

# Evaluation of raw and chemically treated waste phosphogypsum and its potential applications

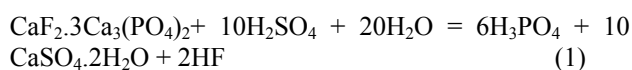
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**Abstract.** A million tons of Phosphogypsum (PG) is stacked in the environment every year and is progressively considered an asset. South African construction industry is expanding as a result of infrastructural developments in the country, the reuse of PG in this industry is considered for recycling and reducing the stacks in landfills. Phosphogypsum is known for its limited ability to use in cement industry due to its phosphorus and radionuclides impurities. This study was conducted to reduce these impurities and investigate the probability of PG application in building and construction. Leaching of PG with citric acid was conducted whereby a relative proportion of  $P_2O_5$  and radionuclides was reduced in the material, constituents which contributes to strengths reduction. Optimum moisture Contents and maximum dry densities were determined for various PG content mix designs in which Lime and Fly Ash were added to stabilise PG material. The composites were compacted at various moisture contents and cured at low and elevated temperatures of at 40 °C and 80 °C for 4 days. The results obtained shows that for unconfined compressive strengths; the composites produced from PG, and cured at high temperature qualified for the use in construction industry.

## 1 Introduction

Environmental problems do not only take a lead in the reported crisis but also threatens the existence of humanity in the near future. Designing an environmental friendly, sustainable products and processes is a major problem in the developing country like South Africa. In addition to that, engineers have to find new ways to recycle and re-use all the alleviating percentage of accumulated by-products. South Africa has limited resources and this makes it a necessity for the adoption of a number of policies, such as pollution prevention, and recycling of waste material for better use. South Africa has a highly developed domestic and export oriented phosphate industry, with the largest igneous phosphates deposits located in Phalaborwa in the northern province of the country [1]. Residual deposits of Phosphogypsum are readily available in large quantities in South Africa and currently are landfilled or pumped into the sea [2]. Waste Phosphogypsum is produced as a by-product during the treatment of phosphate concentrates with sulphuric acid to produce phosphoric acid according to the following simplified chemical reaction [3].



The Phosphogypsum produced can appear as a di-hydrate ( $CaSO_4 \cdot 2H_2O$ ) or hemi-hydrate ( $CaSO_4 \cdot 1/2H_2O$ ) form depending on the processing form [3]. This by-product is then filtered from the produced phosphoric acid aqueous solution and then transferred as a wet cake to open air

storages [4]. The storage of PG without any prior treatment requires large land areas and may lead to serious environmental contamination of soils, water and the atmosphere. For instance the elements present in the PG may be leached and deposited into nearby soil and water systems, and finally to animals and humans. Soil compaction means applying external pressure to the soil mass so that its characteristic properties improve with regard to construction purposes. 100×100mm mould were used for compaction of material after stabilising with Fly Ash and lime. Three layer techniques was used for specimen casting.

With reference to TRH4 [5], Phosphogypsum is classified under Cemented Materials (C1-C4) this is due to that it is initially elastic and have limited tensile strength. They also crack during drying as a result of shrinkage. Thus it is necessary treat it with lime to reduce the cracks. A C2 material may be used when a non-pumping, erosion resistant layer is required. Both C3 and C4 materials can be used in place of natural gravel layers in base and subbase. They can either be cement treated or lime treated depending on the natural properties of the material. However their long term Durability and resistance to erosion has to be carefully tested [TRH4] [5].

The aim of this research was to enhance the geochemical and geotechnical properties of Phosphogypsum (PG) for the use as a building and construction material.

## 2 Experimental

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## 2.1 Leaching of and preparation of phosphogypsum Elemental compositions before leaching

A 20 L reactor was used for the experiment and 0.5 M of citric acid was used as the concentration for the leaching reagent. Leaching tests were carried over 24 hours, thereafter the sample was filtered, the solids were dried in the oven at 50 °C and the solution was stored for further analysis. The lumps of the dried solids were broken to 80%-75 μ. This is the material referred to as treated PG. After treating PG, geotechnical and geochemical tests were conducted. Maximum dry density (MDD) and Optimum Moisture Content (OMC) of the treated PG was determined. A schematic diagram for the leaching process conducted is shown in Figure 1.

