People's Democratic Republic of Algeria

Ministry of the High education and Scientific Research

University A. Mira - Bejaia

Faculty of Technology

Mines and geology department

Option: Valorisation of Mineral Resources

# Master Dissertation

## Theme

# *Characterization and valorisation of Bou-Caid's barite rejects*

Represented on 27th June 2016 in front of:

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Examiner: Mr Imad Bel Abbas

Year 2015 - 2016

# *Acknowledgment*

*This work was carried out on the level the university A. Mira Bejaia.*

*I express my deep sense of gratitude to Mrs Bouzidi Nedjima for her extreme help* and supervision and support during the entire work *and her instructions and advice.*

*I am very thankful to Prof. A. Souici and Prof. I. Bel Abbas for evaluating my work.*

*And I express my deep appreciations for Mrs Souici for her permanent help and concern.*

*Many thanks go in particular to Mr Belhouchet and the physics department in the University of M'Sila and all the staff of Bou-Caid unit.*

# *Dedication*

Thank you #Allah with every breath I take.

#My_Mother_And_Father

#My_ Sister

#My_Two_Brothers

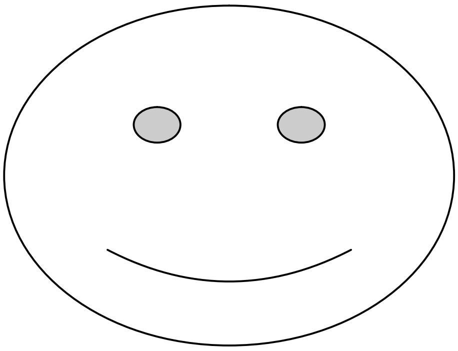
#All_My_ Big_ Family

#All_My_ Beloved_Friends

#I_Love_You_All

#Allah_Bless_You_All

#Hanane



# ***List of figures***

## List of tables

|  |  |  |
|---|---|---|

# *Table of contents*

## Chapter I: Overview of Barite and the treatment process of its rejects.

## Chapter II: Methods and materials.

## Chapter III: Characterization of Barite rejects and their elaboration with ceramics.

## Chapter IV: The physicochemical proprieties of ceramics composites.

# *General introduction*

# *General introduction*

Barite is an abundant mineral that can be found in different geological environments, due to its various applications and intensive exploitation; it largely contributes in the economical and the industrial development of countries, it is well-known by its own significant physical and chemical proprieties, which allow it to be widely used in the petroleum industry and many other industries [1].

Worldwide, barite occupies an important place among the abundant industrial minerals, and because of its large use, the demand is extremely increasing, so as a result the Algerian mining industry deals with the barite exploitation namely in Bou-Caid in Tissemsilt and in Ain Mimoun in Khenchela[1,2] .

In our framework we are interested by the rejects of barite in the case of Bou-Caid unit, where the barite ores are enriched by wet gravimetric separation, though this separation process increases the productivity of the unit, and the recuperated concentrate is of a high quality, but it generates high amounts of rejects that occupy a very large area.

The aim of our research is the characterization of these rejects and the attempt of valorizing them by elaborating them with ceramics. We divided our work into four chapters, while chapter one is devoted to an over view of barite and its different deposits and its extraction methods and its uses worldwide, then focusing on the Algerians ores namely Bou-Caid ones, and the treatment process of barite on the level of this unit and the rejects resulted by it, and the attempt of valorizing them by the flotation method. Then we took an over view of ceramics and their different types and uses. Chapter two brightens the materials and the methods we used for the sake of obtaining representative samples of our rejects, starting from their mechanical preparation and its material to the sampling and the sieving methods until the XRD analysis. Chapter three is consecrated to the results of the characterization of barite rejects by XRD analysis, and their use as a raw material in the fabrication of ceramic composites. Chapter four is devoted to the physical and the chemical proprieties of the ceramic composites, and it displays of the multiple results obtained from the applied tests, with a discussion within.

Then we finish our work by a general conclusion and some perspectives.

# Chapter I

# Overview of Barite and the treatment process of its rejects

## I.1 Introduction

The word barite comes from the Greek word barus, which means heavy, it is also known as barite or barytes. Barite has been found in many areas around the world and it is mined and processed in numerous countries including Algeria. Because the mineral has significant physical and chemical proprieties, it is used in different industries and applications.

The purpose of this chapter is to identify barite, locate the mineral, and understand its uses worldwide, and to line the Algerian barite ores and their treatment process until the obtaining of the rejects and the methods used for their valorization.

## I.2 Barite

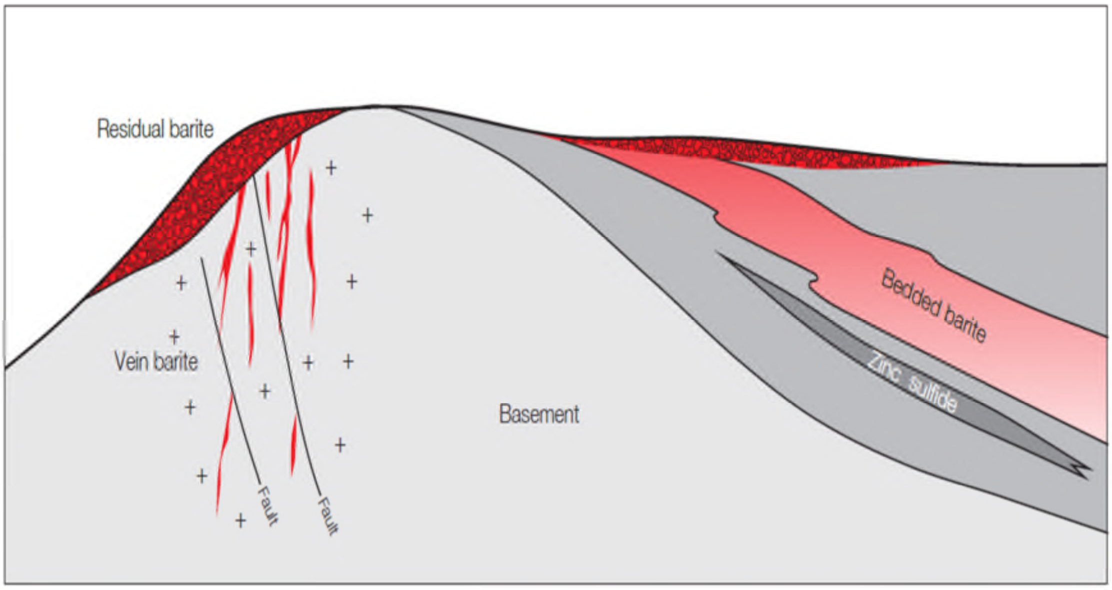
### I.2.1 Definition

Barite is a naturally occurring mineral consisting of barium sulphates $BaSO_4$ in proportion 65.7% BaO and 34.3% $SO_3$ in pure samples. Barite belongs to the orthorhombic crystal system, commonly in well formed crystals which are thin to thick tabular or rectangular and flat parallel to the basal pinacoid or elongated parallel to the a or b axis; it can be identified by its high specific gravity which is 4.50 g/cm3 when in pure form and its chemical inert. The mineral has a hardness of 3.0 to 3.5 on Mohs hardness scale; it has a perfect cleavage on {001}, and less perfect on {210}, and imperfect on {010}, it is transparent to translucent and it also may be found colorless, or in different colors like yellow, white, brown, gray, pale shades of red, green, and blue [1,3,4,5,6].

**Figure I.1:** Barite [7]

### I.2.2 Origin and mode of occurrence

Barite forms in many geologic environments in sedimentary, igneous, and metamorphic rocks and it can be found with both metallic and nonmetallic minerals. In most cases, barite must be a major component of the material and must be of substantial thickness for the ore to be economic. There are three main types of barite deposits: vein, residual, and bedded as it is shown in the figure II.2 [3, 4, 6].



Source: IMR (mineralisation styles after Clarke et al., 2004; Harben & Kuzvart, 1996)

**Figure I.2:** Types of barite deposits [8]

### I.2.2.1 Vein cavity-filling deposits

The vein deposits are of hydrothermal origin with barite precipitated from solution and filling or replacing rocks along fractures or other structures, the host rocks are igneous, metamorphic, or sedimentary rocks of Precambrian to Tertiary age. Most of these deposits are associated with faults, gashes, joints, bedding planes. Because of the nature of the deposit, the barite-mineralized zone can vary greatly in length and width. It is not uncommon for the main mineralized zone to pinch and swell along the fracture structure, and these zones tend to pinch out on each end. The deposit can have fractures filled with barite radiating from the main barite zone [3, 4, 6].

- **Mineralogy of the ores**

Barite in veins and cavity fillings is generally dense, hard, and gray, to white. It is commonly associated with purple, green, or colorless fluorite, calcite, dolomite, ankerite, quartz, and many sulfide minerals including pyrite, chalcopyrite, galena, sphalerite, and their oxidation products, even gold and silver minerals can be common associates [4].

- **Origin of deposits**

The minerals of the vein and cavity-filling deposits are typical of the epithermal suite precipitated from low-temperature hydrothermal solutions, such as the most of vein deposits containing barite in the Western States of the United States of America; the term "tele-thermal" has been applied to such deposits, this term implies that the solutions probably traveled farther from their source, and therefore, were probably somewhat cooler than those termed "epithermal" [4].

### I.2.2.2 Residual deposits

Residual barite deposits occur in unconsolidated material and are formed from the weathering of pre-existing deposits. Following Hull's usage (1920, p. 14), the restriction of weathering "in place" is omitted from the definition so as to include accumulations in alluvium and colluvium that might supplement the deposits formed in place. Stream and frost action, soil creep, and gully wash are the agents in what might be called a secondary accumulation in alluvium and colluvium. The residual deposits are formed by the dissolution of the host rock of vein or bedded deposits leaving irregular masses of barites in clay matrix. Deposits are extremely variable in size and shape, but can extend over several kilometers [3, 4].

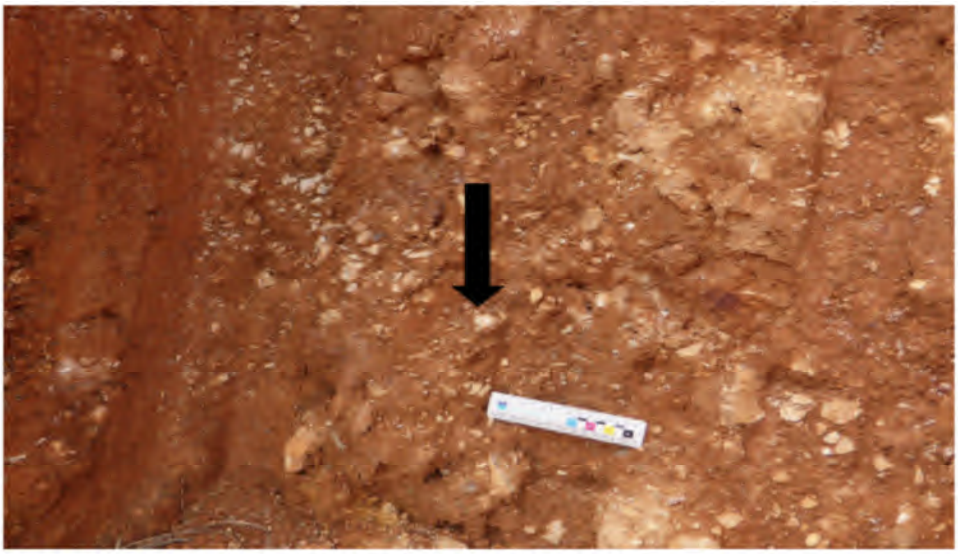


**Figure I.3:** Residual barite [8]

- **Mineralogy of the ores**

Most of the residual barite is white, and translucent to opaque, it occurs in fibrous, or dense fine-grained masses. The surface of the barite is pitted and stained with clay. Some masses or crystals are covered with quartz crystals. Residual barite derived from circle or solution channel deposits forms dense white masses with rough to rounded surfaces. Pyrite, galena, and sphalerite occur in or on some barite, and locally lead or zinc may be byproducts of barite mining. Chert and jasperoid also are abundant in many deposits. Undissolved rock fragments and red, yellow, or brown clay make up the rest of the deposit.

Barite masses of residual deposits range from microscopic particles to irregular boulders weighing hundreds of pounds. Most masses, however, range from 1 to 6 inches in the greatest dimension [3, 4].

- **Types of residual deposits**

Deposits derived from veins are generally elongate, as are those derived from the weathering of mineralized fault zones. In some areas it is impossible to distinguish the original type of deposit. Barite from these deposits locally contains inclusions of pyrite, galena, and sphalerite. Some deposits also contain mineralized fragments of chert [4].

Residual deposits derived from bedded or replacement deposits commonly are large. In general, fragments from beds of fine-grained barite are angular. Barite from incompletely replaced beds is porous. Barite in residual concentrations derived from beds containing oolites, pisolites, rosettes, and disseminated crystals of barite would probably retain enough of their characteristics to make the origin of the deposit readily identifiable [2].

### I.2.2.3 Bedded Deposits

Bedded deposits (also called stratiform deposits) are those formed by the precipitation of barite at or near seafloor or sedimentary basins [3, 4].

The brines are generated by migration of reduced saline fluids, and are concentrated by major basin controlling faults, they are often associated with base metal sulphides mainly zinc-lead .They occur in rocks varying in age from Precambrian to Cenozoic [3].

- **Mineralogy of the ores**

Sequences of sedimentary rocks having barite-rich beds or groups of barite-rich beds may contain many rock types including conglomerate, sandstone, shale, and limestone. The shale and limestone sequences contain most of the deposits. The individual beds of barite are generally light to dark gray (the gray color is the result of included organic matter) and range in thickness from a few inches to about 10 feet [4].

Barite in bedded deposits is generally extremely fine grained and accompanied by quartz and chert, pyrite and secondary iron oxides, dolomite, calcite, siderite, witherite, and strontianite; and clay minerals [4].

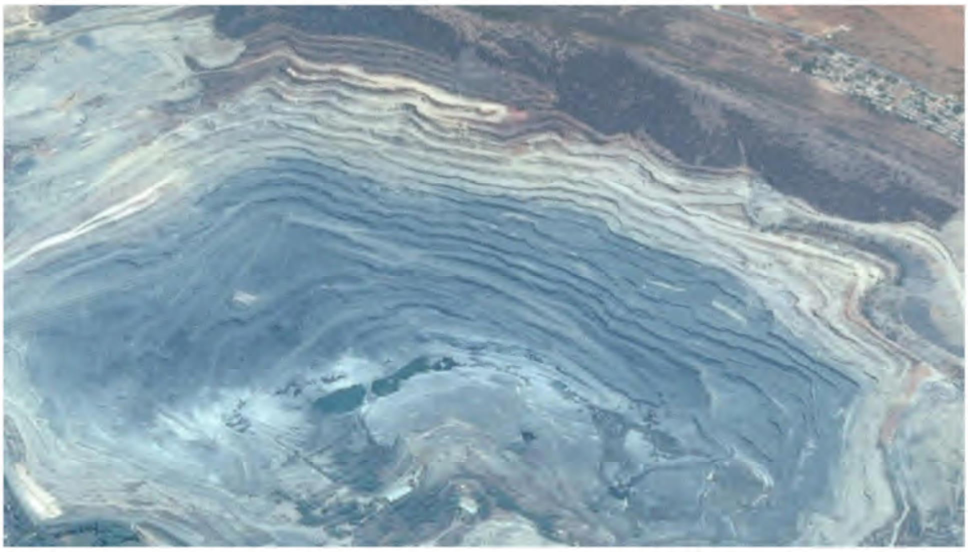


**Figure I.4:** Spatial image of bedded barite deposits [8]

- **Origin of deposits**

Evidence for the origin of the bedded deposits of massive and disseminated barite is conflicting, and suggests that the barite might have originated either as a primary deposit within the sedimentary rocks, or as a secondary deposit formed in the host rocks as a result of replacement by aqueous solutions [4].

### I.2.3 Mining and processing

The geometry and type of barite deposit affects mining economics and processing complexity. Briefly, vein deposits have complex geometry and may often be extracted from surface or underground as a co-product of lead or zinc mining. Residual deposits are shallow enough to be mined opencast using dozers, excavators or front end loaders. Bedded barite deposits are more extensive and have more consistent grades; these can be exploited by large-scale open pit methods, followed by relatively simple processing.

Barite is extracted by both surface and underground mining, generally followed by simple physical processing methods to produce correctly sized product, and to remove extraneous (mainly silicate gangue) materials [3, 9].

## I.3 Barite reserves and production worldwide

### I.3.1 Barite reserves

Barite deposit are found throughout the world in variety of geological environments, and as we already mentioned earlier the three major types of barite deposits are bedded, vein and residual.

No reliable information is available with regard to the total world reserves of barite; however the US Geological Survey (USGS) estimates 350 million tons of reserves of which China, India and Kazakhstan are claimed to account for 219 million tons (63% of world reserves). This global reserve base should be sufficient for more than 40 years' life at current production rate and prices. The table bellow is based on information supplied by (USGS), which outlines the world reserves of barite in 2002 and 2003 [3, 6, 9].

**Table I.1**: Barite reserves of some countries [3, 6]

| **Country** | **Reserves (Million tons)** | **Reserve Base (Million tons)** | **% Reserves** |
|---|---|---|---|
| India | 53 | 80 | 26.5 |
| USA | 26 | 60 | 13.0 |
| China | 62 | 360 | 31.0 |
| Algeria | 9 | 15 | 4.5 |
| Morocco | 10 | 11 | 5 |

The reserve base is the in-place demonstrated (measured plus indicated) resource from which reserves are estimated. The reserve base includes those resources that are currently economic and marginally economic, along with some that are not currently economic. Not all barite reserves have been identified. There are still possible locations for new or additional barite reserves [6].

### I.3.2 Barite production

The four top barite-producing countries in the world are China, India, Morocco, and the United States, according to the information compiled and reported by the U.S. Geological Survey (USGS) in 2004 [6,9,10].

World barite production is directly linked to oil and gas-well drilling activity where more than 80% of barite produced is used as a weighting agent. Barite production has increased from around 5 million tons per year in the 90s to around 8.5 million tons per year in 2013 [8, 9].

When considering barite reserves suitable for use in drilling fluids, there are relatively few major sources with China, India, the US and Morocco, Mexico and Turkey accounting for about 80% of global production. China accounts for around 45% of world production with India, US, Morocco and Turkey making up a further 35%, as it is shown in the figure I.5 [6, 7].

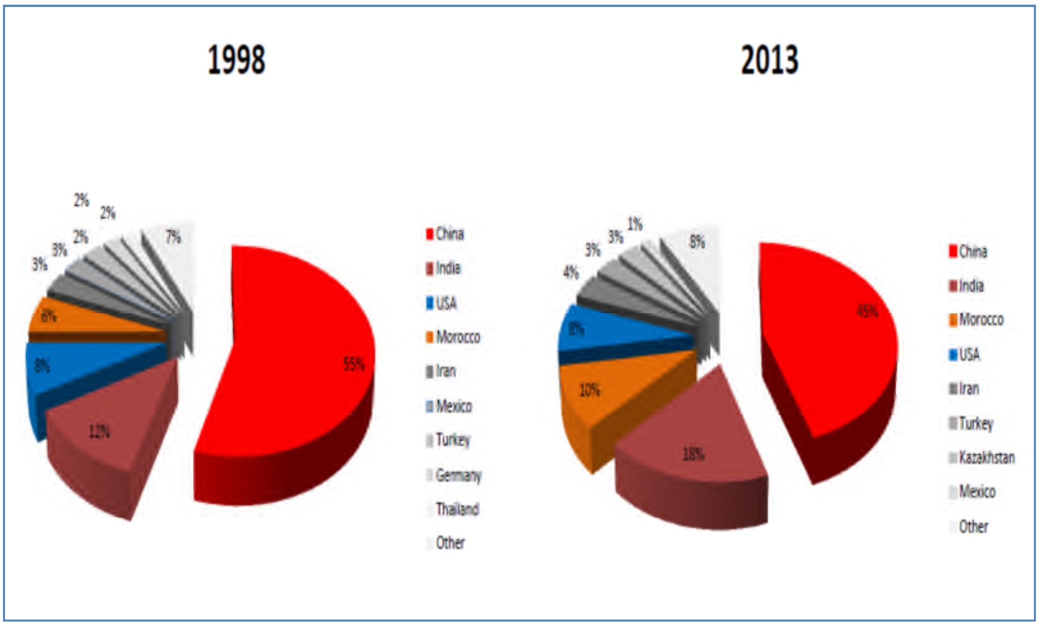


**Figure I.5:** Barite production – Global Proportions [8, 9]

### I.3.3 Barite consumption

The US is the largest barite consumer (around 3 million tons per year), accounting for more than 30% of annual shipments. It is followed by China, which consumes around 1.1 million tons per year of barite [9].

