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Development of hydrometallurgical purification process for Nigerian gypsum ore in hydrochloric acid. Part II: Recovery of pure gypsum from leached liquor

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***Abstract*—As the world grapples with the challenges of resource scarcity and sustainability, the need to develop indigenous raw materials has gained paramount importance. To achieve self-sufficiency and reduce dependence on foreign sources, harnessing hydrometallurgical processes to extract valuable elements from ores presents a promising solution. Raw gypsum from Postikum, Nigeria, was leached in hydrochloric acid to obtain a pure calcium sulphate dihydrate. The dissolution kinetics have been reported elsewhere. This present study focused on optimizing the recovery of pure gypsum by varying acid concentration, temperature, and solid-liquid ratio. Additionally, the recyclability of regenerated hydrochloric acid was tested. The characterization of the raw gypsum ore (RWG), leached residue (LR), and recovered pure gypsum (RCG) was done using SEM-EDS, XRF, and XRD, respectively. The recovered gypsum was characterised by a brilliant white colour in contrast to the initial brown colour of the ore. XRF results show that RWG contains 50.48% SO_3 while RCG contains 57.72 %. XRD results revealed that RWG contains gypsum, magnesite, mordenite, witherite, and calcite, LR contains mordenite, witherite and quartz while RCG consists of gypsum crystal phase only with no impurities. Remarkably, 85% RCG was successfully recovered at the fourth recycle stage of HCl lixiviant. These findings demonstrate that hydrometallurgical treatment of gypsum ore with hydrochloric acid can produce very pure gypsum.**

***Keywords*—Resource scarcity, indigenous materials, hydrometallurgy, leaching, gypsum**

I. INTRODUCTION

The development of cheap alternate routes for production with readily available materials is one of the challenges for researchers in developing countries and indeed around the globe. It is estimated that there are about 1 billion metric tonnes of gypsum in several parts of Nigeria such as Nafada/Bajoga in Gombe State, Fika in Yobe State, Guyuk/Gwalura in Adamawa State, Wurno in Sokoto State and Igankoto in Ogun State [1].

Diverse gypsum deposits exhibit variations in their purity, structure, and color. The primary impurities found include calcium carbonate (limestone), mordenite, witherite, quartz, dolomite, and, on rarer occasions, silica, bitumen, glauberite, and polyhalite. [2]. The purity of gypsum ore is usually above 80% except for some low-grade gypsum with 50 – 80% purity [3]. Utilization of abundantly available gypsum in Nigeria is limited by the presence of impurities which affects its mechanical performance and aesthetics. Previous efforts on the purification of gypsum mainly include the mechanical removal of mud, clay and other associated particles by washing with water [4] and elutriation in hot water (60-90ºC) to remove organic impurities [5]. These methods remain ineffective in removing chemically bounded impurities. Hot fluorosilicic acid (F_6H_2Si / H_2SiF_6) has been employed to purify gypsum and it resulted in a high percentage purity [6]. However, this acid is not readily available and is expensive. Removal of impurities in gypsum to obtain highly pure products that meet industrial applications should be carried out at a minimum cost.

The solubility of gypsum has undergone thorough investigation across various mediums. [7-12]. However, the study of the recovery of gypsum from solution and evaluation of its purity is scarce. Therefore, the present study is focused on developing a method of purification of gypsum ore via a hydrometallurgical route. Gypsum dissolves in various solvents, but, recovering its pure phase from most of these solvents is a difficult task. For example, hydrogen trioxonitrate can dissolve most ores because it readily ionises but the recovery of pure gypsum from the solution would require the addition of sulphuric acid [7,10]. This study seeks to establish the efficiency of hydrochloric acid as a viable option for the development of a hydrometallurgical route for gypsum ore purification. We have reported the dissolution kinetics of the gypsum ore in HCl elsewhere [13]

II. MATERIALS AND METHODS

A. Sample collection and preparation

The gypsum ore sample utilized in this investigation was sourced from a gypsum quarry located in Potiskum, Yobe State, Nigeria. The sample underwent a pulverization process and subsequent sieving to achieve a particle size of -90 to +63µm. For solution preparation, Hydrochloric acid of Chemie Lobal analytical grade and distilled water were employed.

B. Gypsum Ore Leaching and Pure Gypsum Recovery Procedure

The leaching method employed in this study has been previously documented [13]. Following leaching, the leached liquor was subjected to hot suction filtration to separate insoluble impurities. Subsequently, the cooled solution allowed for the precipitation of pure gypsum, which was then filtered, rinsed, and characterized. The study also evaluated the influence of experimental variables like hydrochloric acid concentration, leaching duration, temperature, and the ratio of solid to liquid. Furthermore, the potential for recycling hydrochloric acid was explored.

