OPTICAL CHARACTERIZATION AND X-RAY DIFFRACTION STUDIES OF SYNTHETIC PLASTER OF PARIS

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ABSTRACT

Gypsum samples were produced by reaction of dilute hydrochloric acid with hydrated lime and the resulting calcium chloride solution was reacted with dilute sulphuric acid. Calcinations were done at a constant temperature of 120°C for a period of four hours. The choice of the production parameters was guided by the findings of previous studies. Optical absorption spectra of the samples were measured with respect to a reference standard (imported) plaster sample. This helped to identify the material sample by determining absorption maxima. Four characteristic absorption peaks were notable in the spectrum for the synthetic sample. These occurred, in descending order of intensity, at 1149.7 Å, 3405.3 Å, 1631.1 Å and 2136.4 Å respectively. Similar peaks feature in the spectrum for the reference plaster, though with small shifts in wavelength. X-ray diffraction analysis and x-ray fluorescent spectrometry were carried out on the samples to determine crystal structures and lattice parameters, as well as the elemental composition of the synthetic sample for impurity level assessment. The XRD analysis indicated the presence of hannebachite, gypsum and predominant calcium sulphate hemihydrate in the synthetic plaster. Its crystal structure was revealed as orthorhombic with lattice parameters a, b, c as 9.82 Å, 10.67 Å and 6.50 Å respectively. The structure found in the synthetic plaster was essentially similar to those in the reference sample. The level of possible impurity in the synthetic sample was established as minimal, since XRF analysis did not reveal the presence of elements with atomic mass higher than calcium.

Keywords: Optical Characterization, X-ray Diffraction, Synthetic Plaster of Paris.

INTRODUCTION

Plaster of Paris (or simply plaster) is obtainable from heating gypsum powder (calcium sulphate dihydrate). The natural gypsum is a common mineral found in evaporate beds of sedimentary rock deposits. Notable occurrences are found in Canada, Mexico, Pakistan, Spain, Utah, Colorado, USA, Chile and France.

Plaster has been used in the construction of roads, bridges, sidewalks, protection of walls, as foot creams, shampoo and other hair care products because of its water-solubility. It is used in cement production to prevent flash setting of concrete and as binders in fast dry tennis courts. More importantly, it has application as support frame for broken bones and in dentistry to obtain dental impression recording of jaws (Abioye *et al.*, 1993). Its applicability for multipurpose use lies in the ease of modification of its properties. Consequently, it has been used in treating infrabony periodontal defects in humans (Shaffer and App, 1971), for the regeneration of bones (Coetzee, 1980) and as bone substitutes (Van Rens, 1987; Tay *et al.*, 1999).

The usual colour presentation is white but may occur as yellow, tan, blue, pink, brown and reddish brown or gray depending on the type and amount of impurities present. It is soluble in hot dilute hydrochloric acid and has a specific gravity of about 1.82 2.4 (Akinnifesi and Ogunbodede, 2011) depending on the atomic weight of the constituent elements and their manner of packing. The crystal system is monoclinic with good cleavage in the {010} direction. An important property in the comparison of dental restorative material is the hardness value (Mohsen, 2011). Its measurement delineates the abrasiveness of the material to which natural dentition may be submitted (Albakry *et al.*, 2003).

The chemical production process involves heating at a controlled temperature, without melting, to drive off volatile components from the material. This process of calcination results in three important relatively pure products used in dentistry: dental plaster or beta form of the hemihydrate, stone or alpha form, and high strength stone (hss). They have the same chemical

formula, $CaSO_4.O.5H_2O$ but different physical properties depending on how the water of crystallization is driven off. This makes it useful in different dental situations.

The plaster setting time is the time elapsing from the end of mixing the powder with known quantity of water (determined by water/powder ratio) and the time when the cast is formed, as ascertained by a penetrometer (Skinner and Phillips, 1960). Setting time is minimal for low w/p ratio, however too low values will make the mixture too viscous to flow into requisite details of dental impression while too high values will be too fluidy to remain in position to record details. Setting expansion may be hygroscopic (Ruge and Fairhurst, 1956) since the dihydrate formation is thermodynamically more stable in the presence of water than the hemihydrate (Ishikawa, 2010). The setting time is influenced by the presence of impurities (Abioye *et al.*, 1993). The setting and hardening of the hemihydrate has been used to explain phase transformation based on dissolution-precipitation reactions in apatite cement fabrication (Sekiya, 1964; Mohsen, 2011).