The US uses over 95% of its barite output for the oil drilling industry, highlighting a general correlation between rig activity and barite consumption [9].

## I.4 Specification and uses

As we already mentioned before, accounting for 88 % of 2003 world barite production is used as weighting agent in oil and gas well drilling fluids or ‘mud’.

Barite is added to the drilling mud (mainly water with other chemicals to enhance its performance) to increase the density of the column of mud above the drill bit, and thus assist in preventing a blowout [3].

Ground barite can form up to 40% of the mud by weight. Although there are alternatives, barite is the favoured weighing agent as it is non corrosive, non abrasive, insoluble and non toxic and it is also relatively cheap and easily available [3].

The normal specifications are provided by the American Petroleum Institute APE which requires the following conditions:

- The density of pure barite is about 4.5 g/cm$^3$, while the density for drilling mud must be equal or greater than 4.2 g/cm$^3$, with at least 90% ground to less than 45µm.
- In offshore drilling in the USA the U.S Environmental Protection Agency limits the content of mercury to 1 milligram per kilogram of barite and that of cadmium to 3 milligrams per kilogram of barite [3, 9].

Barite's particular qualities of high density, low solubility, high brightness and whiteness, chemical inertness, softness and relative cheapness also make it available in many other applications. These include [3]:

- As a filler in paint and plastics;
- As the main source of barium for the chemical industry;
- The production of lithopone, which is a high performance white pigment, composed of mixture of chemically precipitated and calcined zinc sulphide and barium sulphate.
- In glass manufacture as a flux and to add brilliance and clarity;
- Minor uses as an absorber of gamma and X-ray radiation, e.g. special concrete to shield nuclear and X-ray installations.

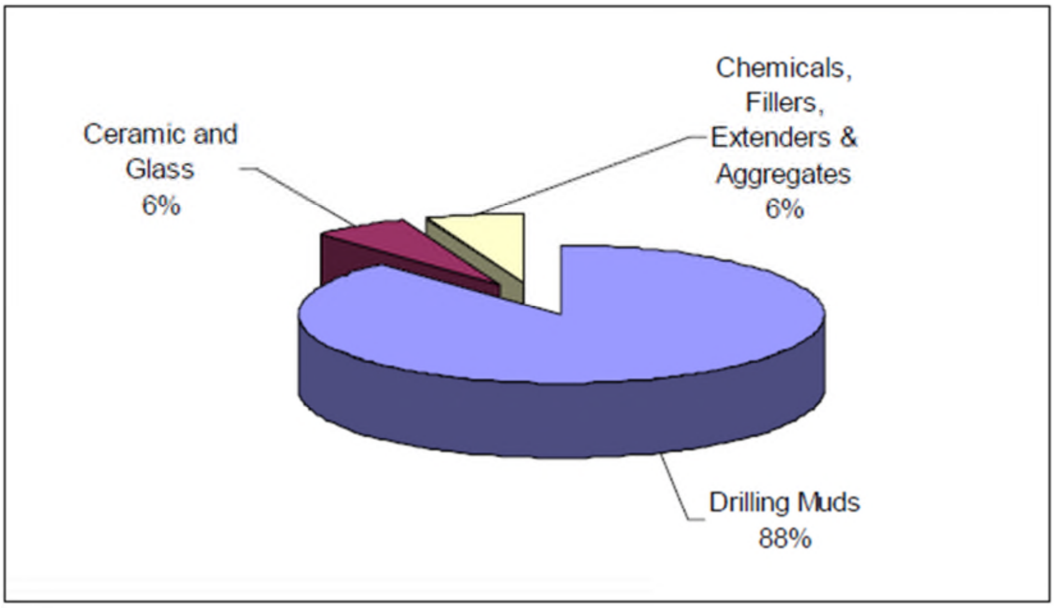


**Figure I.6:** Portions of the global different uses of barite [3]

Figure III.3 shows the global portions of the different industrial application of barite worldwide and as we notice the petroleum industry takes the lead of barite's uses worldwide by more than 88% which confirms all what we have mentioned earlier.

## I.5 Barite –Focus on Algeria

In spite of the availability of barite ores, Algeria is classified as an importer of barite due to the increasing need of barite in the oil fields, and the lack of the new updated generating stations, and the absence of the technological initiative of the improvement of the valorization process of these barite ores, however there are some national companies that are active in barite's exploitation, treatment and production such as Ain Mimoun unit in Khenchela in the Algerian east and Bou-Caid unit in Tissemsilt in the Algerian west.

### I.5.1 Bou-Caid's ore

#### I.5.1.1 Presentation of Bou-Caid unit in W. Tissemsilt

The unit of Bou-Caid W. Tissemsilt was created in 1876 by the Franco-Belgian company "vieille montagne" (old mountain). After the Algerian independence in 1962 and until 1966 it was called BAREM (Bureau Algerien de recherches et d'exploitions minières), then from 1966 to 1983 it was called SONAREM (Société Nationale de Recherches et d'Exploitation Minières), then from 1983 to 2001 it was called ENOF

(Enterprise National des Produits Miniers Non ferreux et des substances Utiles), then from 2001 to 2015 it was called SOMIBAR (Société des Mines de Barite d'Algérie) and now it is called ENOF once again.

ENOF is an Algerian company that exploits and treats and produces barite which 98% of it is intended for the Algerian petroleum industry.

### I.5.1.2 History of Bou-Caid Mine [11]

The mine of Bou-Caid was created at the end of 19th century with the exploitation of the polymetallic ore of lead and zinc following the studies carried out by the French geologist Mr. Fournel in the 40s.

After the nationalization of mines in 1966, and parallel to the exploitation of the polymetals, SONAREM started prospection studies and systematic recognition of the layer in 1967.

In 1975, during a geological survey of 1/5000 of Sidi Belabbes' cover, there was the discovery of powerful baritized structure of 850 meters in length. This baritized structure was the subject of prospection and evaluation studies from 1977 to 1981, but the exploitation and the treatment of barite started in 1976.

The unit of Bou-Caid is composed of several small ores of underground exploitation of barite in the surrounding zone (Lakhdar, North, Sidi Belabbes, Colonne 2, Belkheiret, Ammal, Sidi Djiar and Sidi Ouadah) and of a treatment plant in the county town of Bou-Caid [10,11].

### I.5.1.3 Localization [11]

- **Geographical situation**

Tissemsilt is located at the Mid-west of Algeria, it is limited by Medea from the east, and by Ain Defla and Chlef from the north, and by Relizane from the west and by Tiaret from the south.

- **Localization of the unit**

The unit of Bou-Caid is located on the Northern side and beneath the culminating solid masses of the mountainous chain of Ouarsenis, with 1100 m of altitude. The unit and the installations of treatment are with the accesses of the NR19 as it is shown in the figure I.7.

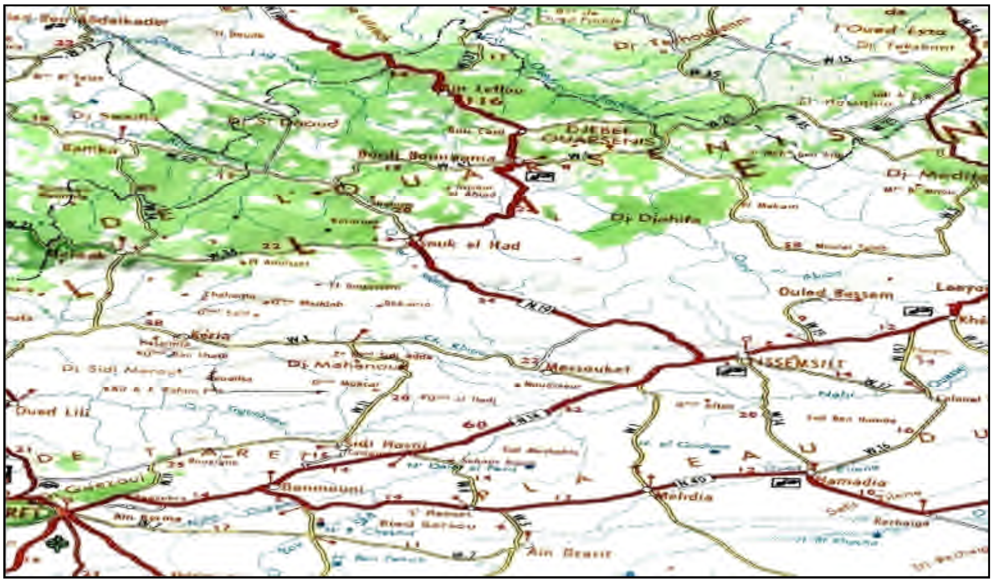


**Figure I.7**: Geographical localization of the Mine of Bou-Caid (Tissemsilt) [11]

- **Geology of the ores of Bou-Caid**

The culminating solid mass of Ouarsenis' chain consists of sedimentary deposits of secondary age formed since the Triassic age until the middle cretaceous:

- Trias: dolomitic and gypseous – metamorphic rocks- clays.
- Lias : dolomites - dolomitic limestones - barite and calcite veins.
- Middle lias**:** white limestone benches - conglomerates - intense barite and calcite seams - local conglomerates.
- Upper lias: limestone deposits, oolitic - limestones with flint- conglomeratic levels and abundant fossils.
- Middle Jurassic: poudinguiformes formation with micro-organisms - limestones with flint layers - limestones layers - abundant fossils.
- Late Jurassic: marmot benches - limestones - Alternations of multi-colored limestones - schistoid marls - abundant fossils - yellowish marl and limestones - limestones with fine grains.
- Cretaceous: limestones variegated in flagstones - marls - pyritous ammonites - marls and schists - sandstones lenses - conglomerated oysters.

- **Genesis of the mineralization**

The metalliferous deposits of Ouarsenis are especially zinciferous, and the presence of fluorite in the gangue, and other characters result in arranging the mineralization in the mesothermale category.

- **The morphology of the ore**

The morphology of the ore of Ouarsenis is conditioned by the tectonic movements which are undergone by the grounds, and in generally the two possible arising forms of ores:

- Seams: the mineral-bearing body which has three dimensions is naturally characterizes by the importance of one of these dimensions. The mine of Bou-caid is characterized by Sidi Djbar, Northern seams.

- Clusters: In this case the three dimensions of the mineral-bearing body are almost the same; it is also called “body” (body Lakhdar).

➢ **Reserves**

The ores’ reserves in Lakhdar, North and Ammal are estimated by 626 000 tons as geological reserves, and by 550 000 tons as exploitable reserves.

➢ **Mode of mining**

Due to the morphology of Bou-Caid ore, it is opened by adits which are an access road to the ore and evacuation means of the raw material, and the mining methods used in Bou-Caid are:

*a. Room and pillar mining;*

*b. Sublevel caving;*

*C. Shrinkage stopping;*

## I.6 Barite treatment in Bou-Caid unit [11]

Barite production unit in Bou-Caid is composed of:

➢ Barite production’s workshop:

- Reception of the ore in the shape of blocks, crushing, and screening, gravimetric treatment and drying, pulverization and conditioning;
- Quality control;
- Maintenance workshop, tools store;
- Administration;

### I.6.1 Barite treatment process in Bou-Caid plant

Bou-Caid plant treats and enriches the barite coming from the underground districts, with the aim of obtaining a commercial product in conformity with the API standards. Barite blocks , with a maximum size of 500 millimeters and an average content varying these last years from 58% to 62 % of $BaSO_4$, is treated in three significant operations as it is shown in figure I.8.

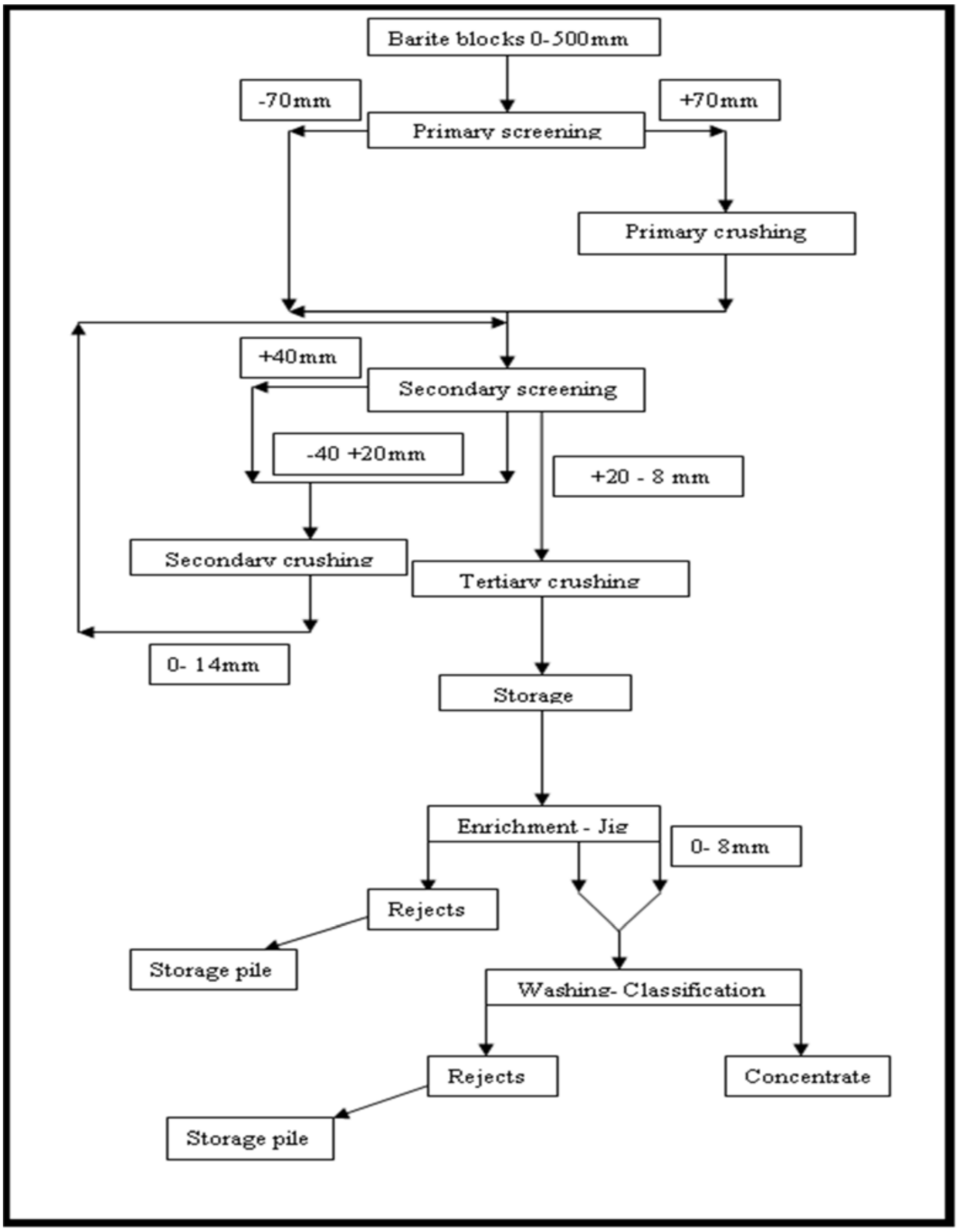


**Figure I.8:** Diagram of barite's treatment process [10, 11]

### I.6.1.1 Mechanic preparation [11]

The goal of this operation is to reduce barite blocks to a final size for the gravimetric treatment.

*a. Primary screening*

Raw material feeding starts from storage pile with a capacity of 5000 tons in a receiving hopper with a capacity of 120 tons of a maximum size of 500 meters. This operation allows in particular:

- Particles with a size inferior than 70 mm to join directly the crushing circuit, thus relieving the primary crushing from a considerable quantity of fine and average elements;

- Particles with a size superior than 70 mm to supply the primary crushing.

*b. Primary crushing*

The reduction of the particles' size to 70 mm by a jaw crusher type VB67 Bergeaud with a capacity of 52t/h.

*c. Screening and secondary crushing*

The reduction of the particles' size in the order of 14 mm to 20 mm. The screening is made up by three stages 40mm, 20 mm and 10 mm, the particles of 40mm and 20 mm are led towards a cone crusher of capacity of 22t/h to reduce them to a 14mm and then they pass by the screens once again, while the particles of 10 mm pass directly to the next step.

c*. Tertiary crushing and storage*

After being screened and crushed to a size of 10 mm, the particles are led to cylindrical crusher with a capacity of 16t/h to be reduced to a size inferior to 10 mm (0-3mm) , and then they are stored in three hoppers with a capacity of 120 tons for each one of them.

The total yield of the crushing installations is about 30t/h.

### I.6.1.2 gravimetric treatment [10, 11]

In this step, crushed barite undergoes a wet gravimetric separation in a device called Remer-Jig brand WEMCO.

The heavy product, which is barite (concentrate), is recuperated from the bottom of the Remer-Jig in a spiral classifier, and then it is evacuated towards dripping rooms.

The light product which is the reject is conveyed on the surface with water towards a decantation dam. Water used in this operation is stored and recycled and clarified.

The concentrate is stored in a storage pile with a capacity of 9000t, and the total yield of this treatment is about 12t/h.

### I.6.1.3 Pulverization and conditioning [10, 11]

This operation allows obtaining a final product in conformity with the standards.

*a .Drying*

The concentrate, with a maximum humidity of 12% at the entrance, undergoes a drying operation in a rotary dryer of 14 m in length and 2 m in diameter, where the humidity is reduced to a rate below 1% under the effect of 600°C.

*b. Pulverization*

The dried product undergoes a fine grinding in pendulum mill with an average yield of 14 t/ h ,and a particle size separation in a static separator where particles smaller than 74 microns are stored in a storage hopper of the final product.

*c. Conditioning*

Ground barite (74 microns) is set in big bags and weighed on an electronic scale.

The product packed in big bags (each big bag weights 1.5 tons) represents the final product intended for use as a drilling mud in the petroleum industry.

#### I.6.1.4 Analyses of laboratory

The various analyses are carried out by the laboratory service on samples of the final product, so as to value the density (4,20 in minimum), alkaline-earth metals (250 mg/kg), the residues with a size higher than 75 microns (3% in weight max), particles inferior to 6 microns (30% in weight max) according to the API standards, and at the end each batch is associated with a certificate which contains the various results to ensure the good quality of the final product.

### I.7. Methods of barite rejects' treatment in Bou-Caid [10]

The estimation of the volume of the rejects' storage pile was carried out by the operation of cubage on the level of the plant in ENOF on 22/08/2015, on various significant surfaces of the rejects' storage (rejects of gravimetric treatment), and the topographical surveys were also realized on the various zones of the rejects' storage pile, and the data were treated on software **SURFER8** to lead to the corresponding volumes. Tonnage obtained corresponds to the multiplication of the volume obtained which is about 136 650 $m^3$ with the density of the reject which is about 3,111 t/m3, so the tonnage is about 424 981 $t/m^3$.

**Figure I.9**: View of the rejects of the gravimetric treatment’s storage pile [10]

Compared to the initial estimation of the stock of the gravimetric treatment’s rejects which was about 500 000 tons, the lack of tonnage in the cubage is mainly due to:

-Dispersion of small surfaces of the storage that the operation of cubage could not completely consider

-The local transfer of small quantities of these rejects for the needs in the infrastructures.

### I.7.1 Available data on the analyses of the reject on Bou-Caid [10]

- **Chemical analyses**

These analyses were done on the rejects resulting from barite's treatment which were in the dam of decantation of the treatment's water in 2014, the results are illustrated the table I.2.