The microstructural features, surface morphology, and elemental makeup of the original gypsum ore (RWG), the residue after leaching (LR), and the gypsum recovered (RCG) were examined using a Leo 1450 Scanning Electron Microscopy with Energy Dispersive Spectroscopy (SEM-EDS). The imaging was carried out at magnifications of 200X and 1.0KX, with a working distance of 13 mm and carbon coating. For element analysis, an Esprit 1.82 software-equipped Brinker X-Flash detector was used. The chemical composition of the samples was investigated using an EDX3600B Skyray X-ray fluorometer. Phase identification was accomplished using a GBC-enhanced mini-materials analyzer (eMMA) X-ray diffractometer.

III. RESULT AND DISCUSSION

A. Effect of Hydrochloric Acid Concentration

Fig. 1 illustrates the influence of hydrochloric acid concentration on the fraction (α) of dissolved gypsum ore (RWG) and the subsequent recovery of pure gypsum (RCG). In alignment with the observations by Baba et al. [14], it was noted that the dissolution of RWG escalates with higher concentrations of hydrochloric acid. The maximum dissolution rate, reaching 95%, was attained with a hydrochloric acid concentration of 6.0 M. Following the filtration to isolate undissolved impurities and subsequent cooling, a distinct transformation occurred: the initial brown hue of the ore (RWG) transitioned into a brilliant white precipitate of pure gypsum (RCG).

Furthermore, the quantity of RCG obtained exhibited a direct positive correlation with the acid concentration. As the acid concentration increased, so did the amount of RCG recovered. The maximum recovery rate, reaching 46%, was observed at a hydrochloric acid concentration of 6.0 M. The dissolution of gypsum in HCl is described by Equation 1. However, it is important to note that the calcium chloride formed is highly soluble, thus favoring the formation of less soluble $CaSO_4$.

$$CaSO_4.2H_2O + 2HCl_{(aq)} \underset{\text{Cooling}}{\overset{\text{Heating}}{\rightleftarrows}} CaCl_{2(aq)} + H_2SO_{4(aq)} + 2H_2O_{(l)} \quad (1)$$

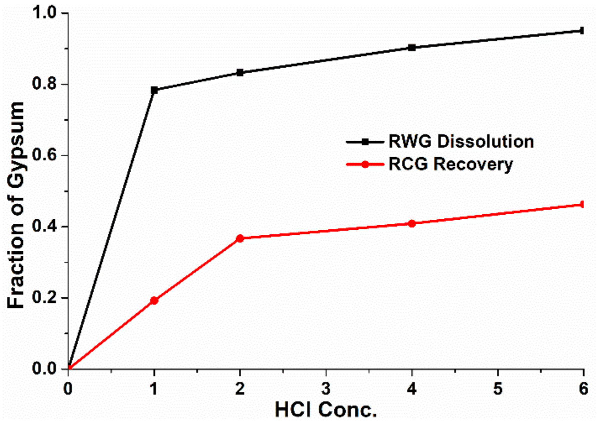

Fig. 1. Fraction of gypsum recovered at different concentrations of hydrochloric acid.

B. Effects of Reaction Time

The effect of leaching time on the dissolution and recovery of pure gypsum at a hydrochloric acid concentration of 6.0 M is illustrated in Fig. 2. Dissolution of the ore has an upward trend in correlation with time, peaking after the fifth minute. This was followed by an abrupt decline due to oversaturation and spontaneous precipitation of RCG prior to the separation of LR. Thus, prolonged leaching time leads to the co-precipitation of RCG along with impurities.

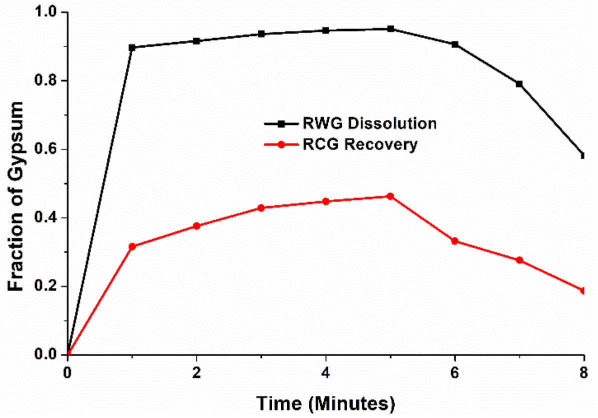

Fig. 2. Fraction of RWG dissolved and RCG recovered at different leaching times.

