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Chemical treatment of phosphogypsum and its potential application for building and construction

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Abstract

This study investigated the use of a chemical treatment process to treat phosphogypsum waste generated from a phosphoric acid production plant and render the final product useful for building and construction applications. Four reagents namely; citric acid, oxalic acid, sodium carbonate and sodium bicarbonate were used for the reduction and removal of hazardous and radioactive constituents in the material. The results for the untreated gypsum revealed that phosphogypsum used in this study was radioactive and laden with radionuclides such as ^{210}Pb , ^{214}Pb , ^{214}Bi , ^{226}Ra , ^{208}Tl , ^{228}Ac , ^{40}K . The best leaching reagent was found to be 0.5 M citric acid as it reduced the relative proportion of contaminants contained in the material. The treated product was blended with lime and fly ash and the effect of curing temperature and phosphogypsum content on the unconfined compressive strength was investigated. Curing at higher temperatures proved to improve the strength of the specimen, the highest strength were obtained at PG content of 30%.

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1. Introduction

Phosphogypsum is worldwide generated at an estimate of around 100-280 million tons/year [1]. An export orientated and a high domestic industry has been developed over the years in South Africa, with the largest igneous phosphate deposit in Africa [2]. Phosphogypsum is a by-product from the treatment of phosphate concentrate with sulphuric acid in a wet process to produce phosphoric acid, according to equation 1, and is mostly used in making fertilizers [3]. The process produces calcium sulphate, which is separated from phosphoric acid by filtration. In the three crystals formed (anhydrite, hemihydrate, dihydrate), dihydrate: $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$ is the most common crystal type found [4]. The phosphogypsum generated in most instances is either disposed in stockpiles (landfilled) or discharged to rivers and the sea. Landfilling results in the formation of leachate that normally mobilizes hazardous constituents by transporting them to the groundwater and underlying soils [5]. The migration of gasses and leachate from the landfill boundaries and the release into the surrounding environment presents an environmental problem of a great concern to the existing and new facilities [6]. Open yards or stack yards disposal of the radioactive sludge poses a major threat to the environment. Management and handling of phosphogypsum is a major problem in phosphoric acid plants due to the large volumes, large area required and the potential release of dust, fluoride and heavy metals in seepage [7]. Naturally occurring uranium, radium and other radionuclides in the phosphate ore are present in phosphogypsum, rendering it radioactive. In the phosphoric production process uranium tend to remain with the product but radium is removed and end up in the waste stream [7]. The study performed by Bolivar et al., 2000, showed that about 80% of the ^{226}Ra , 90% of the ^{210}Po and 20% of the ^{238}U and ^{234}U originally present in the phosphate rock remains in phosphogypsum [8]. Thus, treatment with sulphuric acid leads to the production of phosphogypsum which retains about 80% of ^{226}Ra and 30% of ^{232}Th and 14% of ^{238}U . Uranium occurs naturally as radioisotopes ^{238}U and ^{235}U , while thorium occurs as ^{232}Th [9]. Other treatment processes reported to use PG waste as it is without prior treatment are expensive and consume high energy [10-14]. This study aimed at developing a suitable chemical treatment process to treat waste PG and recommend its application in building and construction. Phosphogypsum was evaluated to assess the radioactivity of the material obtained from a phosphoric acid manufacturing plant, develop a chemical treatment process to remove or reduce the radionuclides and produce a product that can be utilized for construction and building applications.

2. Experimental

Samples of phosphogypsum were collected from a phosphoric acid manufacturing plant in the Phalaborwa, South Africa. Based on the previous studies by [13-14] the concentration of 0.4 M citric acid, 0.5 M oxalic acid, 0.5 M sodium bicarbonate and 0.5 M sodium bicarbonate were prepared and used as leaching reagents. The phosphogypsum samples were dried in an oven for 24 h at 50 °C prior to conducting the leaching test work. The dried sample was then pulverized. An Eriez Magnetic Rotary Riffler was used to divide the sample and obtain a representative sample for characterization. Phosphogypsum specific gravity was determined using a gas pycnometer and a pH meter was used to measure pH. The semi quantitative chemical composition of the phosphogypsum material was determined by X-ray Fluorescence (XRF, Rigaku ZSX Primus II). Mineral species in the raw and treated material were determined by X-ray diffraction (XRD, Rigaku Ultima IV). The concentrations of radionuclides contained in the sample were measured by Gamma Ray Spectroscopy (GRS). The leaching reagents (citric acid, oxalic acid, sodium carbonate and sodium bicarbonate) were each added to the phosphogypsum at 15% solid loading. To conduct the leaching experiments a thermostatic shaker and 8 flat bottom beakers containing the homogenous material were used. The solutions were placed in a thermostatic shaker at 35 °C, and agitated at 170 rpm for 4 h. After 4 h the thermostatic shaker was switched off, the samples were filtered, the solution stored for further characterization. The solids were dried in an oven at 50 °C, after drying; the solid products were analysed using XRF, XRD and GRS. The treated and raw phosphogypsum was blended with fly ash and lime cast in 100mm x100mm moulds and cured at 80 °C for 4 days and the unconfined strength was determined.