**Table I.2**: Results of the analyses of the treatment's rejects and the mud of the recycling basin [10].

| **Parameters** | **Units** | **Sample n°1** | **Sample n°2** |
|---|---|---|---|
| Cr | mg/kg | <20 | <20 |
| Cu | mg/kg | 121.3 | 214 |
| Pb | g/kg | 13.7 | 16.9 |
| Cd | mg/kg | 18,6 | 42.2 |
| Co | mg/kg | <20 | 25 |
| Ni | mg/kg | <20 | 101.6 |
| Mo | mg/kg | <10 | <10 |

These solid rejects of polymetallic mines, just like those of El-Abed (Sebdou, W.Tlemcen) and of Kherzet Youcef and Chaâbet El Hamra (Ain Azel, W.Sétif), were used as building material, in the form of sands.

And also there were other analyses on the rejects of the treatment and solid rejects in 2007, and the results are illustrated in the tables below:

**Table I.3**: Results of the analyses of the treatment rejects [10].

| **Chemical Composition** | **Percentage (%)** | | |
|---|---|---|---|
| | **Sample n°1** | **Sample n°2** | **Sample n°3** |
| $Fe_2O_3$ | 2.61 | 2.35 | 5.32 |
| Hg | Non-existent | Non-existent | Non-existent |
| ZnO | 0.51 | 0.54 | 1.53 |
| PbO | 0.41 | 0.61 | 0.81 |
| MnO | Trace | Trace | Trace |
| CuO | Trace | Trace | Trace |
| Cd | Non-existent | Non-existent | Non-existent |

It is to be announced the existence of arsenic **(**As**)** in two (2) samples:

-Sample n2 with a rate of 0.16 %;

-Sample n3 with a rate of 0.20 %;

**Table I.4**: Results of the analyses solid reject [11].

| Parameters | Units | Sample 1 | Sample 2 |
|---|---|---|---|
| Fe | g/kg | 48 | 44 |
| Mn | mg/kg | 540 | 740 |
| Zn | g/kg | 37 | 18 |
| Pb | mg/kg | 9.2 | 8.9 |
| Cr | mg/kg | 50 | 50 |
| Cu | mg/kg | 200 | 130 |
| Ni | mg/kg | <40 | <40 |
| Co | mg/kg | <40 | <40 |
| Cd | mg/kg | 32 | 35 |
| Hg | mg/kg | 89 | 11 |

As already indicated above, these solid rejects are used as building materials, in the form of sands.

For the existence of arsenic (As), the expert had already suggested to ENOF Bou-Caid to remake the analyses by another laboratory, such as that of the National Observatory of the Environment and the Durable Development (EPIC - ONEDD) before concluding definitively the quality of these solid rejects [10].

### I.7.1.1 Test of valorization by flotation of the gravimetric treatment rejects in Bou-Caid [10]

- **Aim of the test**

Indeed, it was estimated that the rejects of the jig of Bou-Caid, increased year by year in quantity, in a rate of 20 to 25 % of $BaSO_4$ and even sometimes exceeding 30 %.

The goal of these tests was to know if it is possible to obtain from these rejects a concentrate higher or equal to that obtained of the gravimetric treatment.

- **Preparation of the sample**

The sample was taken during one week, every 30 minutes, was dried with the free air, homogenized and prepared for the various analyses.

- **Crude ore**

.*a. Particle size analysis*

The table below shows the particle's size distribution and the content of each class.

**Table I.5:** The particle's size distribution and the percentage of barite in each class [10].

| Class (mm) | Weight (%) | $BaSO_4$ (%) |
|---|---|---|
| **+ 5 mm** | 24.60 | 7.48 |
| **- 5 + 2.5** | 22.95 | 5.92 |
| **- 2.5 + 1.6** | 6.68 | 12.18 |
| **- 1.6 + 0.630** | 7.70 | 17.32 |
| **- 0.630 + 0.400** | 2.10 | 9.84 |
| **- 0.400 + 0.250** | 1.65 | 14.26 |
| **-0.250 + 0.125** | 2.16 | 7.66 |
| **- 0,125** | 31.96 | 61.60 |
| **Raw material re-established** | 100.00 | 25.66 |
| **Raw material determined** | | 22.34 |

*b. Grinding*

The study of grinding quality was made on crushed ore with a size of 1 mm, and the results are indicated in the table below:

**Table I.6:** Grinding results of 1mm ore [10].

| Temps (min) / Class (µ) | 5 | 10 | 20 | 30 |
|---|---|---|---|---|
| **- 80** | 60.53 | 69.10 | 80.15 | 84.02 |
| **+ 80 – 125** | 7.02 | 11.97 | 7.75 | 8.58 |
| **+ 125 – 200** | 28.70 | 12.29 | 11.95 | 7.30 |
| **+ 200** | 3.75 | 0.64 | 0.15 | 0.10 |

c. *The mineralogical study*

The mineralogical study of each class showed that in the heavy fraction, the barite (more than 80 %) is covered with a carbonate film, of quartz and iron oxide; in the electro-magnetic fraction, it is oxidized, carbonated, while in the light fraction, the presence of carbonates (calcite) is noticed.

For better optimizing the time of grinding, and in order to approach as much as possible a suitable particles' size to flotation, tests were carried out by eliminating the class

+200µ which is negligible so much in quantity than in content (between 1,9 and 2,3 % $BaSO_4$).

These tests were carried out with the following parameters:

- Cetylsulfate of Na = 500 g/t ;
- $Na_2SiO_3$ = 1 kg/t;
- pH ($Na_2CO_3$) = 10;

Mode of flotation was simple followed by a control with a small quantity of collector. With a grinding to approximately 70 % < 80µ, the obtained results were acceptable with a good recovery in the concentrate. It is noticed that more the softness of grinding increases, the selectivity of flotation decreases, it is completely logical phenomenon because the fine particles obstruct the flotation considerably.

- **Tests of flotation**

Study of the depressant: before continuing to improve the quality of the concentrate, it was necessary to fix the quantity of Na silicate. It is pointed out that this reagent is not available within the laboratory so it was replaced by the silicate out of ceramics, which according to its density, it approaches much that used like depressant in various laboratories.

The mode consisted of a principal flotation and a washing, and the tests were carried out with the following parameters:

- Cetylsulfate of Na = 500 g/t;
- $Na_2 SiO_3$ = 1 kg/t;
- pH = 10;

The results showed that more the quantity of sodium silicate increases, more recovery decreases and the content of the rejects increases although that of the concentrate remains relatively constant.

Based on the preceding experiment, the flow-sheet of a flotation of control by increasing gradually the quantity of the collector is completed:

-Principal flotation: Cetylsulfate of Na = 500 g/t;Na2 SiO3 = 1 kg/t; pH = 10.

-Flotation of control: Cetylsulfate of Na = 100, 200, 400 and 500 g/t; Na2 SiO3 = 0.5 kg/t; pH = 10.

-Rewashing: without reagents.

The results made it possible to note that decreasing the content of the reject can happen by increasing the quantity of the collector, which brings to test the following flow-Sheet.

This new approach consists in trying to collect all possible barite by increasing the quantity of collector, carried out of a principal flotation followed by 2 rewashing practically without reagents:

-Principal flottation: Cetylsulfate of Na=800, 1000, 1200, 1400g/t; $Na_2 SiO_3$ = 1 kg/t; pH = 10.

- 1st rewashing: $Na_2 SiO_3$ = 250 g/t;

- 2nd rewashing: without.

It came out of this test that increasing the quality of the concentrate with 2 rewashing comes first, and then it is followed by decreasing the content of the rejects.

- **Classified ores**

While referring to the preceding particles' size analysis, a cut was made to 3 mm, although the retained of this class titrates on average 10 % and exceeds 50 % in weight.

- Class +3 mm: Weight = 56.42 % - Content = 12 %

- Class -3 mm: Weight = 43.58 % - Content = 38.56 %

*a. Particle size analysis*

A pushed analysis was made on the class - 3 mm, and the results are shown in the table below:

**Table I.7**: Results of Particle size analysis on the class - 3 mm [10].

| Class (mm) | Weight (%) | $BaSO_4$ (%) |
|---|---|---|
| **+1.6** | 22.94 | 10.00 |
| **-1.6 +0.630** | 16.00 | 18.40 |
| **-0.630 +0.200** | 9.00 | 14.00 |
| **-0.200 + 0.100** | 4.14 | 12.80 |
| **-0.100 + 0.040** | 10.04 | 61.20 |
| **-0.400** | 36.88 | 63.20 |
| **Total** | 100.00 | 36.48 |

It shows, like the preceding test, that barite is found in fines from where attention to avoid the formation of sludge.

The retained of 3 mm comprises a considerable quantity of barite (almost half of the total quantity).

*a. Tests of flotation*

The ore was previously crushed to 200 µm, the mode and the parameters of flotation remain the same, namely:

-*Principal flotation*: Cetylsulfate of Na = 500, 800, 1000, 1200, 1400 1500 g/t; Na2 SiO3 = 1 kg/t; pH = 10.

-*1st rewashing*: Na2 SiO3 = 250 g/t;

- *2nd rewashing*: without.

The results showed, like previously, obtaining a good concentrate is possible by increasing the quantity of the collector, but nevertheless here the rejects are a little rich, this is due to the percentage of fines which obstruct flotation enormously.

- **Comment**

The various tests show that the barite rejects resulting from the gravimetric treatment in Bou-Caid can be enriched by flotation with Cetylsulfate of sodium.

The concentrates obtained are of good quality and in uniformity with the most demanding standards; however, to optimize the parameters for an adequate combination gravimetric treatment - flotation, semi-industrial tests are necessary.

So Bou-Caid unit tried to valorize the gravimetric treatment’s rejects by flotation, and though the tests’ results are very encouraging no step was taken towards this aim due to many reasons, mainly the lack of installations and the expensive amount of flotation and its reagents and also its menace on the environment, however the rejects’ enormous volume is still a problem for the unit and has to be solved by other means of valorization which is the aim of our work in the upcoming chapters.

## I.8 Ceramics

### I.8.1 Historical origins [12, 13]

The term ‘ceramics’ is derived from the Greek word ‘keramos’ meaning ‘burned earth’ and is used to describe materials of the pottery industry. Recent research shows that the processing of clay started around 19000 BC. The oldest findings of pottery in southern Japan are dated between 8000 BC and 9000 BC. As early as 4000 BC fired bricks were used for the construction of temple towers, palaces and fortifications. More than 2000 years ago the Romans spread the technique of brick making into large parts of Europe. In Egypt, glazed ceramic plates were used as wall decorations for the pyramids in 2600 BC and in China, the art of china porcelain making has been known since 1000 BC.

### 1.8.2 Characteristics of ceramics [13]

Generally the term ‘ceramics’ (ceramic products) is used for inorganic materials (with possibly some organic content), made up of non-metallic compounds and made permanent by a firing process. In addition to clay based materials, today ceramics include a multitude of products with a small fraction of clay or none at all. Ceramics can be glazed or unglazed, porous or vitrified.

Firing of ceramic bodies induces time-temperature transformation of the constituent minerals, usually into a mixture of new minerals and glassy phases. Characteristic properties of ceramic products include high strength, wear resistance, long service life, chemical inertness and non-toxicity, resistance to heat and fire, (usually) electrical resistance and sometimes also a specific porosity.

### 1.8.3 Types of ceramics [13]

Ceramics greatly differ in their basic composition. The properties of ceramic materials also vary greatly due to differences in bonding, and thus found a wide range of engineering applications. Classification of ceramics based on their specific applications and composition are two most important ways among many.

Based on their composition, ceramics are classified as oxides, carbides, nitrides, sulfides, fluorides, etc.

The other important classification of ceramics is based on their application, such as:

- ***Glasses:*** Glasses are a familiar group of ceramics; containers, windows, mirrors, lenses, etc. They are non-crystalline silicates containing other oxides, usually CaO, $Na_2O$, $K_2O$ and $Al_2O_3$ which influence the glass properties and its colour. Typical property of glasses that is important in engineering applications is its response to heating. There is no definite temperature at which the liquid transforms to a solid as with crystalline materials. A specific temperature, known as glass transition temperature or fictive temperature is defined based on viscosity above which material is named as super cooled liquid or liquid, and below it is termed as glass.

- ***Clay products:*** Clay is the one of most widely used ceramic raw material. It is found in great abundance and popular because of ease with which products are made. Clay products are mainly two kinds – structural products (bricks, tiles, sewer pipes) and white-wares (porcelain, chinaware, pottery, etc.).

- ***Refractories:*** These are described by their capacity to withstand high temperatures without melting or decomposing, and their inertness in severe environments. Thermal insulation is also an important functionality of refractories.

- ***Abrasives:*** These are used to grind, wear, or cut away other material. Thus the prime requisite for this group of materials is hardness or wear resistance in addition to high toughness. As they may also exposed to high temperatures, they need to exhibit some refractoriness. Diamond, silicon carbide, tungsten carbide, silica sand, aluminium oxide corundum are some typical examples of abrasive ceramic materials.

- ***Cements:*** Cement, plaster of Paris and lime come under this group of ceramics.

The characteristic property of these materials is that when they are mixed with water, they form slurry which sets subsequently and hardens finally. Thus it is possible to form virtually any shape. They are also used as bonding phase, for example between construction bricks.

- ***Advanced ceramics:*** These are newly developed and manufactured in limited range for specific applications. Usually their electrical, magnetic and optical properties and combination of properties are exploited. They are used in typical applications: heat engines, ceramic armors, electronic packaging, etc.

### 1.8.4 Applied processes and techniques in ceramics [13]

- ***Raw materials (ceramic powders)***

A wide range of materials is employed by the ceramic industry to match the diversity of its product collection. Both natural and synthetic materials are used, so ceramic raw materials can be divided into two groups, as shown in the figure I.9.

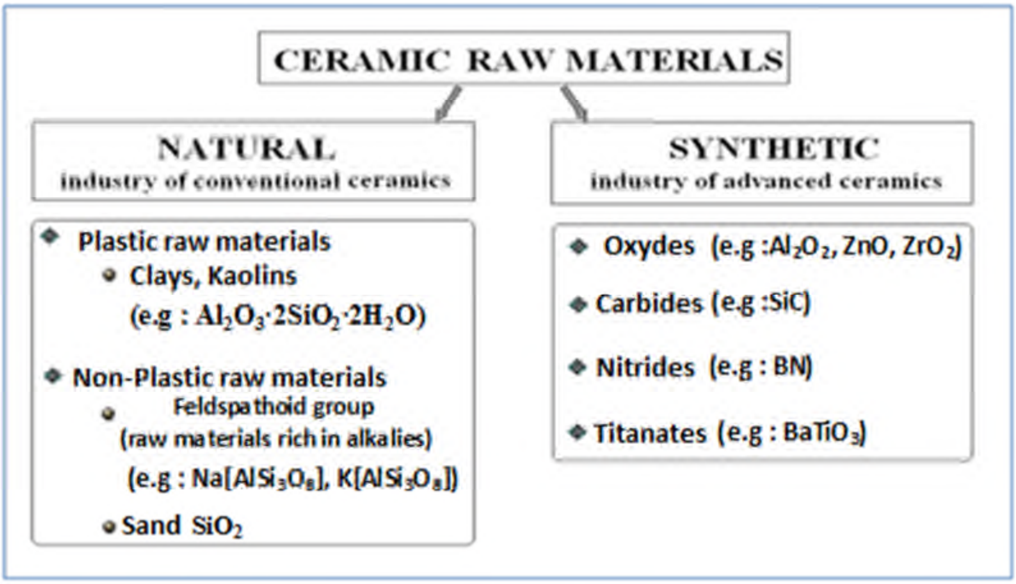


**Figure I.10:** Raw materials of ceramics [14].

Formulas (or bodies) of clay based ceramics may consist of one single clay or more clays, mixed with mineral modifiers, so-called ‘non-plastics’, such as powdered quartz and feldspar. Common clay minerals (‘plastic clays’) are hydrated aluminium silicates that have resulted from the weathering of rocks. There are a number of mineral species called clay minerals, but the most important are ‘kaolinite’, $Al_2O_3 \cdot 2SiO_2 \cdot 2H_2O$, ‘montmorillonite’, $Al_2O_3 \cdot 4SiO_2 \cdot H_2O$, and ‘halloysite’ $Al_2O_3 \cdot 2SiO_2 \cdot 4H_2O$ [12].

Advanced ceramic products, which contain only a small fraction of clay or none at all, are based on the following materials: oxides, carbides, nitrides and borides of Al, Mg, Mn, Ni, Si, Ti, W, Zr and other metal ions. Typical examples are $Al_2O_3$ (alumina), MgO (periclase or dead burned magnesia), SiC (silicon carbide), TiN (titanium nitride) and $WB_2$ (tungsten boride) [12].

### 1.8.5 General production process description

The manufacture of ceramic products takes place in different types of kilns, with a wide range of raw materials and in numerous shapes, sizes and colors [12].

Ceramic powder processing consists of powder production by milling/grinding, followed by fabrication of green product, which is then consolidated to obtain the final product. Concerning the molding (forming), there are many methods used to process powders into a desired shape to form what is known as green ceramic, among those methods we name compaction, tape casting, slip casting, injection molding and extrusion [13].

The green ceramic is then consolidated further using a high-temperature treatment known as sintering or firing which is a process applied to increase the green ceramic's strength. Sintering is carried out below the melting temperature thus no liquid phase presents during sintering. However, for sintering to take place, the temperature must generally be maintained above one-half the absolute melting point of the material. During sintering, the green ceramic product shrinks and experiences a reduction in porosity. This leads to an improvement in its mechanical integrity [12, 13].

As a general summery, we can say that raw materials are mixed and cast, pressed or extruded into shape. An irreversible ceramic structure for the product is reached during the firing process in the kiln. This demands a very accurate temperature gradient during firing to ensure that the products obtain the right treatment. Afterwards controlled cooling is necessary, so that the products release their heat gradually and preserve their ceramic structure. Then products are packed and stored for delivery [12].

During the process, water is regularly used for a thorough mixing and shaping. This water is evaporated in dryers and the products are either placed by hand in the kiln (especially in the case of periodically operated kilns) or placed onto carriages that are transferred through continuously operated kilns. In most cases, the kilns are heated with natural gas, but liquefied petroleum gas, fuel oil, coal, petroleum coke, biogas/biomass or electricity are also used [12,13].

### 1.8.6 Ceramics sectors [13]

The fundamental methods and steps in the production processes hardly differ in the manufacture of the various ceramic products, besides the fact that, for in the manufacture of e.g. wall and floor tiles, and household ceramics, sanitaryware and also technical ceramics, a multiple stage firing process is used. This is one historical reason why the various ceramics sectors can be summarized in two groups, the group of 'coarse' or 'construction' ceramics including the bricks and roof tiles, vitrified clay pipes, refractory products and expanded clay aggregates sectors and the group of 'fine' or 'traditional and industrial ceramics', including the wall and floor tiles, and sanitaryware, technical ceramics and inorganic bonded abrasives sectors.

The technical realization, however, can be very different, according to specific requirements of the products and the characteristics of the raw materials used.

For example, there are various continuously operated (e.g. tunnel kilns) and periodically operated (e.g. shuttle kilns) kilns used for firing the same or different ceramic products.

- ***Construction ceramics***

*a- Bricks and roof tiles*: Brick products are produced in large quantities, which are used as materials in numerous branches of building and contracting. For the most part, bricks and tiles are not designated according to the shaping technique used, but according to the intended application.

*b- Vitrified clay pipes:* Vitrified clay pipes and fittings are used for drains and sewers, but also as tanks for acids and products for stables.

*c- Refractory products:* Refractory products are ceramic materials capable of withstanding temperatures above 1500 ºC. Numerous refractory products in a wide variety of shapes and forms are used in many industrial applications of the steel, iron, cement, lime, glass, ceramic, aluminium, copper and petrochemicals industries, in incinerators, power plants, and house heating systems including night storage heater blocks. They are vital to high temperature processes and resist all types of stresses (mechanical, thermal, chemical) such as erosion, creeping deformation, corrosion and thermal shocks.

The resistance of refractory materials to high temperatures is defined so that their softening point is not less than 1500 ºC. A classification of ‘refractory materials’ with a softening point of between 1500 and 1800 ºC and ‘high refractory materials’ with a softening point of more than 1800 ºC is commonly used.