C. Effect of Temperature

The experiment on the effect of temperature shows (Fig. 3) that 80 °C is optimum for obtaining the highest yield of RCG from RWG. The study was constrained to a maximum temperature of 80 °C to prevent substantial evaporation of HCl at elevated temperatures. [15]. Besides this, a further increase in temperature led to spontaneous precipitation of RCG before a substantial quantity of RWG dissolves thereby decreasing the fraction of RCG obtained.

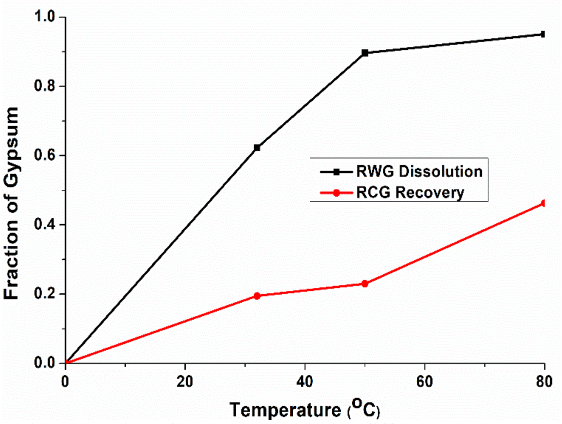

Fig. 3. Fraction of gypsum recovered at different temperatures.

D. *Effect of Solid-Liquid Ratio*

RWG was leached at different solid-liquid ratios maintaining other experimental conditions such as HCl conc. of 6.0 M, temperature of 80 °C, stirring speed of 400 rpm, and reaction time of 5 minutes. The results in Fig. 4 indicate that as the solid-liquid ratio increases, the dissolution of RWG decreases. This result is similar to other reports on the effects of solid-liquid ratio on dissolution [14], [15]. The sharp decrease obtained after 80 g/L is due to supersaturation and spontaneous precipitation of RCG before the leached residue was filtered off. The percentage yield of RCG however, increases with an increase in solid-liquid ratio until it reaches maximum at 80 g/L.

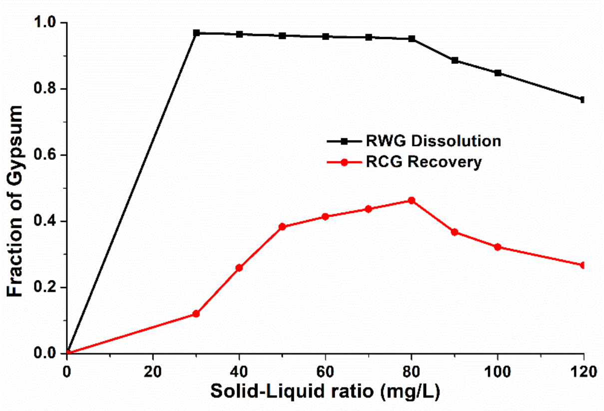

Fig. 4. Fraction of gypsum recovered at different temperatures.

E. *Effect of Recycling HCl lixiviant*

HCl lixiviant recovered after leaching at optimum conditions proved to be useful for further leaching with better RCG yield. Several experiments were conducted to study the effect of serial leaching with recovered HCl at the optimum condition of 6.0 M HCl, 80 °C, RWG particle size of -90+63 μm and dissolution time of 5 minutes,. The results of this investigation are presented in Fig. 5. It was demonstrated that the dissolution of RWG decreases with an increase in the number of HCl recycles due to the presence of already dissolved gypsum. The yield of RCG increased significantly with an increase in the number of times the lixiviant was recycled up to 85.2 %. The yield, however, began to decrease after the fourth cycle due to spontaneous precipitation caused by over-saturation. Fig. 5 also shows that the quantity of recycled lixiviant recovered decreases with subsequent usage which was lost to rinsing during RCG recovery.

