# Facile purification of locally mined gypsum and its use for preparing nano-hemihydrates

Luqman Ayodeji ADAMS[1,*], Enobong Reginald ESSIEN[2], Taiwo AIYELERO[2], Stella OSEYOMON[1], and John MAKANJUOLA[3]

[1] *Department of Chemistry, University of Lagos, Nigeria*

[2] *Department of Chemical and Food Sciences, Bells University of Technology, Ota, Nigeria*

[3] *Department of Dentistry, College of Medicine, University of Lagos, Nigeria*

**\*Corresponding author e-mail:** ladams@unilag.edu.ng

**Abstract**

Gypsum has a wide range of applications, in interior decorations, building construction, supplements or implants in orthopaedics to mention a few. However, in many developing countries including Nigeria, there is still a large-scale importation despite huge available natural deposits. In this study, a facile method to purify locally-mined gypsum has been explored based on the mineral retrograde solubility in water. The purified gypsum was investigated for its elemental composition in comparison to the crude sample and a commercially obtained medical-grade gypsum using X-ray fluorescence (XRF). The results showed that the purified gypsum contained 94.05% $CaSO_4$ compared with the crude which had a $CaSO_4$ content of 58.10%. Hemihydrates obtained by the treatments of the purified gypsum in an oven, autoclave and microwave gave different morphologies when observed under a scanning electron microscope (SEM). Transmission electron microscopy (TEM) showed that particle sizes of all the hemihydrates were within the range 9 nm to 32 nm, but the microwave-derived sample exhibited the most desirable morphological characteristics which could impart high mechanical performance. We have reported here a new facile method for purifying gypsum ore that can have huge commercial benefits.

## 1. Introduction

Gypsum which is known chemically as calcium sulphate dihydrate ($CaSO_4.2H_2O$) is a mineral that occurs naturally as a white powder. It is known to be a sedimentary rock, which settled through the evaporation of sea water, trapped in lagoons. It can exhibit various colours depending on the nature of impurities presented, ranging from white to brown, yellow, grey and pink [1]. It is an important material and one of the oldest still being used in construction [2]. Furthermore, applications of gypsum in products, such as renders, plasters, indoor finishings, retardants for cement, ceramics and medical supplements or implants are well documented [3-9].

Apart from its natural origin, gypsum can be in synthetic forms such as phosphogypsum, desulfogypsum or gypsum from chemical neutralization in certain industrial processes. Irrespective of its sources, gypsum contains impurities which could constitute nuisance and thereby compromise its properties such as the setting kinetics of the plaster, the lack of whiteness of the various chemical and crystalline forms of calcium sulfate (through heat transformation of the gypsum), especially for pigment applications, or appearance of the crystalline structures themselves. The presence of impurities can also affect the control of the morphology and/or the shape factor and cause pollution, which becomes more serious when it involves radioactivity.

In Nigeria, for instance, there is over a billion tonnes of gypsum deposit spread across different locations in the country [10]. In spite of these huge deposits, Nigeria's gypsum imports over three years netted $56 million [11].

Therefore, the purification of raw gypsum to increase access and reduce cost is of utmost interest to users of the commodity. Whilst the percentage purity of Nigerian gypsum is considered low, averaging 60% to 65%, it is however adequate for one of the biggest users - the cement industry [12] which unfortunately does not meet the minimum specification for biomedical applications.

The most common impurities associated with gypsum are organic compounds like humic acids, inorganic compounds, such as halogenides, sulfates, calcium carbonate, magnesium carbonate, strontium carbonate, radium carbonate (and other carbonates), and also complex inorganic compounds such as clays, sodium fluorosilicate, aluminum fluoro-silicate, calcium fluorosilicate, radioactive components, $P_2O_5$ and fluoro-phosphates ($FPO^{3-}$) [13]. These impurities are largely insoluble or minimally soluble in water, and, hence, can be removed by dissolving gypsum in water. Most of the available methods in literature focus on the purification of phosphogypsum using physical, thermal and chemical techniques [14-21], rather than direct use of the mined ore deposit.