- ***Traditional and industrial ceramics***

*a- Expanded clay aggregates*: Expanded clay aggregates are porous ceramic products with a uniform pore structure of fine, closed cells and with a densely sintered, firm external skin. They are manufactured from raw materials containing clay minerals. The raw material is prepared, molded and then subjected to a firing process at temperatures between 1100 and 1300 ºC, resulting a significant increase in volume due to expansion.

The products can be manufactured in any quantity and with precisely adjustable grain size and characteristics to meet a wide range of technical requirements for numerous areas of application. They are used as loose or cement bound material for the construction industry (for instance loose fillings, lightweight concrete, blocks and other prefabricated lightweight concrete components, structural lightweight concrete for on-site processing) and also loose material in garden and landscape design (e.g. embankment fillings in road construction, substrates for green roofs, filter and drainage fillings).

The diverse range of industrially produced lightweight aggregates (LWA) covers a wide spectrum of technical characteristics. Properties such as grain size, porosity, and weight and grain strength can be controlled during the manufacturing processes. Aggregates with grain densities between 0.15 and 1.7 kg/dm³ are available to suit a wide range of requirements and applications. These lightweight aggregates have excellent insulating characteristics.

In addition to expanded clay aggregates, industrially produced lightweight aggregates also include expanded slate and shale, bottom ash, sintered hard coal flue dust and expanded glass.

*b- Wall and floor tiles:* Ceramic tiles are thin slabs made from clays and/or other inorganic materials, generally used as coverings for floors and walls. Ceramic tiles are usually shaped by extrusion or dust pressing at room temperature, then dried and subsequently fired at temperatures sufficient to develop the required properties.

The most common tile shapes are squares and rectangles, but other polygonal shapes (hexagons, octagons, etc.) are also available. As for size, tile sides range from only a few centimeters (mosaics) to slabs with 60 – 100 cm sides. Thickness ranges from around 5 mm for wall tiles to over 25 mm for some extruded tiles.

*c- Table and ornamentalware (household ceramics):* The manufacture of household ceramics covers tableware, artificial and fancy goods made of porcelain, earthenware and fine stoneware. Typical products are plates, dishes, cups, bowls, jugs and vases.

*d- Sanitaryware:* Ceramic goods used for sanitary purposes are all included under the collective name sanitaryware. Typical sanitary ceramic products are lavatory bowls, bidets, wash basins, cisterns and drinking fountains. These products are mainly made of vitreous china (semi-porcelain) or earthenware.

The manufacture of sanitaryware follows processes similar to those applied to all the other ceramic products. The raw materials are mixed with water to produce a clay slip of the required characteristics. The clay slip is then stored in tanks and used for slip casting in separate moulds or in pressure casting machines. The product is produced directly from the pressure casting machines or is released from the moulds used for the slip casting process. Pieces must be dried before they can be worked further, or transported.

Glazing is applied directly to the clay surface and fired at the appropriate temperature of the product concerned; normally between approximately 1200 – 1210 ºC for vitreous china and at about 1220 ºC for fireclay. Spraying of the glaze provides the color and 'vibrancy' to the underlying shape. The color or color combinations required are achieved by using pigments in association with the glaze. The majority of pigments are metal oxides. The quantities of pigments used are minimal compared with the weight of raw materials (clays) and other constituents.

The finished product enters the warehouse or storage facility for selection, dispatch and distribution.

*e- Technical ceramics*: Technical ceramics are applied in many industries and cover both, established products like insulators and new applications. They supply elements for the aerospace and automotive industries (engine parts, catalyst carriers), electronics (capacitors, piezo-electrics), biomedical products (bone replacement), environment protection (filters) and many others.

*f- Inorganic bonded abrasives*: Abrasive products, which apply this principal characteristic, are tools widely used in working every kind of materials, not only grinding, but also cutting-off, polishing, dressing, sharpening, etc, for metals, plastics, wood, glass, stones etc.

An inorganic bonded abrasive (or ‘vitrified bonded grinding wheel as manufacturers say) is a tool where a synthetic abrasive – contemporary abrasive materials are special fused alumina, synthetic corundum, silicon carbide, cubic boron nitride (CBN) or diamond, pre-screened in uniform grit size – is blended with a vitrified. Then the product is fired at a temperature at which the body (e.g. glass, clay), that constitutes the bonding element, vitrifies and, after cooling down, binds together the abrasive grains.

### I.8.7 Comment

Ceramics are definitely the materials of man kin’s future since they invaded almost all the industrial fields that we mentioned some of them in this chapter, and many others such as the healthcare where ceramic components are used extensively in medical laboratories, and pharmaceutical instruments, as well as in blanks for the production of crowns, bridges and implants in dentistry, and also in implantable medical devices such as pacemakers or hip replacements. Ceramics even entered in the field of security, and transport applications where we can find technical ceramics included in bulletproof vests and infrared night vision devices, in jet engine turbine blades, disc brakes and bearing components etc, also the renewable technologies fields require high-quality products that can only be manufactured with high-quality abrasives, refractories and technical ceramics; further research is conducted into the use of nanoengineered ceramic materials to store energy, particularly from wind turbines and solar arrays, so ceramics, one of the most ancient technologies in human history, could therefore be key to unlocking next-generation energy storage and enabling future generations to harness renewable technologies.

## I.9 Conclusion

As we arrive to the end of this chapter that was consecrated to identify and locate barite and to well understand its uses, and to line the Algerian barite ores and their extraction and treatment process, and the valorization of the rejects in the case of Bou-Caid unit, and to have an overview on ceramics. We conclude that barite is an abundant mineral that can be found in different geological environments, and different types of deposits mainly the bedded, the residual and vein ones.

Barite is well-known by its own significant physical and chemical proprieties which allow it to be widely used in the petroleum industry as a drilling mud due to its high density, and its chemical inertness however it is also used in many other industries.

In Algeria there are some national companies that are active in barite’s exploitation, treatment and production such as Ain Mimoun unit in Khenchela in the Algerian east, and Bou-Caid unit in Tissemsilt in the Algerian west. While focusing on Bou-Caid mine, and its reserves, and its process of barite treatment and the tests of the valorization of the gravimetric treatment’s rejects by flotation, we conclude that this reject can definitely be treated by this method due to the hopeful results obtained, however it is not applicable for the moment due to the lack of installations, and the expensive amount of flotation and its reagents, and also its menace on the environment, this fact requires the use of other methods of valorization in short terms to reduce the enormous volume of these rejects.

Concerning ceramics we concluded that they have become indispensable in cutting-edge technologies. Advanced technical ceramics have unique mechanical, electrical, thermal and biochemical properties that enable their use in a variety of applications in the automotive industry, electronics, medical technology, energy and environment and in general equipment and mechanical engineering.

# Chapter II

## *Methods and materials*

## I.1 Introduction

Various methods and techniques of analyses can be used to characterize the different types of materials; particularly we name the X-ray diffractions, TGA and TDA, X-ray fluorescence. This chapter is devoted to the methods and the materials used within our framework to characterize barite rejects of Bou-Caid mine W.Tisemssilet.

## II.2 Preparation of barite rejects

The preparation of our barite rejects of Bou-Caid mine started by crushing operation using a laboratory jaw crucher. The rejects were crushed to d=2mm.

The mechanism of crushing is either by applying impact force, pressure or a combination of both.

The jaw crusher is primarily a compression crusher while the others such as gyratory crusher and roll crushers operate primarily by the application of impact.

### II.2.1 Jaw Crusher [15]

- ***Design of Jaw Crushers***

Jaw crushers are designed to impart an impact on a rock particle placed between a fixed and a moving plate (jaw). The faces of the plates are made of hardened steel. Both plates could be flat or the fixed plate flat and the moving plate convex. The surfaces of both plates could be plain or corrugated. The moving plate applies the force of impact on the particles held against the stationary plate. Both plates are bolted on to a heavy block. The moving plate is pivoted at the top end (Blake crusher) or at the bottom end (Dodge-type crusher) and connected to an eccentric shaft. In universal crushers the plates are pivoted in the middle so that both the top and the bottom ends can move.

The Blake crushers are single or double toggle drives. The function of the toggle(s) is to move the pivoted jaw. The retrieving action of the jaw from its furthest end of travel is by springs for small crushers or by a pitman for larger crushers. As the reciprocating action removes the moving jaw away from the fixed jaw, the broken rock particles slip down, but are again caught at the next movement of the swinging jaw and crushed. This process is repeated until the particle sizes are smaller than the smallest opening between the crusher plates at the bottom of the crusher (the closed set). For a smooth reciprocating action of the moving jaws, heavy flywheels are used in both types of crushers.

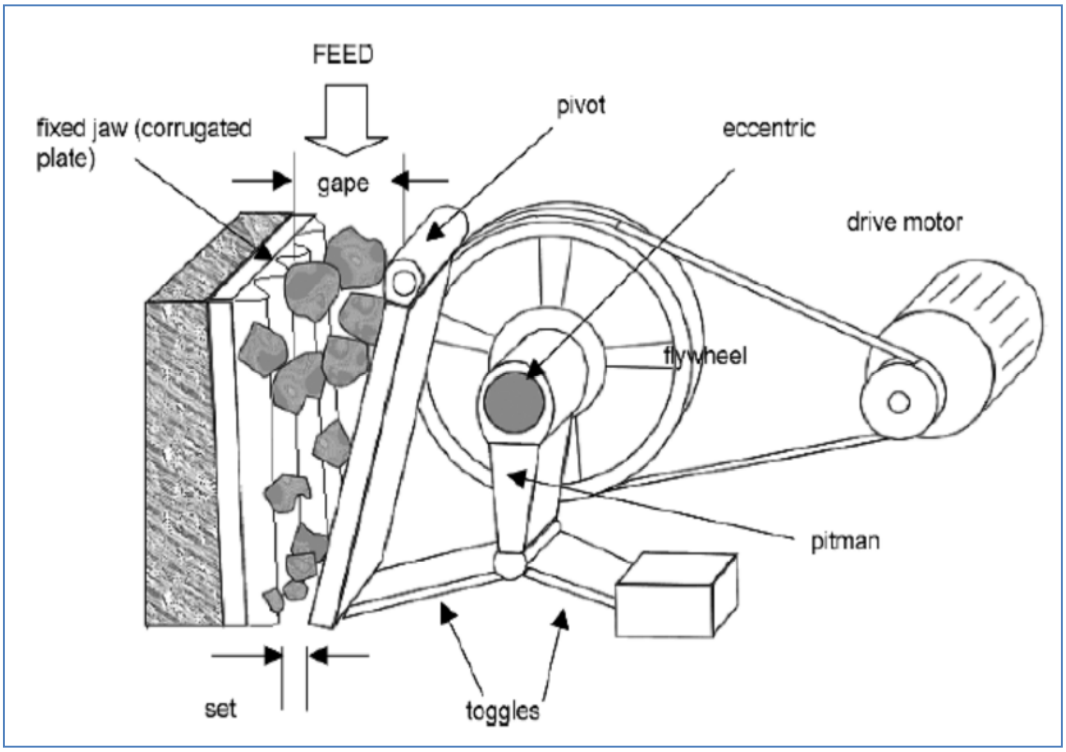


**Figure II.1**: Sketch of a Double-toggle jaw crusher [15]

Dodge type of crusher. They are comparatively lower in capacity than the Blake crushers and are more commonly used in laboratories.

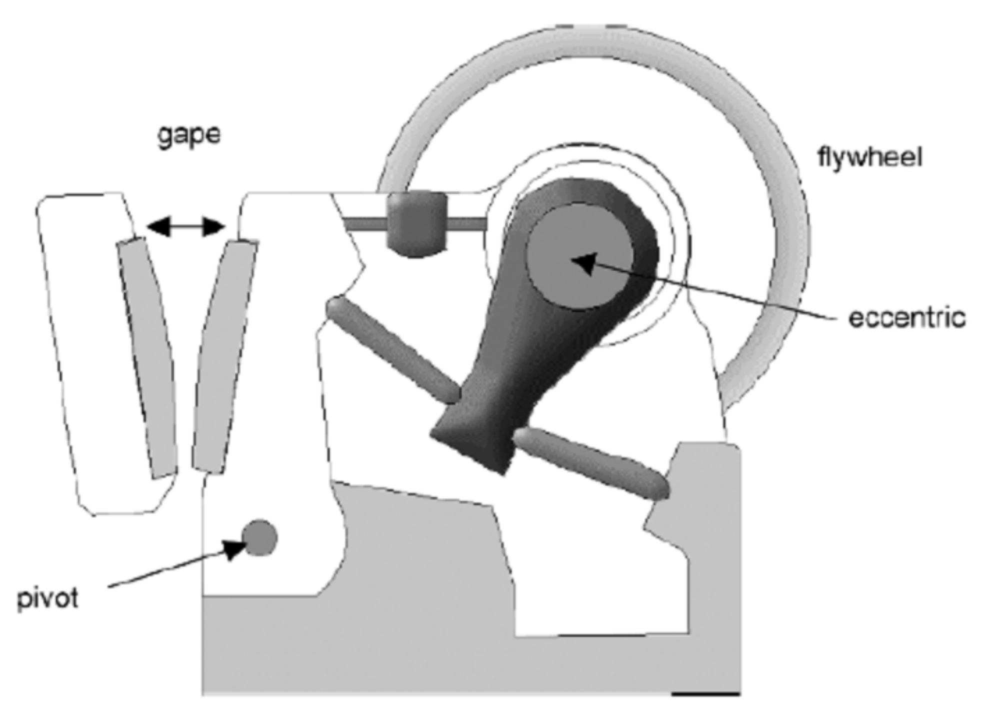


**Figure II.2**: Sketch of Dodge jaw crusher [15]

- ***Operating functions***

The ore or rock is fed to the crusher where the jaws are furtherest apart, i.e. at the maximum opening or gape. When the jaws come together the ore is crushed into smaller sizes and slip down the cavity. In the return stroke, further reduction of size is experienced and the ore moves down further. The process is repeated till particles having size less than the bottom opening or set pass through as product.

### II.2.2 Sampling method- Quartering

After crushing our barite rejects, we uses the quartering as a method of sampling.

- ***Quartering***

In this method the material is first thoroughly mixed on a hard, clean surface and then formed into a cone in the centre of the surface.

If the material is inclined to segregate, the cone should be reformed so that the material is thoroughly mixed, then the cone is flattened and divided into four quarters that should be separated from each other, then each two opposite quarters are removed and the two remaining quarters are mix together again, this process is repeated until a sample of the required size is obtained.

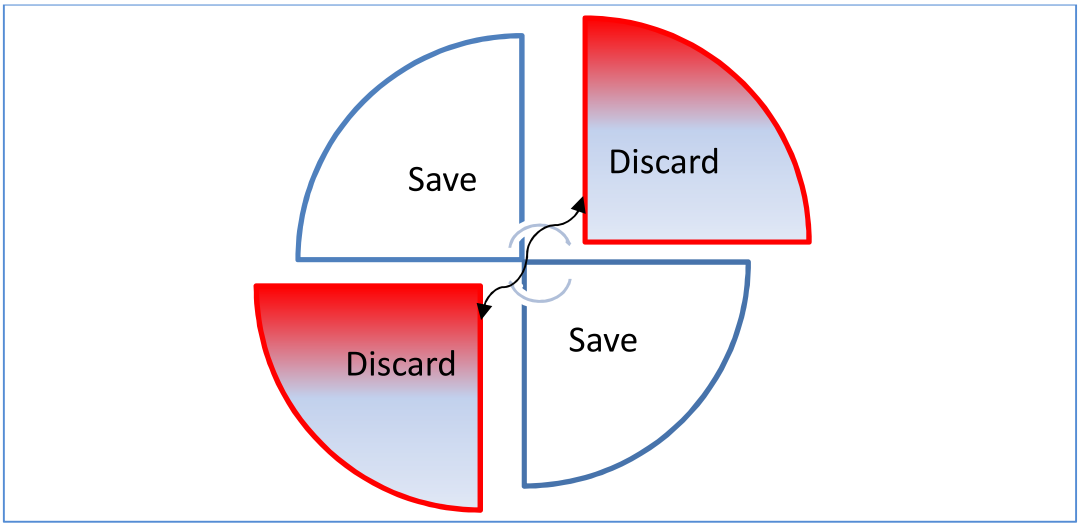


**Figure II.3**: Sketch of quartering method (Top view)

## II.3 Characterization methods of barite rejects

At the end of the different preparation steps, our barite rejects were ready to start the characterization analyses after going through a sieving test during 20 minutes, and the selected mesh sizes of the sieves stacks were successively 2.5mm, 1mm, 500µm, 250µm, 125µm, and < 125µm.

For the characterization of bulk goods of different forms and sizes, the knowledge of their particle size distributions is essential. The particle size distribution is responsible for important physical and chemical properties such as solubility, flowability and surface reaction. In many industries such as food, pharmaceutics and chemistry traditional sieve analysis is the standard for production and quality control of powders and granules [16].

Advantages of the sieve analysis include easy handling, low investment costs, precise and reproducible results in a comparably short time and the possibility to separate the particle size fractions. Therefore, this method is an accepted alternative to analysis methods using laser light or image processing [17].

- ***Sieving Methods*** **[17]**

During sieving the sample is subjected to vertical movement (vibratory sieving) or horizontal motion (horizontal sieving). With tap sieve shakers both movements are superimposed. During this process the particles are compared with the apertures of every single sieve.

Single sieving is carried out with one test sieve of a defined mesh size and is used to determine the percentages of undersize and oversize. It is used to get a general idea of the sample characteristics (sieve cut). A particle size distribution in the actual sense is not obtained with this method.

If more fractions are required (just like in our case), a set of sieves is used. The sieves are arranged in a stack with the mesh size increasing from bottom to top. The sample is then placed on the top sieve. The appropriate sieving method depends on the degree of fineness of the sample material).

Dry sieving is the preferred method for the size range between 40 µm and 125 mm. However, the measurement range is limited by properties of the sample such as a tendency to agglomerate, density or electrostatic charging. Wet sieving extends the measurement range to 20 µm. If wet sieving is not permitted, air jet sieving is an alternative which provides acceptable results down to 20 µm.

*a- Vibratory Sieving*

The sample is thrown upwards by the vibrations of the sieve bottom and falls back down due to gravitation forces. The amplitude indicates the vertical oscillation height of the sieve bottom. With vibratory sieving, the sample is subjected to a 3 dimensional movement; a circular motion superimposes the vertical throwing motion. Due to this combined motion, the sample material is spread uniformly across the whole sieve area.

*b- Horizontal Sieving*

In a horizontal sieve shaker the sieves move in horizontal circles in a plane. Horizontal sieve shakers are preferably used for needle-shaped, flat, long or fibrous samples. Due to the horizontal sieving motion, hardly any particles change their orientation on the sieve.

*c- Tap Sieving*

In a tap sieve shaker a horizontal, circular movement is superimposed by a vertical motion generated by a tapping impulse. Tap sieve shakers are specified in various standards for particle size analysis.

*d- Air Jet Sieving*

The air jet sieve is a sieving machine for single sieving, i.e. for each sieving process only one sieve is used. The sieve itself is not moved during the process.

The material on the sieve is moved by a rotating jet of air: A vacuum cleaner which is connected to the sieving machine generates a vacuum inside the sieving chamber and sucks in fresh air through a rotating slit nozzle. When passing the narrow slit of the nozzle the air stream is accelerated and blown against the sieve mesh, dispersing the particles. Above the mesh, the air jet is distributed over the complete sieve surface and is sucked in with low speed through the sieve mesh. Thus the finer particles are transported through the mesh openings into the vacuum cleaner or, optionally, into a cyclone.

*e- Wet Sieving*

Most sieve analyses are carried out with dry materials. However, there are many applications in which wet sieving cannot be avoided, e.g. if the material to be tested is a suspension or if a very fine sample (< 45 µm) that tends to agglomerate has to be sieved. Dry sieving would lead to blockage of the sieve.

## II.4 X-Ray Diffraction analysis [18]

After the sieving test our barite rejects were obtained as different fractions that were manualy ground to fine powders, and then they were set for XRD analysis.