3. Results and discussion

3.1. Radioactivity analysis

The activity concentrations of radionuclides in phosphogypsum, measured by GRS are shown in Table 1.

Radionuclide	210Pb	214Pb	214Bi	226Ra	40K	228Ac	208Tl
Bq/kg	111.51	95.46	98.85	104.53	11.1	201.21	200.83

The results revealed that the contributors to the radioactivity in the raw phosphogypsum are Tl, Ac, ^{210}Pb , ^{226}Ra , ^{214}Bi , ^{214}Pb and ^{40}K . During the phosphoric acid process the radioactive equilibrium is broken, and every radionuclide is distributed differently according to its stability. Thus, uranium mainly remains in phosphoric acid (under oxidizing conditions, up to 90%), while most of the radium is transferred into phosphogypsum [15]. The results obtained are in agreement with this behaviour, thus the activity of 226Ra and 210Pb in the uranium decay series are higher in terms of activity concentration. Numerous studies conducted show that phosphogypsum is laden with uranium; however no uranium was detected in the phosphogypsum used in this study. The major radioactivity was due to 208Tl, 228Ac, radionuclides in the thorium decay series, 226Ra, 214Bi, 210Pb and 214Pb with minor contribution of 40K. The radioactivity in phosphogypsum was from the radioisotopes in the uranium and thorium decay series.

3.2. Chemical composition of untreated phosphogypsum

Table 2. Composition of major species and impurities in raw phosphogypsum.

Na ₂ O	MgO	AlO ₃	SiO ₂	P ₂ O ₅	SO ₃	Cl	K ₂ O	CaO	Fe ₂ O ₃
0.01	0.02	0.08	0.79	1.45	53.5	0	0.01	43	0.07
SrO	Y ₂ O ₃	La ₂ O ₃	CeO ₂	Nd ₂ O ₃					
0.49	0.01	0.12	0.25	0.14					

The results showed that the concentration (% weight) of S and Ca is more than 90% of total weight, with relative proportion of 53.5 wt% and 43wt%, respectively, Table 2. Some of the major impurities in phosphogypsum were P₂O₅, SiO₂, Al₂O₃, traces of radionuclides and to a lesser extent, Na₂O, MgO, Fe₂O₃ and K₂O. Similarities can be observed in the composition of components contained in phosphogypsum when comparing the obtained results to those reported in the literature [1,3]. In phosphogypsum samples, SiO₂ may be found as quartz, and together with Al₂O₃ and Na₂O/K₂O, might indicate the presence of clay minerals [15]. The heavy metals contents in phosphogypsum are usually very low. However, some phosphate rocks show a significant strontium and rare elements level, up to 3% [16]. In this study the relative proportion of strontium was measured to be 0.49 wt%.

3.3. Mineralogy of phosphogypsum

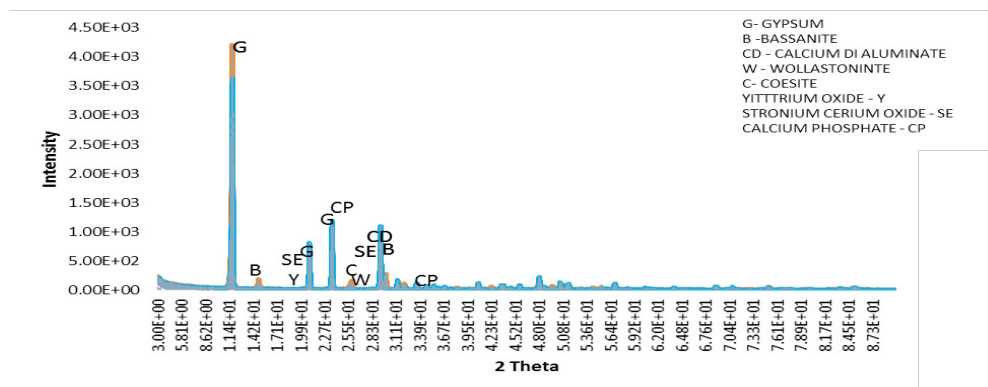


Fig. 1. XRD analysis of phosphogypsum.