Gypsum is known to be exothermic when it dissolves in water [22] whereby it exhibits retrograde solubility, i.e., its rate of dissolution increases at a lower temperature. In general, temperature affects the solubility of a given solute in a given solvent. The solubility of many salts increases dramatically as the temperature rises. This can be explained in the following way. The average kinetic energy of the molecules that make up a solution increases as the temperature of the solution rises. The solvent molecules can more effectively break apart the solute molecules that are locked together by intermolecular interactions because of the increase in kinetic energy. As the temperature rises, the average kinetic energy of the solute molecules rises as well, destabilizing the solid state. Because the solute molecules' kinetic energy is higher, they are less able to hold together and dissolve more easily.

Some solutes, such as calcium sulfate, become less soluble in water with increase in temperature. Retrograde or inverse solubility is a term used to describe this inverse temperature dependence. The advantage is that this reverse solubility behaviour can used to purify gypsum and other ores if the solubility data of their contaminants are available. There is no extensive study on the purification of gypsum from its natural deposits based on this physico-chemical characteristic which to the best of our knowledge is yet to be reported.

## 2. Experimental

### 2.1 Materials

The crude gypsum (CG) was obtained from Igbesa in Ogun State, south-west Nigeria, die stone powder (SG) (UnoDent) was used as a standard reference, while calcium chloride ($CaCl_2$) used for preparing type IV dental stone was purchased from Sigma-Aldrich.
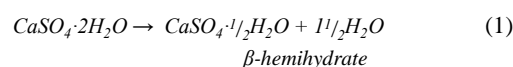
### 2.2 Purification of the crude gypsum

The crude gypsum was first manually to separate larger pieces from smaller sized ore samples. Then it was ground to fine powders before passing through a 90 μm ASTM graded sieve. Thereafter, the fine powders were dispersed in de-ionized water cooled to 20°C, and stirred for 5 min to achieve proper mixing. The resulting aqueous mixture was then refrigerated at a controlled temperature of 20°C for 48 h to allow for dissolution of pure gypsum ($CaSO_4.2H_2O$) presented in the sample. After removal from the refrigerator, the mixture was decanted and filtered, while maintaining the temperature of the mixture at 20°C in an ice bath. The pure gypsum was recovered by evaporating the filtrate to dryness at a temperature of 105°C in an oven equipped with a fan.

### 2.3 Preparation of hemihydrates

The purified gypsum was heated in a petri dish to 120°C for 1 h to drive off part of the water of crystallization to afford β-hemihydrate as shown in Equation 1. Furthermore, α-hemihydrates were prepared from two wet methods. First, the gypsum was heated in an autoclave at 121°C for 15 min. Afterwards the autoclave was allowed to cool to withdraw the sample. In the second method, 10 g of gypsum was initially dissolved with 50 mL of 30% $CaCl_2$ solution at 110°C. The mixture was placed in a microwave oven at a temperature rating of P40 (110°C to 140°C) for 20 min. The obtained crystals were washed with boiled water and dried in an air oven at 75°C.

$$CaSO_4 \cdot 2H_2O \rightarrow CaSO_4 \cdot {}^1/_2 H_2O + 1{}^1/_2 H_2O \qquad (1)$$
$$\textit{β-hemihydrate}$$

### 2.4 Characterization

Elemental composition of the crude and purified gypsum samples was evaluated using X-ray fluorescence (XRF) (XRF: Phillip PW-1800). The microstructure of the samples was investigated by scanning electron microscope (SEM: JEOL JSM 7660F). The particle size and shape of the samples were assessed using transmission electron microscopy (TEM: JEM-ARM200F-G).