X-ray diffraction is a technique that provides detailed information about the atomic structure of crystalline substances. It is a powerful tool in the identification of minerals in rocks and soils. X-rays are electromagnetic radiation of wavelength about1 Å (10-10 m), which is about the same size as an atom. The discovery of X-rays in 1895 enabled scientists to probe crystalline structure at the atomic level. X-ray diffraction has been in use in two main areas, for the fingerprint characterization of crystalline materials and the determination of their structure.

Each crystalline solid has its unique characteristic X-ray powder pattern which may be used as a "fingerprint" for its identification. Once the material has been identified, X-ray crystallography may be used to determine its structure.

- ***Generation of X-rays***

X-rays are produced by the rapid deceleration of fast-moving electrons as they impinge on matter. Production of X-rays for XRD analysis is accomplished using an X-ray tube consisting of a filament electron source and a metal target. The tubes are evacuated to minimize absorption of electrons accelerated from the filament (cathode) to the target (anode). Activation of the tube entails passing a current through the filament to establishing a current (e.g., 10–30 mA) under high voltage (e.g., 30–50 kV) between the filament and the target. X-rays generated from the target during the rapid deceleration of electrons from the filament emerge from windows in the tube. The material comprising the window has a minimal tendency to absorb X-rays [18].

- ***X-ray Diffraction***

X-ray diffraction occurs when X-rays are scattered by atoms arranged in an orderly array in crystals. The atoms serve as scattering centres, reemitting X-rays at the same wavelength as the incident radiation in all directions (coherent scattering). The orderly arrangement of atoms results in the scattered X-rays within the crystal being in phase in specific directions dictated by symmetry and atomic spacings and out of phase in all other directions. The X-rays that are in phase constructively interfere and emerge as intense beams (diffracted beams) from the crystal, while, those that are out of phase destructively interfere and hence have minimal emergence. This systematic combination of constructive and destructive interference arising from the periodicity of atoms in crystals is X-ray diffraction. Detailed information about the internal symmetry and arrangement of atoms in crystals can be gained from XRD. The distance between a given set of planes is termed d-spacing. The d-spacing, although on a scale of Angstroms, can be determined quite accurately using XRD. The principles under laying this determination are elegantly expressed by the Bragg equation: $n\lambda = 2d \sin \theta$ [18].

### II.4.1 X-Ray Powder Diffraction Analysis

Obtaining useful information from XRD requires the ability to control and/or measure angular relations between incident and diffracted radiation. Two types of instruments have been used to perform X-ray powder diffraction analysis: the XRD powder camera and the X-ray diffractometer. The powder camera approach entails recording diffraction maxima “cones” on cylindrically mounted photographic film surrounding the specimen. The diffractometer records the intensity of the diffracted beam electronically at precise angles as the specimen is scanned over an angular. Modern diffractometers have a number of advantages over the powder camera and are the more commonly used instruments in soil mineralogy, but the d-spacing and intensity data obtained from either type of instrument are interpreted the same way [18].

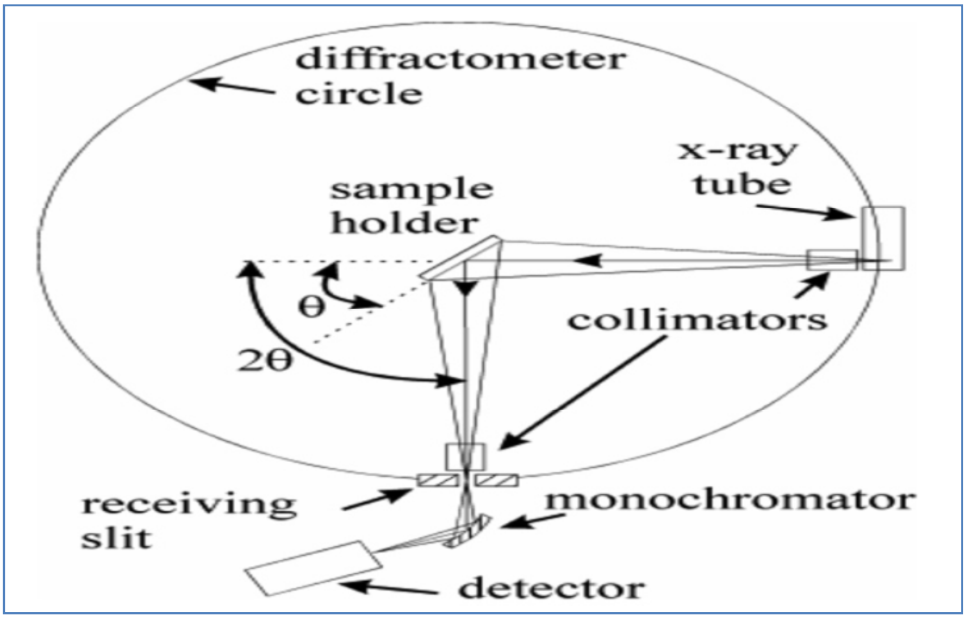


**Figure II.4**: Schematic representation of the components of an X-ray diffractometer [18]

## II.5 Conclusion

As we come to the end of this chapter that was consecrated to the methods, and the materials we used within our framework, we can assure that for the sake of obtaining representative samples ready for chemical analyses we followed the most known methods starting from the mechanical preparation to the sieving tests until arriving to the X-ray.

# Chapter III

# *Characterization of Barite rejects and their elaboration with ceramics*

## III.1 Introduction

In the precedent chapter we named and defined the different methods that we used to characterize our barite rejects, so in this chapter we are going to display the different results that we obtained and their suitable interpretations.

## III.2 Sieving test

As we mentioned earlier, before the sieving test, 2 Kg of our barite rejects received a mechanical preparation by a laboratory jaw crusher (figure III.1) with power = 2200 w, current = 4.95 A and frequency = 50 Hz, so as to reduce their sizes into 2 mm.

**Figure III.1**: Photo of our laboratory jaw crusher

After the crushing operation we used the quartering as a sampling method in a purpose to obtain a representative sample destined for the sieving test. It is to declare that the representiveness of the sample is verified by the fundamental law of RICHARDSE, so before operating, it is necessary to know if the initial quantity is sufficient enough for the preparation of the sample that is destined to serve in the next analysis, for this reason the relation $Q_{1} \geq kd^{2}$ must be verified, while Q is the quantity of the sample (g), K is a constant, d is the size of the sample (mm).

The different steps of the quartering are illustrated in figure III.2.

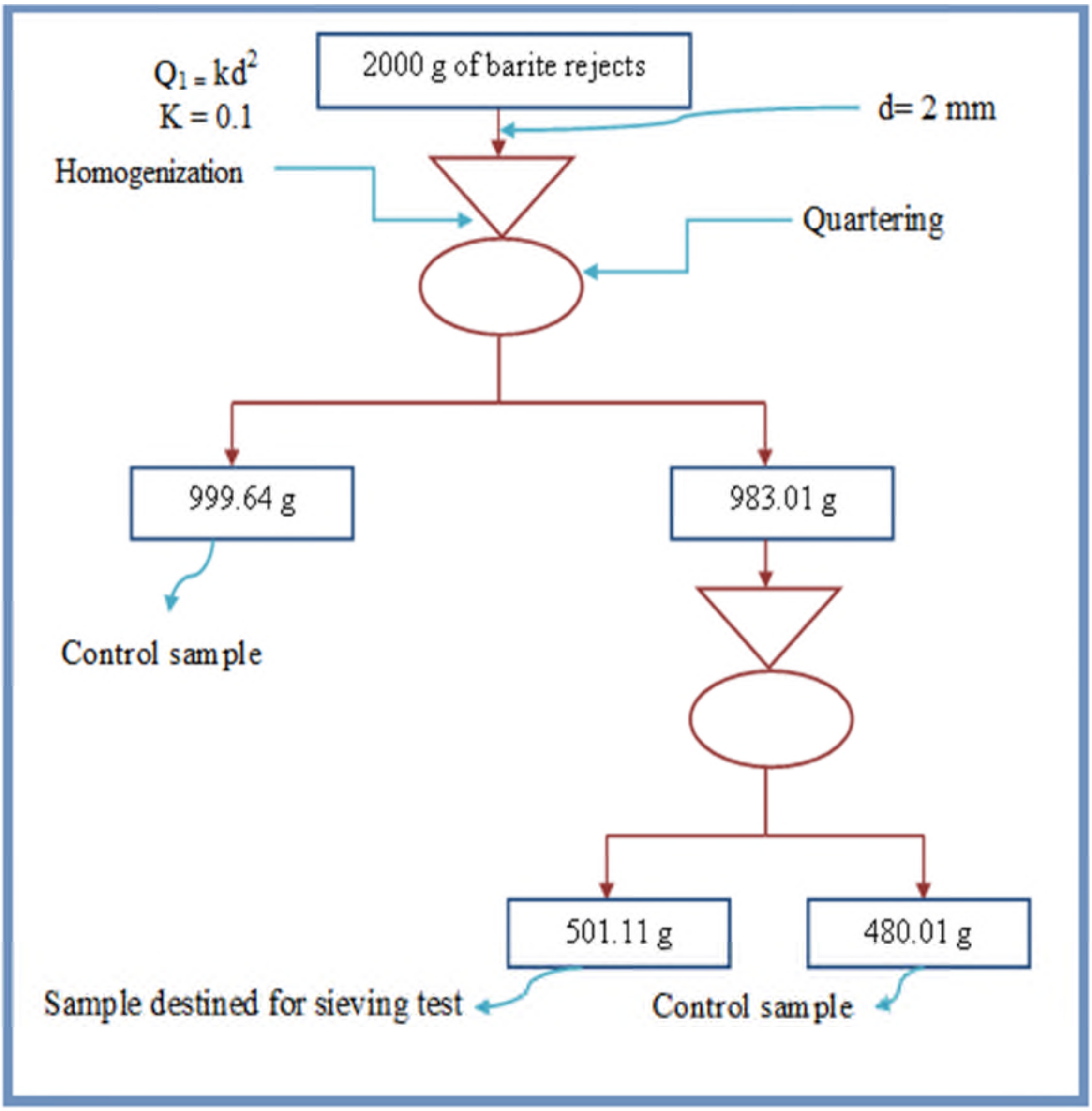


**Figure III.2**: Diagram of quartering process

After the quartering we obtained a sample of 501.11 g that was set for the sieving test.

- *Objective of sieving*: It allows us to find out the liberation size of barite mineral contained in our rejects.
- *Sieving tests:* We applied vibratory sieving on our sample during 20 minutes. The sieves apertures that we used are: 2.5 mm, 1 mm, 500 µm, 250 µm, 125 µm.

Our sieves are ISO type; they are made in the United Kingdom from a stainless steel (figure III.3).

**Figure III.3**: Sieves column and its shaker

When the 20 minutes of sieving were finished, we weighed each retained mass in the bottom of each sieve using a balance.

The results of the sieving test are shown in the table below.

**Table III.1**: Results of the sieving test.

| Sieves' classes (mm) | Mass retained (g) | Cumulative mass retained (g) | Percent retained (%) | Percent passing (%) |
|---|---|---|---|---|
| > 2.5 | 152,16 | 152,16 | 30,45 | 69,55 |
| 2.5-1 | 109,72 | 261,88 | 52,41 | 47,59 |
| 1-0.5 | 53,52 | 315,40 | 63,10 | 36,9 |
| 0.5-0.250 | 41,68 | 357,08 | 71,44 | 28,56 |
| 0.250-0.125 | 39,20 | 396,28 | 79,30 | 20,7 |
| <0.125 | 103,50 | 499,78 | 100 | 0 |
| Total weight = | 499,78 (g) | | | |

Based on the results of the table III.1, we drew the curves of the particles distribution of our sample (figure III.4).

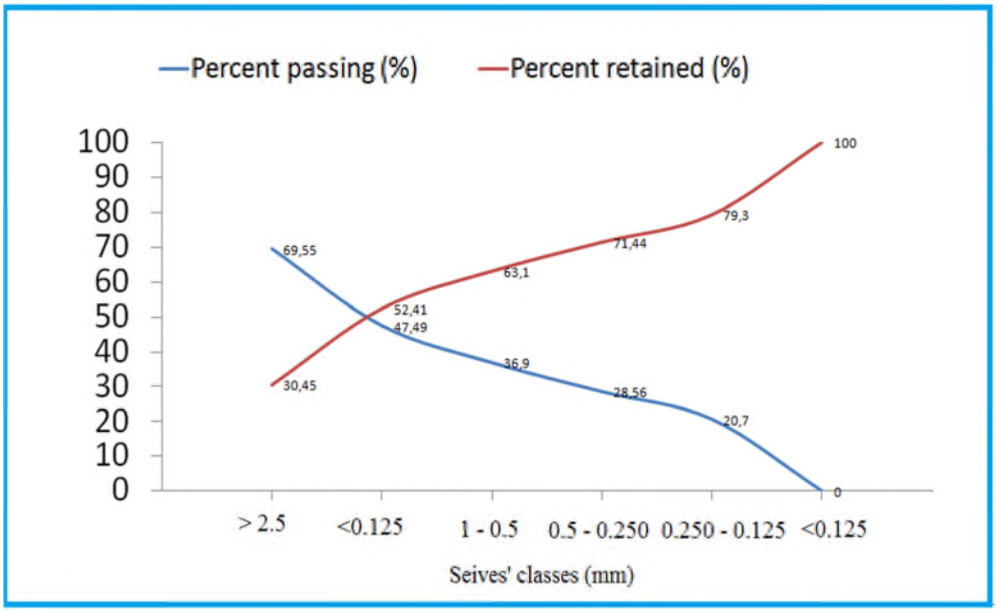


**Figure III.4**: Particles distribution curves

The percentage of our sieving test is calculated by the following relation:

% sieving = (Mc/Mt)*100;

While Mc is the cumulative mass (g), Mt is the total mass used at the beginning.

- Numerical calculation

% sieving = (Mc/Mt)*100 = (499.11/501.11)/100 = 99.73 %

This percentage indicates that our sieving test was highly successful.

- ***Comment***

According to our sieving test's results, particles of large diameters (classes: >2.5 mm; 2.5 mm - 1 mm) represent 52.39 % of our global sample, and the particles of medium diameters (classes: 1 mm - 500 µm, 500 µm - 250µm, 250 µm - 125 µm) represent 26.71% of our global simple, and the particles of the smallest diameters (fine particles) (class: < 125 µm) represent only 20.71 % of our global simple, therefore our rejects are more coarse.

## III.3 Preparation of the samples for XRD analysis

Since more than 50 % of our global sample is composed of particles of large diameters we were obliged to apply a manual crushing using porcelain mortar and pestle (figure III.5), so as to obtain fine powders suitable to receive the XRD analysis. All the classes were concerned by this operation except the final class (< 125 µm).

**Figure III.5**: Mortar and pestle

## III.3.1 XRD analysis results

Figure III.6 represents the different patterns obtained during our analysis that took a place in our university on the level of GP laboratory.

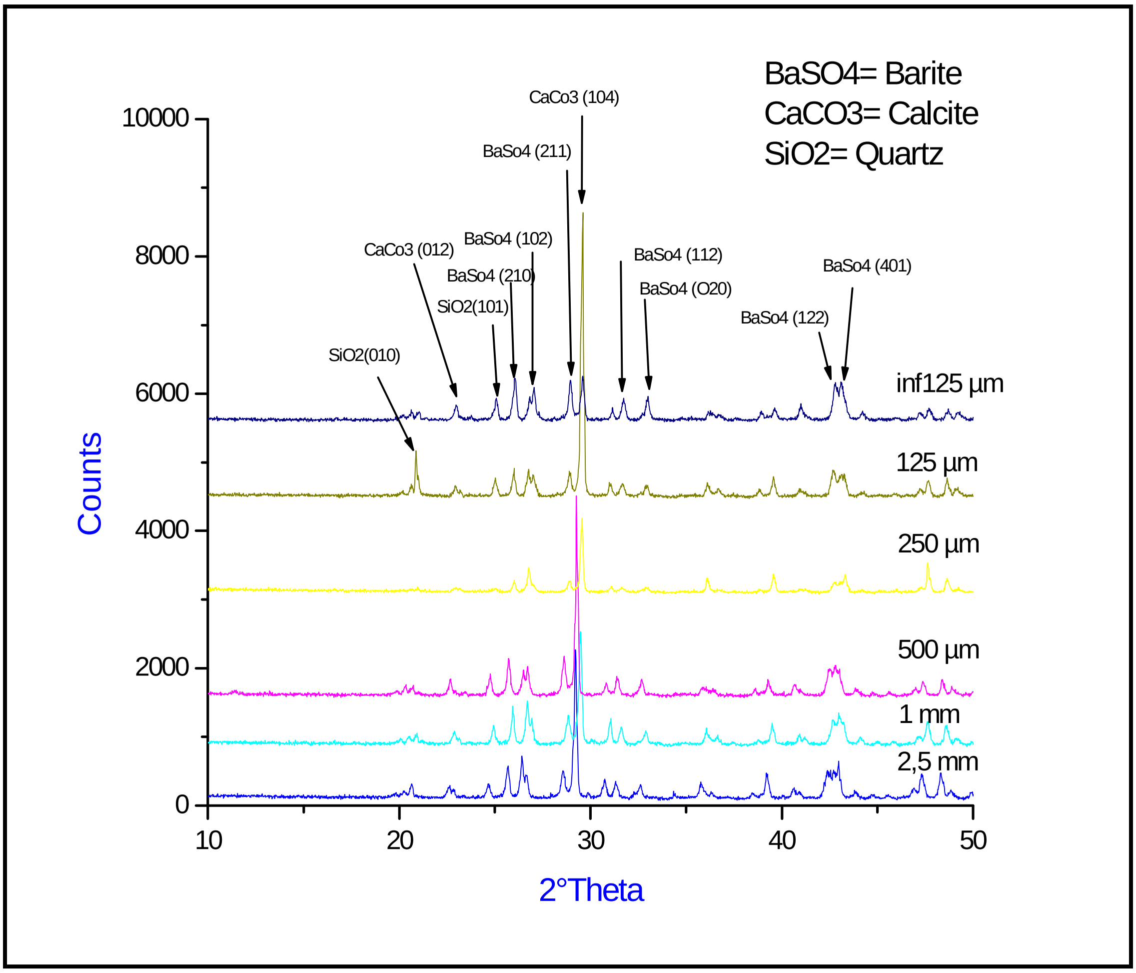


**Figure III.6**: Powder diffraction patterns of the different apertures

### III.3.1.1 Identification of the graph

The research of major phases in any pattern consists in the selection of the most intense peaks, the values of the different intensities is compared to those that are found in the Database, or even sometimes in articles.

***a. Pattern of 2.5 mm***

After smoothing so as to eliminate the non intense peaks, we obtained 33 peaks, 26 peaks correspond to barite ($BaSO_4$). Based on the mineral data of barite, in our pattern of 2.5 mm we found four intense peaks of barite as it is shown in the table below.

**Table III.2**: Barite peaks in the Pattern of 2.5 mm.

| Number of the peak | h k l | d[A] | 2Theta(degree) | Intensity (%) |
|---|---|---|---|---|
| 3 | 011 | 4.31989 | 20.543 | 77.7 |
| 7 | 210 | 3.43024 | 25.954 | 100.0 |
| 8 | 102 | 3.30679 | 26.941 | 85.0 |
| 9 | 211 | 3.09112 | 28.860 | 79.0 |

Calcite ($CaCO_3$ ) was found in our pattern of 2.5 mm with 3 intense peaks as it is shown in the table below.

**Table III.3**: Calcite peaks in the Pattern of 2.5 mm.

| Number of the peak | h k l | d[A] | 2Theta(degree) | Intensity (%) |
|---|---|---|---|---|
| 2 | 104 | 3.01993 | 29.556 | 100.0 |
| 4 | 110 | 2.48350 | 36.139 | 14.1 |
| 5 | 113 | 2.27384 | 39.603 | 18.7 |

***b. Pattern of 1 mm***

In this pattern we obtained 34 peaks, while 26 peaks of them correspond to barite ($BaSO_4$); in comparison with the mineral data of barite only two of these peaks are intense as it is shown in table III.4.

