Abstract—Gypsum is a favourite when it comes to mimicking certain features of human body and enhancing some properties of industrial products made from it. Gypsum is widely used for medical purposes such as design of dental prosthetics and limbs support in orthopaedics; but the gypsum powder used for these products are usually well processed. Gypsum ore samples were obtained from a mine at Ibese in Ogun State, Nigeria and processed in a multistage de-gritting operation to obtain a grit-free powder which was converted to gypsum plaster (Plaster of Paris, POP) at about 220°C. The plaster powder so produced was used with property enhancing additives like calcium carbonate, sodium chloride, warm water and others to produce some medical and industrial products. Some of the medical products were tested at the State Specialist Hospital Ado-Ekiti and were found to conform with the required standard for such applications in medicine (especially dentistry and orthopaedic). Other products such as chalk and wallboards were also produced from the processed gypsum and these also performed satisfactorily. Results of property tests showed that the products will have long service life.

Keywords— multistage processing, de-gritting, property enhancer, dewatering, durability, dental, orthopaedics.

1 INTRODUCTION

Gypsum is a hydrated sulphate of calcium, found usually in clays and limestone and sometimes associated with sulphur (Garcia-Ruiz et al., 2007; RMDC, 2010). It is the principal commercial form of hydrated calcium sulphate (CaSO\(_4\cdot2\)H\(_2\)O). It is usually formed by either the evaporation of salt (brines) in shallow inland seas or by the decomposition of pyrite (FeS\(_2\)) in the presence of calcium carbonate. (ASTM 2010; USGC 2010; Al-Rafidain 2010). Gypsum is chemically known as “calcium sulphates dehydrate”. It contains calcium and sulphur bound to oxygen and water (CaSO\(_4\cdot2\)H\(_2\)O). Gypsum has been known for many centuries around the world. It was used by the Egyptians for decoration and construction as far back as 4 B.C.E. The White Sands National Monument in New Mexico is the world’s largest gypsum dune field known till date Al-Rafidain, 2010). Gypsum is found in many locations in Nigeria including locations in Anambra, Delta, Edo, Imo, Sokoto and Yobe States (RMDC, 2010).

Gypsum is useful to humans, animals, plant life, and the environment (Anthony et al., 2003). While the majority of gypsum produced in Nigeria is used to manufacture gypsum board and as building plasters, gypsum is used in many other ways. It is an important input material in production of cement. It finds uses also in production of POP (Plaster of Paris which is used in a variety of home, office and industrial products), chalk production for various uses, in construction and decoration and many other applications. Gypsum is used in such areas in medicine as in dentistry for oral impression casting and in orthopedic for fractures correction. Two sources of gypsum are natural gypsum and gypsum obtained from flue-gas desulphurization (USGC, 2010). Natural gypsum occurs in nature in several different forms such as rock or amorphous gypsum, selenite, satin spar, and gypsumite or earth gypsum. Anhydrite (calcium sulphate - without water of crystallization) is closely related to gypsum and occurs intimately associated with it (Ciullo, 2006; Snider, 2005).

According to the Raw Materials Research and Development Council (RMDC), (2010), about one billion tons of natural gypsum material are spread over many deposits in a number of states in Nigeria. However, due to the poor quality of plaster (POP) produced from locally mined gypsum in Nigeria (as compared to imported gypsum products), demand for local plasters has not been encouraging. Most of the large consumers of processed gypsum in Nigeria (epicyclically cement producers) import gypsum from major producing countries. Similarly, most gypsum material used for dental applications are imported because of the high quality of gypsum required for such products. Although there are good gypsum deposits in Nigeria, the plaster powder produced from them do not meet most modern service requirements possibly due to poor quality of the processed products stemming from inadequate technical understanding of the behaviour of the mineral. Many attempts have been made to improve the demand for local plaster by improving the quality of plaster produced from local gypsum, yet the mineral is still largely imported for the same reasons. Thus, the aim of this research is to process gypsum samples obtained from some locations in Nigeria to meet requirements for use in medical and some industrial processes (Pankaj, 2014; McCabe, 2012; USGC, 2010).