## 3. Results and discussions

### 3.1 The purification method

The crude gypsum was light brown in colour as presented in Figure 1(a), but improved in whiteness significantly after the purification (Figure 1(b)). This is due to the removal of most of the impurities as residue through reverse solubility at 20°C. During this stage, the dissolution of gypsum in water is based on a simple two-phase dissolution (solid and solvent) (Equation 2). Gypsum becomes more soluble as temperature decreases due to its exothermic reaction with water, while the impurities become less soluble. According to Le Chatelier principle, the position of the equilibrium (Equation 2) will shift to the right, that is, in a direction when the process is exothermic to counter the disturbed equilibrium, consequently, the dissolution process will be accelerated. Solutes which are not gypsum, including $CaSO_4$ (anhydrite) will be undissolved in water during this condition [23]. This is because at ambient conditions, the anhydride is in equilibrium with the solid phase of gypsum, but not with the anhydrite. Hence, if non-equilibrium of the solid-solvent system occurs, gypsum precipitates. This has been attributed to "the instability of anhydrite under normal surface and shallow sub-surface thermobaric conditions" [23].

$$CaSO_4 \cdot 2H_2O \rightleftharpoons Ca^{2+} + SO_4^{2-} + 2H_2O \qquad (2)$$
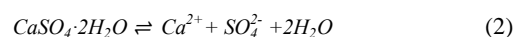


**Figure 1.** Photo shot of the (a) crude gypsum and (b) purified gypsum showing significant improvement in whiteness.

## 3.2   Composition

The compositions of the crude gypsum (CG), purified gypsum (PG) and standard reference die stone (SG) determined by XRF are provided in Table 1. As observed, the impurities decreased significantly, and, in some cases were eliminated completely. This was further justified by the improved physical white appearance of the purified sample (Figure 1). Furthermore, the concentration of CaO and $SO_3$ showed appreciable increase in the sample. Interestingly, the retrograde solubility method used led to improvement in purity from 58.10% in (CG) to 94.05% in (PG). The purity level of purified gypsum was remarkable, when compared with the gypsum composition from the standard commercial sample (SG), which was 97.94% (Table 1), and hence, confirms the validity of the method adopted in this study. However, oxides such as MgO, $Al_2O_3$ and SrO were still presented in amounts that affected the overall purity of the sample. To overcome this drawback, the recovery process could be optimized by subsequently introducing a primer to crystallize pure $CaSO_4$ from the filtrate.

## 3.3   Morphology

The SEM images (Figure 2) show the hemihydrates obtained at different heating conditions of the gypsum. The β-hemihydrate formed from dry calcination of the gypsum at 120°C for 1 h in a ventilated oven shows a compact architecture (Figure 2(a)). The morphology appears to be highly agglomerated, flaky and composed of small crystals, which is in line with a previous report [24]. When the gypsum was subjected to autoclave pressure steam heating, the morphology transformed to particles appearing more regular in shape and on the brink of isolation (Figure 2(b)). There is clearly a reduction in the void fraction, and consequently a lower porosity than the β-hemihydrate in Figure 2(a). This transformation suggests better bonding between crystals of the gypsum, leading to formation of α-hemihydrate.

The microstructure of the α-hemihydrate obtained from heat treatment of the gypsum using microwave energy (Figure 2(c)) presents a markedly different morphology from the sample derived from autoclave condition. Tiny particles are seen distributed over the surface of thicker and agglomerated ones to form a regular porous matrix with large surface area. The result indicates that individual crystals of the gypsum experienced more thermal energy under the microwave condition leading to their further breakup. The effect of various thermal treatment methods on the morphology of gypsum could provide useful information for the optimization of mechanical

properties of gypsum, since mechanical properties depend on micro-structure of gypsum system [25]. Particle and pore size have inverse relationship with mechanical properties. Smaller particles sizes result in better grain in a material, and hence, enhanced mechanical properties. Whereas large pore sizes would adversely affect mechanical properties. The reason for this is that the voids could trap air bubbles, such as carbon dioxide which could reduce compressive strength [26].