**Table III.4**: Barite peaks in the pattern of 1mm.

| Number of the peak | h k l | d[A] | 2Theta(degree) | Intensity (%) |
|---|---|---|---|---|
| 7 | 210 | 3.44305 | 25.856 | 97.6 |
| 9 | 211 | 3.10244 | 28.753 | 100.0 |

Calcite ($CaCO_3$) was found with 3 intense peaks as it is shown in the table below.

**Table III.5**: Calcite peaks in the Pattern of 1mm.

| Number of the peak | h k l | d[A] | 2Theta(degree) | Intensity (%) |
|---|---|---|---|---|
| 2 | 104 | 3.03507 | 29.405 | 100.0 |
| 4 | 110 | 2.49400 | 35.981 | 14.6 |
| 5 | 113 | 2.28402 | 39.420 | 18.5 |

### *c. Pattern of 500 µm*

In this pattern we obtained 32 peaks, 27 peaks match up with barite, but only two of these peaks are intense, and they are exactly the same shown in table III.4.

The calcite was also found with three intense peaks and they are exactly the same shown in table III.5.

### *d. Pattern of 250µm*

In this pattern we got 19 peaks, 13 peaks of them match up with barite; three of them are intense, they are exactly the same with those mentioned in the table III.4 with one new peak as it is shown in the table below.

**Table III.6**: Barite peaks in the Pattern of 250 µm.

| Number of the peak | h k l | d[A] | 2Theta(degree) | Intensity (%) |
|---|---|---|---|---|
| 7 | 210 | 3.44305 | 25.856 | 97.6 |
| 8 | 201 | 3.31934 | 26.837 | 66.8 |
| 9 | 211 | 3.10244 | 28.753 | 100.0 |

Also calcite was present by three intense peaks, they are the same peaks mentioned in the table III.5.

***e. Pattern of 125 µm and Inferior to 125µm***

In the pattern of 125 µm we obtained 36 peaks and 26 of them match up with barite, while in the pattern of inferior to 125µm we obtained 33 peaks, 29 peaks of them correspond to barite and in both patterns we found 7 intense peaks as it is shown in the table below.

**Table III.7**: Barite peaks in the patterns of 125 µm and Inferior to125µm.

| Number of the peak | h k l | d[A] | 2Theta(degree) | Intensity (%) |
|---|---|---|---|---|
| 3 | 011 | 4.31989 | 20.543 | 77.7 |
| 4 | 111 | 3.88209 | 22,890 | 49.5 |
| 7 | 210 | 3.43024 | 25.954 | 100.0 |
| 8 | 102 | 3.30679 | 26.941 | 85.0 |
| 9 | 211 | 3.09112 | 28.860 | 79.0 |
| 10 | 112 | 2.82429 | 31.655 | 47.9 |
| 13 | 020 | 2.71500 | 32.965 | 46.0 |

The intense peaks of calcite are the same mentioned in the table III.5.

### III.3.1.2 Identification of the XRD graph of pure barite (final product of Bou-Caid) and comparison with the pattern of Inf125 µm

We set a sample of pure barite to XRD analysis, and the resulted pattern is compared to that of inferior to 125 µm (figure III.7).

- ***Comment**:*

From the barite pattern in figure III.7 and its comparison with the pattern of inferior to 125 µm, we found that 6 of 7 intense peaks were identical in both patterns, which allow us to declare that the liberation size of barite contained in our rejects is in the apertures inferior to 125 µm

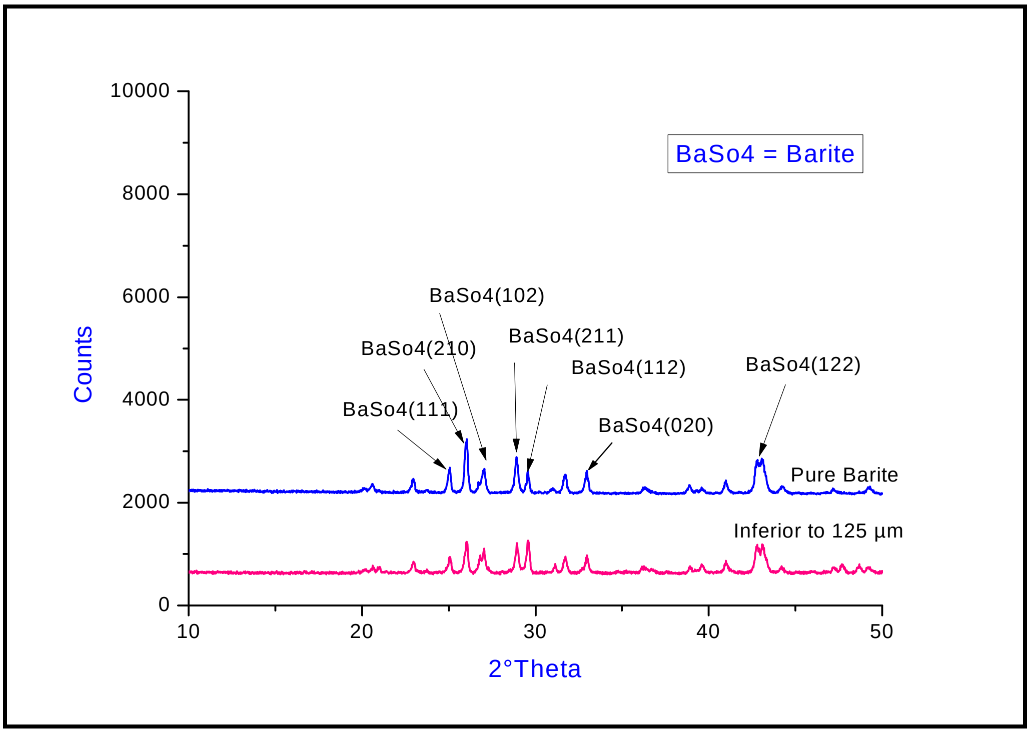


**Figure III.7**: Powder diffraction patterns of pure barite and the aperture inferior to 125 µm

After the characterization of our barite rejects and the determination of their liberation size, we started the second part planned within our framework in the aim to elaborate them with ceramics.

## III.4 Raw materials

In the fabrication of our ceramics we used kaolinite, quartz, and feldspar plus our calcined barite rejects as raw materials.

- ***Kaolinite***: Its chemical formula is $Al_2O_3 \cdot 2SiO_2 \cdot 2H_2O$ (figure III.8), it belongs to the kaolinite-serpentine group; it replaces other aluminosilicate minerals during hydrothermal alteration and weathering, and it is a common constituent of the clay-size fraction of sediments, where it may be formed by direct precipitation. Kaolinite is normally associated with quartz, feldspar, and muscovite [19].

**Figure III.8**: Kaolinite

- ***Quartz:*** Its chemical formula is $SiO_2$ (figure III.9), it occurs in hydrothermal veins, epithermal to alpine; in sandstones and quartzites; in hydrothermal metal deposits; less abundant in other rock types. It is also common in carbonate rocks; a residual mineral in soils and sediments, generally it is associated with calcite, fluorite, feldspars, chlorite, micas, zeolites, many other species [20].

**Figure III.9**: Quartz

- ***Feldspar***: Feldspar is a common name that applies to a group of minerals with a general chemical formula of x $Al(Al,Si)_3O_8$, where x can be sodium (Na) and/or calcium (Ca) and/or potassium (K). Feldspar occurs in igneous, metamorphic and sedimentary rocks and thus can be found throughout different geological environment. It is more commonly found in igneous and metamorphic rocks. Feldspar weathers to kaolin which is the main clay mineral used in ceramics and fine pottery [21, 22, 23].

**Figure III.10**: Feldspar

- ***Calcined barite rejects:*** Our barite rejects were introduced into a kiln on the level of the technology hall in our university, so as to undergo a thermal decomposition process. This process occurred for 2 hours in a temperature equals 950°C (figure III.11).

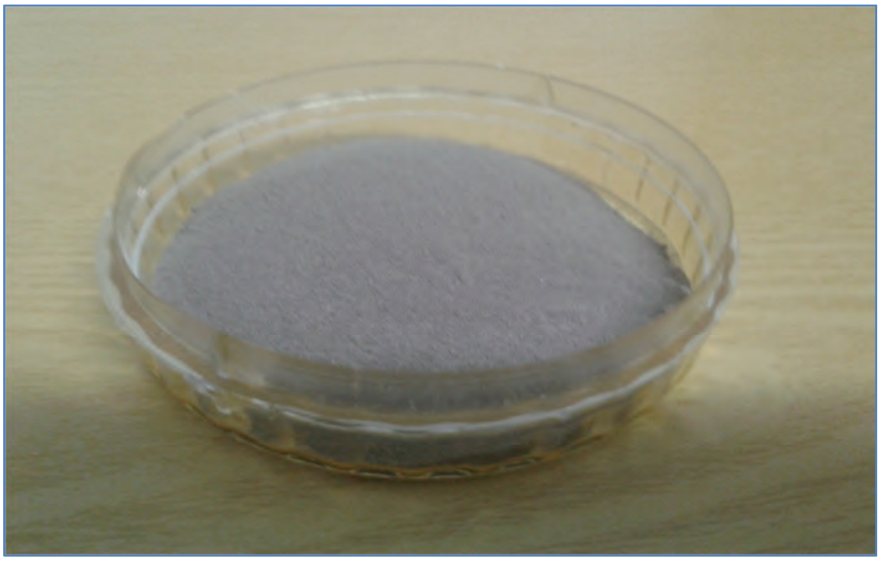


**Figure III.11:** Calcined barite rejects

After preparing our raw materials, we started the fabrication of our ceramic samples, while varying the percentages of barite rejects and feldspar whereas keeping the same percentages of quartz and kaolinite as it is shown in the table below.

**Table III.8**: Percentages of raw materials in our ceramics.

| Raw materials | Ceramics of 0 % rejects | Ceramics of 10% rejects | Ceramics of 15 % rejects | Ceramics Of 25 % rejects |
|---|---|---|---|---|
| Kaolinite | 50 | 50 | 50 | 50 |
| Quartz | 30 | 30 | 30 | 30 |
| Feldspar | 20 | 10 | 15 | 5 |
| Barite rejects | 0 | 10 | 15 | 25 |

- ***Comment:*** We fabricated four samples for each ceramic composition with a total of 16 samples.

The free barite rejects composition (reference ceramics) of our ceramics is the same of vitreous sanitary ware ceramics.

## III.5 Ceramics fabrication

We prepared 5 g of each composition and we crushed them using mortar and pestle so as to obtain fine and homogeneous powder, then they were pressed under 2t of pressure for five minutes, to form small cylindrical ceramic samples (figure III.12).

**Figure III.12**: Photo of samples ceramic composites

After their fabrication, our samples were dried for two hours at 100°C using Memmert oven on the level of our laboratory (figure III.13), this process aims to get rid of water molecules contained in our ceramics.

**Figure III.13**: Memmert oven

After their drying process, we weighed each sample using a balance, and we measured the diameter and the thickness using a caliper then we carried them to M'Slia's university for sintering.

As we mentioned earlier in chapter one, sintering or firing is a process applied to increase the green ceramic's strength.

Our samples were divided into two groups, eight samples were fired at 1200°C, and the other half were fired at 1300°C during two hours with the augmentation of 10°C in each minute, figure III.14 shows the ceramics of 10 % of barite rejects after their sintering.

**Figure III.14**: Ceramics of 10% of barite after sintering

After the sintering process, we weighed and measured the diameter and the thickness of each sample; then eight samples were set for XRD analysis, and the others were set for the tests of water absorption, and acid (HCl) and basic (NaOH) attacks.

## III.6 Conclusion

At the end of this chapter that lightened our sieving test and its results, plus the XRD analysis and the graphs obtained and their identifications, and the elaboration process of barite rejects with ceramics , we concluded that our rejects contain a large potential calcite which is normal since it is the main gangue of Bou-Caid ores, in addition of barite in all the samples of each retained mass, however the largest potentials of this latter were registered in the small sizes namely those that are inferior to 125 µm, so as a result the rejects of this aperture is the ones that we elaborated with ceramics.

# Chapter IV

# *The physicochemical proprieties of ceramics composites*

## IV.1 Introduction

In this chapter we are going to display the different results obtained by the different methods, and the tests we applied on our ceramic composites.

## IV.2 Results and Discussion

### IV.2.1 Physicochemical proprieties of ceramic composites

### IV.2.1.1 Mass variation before and after sintering

As we mentioned before our ceramic composites were weighed before and after sintering, while in this latter two temperatures (T= 1200°C, and T=1300°C) were used to fire our samples and the results obtained are shown in the tables IV.1, and IV.2 while:

Mi: Initial mass (g) (before sintering);

Mf: Final mass (g) (after sintering);

Δm: mass loss (%), it is calculated by the following relation:

$$\Delta m = [(Mi - Mf)/ Mi]*100\ \%;$$

**Table IV.1:** Mass variation of ceramic composites fired at T = 1200C°.

| Ceramics | Mi (g) | Mf (g) | Δm (%) | Average Δm (%) |
|---|---|---|---|---|
| 0% | 1.59 | 1.46 | 8.17 | 9.33 |
| | 1.43 | 1.28 | 10.49 | |
| 10% | 1.73 | 1.57 | 9.24 | 10.91 |
| | 1.75 | 1.53 | 12.57 | |
| 15% | 1.94 | 1.68 | 13.40 | 12.99 |
| | 1.75 | 1.53 | 12.57 | |
| 25% | 1.88 | 1.63 | 13.30 | 14.28 |
| | 1.77 | 1.5 | 15.25 | |

**Table IV.2:** Mass variation of ceramic composites fired at T = 1300C°.

| Ceramics | Mi (g) | Mf (g) | Δm (%) | Average Δm (%) |
|---|---|---|---|---|
| 0% | 1.65 | 1.49 | 9.7 | 9.7 |
| | 1.65 | 1.49 | 9.7 | |
| 10% | 1.76 | 1.57 | 10.79 | 11.83 |
| | 1.71 | 1.49 | 12.86 | |
| 15% | 1.81 | 1.55 | 14.36 | 14.36 |
| | 1.81 | 1.55 | 14.36 | |
| 25% | 1.99 | 1.67 | 16.84 | 16.62 |
| | 1.95 | 1.63 | 16.41 | |

The variations of the mass loss indicated in the tables above are represented by a histogram in the figure IV.1.

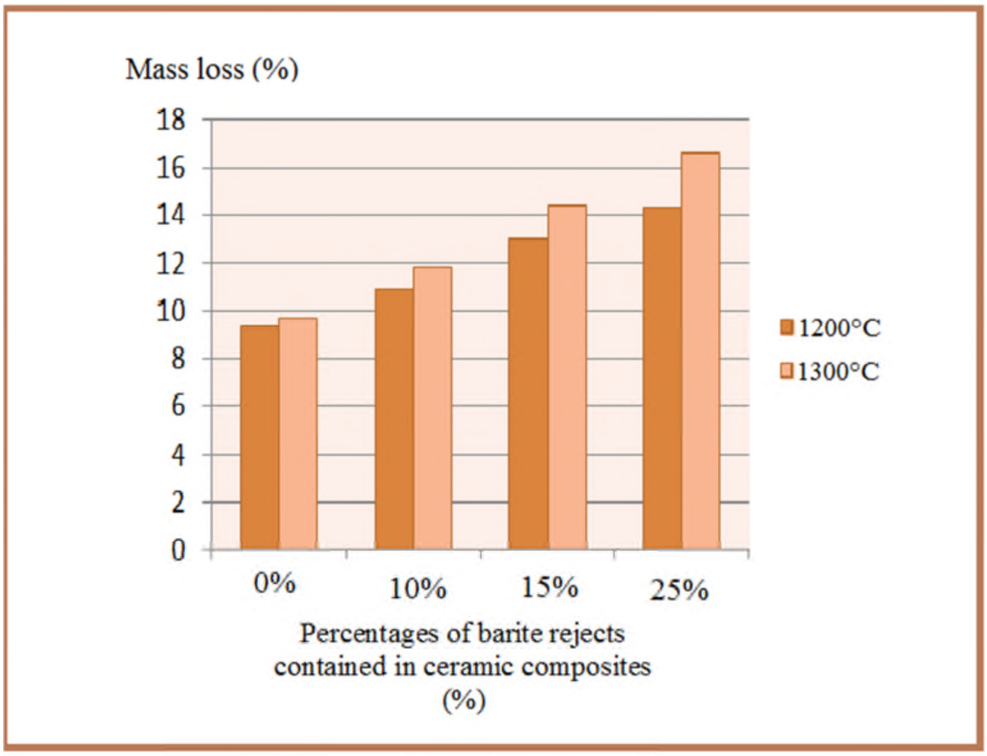


**Figure IV.1**: Histogram of the mass loss of ceramic composites

- ***Comment:*** Based on figure IV.1, we clearly observe that the ceramic composites' mass loss increases with the increase of the barite rejects' percentages contained in them, this is due to the fact that they contain more gases such as $SO_4$ and $CO_3$ which are released.

It is also to notice this mass loss increased with the increase of the sintering temperature. In general during any sintering process the mass loss is a normal result due to the shrinkage of ceramics under the effect of high temperature.

#### IV.2.1.2 Diameter variation before and after sintering

We measured the diameter using a caliper, and the results obtained are shown in the tables IV.3 and IV.4, while:

'ϕi' (mm): Initial diameter of the ceramics (before sintering);

'ϕf' (mm): Final diameter of the ceramics (after sintering);

'Δϕ' (%): diameter variation, it is calculated by the following relation:

$$\Delta\phi = [(\phi i - \phi f)/\ \phi i]*100\ \%;$$

**Table IV.3:** Diameter variation of ceramic composites fired at T = 1200°C.

| Ceramics | 'ϕi' (mm) | 'ϕf' (mm) | 'Δϕ' (%) | Average 'Δϕ' (%) |
|---|---|---|---|---|
| 0% | 13.6 | 12.2 | 10.29 | 9.78 |
| | 13.5 | 12.2 | 9.62 | |
| 10% | 13.6 | 12.3 | 9.55 | 8.18 |
| | 13.2 | 12.3 | 6.81 | |
| 15% | 13.2 | 12.2 | 7.57 | 7.57 |
| | 13.2 | 12.2 | 7.57 | |
| 25% | 13.2 | 12.2 | 7.57 | 7.57 |
| | 13.2 | 12.2 | 7.57 | |

**Table IV.4:** Diameter variation of ceramic composites fired at T = 1300°C.

| Ceramics | 'ϕi' (mm) | 'ϕf' (mm) | 'Δϕ' (%) | Average 'Δϕ' (%) |
|---|---|---|---|---|
| 0% | 13.6 | 12 | 11.76 | 9.66 |
| | 13.2 | 12.2 | 7.57 | |
| 10% | 13.2 | 12.2 | 7.57 | 7.57 |
| | 13.2 | 12.2 | 7.57 | |
| 15% | 13.2 | 12.2 | 7.57 | 7.57 |
| | 13.2 | 12.2 | 7.57 | |
| 25% | 13.2 | 12.2 | 7.57 | 7.57 |
| | 13.2 | 12.2 | 7.57 | |

The diameters' variations of the ceramics composites indicated in the tables above are represented by a histogram in the figure below.