The synthetic production of dental plaster is facilitated by the reaction of HCl with limestone and subsequently with H_2SO_4 to obtain gypsum, which on calcination gives Plaster of Paris. Optimum calcination periods of 4 - 4.5 hours at 120°C 125°C has been reported (Abioye *et al.*, 1993; Akinnifesi and Ogunbodede, 2011). This helps to focus further analyses and characterization on more effective samples.

The synthetic samples can be characterized optically by measuring the absorption spectra with respect to different wavelengths of incident electromagnetic radiation. This is in view of the fact that optical characteristics result mostly from interaction of electromagnetic radiation with electrons in a material. Atoms or molecules can absorb or emit radiation of characteristic wavelengths in which the resulting absorption or emission spectrum is associated with discrete electronic transitions taking place in the material. In the case of absorption, electrons are excited to higher energies on acquiring photon energy $E = hc/\lambda$, where λ is photon wavelength, h is Planck's constant and c is speed of light. On this basis, optical absorption may be interpreted in terms of electronic structure. In $CaSO_4$, the respective electronic structures of O, S and Ca are:

O: $1S^2\ 2S^2\ 2P^4$

S: $1S^2\ 2S^2\ 2P^6\ 3S^2\ 3P^4$

Ca: $1S^2\ 2S^2\ 2P^6\ 3S^2\ 3P^4\ 4S^2$

From these structures, unfilled shells are obvious. Absorption spectra thus help to identify the material by determining absorption maxima (Craig *et al.*, 1973).

For the identification of crystal structure and lattice parameters of the synthetic sample, X-ray powder diffraction analysis technique is a useful tool. In this technique, the diffracted beams from atoms in successive planes, when in phase, interfere constructively to form peaks in accordance with Bragg's law: $n\lambda = 2d\text{Sin}\theta$, where λ is the wavelength of the incident radiation, θ is the angle of diffraction and d is the interplanar distance.

The relative intensity of peaks and their position can be measured and interpreted using a data base. The width and shape of reflections are characteristic of crystallite size in samples. Harcourt and Lautenschlager (1970) have used X-ray diffraction peaks of calcium sulphate hemihydrates to study gypsum product formation, while the setting reactions have been investigated by the same technique (Lautenschlager *et al.*, 1956).

Energy dispersive XRF analysis technique is also capable of measuring the different energies characteristic of fluorescent radiations emitted by the elements of a material sample. Their relative proportions are indicated by the relative intensities. This work is motivated by the need to characterize the synthetic plaster samples with reference to an imported sample for improved physical and structural properties and also to determine the acceptability of the impurity levels in them.

MATERIALS AND METHODS

Sample Preparation: Two methods are possible; the direct reaction route and the indirect reaction route. In the direct reaction route, calcium hydroxide is reacted with H_2SO_4 to give hydrated calcium sulphate and water in equal molar

proportions. Whereas in the indirect route, HCl and $Ca(OH)_2$ are reacted together resulting in $CaCl_2$ which is then reacted with H_2SO_4 to regenerate HCl as a by-product which can be recycled. The latter method has the advantage of abundant availability of starting materials and control of purity and was therefore the preferred option.

90 cm^3 of concentrated HCl in a beaker was diluted with water to obtain 1000 cm^3 of the solution while 27 cm^3 of concentrated H_2SO_4 was diluted with distilled water to obtain 1000 cm^3. 50 g of $Ca(OH)_2$ was mixed with 100 cm^3 of distilled water to obtain a slurry. The HCl specimen was poured to the slurry in excess until it fully reacted. Calcium chloride precipitate was filtered from the solution and reacted with the H_2SO_4 specimen. The mixture was stirred for five minutes and the solution was left for about an hour to ensure complete precipitation. The precipitated gypsum was filtered from the HCl and thoroughly washed with distilled water to expel excess HCl. It was then calcined at 120°C for four hours following the findings of earlier studies (Akinnifesi and Ogunbodede, 2011). A reference (imported) sample was obtained from the Faculty of Dentistry for comparative studies.