## 3.4   Structure and size of particles

The structure and size dimension of the hemihydrates obtained by subjecting the gypsum to the different thermal treatment methods are shown in the TEM images presented in Figure 3. The TEM photographs confirm the observation made concerning the SEM micrographs of the samples. The hemihydrate formed via dry calcination shows polydisperse particles within 50 nm size dimension (Figure 3(a)). The α-hemihydrate formed through autoclave heating is shown as orthorhombic crystals, while that obtained from applying microwave energy are more dispersed, almost spherically shaped with size within the range 14 nm to 34 nm. This result clearly supports the SEM result in Figure 2(a).

**Table 1.** Comparison of the composition of the crude gypsum (CG), purified gypsum (PG) and standard dental stone powder (SG).

| Constituent | Composition (wt%) | | |
| --- | --- | --- | --- |
| | CG | PG | SG |
| $SiO_2$ | 5.22 | 0.17 | 0.01 |
| $Fe_2O_3$ | 0.76 | 0.01 | - |
| CaO | 34.30 | 42.75 | 42.33 |
| $SO_3$ | 23.80 | 51.30 | 55.61 |
| MgO | 0.50 | 0.28 | - |
| $Na_2O$ | 0.03 | 0.01 | 0.01 |
| $K_2O$ | 0.01 | 0.01 | 0.01 |
| $Al_2O_3$ | 0.33 | 0.15 | 0.01 |
| $P_2O_5$ | 0.028 | 0.02 | 0.01 |
| $TiO_2$ | 0.034 | 0.01 | 0.01 |
| MnO | 0.03 | 0.01 | - |
| SrO | 0.42 | 0.18 | - |
| $Cr_2O_3$ | 0.03 | 0.01 | - |
| Zn | 0.041 | 0.02 | - |
| Ni | 0.052 | 0.02 | - |
| Cu | 0.03 | - | - |
| Pb | 0.055 | - | - |
| LOI | 15.2 | 5.05 | 1.01 |
| Total $CaSO_4$ | 58.10 | 94.05 | 97.94 |
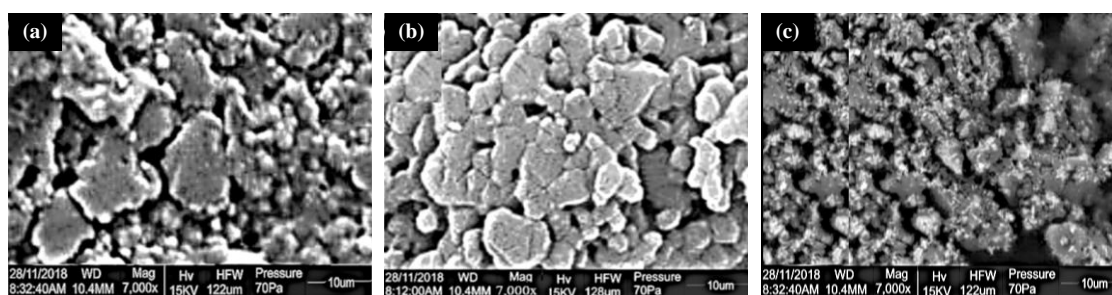