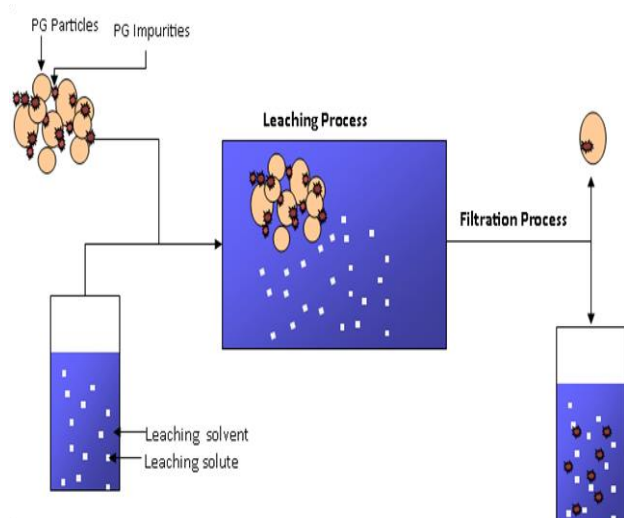


Fig. 1. PG leaching process.

## 2.2 Mix Designs preparations, casting and curing

Four different mix designs were prepared for both Raw and treated PG, the designs were composed of Lime, Fly ash and the material of interest PG. In all designs the percentage by weight (w%) of Lime was kept constant at 20% while PG and Fly Ash were varied. The proportion of PG was decreases by ten percent from 60% in design 1, to 30% in design 4. While Fly Ash proportion was increased by ten percent in each design from 20% in design 1 to 50% percent in design 4. The MDD and the OMC obtained were mixed per design. The mixture was then cast into a 100mm×100mm mould. The moulds were then re-assembled and the moulded sample removed as a specimen. The specimen were tightly covered with a plastic sample bag before being placed into an oven at 40 °C for five days. This procedure was repeated for 80 °C and 100 °C specimen.

## 2.3 Testing of PG specimen

After five days the specimen were removed from the oven and the Unconfined Compressive Strength (UCS) test performed on them. After UCS testing a small portion of a specimen was milled using a rod mill and the

milled sample were analyzed using XRF for elemental composition. Of the four designs at 40 °C, 80 °C and 100 °C, two designs that showed high or better UCS at their respective temperatures were chosen for casting of specimen that were tested for durability. For durability tests two specimen per design were cast, covered with a plastic and cured in the oven for five days. After five days the specimen were removed from the oven weighed (Wi) in a mass scale and fully submerged in water for 24 hours (without plastic). After 24 hours they were removed from the water and weighed (WF) after removing excess water from the specimen, then the UCS test performed.

## 3 Results and discussion

### 3.1 XRF analysis of phosphogypsum

The XRF analyses results for the Raw and Treated PG are illustrated in Table 1.

Component	Raw PG	Treated PG
F	1.06	0.86
Na <sub>2</sub> O	0.07	0.06
MgO	0.08	0.02
Al <sub>2</sub> O <sub>3</sub>	0.23	0.23
SiO <sub>2</sub>	1.37	1.52
P <sub>2</sub> O <sub>5</sub>	1.28	0.84
SO <sub>3</sub>	51.01	50.31
K <sub>2</sub> O	0.02	0.02
CaO	43.65	44.85
Fe <sub>2</sub> O <sub>3</sub>	0.12	0.14
Radionuclides	1.11	0.08

The main targeted impurity was phosphorus and purification was successfully achieved as the relative proportion of P<sub>2</sub>O<sub>5</sub> decreased by an enormous 34.7%. The CaO relative proportion increased by 2.7 %. The relative proportion of F and total radionuclides were also decreased, indicating that these components had a significant reaction with Citric acid concentration reducing the impurities and rendering PG more environmentally friendly by reducing the level of radioactive particles. The constituent that was leached out in a higher percentage is that of Magnesium Oxide MgO with a relative proportion of 72.3%. According to Liz et al. (2004), MgO is an environmentally friendly building material that has strength and resistances due to its very strong bonds between magnesium and oxygen atoms that form MgO molecules [6].