Sample characterization: To measure the absorption spectra of the samples, the double beam SP8-400 spectrophotometer was used. This was capable of giving plots of absorbance (in logarithm of the inverse transmittance) as a function of wavelength (in angstrom units).

The samples for the XRD and XRF analyses were prepared by grinding the powder in a mortar and subsequently compressed at a pressure of 20,000 kg and then forced into pellet of radius 5 mm for the sample holder. XRD analysis of the samples was carried out using the rotating crystal method in which λ is fixed and θ is varied on MD10 mini diffractometer with an angular range of 16° - 70° on the 2θ angle. The CuK_a line (1.5406Å) with a nickel filter was used. Measured values were analyzed using the International Center for Diffraction Data PDS database sets 1 - 44.

The XRF analysis of the synthetic sample was carried out on an Amptek Inc. Eclipse III which was furnished with a digital processor, X-ray detector and X-ray tube, for elemental compositional analysis. The homogeneity of the sample is significant as screening is restricted to the surface layer. Interpretation of spectrum was done against a standard list of calibrated elements.

RESULTS AND DISCUSSION

Figure 1 shows the typical absorption spectrum of the synthetic sample calcined at 120°C for four hours while Figure 2 represents the spectrum for the reference (imported) plaster. The wavelength positions of the respective absorption peaks as well as their intensities are indicated in the spectra.

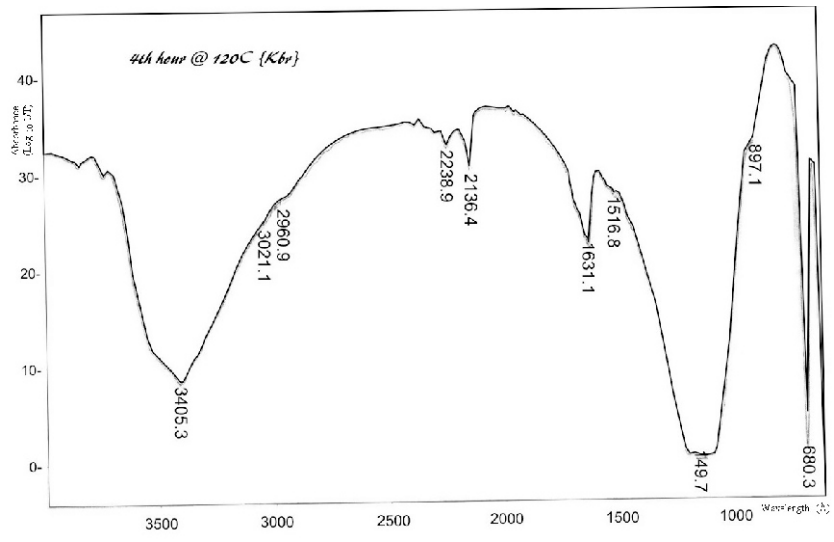

Figure 1: Absorption Spectrum of Synthetic Plaster of Paris Calcinated at 120°C for 4 hrs.