2 MATERIALS AND METHODS

2.1 MATERIALS AND EQUIPMENT

Gypsum samples were obtained from a mining site at Ibese in Ogun State, Southwest Nigeria. Although several gypsum mining sites were operating in the area, samples were collected from two sites in the same mine because of the level of activities in the mine which makes the samples more representative and information from the mines that gypsum materials in all the other mines have the same origin and are exactly the same except for grade especially the percentage composition of gritting material in the samples. Calcium carbonate was obtained and used as setting retardant and visual quality enhancer in some applications. Sodium chloride and warm water were used as setting retardant in other applications. An X-ray fluorescent equipment was used for compositional analysis of sample material and other
equipment like laboratory oven, enhanced gravity separator, pulveriser and ball mill were used at various stages for processing the as-mined gypsum.

2.2 METHODS
The chemical composition of the as-mined gypsum ore was determined after which the samples were crushed and ground for processing. The processing operation involves de-gritting by wet gravity method followed by a mild chemical washing with acidified water to remove some metals (especially iron) by dissolution. The processed gypsum was then converted to plaster powder which was used in some medical and industrial application tests.

2.2.1 CHEMICAL COMPOSITION OF SAMPLES
The composition analysis was carried out to determine the chemical and mineral compositions of the as-mined gypsum samples, using X-ray fluorescence spectrometer (EDX3600B). The result obtained was analysed with the aim of determining the suitability of each sample for use in medical and industrial sectors.

2.2.2 PROCESSING THE GYPSUM SAMPLES
The samples collected were in lumps of average weight of about 5 – 10 kg with a dimension of about 50mm to 100mm and were further broken down manually to sizes suitable for use in the available laboratory jaw crusher followed by grounding with a Denver laboratory ball mill. Gravity separation technique was employed to completely de-grit the samples; producing high grade gypsum powder. The original de-hydrate gypsum powder was treated to produce a hemihydrate product that will be used for various medical and industrial applications. Quality tests such as setting and durability test were also carried out on products obtained from the processed samples. Quality enhancing additives such as lime, sodium chloride and calcium carbonate were used to enhance some properties of the gypsum products. Figure 1 represents the flow sheet for the process. It should be noted however, that the de-gritting stage of the processing (Figure 1) was done in a multistage process emphasized in Figure 2.

2.2.3 DE-GRITTING BY GRAVITY TECHNIQUE
An enhanced gravity separation technique by hindered settling was employed to remove the coarse (or grit) impurities mainly sand from the gypsum sample in a multistage process (Van-Driessche et al, 2012). This involved dispersing the gypsum sample thoroughly in water in a settling column and allowing the feed to settle as underflow and overflow fractions against upward rising current of water in the column. Each of the fraction is further classified as shown in Figure 2.

![Fig. 2: Flowsheet for Multistage De-gritting](image)

The final high-grade gypsum material was dewatered, while the coarse impurities settled as underflow. The dewatering process allowed the fine gypsum material to be collected in a combination of decantation, filtration and drying processes. The dried samples were carefully ground again to produce an unctuous gypsum powder for the remaining stages of the research.

Prior to drying, the wet de-gritted sample was dispersed in an acid solution of pH 4.5 (prepared with a laboratory grade H2SO4 and hydrolysed sucrose to remove any free metal content that was not removed during de-gritting. This acid leaching does not affect the gypsum material, since gypsum is mostly inert to direct acid leaching. The product was washed several times with water to ensure it is free from acid and thereafter dewatered and dried.

2.2.4 CONVERSION TO HEMIHYDRATE
The de-gritted sample was converted to gypsum plaster powder by driving off some of the chemically combined water. The sample was heated to a temperature of about 200°C in a laboratory oven and left at this temperature for one hour; the results being a hemi-hydrate product CaSO4·2H2O also known as Plaster of Paris (POP). This was further heated over several hours resulting in the formation of anhydrite with practically none of the chemically combined water left. Anhydrite sets more slowly and is a slightly stronger plaster than the hemihydrate product.

2.2.5 QUALITY TESTS
The quality tests carried out on the gypsum sample are setting and durability tests. These tests were carried out on cast samples of the hemihydrates product.
Setting Test - The setting test was carried out to determine the natural setting time of plaster (POP) produced from the hemi-hydrate product obtained from the gypsum samples. The test was also carried out on samples with the addition of appropriate quality enhancers. Specimens were produced from the dried powder without addition of quality enhancer and an improvised indenter with a 2kg weight was used to determine the complete setting time at which the indenter rod was unable to make any surface indentation on the cast. As soon as the mixing was complete and poured into the mould a digital timer was started and the indenter rod frequently lowered into the cast. As soon as setting is observed to commence, the frequency of measurement was increased until the indenter rod was unable to make a mark on the surface (ASTM, 2010; Rodriguez, et al., 2008). Another set of samples were prepared with 25g, 50g and 75g each of Sodium Chloride, Calcium Carbonate and warm water were added to 500g of cast mixes and the procedure repeated to determine the setting time for the different casts.