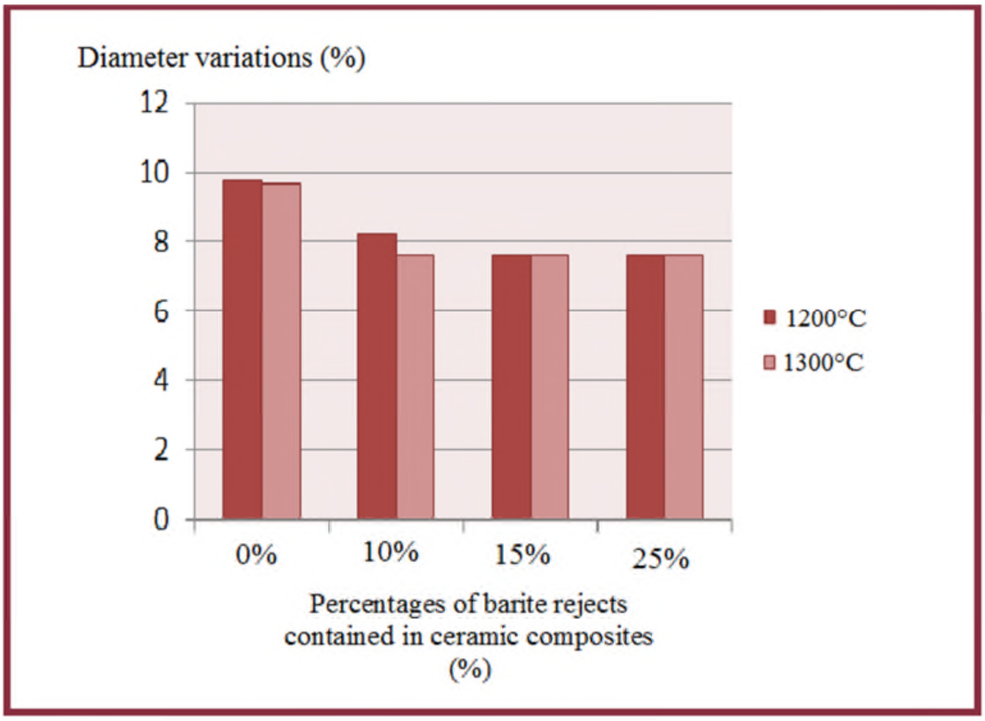


**Figure IV.2**: Histogram of the diameters' variations of the ceramic composites

- ***Comment***

Based on figure IV.2, we clearly observe that the values of the variation of the diameters of the ceramic composites decreased with the increase of the percentages of barite rejects and the temperature, while they remained constant for the ceramics of 15% and 25.

### IV.2.1.3 Thickness variation before and after sintering

We measured the thickness using a caliper, and the results obtained are shown in the tables IV.5 and IV.6, while:

'Ti' (mm): Initial thickness (before sintering);

'Tf' (mm): Final thickness (after sintering);

'ΔT' (mm): Thickness variation, it is calculated by the following relation:

$$\Delta T = [(Ti - Tf)/ Ti]*100$$

**Table IV.5:** Thickness variation of ceramic composites sintered at T = 1200°C.

| Ceramics | Ti (mm) | Tf (mm) | ΔT (%) | Average ΔT (%) |
|---|---|---|---|---|
| 0% | 7 | 6.2 | 11.42 | 11.36 |
| | 6.2 | 5.5 | 11.29 | |
| 10% | 7 | 6.2 | 11.42 | 8.02 |
| | 6.5 | 6.2 | 4.61 | |
| 15% | 7.4 | 7.1 | 4.05 | 8.45 |
| | 7 | 6.1 | 12.85 | |
| 25% | 7.3 | 7 | 4.11 | 8.49 |
| | 7.2 | 6.1 | 12.86 | |

**Table IV.6:** Thickness variation of ceramic composites sintered at T = 1300°C.

| Ceramics | Ti (mm) | Tf (mm) | ΔT (%) | Average ΔT (%) |
|---|---|---|---|---|
| 0% | 7 | 6.2 | 11.42 | 11.42 |
| | 7 | 6.2 | 11.42 | |
| 10% | 7 | 6.3 | 10 | 10 |
| | 7 | 6.3 | 10 | |
| 15% | 7.2 | 6.4 | 11.11 | 11.81 |
| | 7.2 | 6.3 | 12.5 | |
| 25% | 7.3 | 12.4 | 69.8 | 68 |
| | 7.4 | 12.3 | 66.2 | |

The results that are shown in the tables IV.5 and IV.6 are represented by a histogram in figure IV.3.

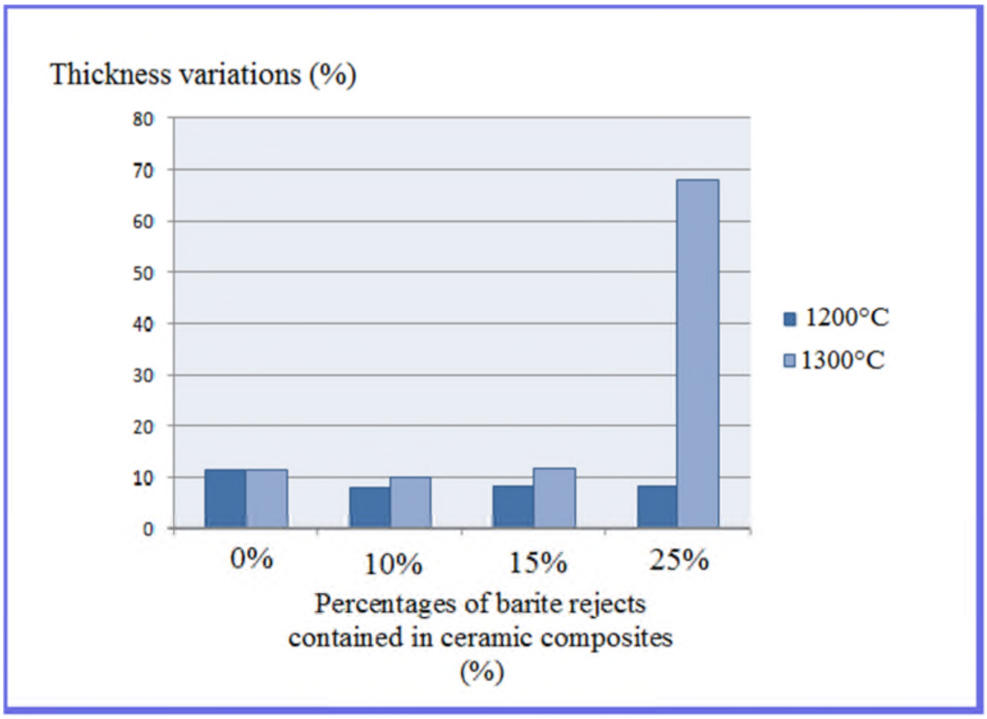


**Figure IV.3**: Histogram of the thickness variation of ceramic composites

- ***Comment***: From the results that we obtained, we can observe that the samples elaborated with barite rejects undergone low thickness variations when they were fired at T= 1200°C comparing to the reference ceramics, but we clearly observe that two samples of 25 % rejects that were fired at 1300°C undergone a big variation in thickness due to the growth phenomenon.

## IV.2.2 Chemical durability of ceramic composites

### IV.2.2.1 Water absorption test

Our samples were weighed ($W_D$), then they were immerged by water ($H_2O$) for two hours, then they were dried using a paper tissue before being weighed again ($W_H$).

This test allows us to calculate the mass gain of our ceramics using the following relation:

W (%) = [(Wh – Wd)/ Wh]*100 while:

$W_H$: Humid weight of ceramics (g);

$W_D$: Dry weight of ceramics (g);

The results obtained are shown in the table IV.7.

**Table IV.7**: Percentage of mass gain of ceramic composites during water absorption test.

| Ceramics | $W_D$ (g) | $W_H$ (g) | W (%) |
|---|---|---|---|
| 0% | 1.46 | 1.52 | 3.95 |
| | 1.57 | 1.58 | 0.63 |
| 10% | 1.57 | 1.62 | 3.1 |
| | 1.49 | 1.5 | 0.66 |
| 15% | 1.70 | 1.75 | 2.86 |
| | 1.55 | 1.58 | 1.9 |
| 25% | 1.54 | 1.58 | 2.5 |
| | 1.63 | 1.81 | 9.94 |

The results of the table IV.7 are represented by a histogram in figure IV.4.

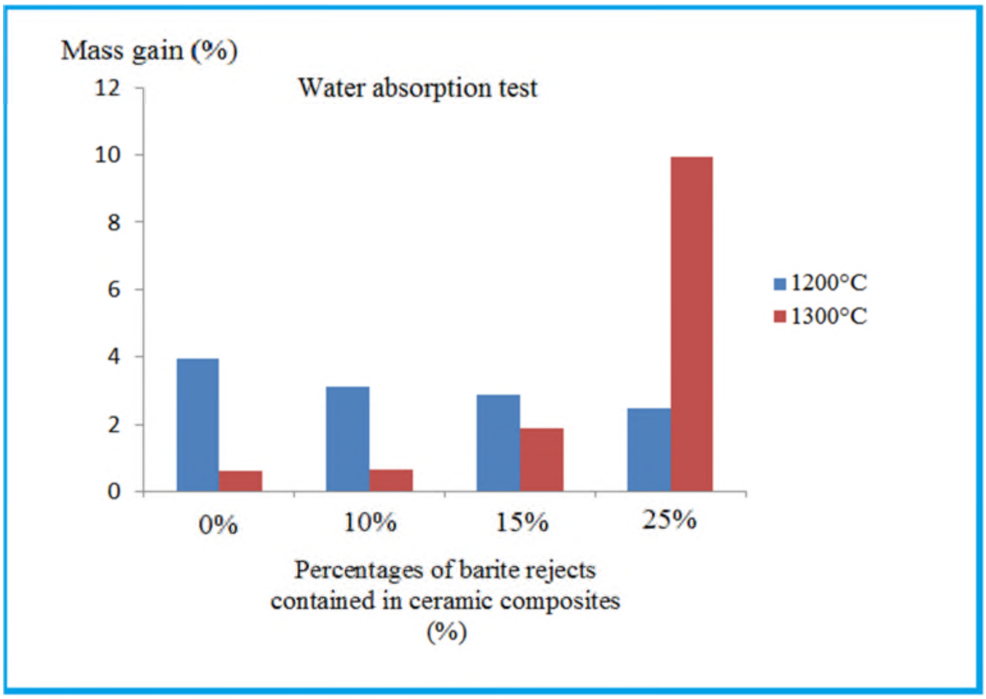


**Figure IV.4**: Mass gain of ceramic composites during water absorption test

- ***Comment***: From the figure IV.4, we can observe that ceramics fired at T= 1300°C registered the lowest mass gain comparing to those that were fired at T= 1200°C, except in the case of ceramics of 25% rejects that registered an enormous mass gain that can be explained by fact that they undergone the growth phenomenon which made them more porous than the other samples, and the ceramics of 10% rejects fired at 1300°C gave close values to those of the reference ceramics.

### IV.2.2.2 Acid attack test

This test was conducted using the same steps as the water absorption test, starting from weighing our samples ($M_D$), then immerging them by 1N hydrochloric acid (HCl) for two hours, then drying them using a paper tissue before weighing them again ($M_H$).

We calculated the mass variations using the following relation:

$$\Delta m\ (\%) = [(M_H - M_D)/\ M_H]*\ 100,\text{ while:}$$

$M_D$ : Dry mass of ceramics (g) (before HCl attack);

$M_H$ : Humid mass of ceramics (g) (after HCl attack);

The results obtained are shown in the table III.13.

**Table IV.8**: Mass variation of ceramic composites during HCl attack.

| Ceramics | | $M_D$ (g) | $M_H$ (g) | $\Delta m$ (%) |
|---|---|---|---|---|
| 0% | 1200°C | 1.52 | 1.54 | 1.3 |
| | 1300°C | 1.58 | 1.6 | 1.25 |
| 10% | 1200°C | 1.62 | 1.63 | 0.61 |
| | 1300°C | 1.5 | 1.52 | 1.25 |
| 15% | 1200°C | 1.75 | 1.8 | 2.77 |
| | 1300°C | 1.58 | 1.61 | 1.86 |
| 25% | 1200°C | 1.58 | 1.63 | 3.1 |
| | 1300°C | 1.81 | 1.81 | 0 |

The results of the table above are represented by a histogram in the figure IV.5.

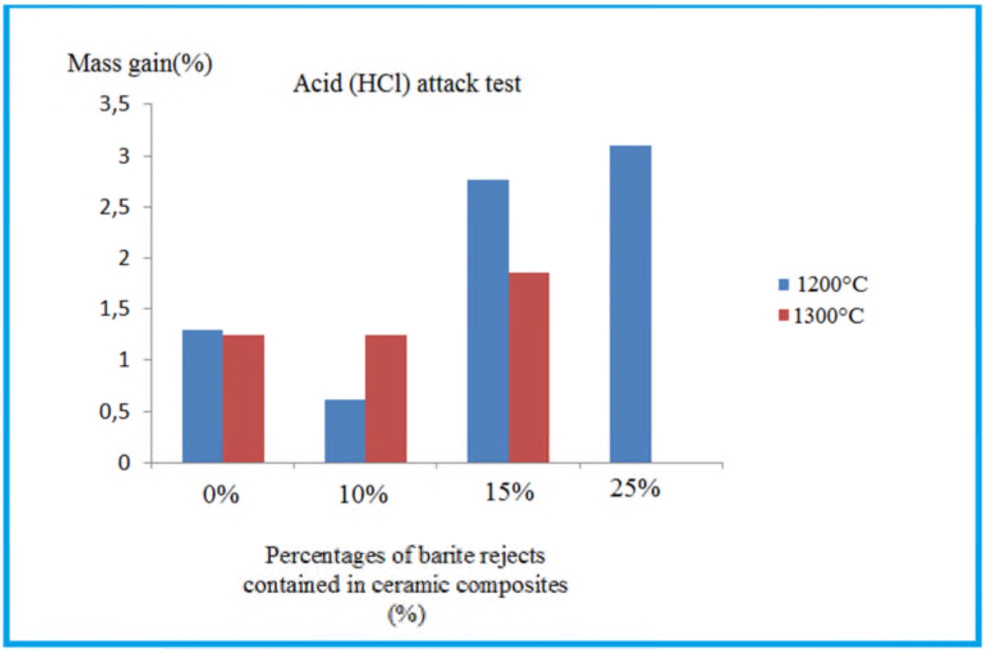


**Figure IV.5**: Mass gain of ceramic composites during HCl attack

- ***Comment:*** During this test there was no color change. From the figure IV.5 we observe that the ceramics elaborated with 10% of rejects registered the lowest mass gain during this test among the ceramics fired at 1200°C, and they registered the same mass gain value of the reference ceramics while being fired at1300°C, and ceramics of 25% rejects registered no mass variation among the ceramics fired at T= 1300°C.

### III.2.2.3 Basic Attack test

This test was conducted using the same steps of the two preceding tests, starting from weighing our samples ($M_D$), then immerging them by 1N sodium hydroxide (NaOH) for two hours, then drying them using a paper tissue before weighing them again ($M_H$).

We calculated the mass variations using the following relation:

$$\Delta m\ (\%) = [(M_H - M_D)/\ M_H] * 100, \text{ while:}$$

$M_D$ : Dry mass of ceramics (g) (before NaOH attack);

$M_H$ : Humid mass of ceramics (g) (after NaOH attack);

The results obtained are illustrated in the table IV.9.

**Table IV.9**: Mass variation of ceramic composites during NaOH attack.

| Ceramics | | $M_D$ (g) | $M_H$ (g) | Δm (%) |
|---|---|---|---|---|
| 0% | Sample 1 | 1,52 | 1,43 | 5.92 |
| | Sample 4 | 1,58 | 1,55 | 1.89 |
| 10% | Sample 1 | 1,63 | 1,59 | 2.45 |
| | Sample 4 | 1,52 | 1,49 | 1.97 |
| 15% | Sample 1 | 1,8 | 1,73 | 3.88 |
| | Sample 4 | 1,61 | 1,58 | 1.86 |
| 25% | Sample 1 | 1,63 | 1,56 | 4.3 |
| | Sample 4 | 1,8 | 1,78 | 1.11 |

The results shown in the table above are represented by a histogram in the figure IV.6.

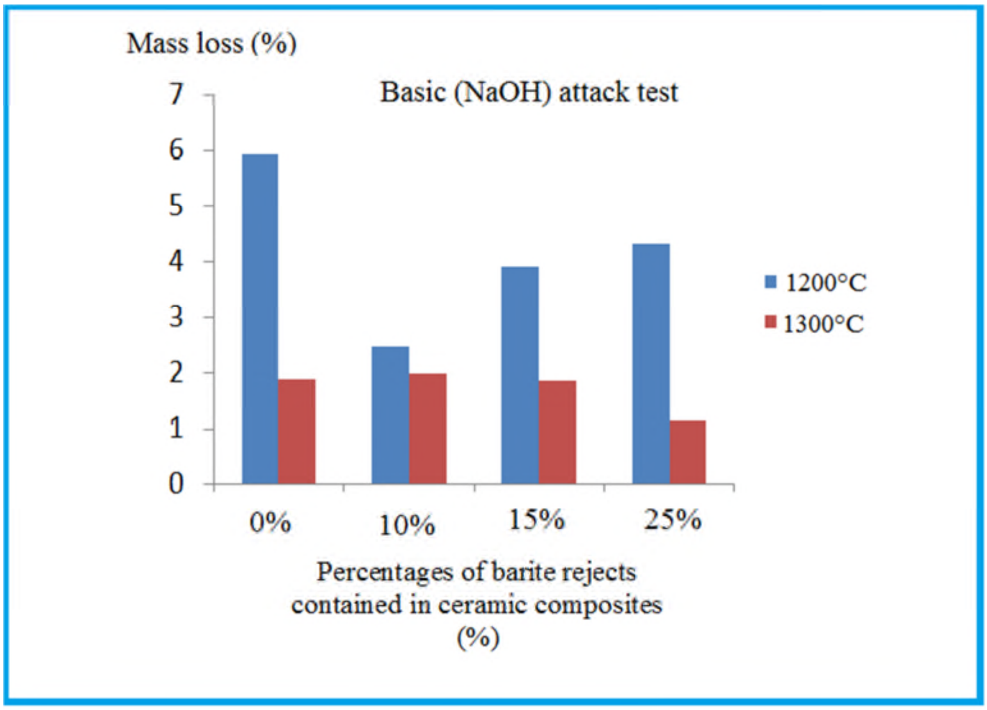


**Figure IV.6**: Mass loss of the ceramic composites during NaOH attack

➢ ***Commen**t*: During this test there was no color change. From the figure IV.6 we can clearly observe that the ceramic composites fired at T=1300C° registered the lowest mass loss comparing to those fired at T= 1200°C, and the ceramics elaborated with rejects registered low mass gain values comparing to the reference ceramics, but the most significant observation derived from the table IV.9 is fact that the addition of barite rejects to the ceramic composites gained them an excellent chemical resistance comparing to the reference ceramics specially in the case of samples fired at T=1300°C.

- ***Conclusion***: Since we have no means to identify the mechanism of mass transfer during the three tests, we based on the observation and the comparison between the ceramics of 0 % rejects' behavior and the other ceramics compositions, so from the results we obtained we can say that during the three tests, ceramic composites of 10 % that were fired at T= 1300°C gave the closest values in the mass variation (gain/loss) to those given by the reference ceramics.

## IV.2.3 Mineralogical composition of ceramic composites after sintering

### IV.2.3.1 XRD analysis

As we mentioned earlier eight samples were set for XRD analysis so as to identify the dominant phases of our ceramics and the raw minerals' evolution through the sintering process.

### IV.2.3.2 Ceramics of 0% rejects

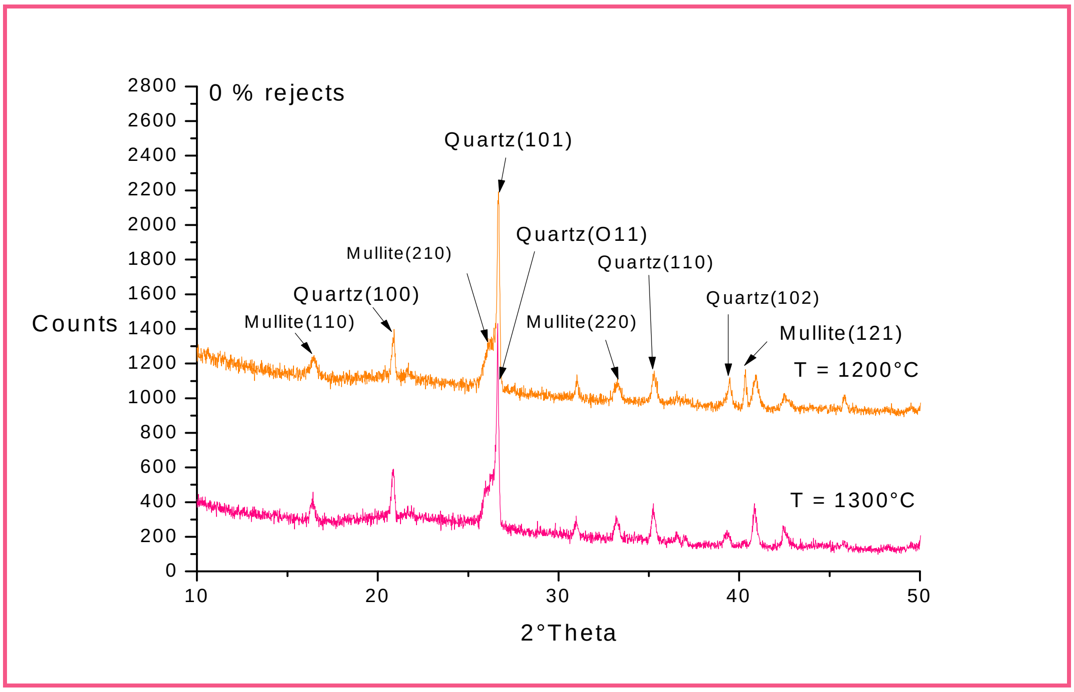


**Figure IV.7**: XRD Patterns of the ceramics of 0% rejects

***a. Patterns of 1200°C and 1300°C***

In the pattern of the ceramics of 0 % rejects that were fired at T = 1200°C, mainly we obtained peaks of quartz and mullite.