### 3.2 Maximum dry density (MDD), optimum Moisture content (OMC) and density for PG mx design

The relationship portrayed in Table 2 shows that at a low PG content of 30% the specific gravity seems to increase and reached a peak  $2.13\text{gcm}^{-3}$  at 40% PG content before continuously decreasing to a low 1.98 at 60% PG proportion. This maximum SG ( $2.13\text{gcm}^{-3}$ ) is lower than  $2.60\text{gcm}^{-3}$ ; this means that PG has high amounts of organic matter or porous particle [ASMTM D 854-92] [7]. With this knowledge, it is safe to deduce that PG has a low holding capacity of water, and becomes saturated very quickly. The MDD of phosphogypsum was the highest at PG 50, indicating that the highest dry density obtained by compaction at its optimum moisture content is  $1204\text{g/cm}^3$  and 22.5% OMC. Table 2.

### 3.3 Unconfined compressive strength (UCS) at different moisture content and temperature

Figure 2 shows the UCS test results against the moisture content percentages added into the mix design 1 and 2 for both raw and treated PG at 40 °C and 80 °C.

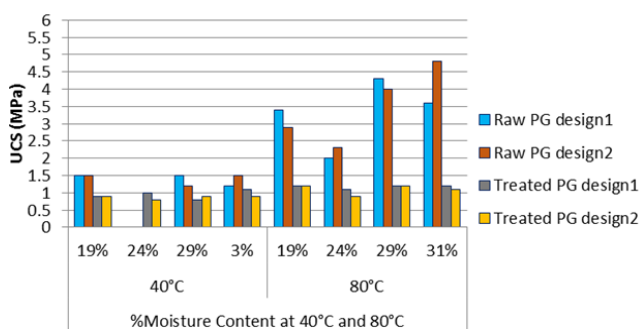


Fig. 2. UCS and moisture content bar graph at 40°C and 80°C.

After curing the specimen in the oven for five days UCS was measured. The UCS values improved at the elevated temperature of 80 °C for both treated and raw PG. However treated PG design specimen have yielded lower UCS values than Raw PG for both temperatures investigated. The UCS for treated PG vary from 0.8 to 1.2 MPa and from 1.2 to 4.8 MPa for Raw PG. In both cases the minimum limit range value is obtained at low temperature of 40 °C and low moisture contents while the maximum range limit is attained at the high temperature of 80 °C and high moisture content. This indicate that compressive strength of specimen is improved by curing at high temperature and high moisture contents.

### 3.4. Water absorption of the produced specimen for raw and treated PG

It is well known that clay-like products expand over time as they absorb water into their structure. According to IS 3495 [8], fly ash specimen are not expected to absorb water more than 20%. To perform water absorption test specimen are oven dried at a certain temperature till they attained a constant weight. They are then cooled at room temperature and weighed ( $W_i$ ). After attaining the initial weight they are totally submerged in water for 24hrs, removed wiped out of any traces of water and weighed immediately ( $W_f$ ). Using the masses measured a water absorption percentage is calculated with an equation below.

$$\text{Water absorption in \% by weight} = (W_f - W_i) / W_i \times 100 \quad (2)$$

It is preferred that specimen absorb as less water as possible (24 hr absorption process) in order for them to give high durability results. After observing that the highest unconfined compressive strength was obtained at 80 °C, it was then decided that specimen that will undergo inundation tests be oven dried at the same temperature (80 °C) for five days. Upon measuring the initial weight ( $W_i$ ) and the final weight ( $W_f$ ), the % water absorption was calculated using Equation 2. The overall water absorption percentage decreases with an increase in moisture content of the specimen for both the raw and treated PG material, Table 3. Even so the Raw PG specimen had the lowest water absorption percentages when compared to the treated PG. According to the South African Pavement Manual [9] the required maximum water absorption for C3 material should be 20% or less, which was achieved by raw PG material at 29% and 31% moisture content. For C4 material the limit for water absorption maximum of 30 % or less which was achieved by treated PG Material from 24 % to 31 % moisture content.