Durability Test - The purpose of the durability test was to determine the stability of products made from the gypsum (hemi-hydrate) powder with time. The test involved a simple procedure of casting cylindrical specimens from the samples with and without addition of quality enhancers and allowed to set completely. A penetrometer was used to impose a constant load on each specimen and the rate of penetration was measured every ten days for six months. This test was also carried out on a building wallboard sample produce about 8 years earlier. The test was repeated on both samples after about 14 months of completion of this project. Although this test is an improvised hardness test, it provided an indication of how weak the material becomes overtime which is also a measure of the durability of the products.

An impact test with a 5kg hammer was also carried out on cast cylindrical samples after 5 days, 1, 3 and 5 months of setting.

2.3 Producing Medical and Industrial Products from Processed Gypsum

Moulds for various medical and industrial products were produced and casts of the required products made from processed and property-enhanced gypsum powder. Calcium carbonate was added to the gypsum powder used for chalk production to whiten and soften the products; Sodium chloride was used for the purpose of controlling the setting time in the mixes for dental products and warm water was used to increase the setting time in some of the applications. The qualities of the various products were tested by carrying out impact and durability tests as applied to specific products. The medical products were tested in hospitals for quality assessment.

2.3.1 Medical Applications

The most common areas of application of processed gypsum in medicine are in dentistry and orthopaedic.

The processed locally mined gypsum was tested in these two major applications in this research.

Dental Application - The gypsum powder produced was used to take the alginate impression (i.e. measurement of the jaws) of the oral cavity of a patient. Water-to-Powder (WP) ratio of 1:3 was used in the procedure for casting the impressions of the jaw cavities with sterilized upper and lower impression trays as shown in Figure 3. The mixture changes from white to pink as water was added and mixing commenced. At this stage, it was loaded into the impression tray and placed in the oral cavity (mouth) of the patient, manually manipulated until it begins to harden and turns white in the patient’s mouth. This was the final setting stage of the impression shown in Figure 3 and it was thereafter withdrawn from the patient’s mouth. The dental mix must be stirred vigorously before pouring into the impression to obtain an adequate viscosity that will produce the appropriate dental stone. It must also be vibrated to avoid entrapment of air bubbles or pore spaces before setting completely. It was then de-cast from the impression and used in the working of artificial teeth.

Fig. 3: Use of Cast Impression

Orthopaedic Application - The areas of application of POP in orthopaedic are generally in broken bones and limbs correction. The POP produced in this research was bitten directly into cotton bandages without any additives or quality enhancer for easy application as shown in Figure 5 and held in position by soft-band, stockinette, and adhesive tape. The injured site is prepared for the application, and further fracture is prevented by assisting to hold affected limb in position of function in a manner that is unobtrusive to the application of cast. Padding is done in layers and on average 6-10 layers are applied in the upper limb and 12-16 layers for lower limb. The padding is then brought out and squeezed slightly to get rid of excess water and for slabs, the wet plaster is run from one end to another to get rid of air bubbles so as to prevent brittleness and separation of the layers when drying. Hole is then created on the manoeuvring jacket around the navel for easy penetration of air as shown in Figures 4-6.
2.3.2 INDUSTRIAL APPLICATION

The specific industrial applications of gypsum covered in this research are; its use in chalk production and in building construction such use in construction of wall boards. The results apply to several similar applications of the material.

Chalk Production - The processed gypsum was used to produce chalk by mixing the POP with little amount of calcium carbonate to increase the whitening and water in the ratio 1:2. The mixing generates an exothermic reaction and the mixture quickly became thicker. It was immediately poured into the assembled chalk mould and vibrated to prevent pore spaces from developing. It was left in mould for about 4 minutes to prevent the chalk sticks from breaking. Thereafter, the mould’s components were taken apart and the chalk sticks gently removed and dried for 24 hours depending on the atmospheric condition to give a quality product. Figure 7 shows the setup of the chalk production process.