The X-ray diffraction pattern of phosphogypsum is reported in Figure 1. While in phosphogypsum, gypsum generally exists as $\text{CaSO}_4 \cdot \text{H}_2\text{O}$. The chemically bound water content in calcium sulphate from phosphogypsum depends on the method of phosphoric acid production, sulphate, temperature and phosphate ion concentration. The results revealed that the main diffraction peak in the raw phosphogypsum corresponds to calcium sulphate (CaSO_4), with a content of 88.46%. This agrees with the XRF results obtained with the predominant chemicals being CaO and SO_3 . The next highest compound was bassanite, due to the reaction between phosphogypsum and sulphuric acid as illustrated in equation 1. From the literature, the majority of phosphogypsum samples showed this composition; and countries such as Brazil, calcium sulphate hemihydrate, in addition to the expected $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$, was also present [17]. P_2O_5 existence is generally in the form of H_3PO_4 , $\text{Ca}(\text{H}_2\text{PO}_4)_2 \cdot \text{H}_2\text{O}$, $\text{CaHPO}_4 \cdot 2\text{H}_2\text{O}$ and $\text{Ca}_3(\text{PO}_4)_2$. Phosphate in the raw phosphogypsum existed as $\text{Ca}(\text{PO}_3)_2$ and contributed 0.2% to the overall constituents in the material.

3.4. pH and density of phosphogypsum

The measured pH for raw phosphogypsum was 4.17 and below what was reported by other authors. Green, 2000, evaluated the use of the by-product phosphogypsum and observed that the pH of phosphogypsum varied based on the depth and that complete leaching of material increased the pH to a value of about 6.4. The minimum pH obtained was 5.3 and maximum 6.4 [17]. The specific gravity of material was 2.516, based on the standard proctor compaction, the specific gravity of phosphogypsum ranges from 2.3-2.6 [18]. The obtained specific gravity for all mix designs ranges from 2-2.13, thus agrees with these stipulated standards.

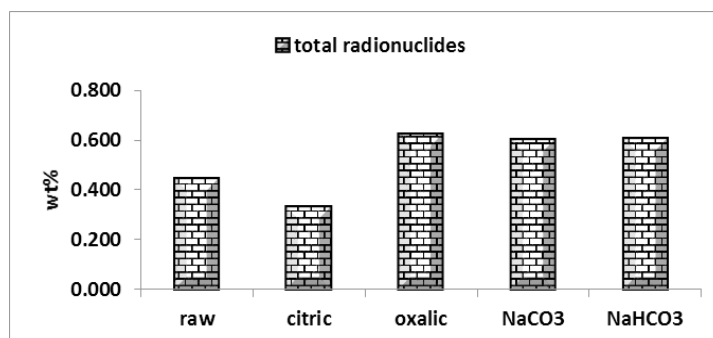


Fig. . Composition of radionuclides in phosphogypsum leaching with all four reagents at 35°C.

Figure 2 shows the relative proportion of total radionuclides in phosphogypsum, determined by XRF, after leaching with 0.5 M citric acid, 0.4 M oxalic acid, 0.4M sodium carbonate and 0.4 M sodium bicarbonate under

these conditions (temperature of 35 °C, mixing for 4 h at 170 rpm). The detected radionuclides were La, Ce, Y and Nd. The raw phosphogypsum was laden with a total of 0.522 wt% relative proportion of radionuclides. Using citric acid as a leaching reagent reduced the relative proportion of the radionuclides by 22%. With oxalic acid, sodium carbonate and sodium bicarbonate, the relative proportion of radionuclides increased, indicating that, instead of leaching out the radioactive elements in phosphogypsum, other elements were leached out, hence the increase. The leaching of other elements contained in phosphogypsum is discussed in detail in the subsequent section.

From the results presented it is evident that the lowest relative proportion (wt%) of radionuclides was obtained when citric acid was used as a leaching reagent, proving that, citric acid under above mentioned conditions can successfully be applied for the reduction of radioactive nuclides such as yttrium, lanthanum, cerium and neodymium in phosphogypsum.

Table 3. Composition of major species and impurities before and after treatment.