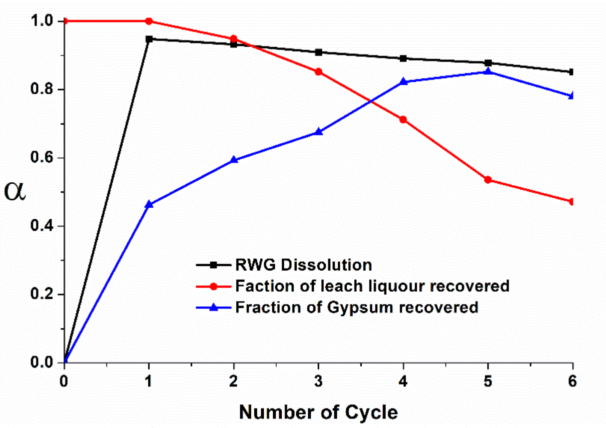

Fig. 5. Fraction of RWG dissolved RCG yield and HCl solution recovered.

F. *X-Ray Fluorescence Analysis of RWG and RCG*

The results of the chemical composition of the raw gypsum ore (RWG) and recovered gypsum samples (RCG) obtained by XRF and expressed as oxide wt% are shown in Table 2. The major oxides in the RWG are CaO (46.23 wt%) and SO_3 (50.48 wt%). Others are SiO_2, Al_2O_3, TiO_2, and MnO. The results also show that TiO_2, MnO and Al_2O_3 have been leached out completely while the amount of SiO_2 reduced significantly ($p < 0.05$) in RCG. This is an indication of an increase in the purity of the gypsum sample.

Table 2: Chemical composition of raw gypsum (RWG) ore and Recovered Gypsum (RCG)

Compound	**CaO**	**SO_3**	**SiO_2**	**TiO_2**	**MnO**	**Al_2O_3**
RWG (Wt %)	46.23	50.48	1.253	0.044	0.039	1.624
RCG (Wt %)	42.59	57.72	0.634	-	-	-

G. *X-Ray Diffractometric Analysis of RWG, LR and RCG*

In Figure 6, the diffractograms of RWG, LR, and RCG were overlaid to facilitate comparison. Phase identification was achieved using the Joint Committee on Powder Diffraction Standard (JCPDS) File number. The results clearly demonstrate that the ore phase (RWG) is predominantly composed of gypsum, corroborating the chemical analysis findings obtained via X-ray fluorescence. The mineral composition of the ore encompasses Gypsum (01-070-0982), Mordenite (49-0924), Witherite (5-0378), and Quartz (46-1045).

Contrastingly, the diffractogram of the leached residue (LR) did not exhibit the presence of gypsum phases. Instead, the prevailing phases were Mordenite, Witherite, and Quartz [2], [17-19]. In the RCG sample, only the gypsum phase (01-070-0982) was discernible. Notably, the diffractogram peaks of RCG manifested as sharp and well-defined, indicating a crystalline nature and confirming the composition of RCG to be solely crystal particles.

Fig. 7 presents scanning electron microscopy (SEM) micrographs of RWG, LR, and RCG. The micrographs provide visual evidence that RWG and LR exhibit a non-uniform microstructure, indicating a heterogeneous phase characterized by the conglomeration of various compounds (Figures 7a and 7b). This observation aligns with the results obtained from X-ray diffractometer analysis, which identified the presence of multiple phases. In contrast, RCG exhibits a uniform microstructure, indicating a homogeneous phase.

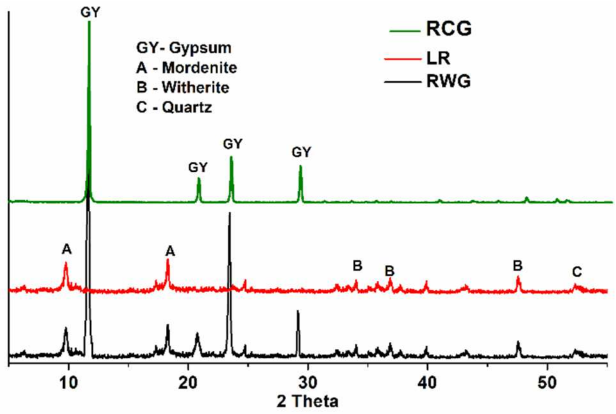

Fig. 6. Diffractogram of RWG, LR and RCG

H. *Scanning Electron Microscopic Analysis of RWG, LR and RCG*

The micrographs at 200X and 1.0 KX magnifications in Figure 7c and 7d, respectively, reveal a cluster of needle-like particles. This finding is consistent with the results obtained from the phase determination of RCG using X-ray diffractometer analysis. The needle-like structure observed also indicates that RCG has the potential to form α-hemihydrate when two-thirds of its water of crystallization is removed. This particular form of hemihydrate is known to possess excellent mechanical properties, as reported in references [20], [21].