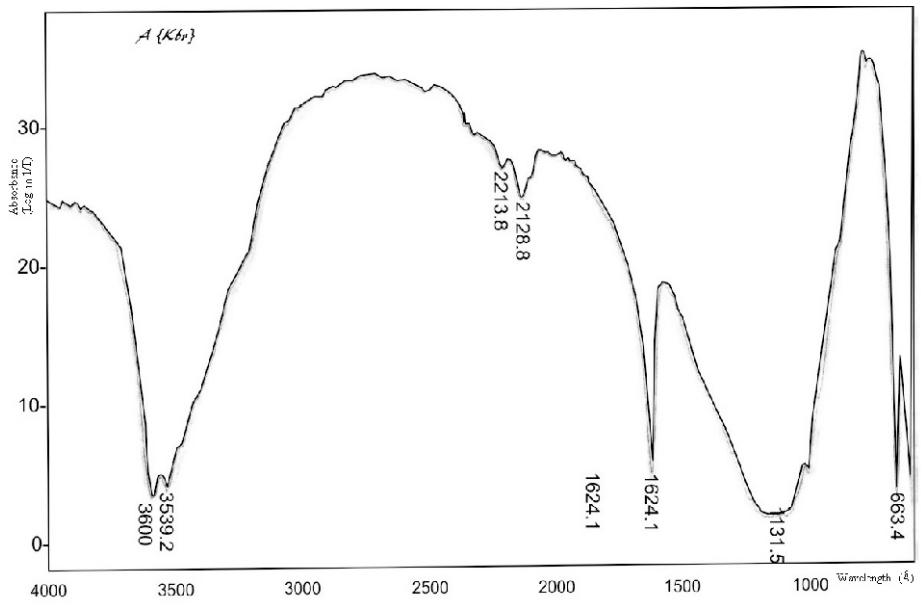

Figure 2: Absorption Spectrum of the Reference (Imported) Plaster of Paris.

Figure 3 shows the XRD spectrum of the locally synthesized sample, identifying the prominent peaks. Analysis shows that the system is orthorhombic with lattice parameters a = 9.82Å, b = 10.67Å and c = 6.50Å. The cell parameters were refined from cell data reported by Scheib *et al.* (1988) in which lattice structure was found to be orthorhombic with lattice parameters a = 9.808Å, b = 10.676Å and c = 6.496Å. The relative standard deviation in intensity of the ten strongest reflections in our sample is 2 %. The main peak for the Bragg's angle (2θ) occurs at 32°. The closest in prominence to this occurs at 14.62° and 29.8°, followed by the peak at 26.01°. Forty-six reflections in pattern were observed as presented in Table 1.

On the other hand, the XRD analysis of the imported calcium sulphate hemihydrate reveals a monoclinic system with lattice parameters a = 12.67Å, b = 6.927Å and c = 12.028Å. The prominent peak (2θ) is at 21.38°. Other peaks occur in this sample than in the locally synthesized sample. 26 reflections in pattern were observed as presented in Table 2.

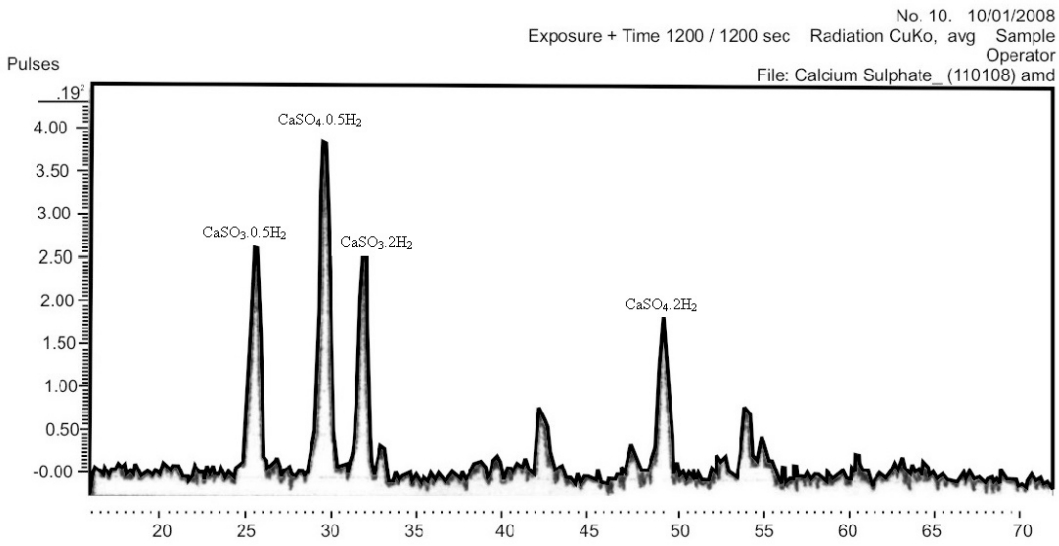

Figure 3: XRD Spectrum of the Locally Synthesized Plaster of Paris

Table 1: XRD Analysis of Locally Synthesized Plaster of Paris; Diffraction Angles are Calculated using Wavelength 1.5406.