### 3.5. Durability of the produces specimen

Since Durability is inversely proportional to % water absorption it is theoretically correct to state that raw PG specimen will be less durable if designed with moisture contents of 24 % and less while treated PG will be less durable with moisture contents of 19% or less. To achieve highest durability results these specified moisture contents must be increased to 31%.

**Table 2.** MDD and OMC.

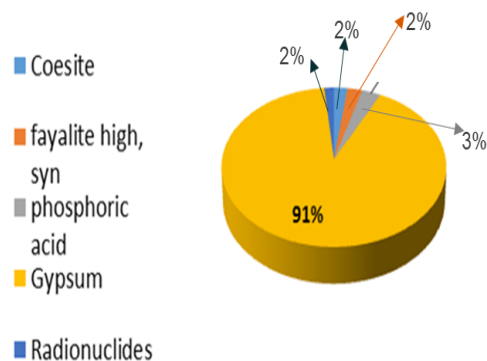
Mix design	Composition	MDD(g)	OMC (%)	Density (g/cm <sup>3</sup> )
Design 4	L20: PG30 : FA50	1126	24	2.04
Design 3	L20: PG40 : FA40	1072	23	2.13
Design 2	L20: PG50 : FA30	1204	22.5	2.05
Design 1	L20: PG60 : FA20	1144	19	1.99

**Table 3.** Water absorption of the produced specimen.

Moisture content (%)	PG content	Raw PG			Treated PG		
		Wi	Wf	%water absorption	Wi	Wf	%water absorption
15	PG60	1193	1618	35.62	1182	1600	35.36
	PG50	1187	1606	35.30	1159	1564	34.94
19	PG60	1222	1608	31.59	1200	1595	32.92
	PG50	1221	1572	28.75	1320	1495	13.26
24	PG60	1260	1562	23.97	1274	1593	25.04
	PG50	1286	1606	24.88	1273	1545	21.37
29	PG60	1297	1564	20.59	1286	1494	16.17
	PG50	1170	1399	19.57	1234	1527	23.74
31	PG60	1358	1559	14.80	1271	1490	17.23
	PG50	1364	1576	15.54	1329	1508	13.47

### 3.6. The mineralogy of the treated PG

The XRD of the treated PG is shown in Figure 3.



**Fig. 3.** Mineralogy of treated PG.

The treatment of phosphogypsum with citric acid transformed the calcium sulphate initially contained in phosphogypsum from  $\text{CaSO}_4$  to  $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$  (Figure 3). The predominant constituent in the citric acid leached material corresponded to gypsum ( $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$ ), 91%, followed by phosphoric acid ( $\text{H}_3\text{PO}_4$ ), 3%, Fayalite ( $\text{Fe}_2\text{SiO}_4$ ) with a content of 2.0% and radionuclides, 2%. Fayalite is a relatively common constituent of acidic and alkaline igneous rocks. This agrees with the XRF results obtained where the predominant elements were Ca and S. Coesite ( $\text{SiO}_2$ ), a mineral normally used in the

manufacturing of glass, electronics, abrasives and building materials was also detected with a content of 1.95%. The remaining constituents were those associated with the radionuclides

### 3 Conclusion

A PG leaching process through a single stage using citric acid as a solute removed 34.7%  $\text{P}_2\text{O}_5$  molecules, while upgrading CaO purity by 2.3%. Furthermore radioactive materials were reduced and a large 72.3%. The leaching process resulted in a more environmentally friendly yet limited strength of PG. The Minimum standard required UCS for load bearing in South Africa is 3.5 MPa. Curing PG specimen at high temperature improved the UCS results to a satisfying maximum 4.8 MPa which made them qualifying for use as building and construction load bearing material. PG developed specimen absorbed as high as 35% water at low moisture content and as low as 13% water at high 31% moisture contents. Citric acid treated PG specimen absorbed a high water percentage when compared to raw PG. When comparing durability strength; raw PG specimen are more durable than treated PG specimen. A 50% and 60% raw PG specimen at high OMC and high curing temperatures of 80 °C qualifies to be used as building, construction and backfill material.

### Acknowledgments

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