- Presence of huge outcrop calcium carbonate reserve in El Minia areas can be mined open cast with low cost.
- El Mina limestone possesses high purity CaCO3 "99.65%" content suitable for industrial purposes, further more paper filler/-coating pigment.
- The calcium carbonate brightness reading ranging from 91 to 93.5% and suitable for paper pigment fillers.
- The more investigation and cooperation with paper Manufacture Company for trial testing using local ores are required.

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