	SO ₃	CaO	SiO ₂	AlO ₃	P ₂ O ₅	Na ₂ O	MgO	K ₂ O	F	Cl	Fe ₂ O ₃	SrO	Radionuclides
Raw PG	53.5	43	0.8	0.8	0.2	0.01	0.02	0.01		0.03	0.74	0.4	0.5
Citric acid	54.4	42.8	0.9			0.02	0.01	0.0			0.04	0.4	0.4
Oxalic acid	39.	57.9	0.9	0.1	0.5	0.04	0.01	0.01			0.1	0.7	0.6
Sodium carbonate	30.2	61.2	1.1	0.2	2.9	3.4	0.03	0.01	0.4	0.02	0.1	0.6	0.7
Sodium bicarbonate	30.9	61.1	1.0	0.2	1.9	3.0	0.03	0.01	0.4	0.0	0.1	0.7	0.7

There was no significant change in the calcium and sulphur relative proportion (wt%) when citric acid was used as a leaching reagent. With oxalic acid, sodium carbonate and sodium bicarbonate as leaching reagents a significant change was observed, sulphur was drastically leached out and calcium relative proportion increased, Table 3. Silicate relative proportion increased in all leaching reagents. Aluminium oxide was leached out in oxalic acid medium, and its relative proportion increased when citric acid, sodium carbonate and sodium bicarbonate were used. As mentioned previously, phosphorus and fluorides in phosphogypsum must be at minimal for the material to be used further in construction applications. P₂O₅ was leached out in citric acid and in oxalic acid, and its relative proportion increased in sodium carbonate and sodium bicarbonate. No fluoride was detected in the raw phosphogypsum, citric acid and oxalic acid leached phosphogypsum, however, when leaching with sodium carbonate and sodium bicarbonate, the fluoride was exposed. Sodium oxides drastically increased when leaching with sodium carbonate and sodium bicarbonate. The increase observed was due to the entrainment of salt, since no sodium was detected in the raw phosphogypsum with XRD. Other impurities MgO, K₂O and Fe₂O₃ were detected to a lesser extent before and after treatment in all the leaching reagents and did not show significant changes. Strontium was leached out in citric acid and the relative proportion, increased in oxalic acid, sodium carbonate and sodium bicarbonate solution.

Table 4. Composition of phosphogypsum by XRD after treatment with: citric acid, oxalic acid, sodium carbonate and sodium bicarbonate.

Phases in citric acid	Content (%)	Phases in oxalic acid	Content (%)
Coesite	1.953	Sisodium disilicate	8.568
Falalite	4.001	Wollastomite	0.134
Gypsum	91.939	Gypsum	87.249
Radionuclides	2.106	Radionuclides	4.049
Phases in sodium carbonate	Content (%)	Phases in sodium bicarbonate	Content (%)
Trisodium	1.606	Calcite	21.664
Gypsum	58.891	Gypsum	76.299
Silicate	28.084	Radionuclides	2.037

The treatment of phosphogypsum with citric acid transformed the calcium sulfate initially contained in phosphogypsum from CaSO_4 to $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$, Table 4. The main diffraction peak in the citric acid leached material corresponded to gypsum ($\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$), 91.9%, followed by Fayalite (Fe_2SiO_4) with a content of 4.0%. 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, 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. With oxalic acid the major compound was gypsum ($\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$) with a content of 89.4%. Disodium catena-disilicate ($\text{Na}_2\text{Si}_2\text{O}_5$) was the second predominant phase in the final product amounting to 8.57%, the remainder being radionuclides. 58.9% of Calcium sulfate (VI) hemihydrate ($\text{CaSO}_4 \cdot 0.5\text{H}_2\text{O}$), was detected when sodium carbonate was used as a leaching reagent. This product is formed as a result of gypsum losing three-quarters of its combined water. 28.1% was Lanthanum Silicate ($\text{La}_2\text{Si}_2\text{O}_7$), usually prepared by solid state reaction (SSR) route using La_2O_3 and SiO_2 [19], and can be used in electrolyte films. The remaining constituents were those associated with radionuclides. Gypsum ($\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$), with a content of 76.3% was obtained in the sodium bicarbonate leached material, followed by 21.7% calcite (CaCO_3). In building and construction applications, calcium carbonate is mainly used as a building material or as the starting material for the preparation of builder's lime by burning in a kiln. Due to the weathering mainly caused by acid rain [20], calcium carbonate in the form of limestone is no longer utilized for building applications on its own, but only as a raw or primary substance for building materials. 2.04% of the sodium bicarbonate leached material consisted of radionuclides.