Based on these two minerals' data we registered four intense peaks for each mineral as it is shown in the tables below.

**Table VI.10:** Quartz intense peaks in the pattern of 0% rejects fired at T = 1200°C**.**

| Number of the peak | h k l | d[A] | 2Theta(degree) | Intensity (%) |
|---|---|---|---|---|
| 1 | 100 | 4.25499 | 20.860 | 16.0 |
| 2 | 101 | 3.34347 | 26.640 | 100.0 |
| 3 | 110 | 2.45687 | 36.544 | 9.0 |
| 4 | 102 | 2.28149 | 39.465 | 8.0 |

**Table IV.11:** Mullite intense peaks in the pattern of 0% rejects fired at T = 1200°C**.**

| Number of the peak | h k l | d[A] | 2Theta(degree) | Intensity (%) |
|---|---|---|---|---|
| 1 | 110 | 5.38561 | 16.446 | 47.6 |
| 5 | 210 | 3.38635 | 26.297 | 100.0 |
| 7 | 220 | 2.69281 | 33.244 | 39.4 |
| 13 | 121 | 2.20642 | 40.867 | 61.6 |

And in the pattern of the ceramics that were fired at T = 1300°C, we obtained peaks of quartz and mullite. The intense peaks are illustrated in the tables below.

**Table IV.12:** Quartz intense peaks in the pattern of 0% rejects fired at T = 1300°C**.**

| Number of the peak | h k l | d[A] | 2Theta(degree) | Intensity (%) |
|---|---|---|---|---|
| 1 | 010 | 4.25738 | 20.848 | 14.6 |
| 2 | 011 | 3.34542 | 26.624 | 100.0 |
| 3 | 110 | 2.45800 | 36.527 | 10.0 |
| 4 | 102 | 2.28283 | 39.441 | 8.3 |

**Table IV.13:** Mullite intense peaks in the pattern of 0% rejects fired at T = 1300°C**.**

| Number of the peak | h k l | d[A] | 2Theta(degree) | Intensity (%) |
|---|---|---|---|---|
| 1 | 110 | 5.39114 | 16.429 | 52.9 |
| 4 | 120 | 3.42668 | 25.982 | 65.3 |
| 5 | 210 | 3.38635 | 26.297 | 100.0 |

➢ ***Comment***: In comparison between the two patterns, the same intense peaks were registered, some of them were identical and some differed. It is to notice that the intensity of mullite peaks increased with the increase of the sintering temperature.

### IV.2.3.3 Ceramics of 10% rejects

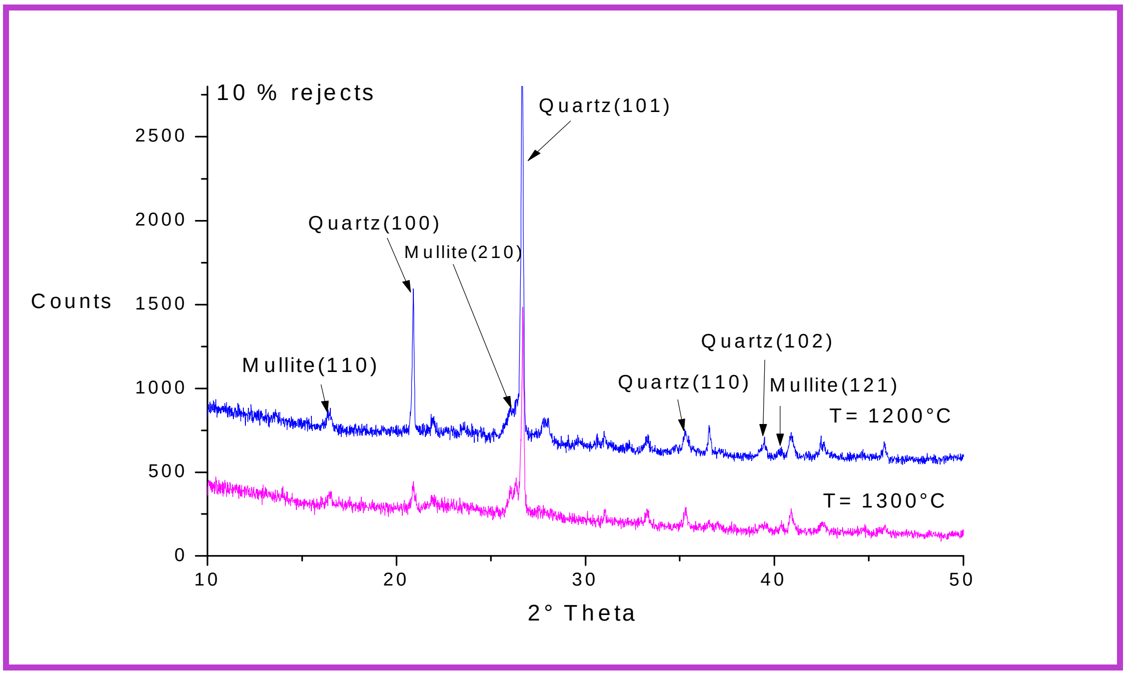


**Figure IV.8**: XRD Patterns of the ceramics of 10% rejects

#### *a. Patterns of 1200°C and 1300°C*

In the pattern of the ceramics of 10 % rejects that were fired at T = 1200°C, we obtained peaks of quartz and mullite.

The most intense peaks of these two minerals are illustrated in the tables below.

**Table IV.14:** Quartz intense peaks in the pattern of 10% rejects fired at T = 1200°C**.**

| Number of the peak | h k l | d[A] | 2Theta(degree) | Intensity (%) |
|---|---|---|---|---|
| 1 | 100 | 4.25700 | 20.850 | 22.0 |
| 2 | 101 | 3.34200 | 26.652 | 100.0 |
| 3 | 110 | 2.45700 | 36.542 | 8.0 |
| 4 | 102 | 2.28200 | 39.456 | 8.0 |

**Table IV.15:** Mullite intense peaks in the pattern of 10% rejects fired at T = 1200°C.

| Number of the peak | h k l | d[A] | 2Theta(degree) | Intensity (%) |
|---|---|---|---|---|
| 1 | 110 | 5.38717 | 16.442 | 49.8 |
| 5 | 210 | 3.38918 | 26.274 | 100.0 |
| 13 | 121 | 2.20618 | 40.871 | 66.6 |

In the pattern of the ceramics of 10 % rejects that were sintered at T = 1300°C, we obtained the same mineralogical phases of quartz that are illustrated the table IV.14, and three peaks of mullite shown in the table below.

**Table IV.16:** Mullite intense peaks in the pattern of 10% rejects fired at T = 1300°C.

| Number of the peak | h k l | d[A] | 2Theta(degree) | Intensity (%) |
|---|---|---|---|---|
| 1 | 110 | 5.38561 | 16.446 | 47.6 |
| 5 | 210 | 3.38635 | 26.297 | 100.0 |
| 13 | 121 | 2.20642 | 40.867 | 61.6 |

- ***Comment***: In comparison between patterns of 0% and 10%, we noticed that quartz peaks enhanced while mullite peaks decreased in intensity.

### IV.2.3.4 Ceramics of 15% rejects

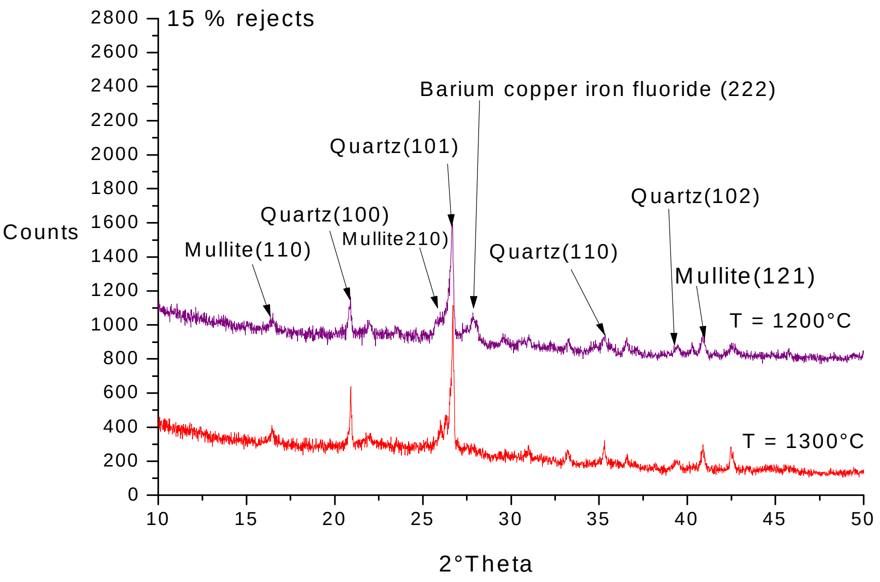


**Figure IV.9**: XRD Patterns of the ceramics of 15% rejects

### *a. Patterns of 1200°C and 1300°C*

In the pattern of the ceramics of 15 % rejects that were sintered at T = 1200°C, the same mineralogical phases appeared as quartz and mullite.

The four intense peaks of quartz are identical to those of the table IV.14, and the peaks of mullite are indicated in the table IV.16.

**Table IV.17:** Mullite intense peaks in the pattern of 15% rejects fired at T = 1200°C**.**

| Number of the peak | h k l | d[A] | 2Theta(degree) | Intensity (%) |
|---|---|---|---|---|
| 1 | 110 | 5.39259 | 16.425 | 47.6 |
| 5 | 210 | 3.39432 | 26.234 | 100.0 |
| 13 | 121 | 2.20707 | 40.854 | 61.6 |

In the pattern of the ceramics of 15% rejects that were sintered at T = 1300°C, we got peaks of quartz and they are identical to those mentioned in the table IV.14, and three others for mullite.

**Table IV.18:** Mullite intense peaks in the pattern of 15% rejects fired at T = 1300°C**.**

| Number of the peak | h k l | d[A] | 2Theta(degree) | Intensity (%) |
|---|---|---|---|---|
| 1 | 110 | 5.39114 | 16.429 | 52.9 |
| 5 | 210 | 3.39288 | 26.245 | 100.0 |
| 13 | 121 | 2.20742 | 40.874 | 66.5 |

- ***Comment:*** The peaks of quartz and mullite decreased in intensity comparatively to those registered in the patterns of 10%, and we also notice the presence of the barium copper iron fluoride.

### IV.2.3.5 Ceramics of 25% rejects

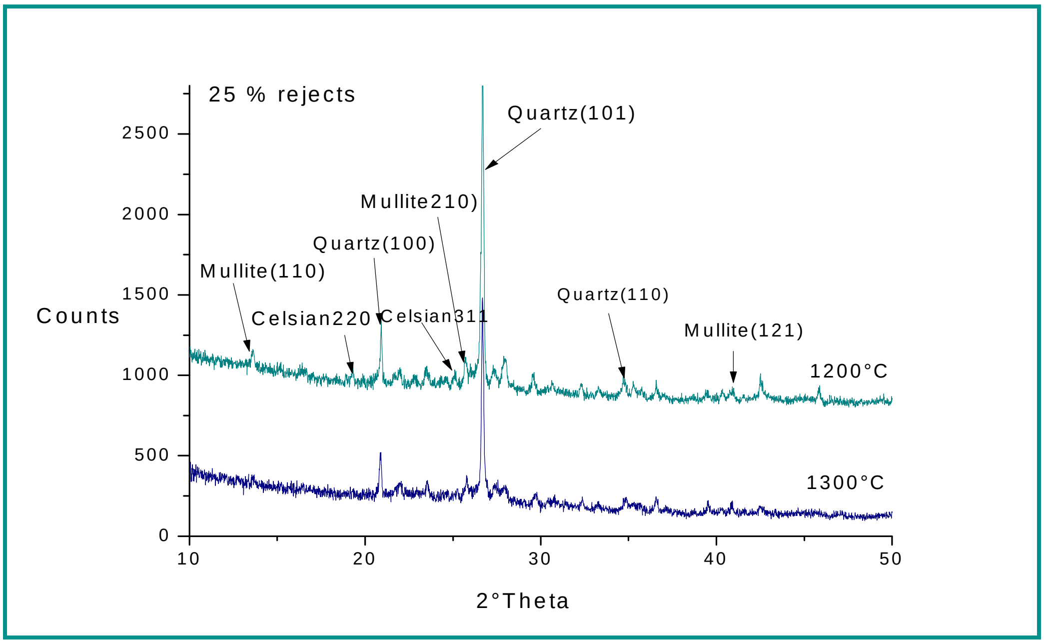


**Figure IV.10:** XRD Patterns of the ceramics of 25% rejects

***a. Patterns of 1200°C and 1300°C***

In the pattern of the ceramics of 25% rejects, we found quartz and mullite, and celsian.

**Table IV.19:** Quartz intense peaks in the pattern of 25% rejects fired at T = 1200°C**.**

| Number of the peak | h k l | d[A] | 2Theta(degree) | Intensity (%) |
|---|---|---|---|---|
| 1 | 100 | 4.25499 | 20.860 | 16.0 |
| 2 | 101 | 3.34347 | 26.640 | 100.0 |
| 3 | 110 | 2.45687 | 36.544 | 9.0 |

**Table IV.20**: Mullite intense peaks in the pattern of 25% rejects fired at T = 1200°C.

| Number of the peak | h k l | d[A] | 2Theta(degree) | Intensity (%) |
|---|---|---|---|---|
| 4 | 120 | 3.46703 | 25.674 | 64.0 |
| 5 | 210 | 3.43349 | 25.929 | 100.0 |
| 13 | 121 | 2.23565 | 40.309 | 63.0 |

**Table IV.21**: Celsian intense peaks in the pattern of 25% rejects fired at T = 1200°C.

| Number of the peak | h k l | d[A] | 2Theta(degree) | Intensity (%) |
|---|---|---|---|---|
| 7 | 220 | 4.61884 | 19.201 | 34.6 |
| 20 | 311 | 3.47329 | 25.627 | 77.6 |
| 21 | 22-2 | 3.35197 | 26.571 | 100.0 |

➢ ***Comment***: We notice in this pattern the enhance of quartz peaks in comparison with the patterns of 15% rejects, and the entrance of celsian which is barium feldspars with the chemical formula $Ba\ Al_8\ Si_8\ O_{16}$, this means that barite rejects we introduced to these ceramic composites entered into the transformations of other phases.

In the pattern of the ceramics of 25% rejects that were fired at T = 1300°C, we got quartz, and barium tetracaesium hexakis of the chemical formula $Ba\ Cs_4\ P_6$ at $2\theta° = 23.515$, and there was no peak corresponding to mullite, the disappearing of this latter lead to the formation of other mineralogical phases like barium aluminium silicate $Ba_{3.19}\ Al_{6.38}\ Si_{9.62}\ O_{32}$ ($2\theta° = 25.632; 26.660; 29.581$), and we also in this pattern the appearance of glass phases.

## IV.3 Conclusion

At the end of this chapter that was devoted to the physicochemical proprieties of the ceramic composites and their mineralogical compositions after sintering, we can summarize it the following points:

- The elaboration of barite rejects with ceramics while varying their percentages and comparing their behavior to free barite rejects ceramics (0% rejects) through the different tests showed that the ceramics of 10% rejects that were fired at T=1300°C relatively gave the closest results to those recorded by the reference ceramics fired at the same temperature, and in the basic attack test we concluded that the addition of barite rejects gained the sample that were fired at T=1300°C an excellent chemical resistance.
- The XRD analysis of ceramics registered quartz and mullite as dominant phases with the appearance of barium in the formation of other phases in the ceramics of 15% and 25% of ceramics.

# *General conclusion and perspectives*

# ***General conclusion and perspectives***

Within our framework we aimed to characterize and valorise Bou-Caid's rejects using the available means we have. Starting from the mechanical preparation passing through quartering and sieving until we arrived to the XRD analysis.

- Based on the XRD analysis results the we concluded that Bou-Caid's rejects contain a good potential of barite in their different fractions, however the highest potentials were registered in the fine sizes and according to our results barite is liberated in the fractions that are inferior to 125µm.
- So as to valorise Bou-Caid's rejects we elaborated them with ceramics and set them to multiple tests such as water absorption and acid (HCl) and basic (NaOH) attacks. Since we have no other means to verify the quality of our ceramics elaborated with rejects we just based on the comparison between them and the reference ceramics.
- In the basic attack test we obtained excellent results showed that the addition of barite rejects to the ceramics gained them an excellent chemical resistance comparing to the reference ceramics specially in the case of the samples fired at T=1300°C.
- From global results we obtained, we can say that ceramics of 10% rejects that were fired at T= 1300°C relatively gave the closest results to those recorded by the reference ceramics fired at the same temperature.
- Based on the identification of the XRD graphs of the different ceramic composites, we conclude that the dominant phase of our ceramic composites is the quartz, and the second dominant phase is the mullite.
- Barium entered the formation of other phases in the case of the ceramic composites of 25% rejects, and the glass phases appeared in the pattern of ceramic composites of 25% rejects that were fired at T=1300°C.
- We definitely can't say that Bou-Caid's barite rejects can be elaborated successfully with ceramics and give them an excellent addition basing only on our results, so those who are going to continue in this theme should determine the mechanical proprieties of the ceramics elaborated with rejects, and try to introduce different percentages of rejects in the ceramics besides those used by us, and it would be better to get the chemical composition of the global rejects using X-ray fluorescence.

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# ملخص

يتمحور عملنا حول تمييز اصدارات معدن الباريت الخاص بوحدة بوقايد, باستخدام تحليل الأشعة السينية بهدف تثمينهم عن طريق خلطهم مع الخزف. انبثقت من هذه الدراسة أن الباريت الموجود في الاصدارات يتحرر في الاجزاء التي مقاسها أقل من ١٢٥ ميكرو متر,و السيراميك المخلوط مع ١٠ بالمئة من اصدارات الباريت و المكلس في درجة الحرارة تعادل ٣٠٠٠ درجة مئوية يمثل الخليط المناسب اعتمادا على النتائج المسجلة من مختلف التجارب.

الكلمات المفتاحية: تحليل الأشعة السينية, اصدارات الباريت ,السيراميك.

# *Abstract*

Our work consists of characterizing Bou-Caid unit's barite rejects using mainly the XRD analysis in the aim of valorizing them by introducing them into ceramics. The results emanated from this study show that barite contained in these rejects is liberated in the fractions that are inferior to 125µm, and the ceramic composites of 10% rejects fired at T=1300°C present the best composition of ceramics elaborated with rejects according to the results of the of different tests.

Key words: XRD analysis, barite rejects, ceramic composites.

# *Résumé*

Notre travail est de caractériser les rejets de barite de l'unité de Bou-Caid, pour des essais de les valoriser dans le domaine des céramiques. Les résultats émanés dans cette études prouvent que la barite contenue dans ces rejets est libérée dans les fractions qui sont inferieures à 125µm. Les échantillons contenant 10% de rejets de barite frittés à T=1300°C présentent la meilleure composition vis-à-vis la microstructure et la durabilité chimique.

Mots clés : Analyse de DRX, rejets de barite, céramiques.