Building Constructions - Wallboards are commonly made from gypsum plaster (POP) for various purposes for use in homes and offices. The plaster product in this research was used to produce wallboard by cleaning and greasing the mould properly with lubricant (dissolved soda soap and groundnut oil). Thereafter, the plaster powder was mixed with water in the ratio 1:2; the mixing was vigorous in order to remove and clear all lumps, gently poured into the prepared mould with loosened fibres shown in Figure 8. The fibres were spread on top of the mixture in the mould, while another mixture was prepared, spread on the fibres to cover it up and the surface was well dressed. The wallboard was left in the mould for about 5 minutes and thereafter removed and used for walls, ceilings and decorative materials.

3 RESULTS AND DISCUSSION

The results of chemical analysis carried out as described in section 2.2.1 and the various processes and application procedures undertaken are shown in tables and figures in this section.

3.1 RESULTS OF COMPOSITIONAL ANALYSIS

The analytical equipment indicated elements between sodium (Na, Z = 11) and uranium (U, Z = 92) with high resolution and fast analysis. The major element contained in both samples that were analysed are calcium (Ca) and sulphur (S) which constitute more than 80% of the gypsum composition. The other minerals present in some appreciable quantities are aluminium (Al) and silicon (Si) which is about 5% of the gypsum sample while phosphorous (P), iron (Fe), nickel (Ni),...
copper (Cu), zinc (Zn), tungsten (W) and gold (Au) are present in very small quantities. The remaining elements exist in negligible quantities of less than 1% as shown in Table 1 for the two samples analysed.

| Element | Sample A (%) | Sample B (%) |
|---------|--------------|--------------|
| Al      | 1.8700       | 1.9762       |
| Si      | 1.3221       | 1.5990       |
| P       | 0.6874       | 0.6601       |
| S       | 54.9473      | 52.7734      |
| Ca      | 27.4919      | 27.0674      |
| Fe      | 0.2856       | 0.3161       |
| Ni      | 0.0171       | 0.0243       |
| Cu      | 0.0181       | 0.0202       |
| Zn      | 0.0350       | 0.0342       |
| Pb      | 0.0017       | 0.0000       |
| W       | 0.0067       | 0.0340       |
| Au      | 0.0145       | 0.0000       |
| Nb      | 0.0000       | 0.0032       |
| Mo      | 0.2375       | 0.2013       |
| Sn      | 0.3775       | 0.4204       |
| Sb      | 0.3700       | 0.4048       |

3.2 RESULTS OF PHYSICAL PROCESSING

The results of multistage gravity separation by hindered settling described in section 2.2.4 was the production of completely de-gritted gypsum powder which was converted to the hemi-hydrate powder used in every other process and application (Figure 9).

The sample treated with acidified water and sucrose was especially suitable for dental application as it became whitened without addition of other additives. This treatment may have converted the insoluble iron (III) oxide which was responsible for the pinkish colour of the as-mined gypsum to the soluble iron (II) form and subsequently removed free iron from the composition.

Dewatering the gypsum slip is the major difficulty encountered with the physical processing, especially the multistage classification process. Obviously in gypsum processing for plaster powder production, total dewatering is required before the gypsum can be converted to plaster powder for use in various applications. In this case, dry processing in pneumatic system provides an advantage over wet processing, but the final plaster powder is not always as free of grits as that obtained from wet processing. Thus, the multistage de-gritting process is done in such a manner that only the final de-gritted slip is carefully filtered and thereafter dried. It should be noted that the dewatering stage in Figure 2 is a combination of filtration processes (which may include both pressure and vacuum filter) preceded by clarification and followed by sun, air or gas drying. In this research, dewatering was done by clarification, careful decantation followed by air and oven drying. This was very slow and thus unsuitable for commercial production.

3.3 QUALITY TEST

Results of durability test carried out on cast POP (Figure 10) show that the products did not deteriorate appreciably with time. The results of measurements taken about five days after setting and drying were compared to those taken after 5 months and 14 months; and were found to be even a little less showing that penetration was still a little easier 5 day after production, than 14 months later. The results were also compared to that of a measurement in the same 14 months interval made on an 8-year old wall board and the penetration was about the same value showing that there is no noticeable deterioration even in the old wallboard for those years.

The results of the measurements on the wallboard sample produced with the processed gypsum powder remained almost the same for the period of 14 months with only about 2.0 mm penetration during two or more of the trials which is possibly an error or that the rate of deterioration is very slow. For most tests, the improvised indenter was not able to make any mark on the board surface after setting.