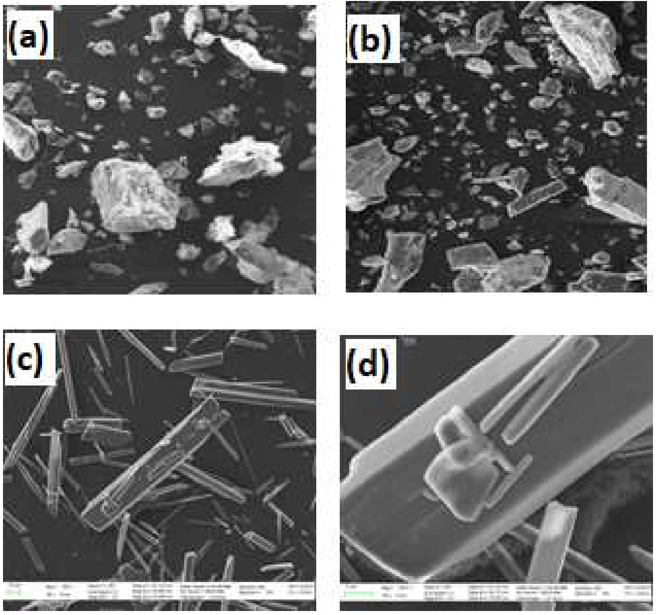

Fig. 7 SEM image of (a) raw gypsum (RWG) at (a) 200 X, (b) leached (LR) at 200 X, (c) pure gypsum (RCG) at 200 X and (d) pure gypsum (RCG) at 1.0 KX magnification

I. *Purification Process Optimisation Flow-Chart*

The gypsum produced exhibited significantly superior quality compared to the initial material, evident from the degree of whiteness as illustrated in Figure 8. The plaster of Paris orthopedic bandage was prepared using RCG. The detailed evaluation of the bandage's physical and mechanical properties has been documented in a separate publication [22]. Taking into account the high quality of the purified gypsum achieved through the refinement process and the established optimal conditions, a comprehensive hydrometallurgical scheme outlining all the analytical procedures is depicted in Figure 9.

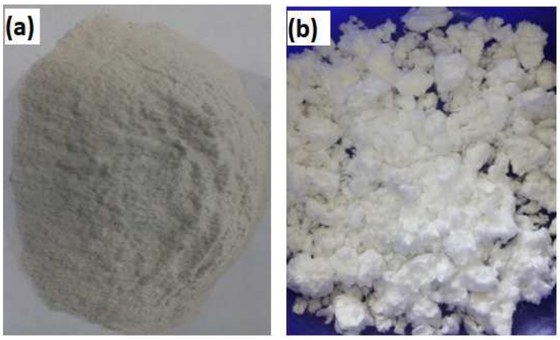

Fig. 8. Images of (a) RWG (b) RCG

IV. CONCLUSION

A hydrometallurgical purification process route was formulated for Nigerian gypsum ore using hydrochloric acid. The optimization study revealed that a 6.0 M hydrochloric acid solution, a temperature of 80°C, a stirring speed of 400 rpm, and a solid-liquid ratio of 80 g/L resulted in the highest yield of pure gypsum. The developed route incorporates the recycling of the lixiviant, thereby enhancing efficiency and reducing the cost of material purification. The recovered gypsum demonstrated exceptional purity, exhibiting a brilliant white color in stark contrast to the original brown hue of the ore. This renders it suitable for applications where aesthetics and high purity are paramount.

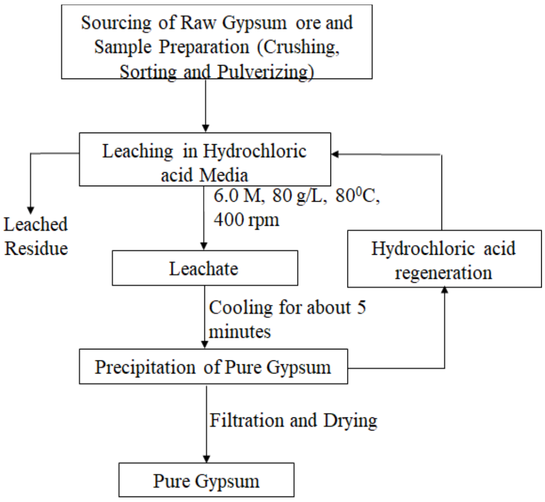

Fig. 9. Hydrometallurgical flowchart for the purification of gypsum ore

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