**Figure 2.** SEM micrographs of the hemihydrates obtained by treating the gypsum (a) at 120°C for 1 h in an oven (b) in autoclave pressure and (c) in microwave, showing different morphologies.
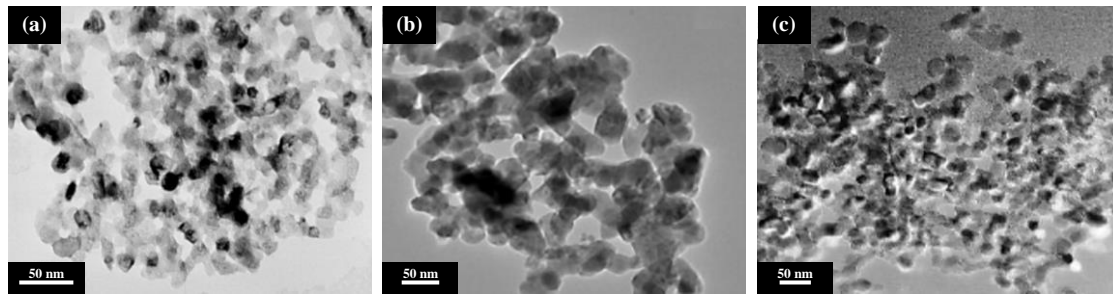
**Figure 3.** TEM images the hemihydrates obtained via (a) dry calcination in the oven, (b) autoclave treatment condition and (c) microwave energy.

## 4. Conclusions

Locally sourced gypsum has been purified by applying retrograde solubility method. The percentage purity of the crude gypsum rose from 58.10% to 94.05%. The purified gypsum when exposed to different thermal treatment methods transformed to hemihydrates having different morphologies with different crystalline structures and size dimensions. The α-hemihydrate formed through microwave assisted heating, in particular, gave the smallest particle size with good distribution to present a large surface area. This study showed that the physical properties of the gypsum depend on method of heat treatment and hence could provide useful insights on how to tune up the mechanical property of gypsum products. More, importantly, the unique method employed in purifying the crude gypsum is cheap and facile and could be further developed and upscaled for large scale purification of gypsum obtained from their natural deposits.

## Acknowledgements

## References

[1] K. Asante – Kyei, "Manufacturing of local plaster of Paris (P.O.P) from salt residue mined in Sege in the Dangme East District of the Greater Accra Region of Ghana," *Research Journal of Environmental and Earth Sciences*, vol. 4, no. 4, pp. 953-958, 2012.

[2] P. Coquard, R. Boistelle, L. Amathieu, and P. Barriac, "Hardness, elasticity modulus and flexion strength of dry set plaster," *Journal of Materials Science*, vol. 29, no. 17, pp. 4611-4617, 1994.

[3] J. Karni, and E. Karni, "Gypsum in construction: origin and properties," *Materials Structures*, vol. 28, no. 2, pp. 92-100, 1995.

[4] M. Arikan, and K. Sobolev, "The optimization of gypsum-based composite material," *Cement and Concrete Research*, vol. 32, no. 11, pp. 1725-1728, 2002.

[5] P.E. Harris, S. Hoyer, T.J. Lindquist, and C.M. Stanford, "Alterations of surface hardness with gypsum die hardeners," *Journal Prosthetic Dentistry*, vol. 92, no. 1, pp. 35-38, 2004.

[6] L.G.N. Melo, M.J.H. Nagata, A.F. Bosco, L.L.G Ribeiro, and C.M. Leite, "Bone healing in surgically created defects treated with either bioactive Glass particles, a calcium sulfate barrier, or a combination of both materials," *Clinical Oral Implants Research*, vol. 16, no. 6, pp. 683-691, 2005.

[7] A. Papageorgiou, G. Tzouvalas, and S. Tsimas, 'Use of inorganic setting retarders in cement industry," *Cement and Concrete Research*, vol. 2, no. 2, pp 183-189, 2005.

[8] C.P. Peters, J.L. Hines, K.N. Bachus, M.A. Craig, and R.D. Bloebaum, "Biological effects of calcium sulfate as bone graft substitute in ovine metaphyseal defects," *Journal of Biomedical Materials Research A*, vol. 76, no. 3, pp. 456-462, 2005.

[9] T. Sievert, W. Wolter, and N.B. Singh, "Hydration of anhydrite of gypsum ($CaSO_4.II$) in a ball mill," *Cement and Concrete Research*, vol. 35, no. 4, pp. 623-630, 2005.