However, experience gathered from interaction with builders who used POP for decoration and finishing in buildings showed that some POP application collapse from building while others remains unchanged even in physical look for as long as 20 years (USGC, 2010). It is also found that most of the quality enhancers used (except CaCO₃) have little or no effect at all on the durability of the products. Most affect only the setting time of the mixes. Once the the mix sets, the effects of such enhancer seize. Addition of calcium carbonate as quality enhancer is the only one that had obvious effects on the durability of the product because the chalk produced with this mix became weaker and whiter as shown by the brittleness of the chalks.
The results of impact breakage of cast cylindrical samples (Figure 10) with hammer produced a split-like breakage into lumps and not the crumble type of breakage that was expected. The breakage although could not be measured in numeric terms, was observed to be similar even with the long interval of time between tests. The also shows that once set, gypsum powder product maintains the strength attained for a long time.

3.4 Water-to-Powder (W/P) Ratio
The proportion of water-to-powder used to make a workable mix of gypsum product is called water-to-powder (W/P) ratio by volume. The w/p ratio for different gypsum applications vary slightly. For example, the ratio for plaster is 1:2, stone 1:3, Chalk 1:2, wall board 1:2, manoeuvring jacket 1:3 and Limb 1:3 as shown in Figure 11. These ratios were used to prevent the mixture from increased or reduced setting time before getting the appropriate product consistency.

![Figure 11: Effect of water/powder ratio on setting time for POP](image)

3.5 Medical Application
3.5.1 Dental
Results of dental and orthopaedic applications both carried out at the state specialist hospital Ado-Ekiti, Ekiti State, Nigeria showed that the locally sourced and processed gypsum meets all the requirements for these applications as much as those imported. The dental stones and orthopaedic supports were amenable to manoeuvring as desired and set readily as planned with the addition of the appropriate property enhancer. The best outcome will however be achieved by remixing and addition of the enhancers and water at very short and regular interval. This is particularly helpful in the case of orthopaedic applications where more time may be required for manipulation before the mix finally sets. Alternatively, the required volume may be prepared in batches with the same composition and consistency but the batch being applied must not be allowed to set before a new batch is ready. Otherwise the material may set with definite interfaces producing layers and sections that will result in ineffective application. Figures 12 and 13 show some of the medical products made from the processed gypsum.

![Figure 12: The Manoeuvring and Limb Jackets](image)

3.6 Industrial Application
3.6.1 Chalk Production
The use of gypsum powder (POP) in industrial application is numerous but only its use in chalk production and building construction are considered here. Although the use of chalk in schools is becoming insignificant due to the availability of digital instructional materials, white board markers, chalk of different types and colours are still being used in elementary schools and for engineering and fabrication purposes. The chalk produced from the processed local gypsum powder (Figure 14) meets all requirements for use. The higher the quantity of calcium carbonate added the softer and weaker the chalk produced and the lower the quantity, the harder the chalk. Hard chalks are useful for engineering purposes because the marks they make on metals are more difficult to erase than other chalks and they still appear legible. The soft chalks are however better for educational instruction. Thus, chalks for classroom instruction should contain from 15% by weight of calcium carbonate while those for metal works should contain less than 10%. Colorants for inducing specific colors on chalks also increase their softness, thus the percent composition of both the colorant and quality enhancer should not exceed 15% for instructional chalk.

The use of gypsum powder (POP) in building and construction is limited to decoration and aesthetic finishing; they are not used where load application of some magnitude is required. The use of fibres for reinforcement is more for achieving cohesion and carrying of load. Thus, only wall board (for which most of the applications of gypsum plaster in building is applied) is produced with the processed gypsum) and the product compared favourably in integrity with those produced from imported plaster as shown by the result of durability test. The Ibese gypsum can therefore substitute favourable for some of the foreign resource gypsum. It also confirmed that gypsum composition and properties are the same. What makes a difference in service performance is the level of purity which is determined by the degree of processing.
4 CONCLUSION

This research has shown that Ibese gypsum is suitable for medical and industrial applications if adequately processed. Processing should involve a multistage degritting operation with the final gypsum slip carefully dewatered and converted to gypsum plaster at about 200°C and the use of any quality enhancer that tends to affect the hardness or softness of the plaster products should be carefully controlled based on the specific application in order to prevent unexpected failure in service.

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