.	Intensity	hkl	θ	Intensity	hkl
15.9271	46	011	49.1811	25	033
16.5878	16	020	60.1201	04	133
18.3460	06	111	50.4792	15	303
23.3848	22	121	50.4792	15	440
27.4123	04	002	51.4989	04	521
28.2412	100	221	52.4068	03	342
28.9090	08	102	54.7234	09	252
30.0332	10	131	56.8519	08	261
31.1161	09	112	56.8519	08	610
31.0380	08	230	57.3119	04	431
31.7043	17	311	58.1230	02	114
33.5832	11	040	58.4096	01	442
34.1236	60	212	59.1915	02	062
36.5806	10	400	60.5770	03	214
40.1171	08	400	60.8677	08	621
40.4175	04	420	60.8677	08	053
40.8981	11	241	62.5586	02	071
41.8667	08	232	62.8367	05	433
42.5258	10	013	63.9074	02	304
43.8741	10	042	63.9074	02	503
46.3214	14	250	64.2333	04	631
47.0721	05	431	64.2333	04	612
49.1811	25	511	65.9335	02	234

Table 2:XRD Analysis of Reference Calcium Sulphate Hemihydrate

θ	Intensity	hkl	θ	Intensity	hkl
14.6859	52	110	49.3831	57	-431
14.6859	52	002	52.7158	14	026
25.6217	47	013	54.1287	38	-433
29.7059	100	004	55.0796	27	-240
31.8900	76	-411	62.8699	10	-417
32.9772	09	-222	64.3680	06	-327
38.2860	09	-413	68.3680	06	-051
39.6550	05	015	70.6409	08	-345
41.3251	63	-422	71.1542	12	-716
42.2153	29	503	72.7656	14	-831
42.7177	05	600	74.9067	06	-428
47.5427	14	206	76.3289	08	-806
49.1840	36	-415	76.5318	04	741

Figure 4 represents the spectrum of the XRF analysis of the locally synthesized plaster sample. As expected, Ca is shown as the main peak. The equipment sensitivity is limited to the detection of elements such as Al, Ca, Fe, K, Na, Si, and Ti. As such the only prominent element detected is calcium and traces of Argon. The analysis revealed a concentration value of 30.29 % ± 0.1022 % for Ca.

In the spectrum for the synthetic sample, four characteristic absorption peaks are more notable at wavelengths 1149.7Å, 3405.3Å and 2136.4Å (in descending order of their intensities). Similar peaks occur in the reference sample at 1131.5Å, 3600Å, 1624.1Å and 2128Å (in descending order of peak intensities) with slight shifts in wavelengths. The peak occurring at 1624.1Å in the reference sample is significantly more intense, whereas a broadening is remarkable in the peak at 3419.1Å for the synthetic sample.