[10] M.D. Dogara, and J.O. Aloa, "Preliminary estimate of gypsum deposit based on Wenner and Schlumberger electrical resistivity methods at Ikpeshi, Edo State, Nigeria," *Scientific World Journal*, vol. 12, no. 2, pp. 19-23, 2017.

[11] Trendeconomy. (2021). Annual International Trade Statistics by country (HS02), Reporting period: 2002-2020. Available: https://trendeconomy.com/data/h2/Nigeria/2520.

[12] U. Lar, Local sourcing of gypsum for industrial utilization in Nigeria, *Nigerian Society of Chemical Engineers Conference*, Abuja, Nigeria, 2016.

[13] J. Moisset, and A. Petit, Process for Preparation of Purified Calcium Sulfate in an Aqueous Medium, *US Patent, Application* 5,173,284 A, 1992.

[14] E.M. van der Merwe, and C.A. Strydom, "Purification of South African phosphogypsum for use as Portland cement retarder by a combined thermal and sulphuric acid treatment method," *South African Journal of Science*, vol. 100, no. 9, pp. 411-414, 2004.

[15] H. Ölmez, and E. Erdem, "The effects of phosphogypsum on the setting and mechanical properties of Portland cement and Trass cement," *Cement and Concrete Research*, vol. 19, no. 3, pp. 377-384, 1989.

[16] Y. Erdogan, A. Demirbas, and H. Genc, "Partly refined chemical by-product gypsums as cement additives," *Cement and Concrete Research*, vol. 24, no. 4, pp..601-604), 1994.

[17] M. Singh, M. Garg, C.L. Verma, S.K. Handa, and R. Kumar, "An improved process for the purification of phosphogypsum," *Construction and Building Materials*, vol. 10, no. 8, pp. 597-600, 1996.

[18] S. Al-Jabbari, F. Faisal, F. Ali, and S. Nasir, "Scientific Research Council," *Baghdad, Building Research, (Baghdad)*, vol. 7, pp. 49-69, 1988.

[19] A. Jarosinski, "Properties of anhydrite cement obtained from apatiapatite phosphogypsum. properties of anhydrite cement obtained from apatite phosphogypsum," *Cement and Concrete Research,* vol. 24, pp. 99-108, 1994.

[20] I. Hammas-Nasri, K. Horchani-Naifer, and M. Férid, "Rare earths concentration from phosphogypsum waste by two-step leaching method," *International Journal of Minerals Processing*, vol. 149, pp. 78-83, 2016.

[21] R. Moalla, M. Gargouri, F. Khmiri, L. Kamoun, and M. Zairi, "Phosphogypsum purification for plaster production: a process optimization using full factorial design," *Environmental Engineering Research*, vol. 23(1), pp. 36-45, 2018.

[22] J. Kaszuba, B. Yardley, and M. Andreani, "Experimental perspectives of mineral dissolution and precipitation due to carbon dioxide-water-rock interactions," *Reviews in Mineralogy and Geochemistry*, vol. 77(1), pp. 153-188, 2013.

[23] A. Klimchouk, "The Dissolution and conversion of gypsum and anhydrite*," International Journal of Speleology*, vol. 25(3-4), pp. 21-36, 1996.

[24] N.B. Singh, and B. Middendorf, "Calcium sulphate hemihydrate hydration leading to gypsum crystallization," *Progress in Crystal Growth and Characterization of Materials*, vol. 53(1), pp. 57-77, 2007.

[25] Q.L. Yu, and H.J.H. Brouwers, "Thermal properties and micro-structure of gypsum board and its dehydration products: a theoretical and experimental investigation," *Fire Materials*, vol. 36(7), pp. 575-589, 2011.

[26] Y. Li, Q. Li, and H. Ma, "The voids formation mechanisms and their effects on the mechanical properties of flax fiber reinforced epoxy composites," *Composites Part A: Applied Science and Manufacturing*, vol. 72, pp. 40-48, 2015.