A high content of $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$ is available in the final treated product in citric acid, oxalic acid and sodium bicarbonate. This is the main constituent in many forms of plaster and in blackboard chalk. For building and construction applications it can be used as a component of Portland cement to prevent flash setting of concrete. Among the impurities present in phosphogypsum, the most important are the phosphorus and fluoro containing compounds along with the organic matter. These materials strongly affect the setting of gypsum products and cement manufactured with phosphogypsum. Although the raw phosphogypsum was laden with phosphorus oxide, this compound was not detected in the final produced products with all the reagents used for phosphogypsum treatment. Most of the phosphogypsums especially those produced by dihydrate method, cannot be used in the construction industry in a raw form [21]. The undesirable contaminations are those containing the phosphates and fluoride ions, both adsorbed and incorporated in the structure, which are transferred to the solution [21]. The chlorides, alkalis, pH and the radioactive elements contents must be limited too.

Only 15% of phosphogypsum is used in the manufacturing of binding materials worldwide [22]. The application of phosphogypsum in production of binding materials is burdened by the presence of phosphate, fluorides and other soluble impurities. Nevertheless, the phosphogypsum is successfully applied for the production of anhydride cement in some countries [23]. Calcium oxide content in building material (Portland cement) and slag cement is 62% and 40%, respectively. Calcium hydroxide, also called slaked lime is obtained by the action of water on calcium oxide and is used as an industrial alkali and as a constituent of mortar, plasters, and cement. Sulphate can be employed as a soil conditioner. The final CaO content when different reagents were used was 43 wt%, 62 wt%, 63.2 wt% and 64.2 wt% for citric acid, oxalic acid, sodium carbonate and sodium bicarbonate respectively. The product obtained when phosphogypsum is leached with citric acid can be blended with other building materials to increase the strength or can be used as slag cement as the CaO content, is almost similar to the slag cement content of 40% CaO. The predominant compound in the raw phosphogypsum was calcium sulphate (CaSO_4).

3.5. Unconfined compressive strength of phosphogypsum

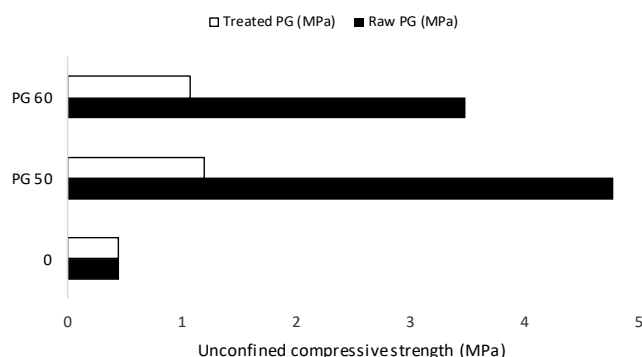


Fig. 3. Unconfined compressive strength of phosphogypsum (raw and treated PG).

Chemical treatment with all the applied reagents transformed the gypsum from anhydride to hydride for citric, oxalic and sodium bicarbonate and hemihydrate for sodium carbonate. The raw PG had the UCS of 0.45 MPa indicating a need for stabilization. PG for both raw and citric acid treated was stabilized with lime (L) and fly ash (FA), Figure 3. PG content of 50% and 60% was then prepared and the UCS measured. The unconfined strength obtained at 80 °C when the specimen were cured for 4 days was measured to be 4.8 MPa and 3.5 MPa for raw PG. For treated PG the UCS was 1.2 MPa and 1.08 MPa. PG before stabilization had the strength of 0.45 MPa, the results shows a significant strength improvement for both raw and treated PG when the material was stabilized with lime and fly ash. The reaction between Lime, fly ash, silica and alumina pozzolans formed strong cementitious bond [24].

4. Conclusion

In this study the chemical treatment and procedure for the leaching of phosphogypsum, a by-product from phosphoric acid manufacturing plant was developed. The raw phosphogypsum sample showed that the highest contributors to the radioactivity are Thallium and Actinium. Citric acid proved to be the best leaching, cost effective and environmental friendly reagent for the reduction of radionuclides contained in the raw phosphogypsum as compared to oxalic acid, sodium carbonate and sodium bicarbonate. In respect to the unconfined compressive strengths obtained, the specimen from treated PG mix designs can be used as a backfill material and stabilised raw PG is suitable for load bearing walls. Phosphogypsum can be treated successfully with citric acid and blended with waste such a fly ash and commercial limestone to produce a product that is usable, thus utilizing two wastes that contaminate the environment and benefiting the waste.

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