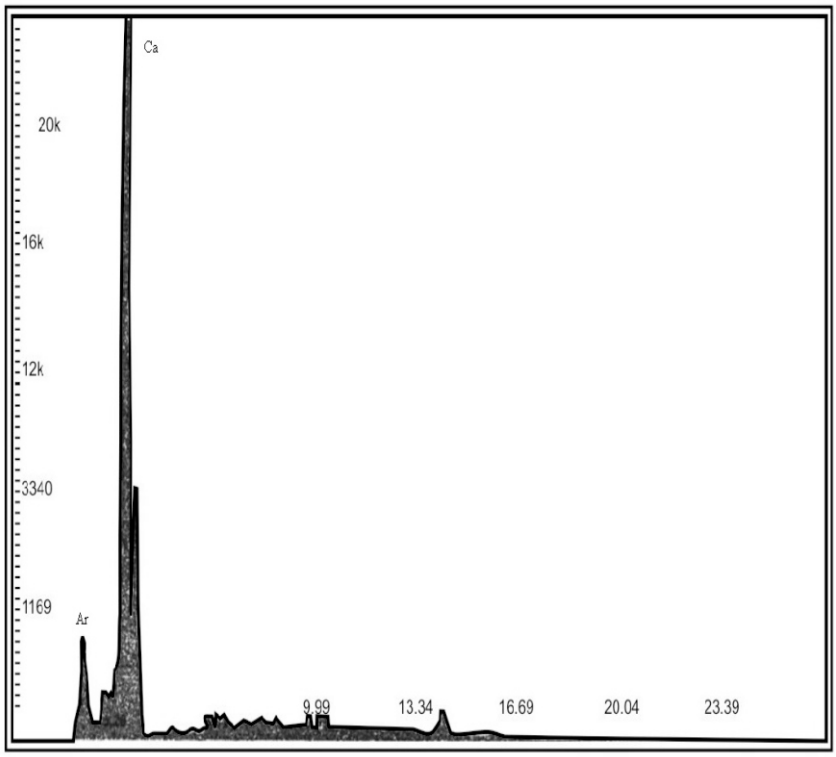

Figure 4: XRF Spectrum of the Locally Synthesized Plaster of Paris

The characteristic allures revealed by the optical spectra may be understood by considering that energy gap arises between filled and empty states in ionic solids. Minor absorption peaks at lower frequencies (high wavelengths) may occur as a result of impurities or interaction of photons with ions at frequencies comparable to that of ionic vibrations. Considerable absorption at higher frequencies are due to interband transitions. The presence of lattice defects locally alters the electronic energy levels and electrons can reside between valence and conduction bands or give rise to new absorption levels. As this occurs in the visible spectrum and may influence optical characteristics, ionic crystals exhibit definite colour depending on the density of defects. Characteristic absorption bands in the visible may also indicate the presence of impurity levels which can give colour to the material. Our samples are consistently whitish, suggesting very low levels of possible impurity or lattice defect.

A comparison of 2θ peak values with ICCD database software reveals the presence of certain compounds in the samples. In the XRD analysis of the locally produced sample with the most prominent peak occurring at 32°, the peaks 14.62° and 29.8° closest in prominence to the main peak suggest the presence of calcium sulphate hemihydrates, the one at 26.01° is representative of hannebachite (synthetic, $CaSO_3.O.5H_2O$) while the peak at 49° represents the presence of gypsum (synthetic $CaSO_4.2H_2O$).

For the imported sample, the prominent peak at Bragg's angle (2θ) occurs at 31.38°. This has closest to it in prominence, the peaks at 20.72° and 11.589° suggesting the presence of gypsum, hannebachite at 28.25° and that of bassanite at 29.69°. Therefore except for the difference in crystal structures, both the synthetic plaster and the imported plaster essentially consist of

identical components. The different preparation procedures would have undoubtedly affected the structural formation. However the excess minor peaks present in the imported sample over those in the locally synthesized sample may be adduced to the presence of additives in the form of accelerators or retarders which are not included in the locally produced sample.

The result of XRF analysis confirms the absence of elements with high atomic masses which are not particularly favourable to the formation of dental POP. These elements with higher atomic masses do not feature in the imported plaster either.

CONCLUSIONS

Synthetic samples of Plaster of Paris were prepared by the reaction of dilute hydrochloric acid with calcium hydroxide and subsequently reacted with dilute sulphuric acid. The precipitate was calcined at 120°C for a period of four hours. Absorption spectrum was measured and interpreted in the light of electronic transitions between filled and empty states. Notable characteristic absorption peaks are revealed at wavelengths of 1149.7, 3405.3. 1631.1 and 2136.4 angstroms.

XRD analysis of the synthetic sample shows the dominant presence of calcium sulphate hemihydrate while the presence of gypsum and hannebachite were also indicated. The synthetic plaster structure was revealed as orthorhombic with lattice parameters a = 9.82Å, b = 10.67Å and c = 6.50Å.The reference (imported) plaster has essentially similar constituents to that of the synthetic plaster.

XRF analysis precludes the presence of elements with atomic masses higher than calcium, indicating the possibility of limited presence of impurity. Production on industrial scale would be environmentally friendly as reaction by-products can be recycled into the production process.

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