


Utilisation of phosphogypsum along with other additives in geotechnical engineering— A review

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ABSTRACT: Various adverse effects and hydro-mechanical failures of soil are the dominant effects of global warming. At the same time, rapid industrial development has produced several by-products on a large scale. The reuse of industrial residues in different engineering fields without compromising the technical characteristics is propitious from the engineering, environmental, ecological and economic points of view. Phosphogypsum (PG) can be used as an alternative civil engineering material as it is rich in calcium sulphate, although it contains some radioactive molecules. Researchers are continuing to investigate the utilisation of PG by mixing it with other traditional materials to convert into alternative materials when the radioactive minerals are within the permissible limits. However, the contamination effect can be reduced by treating with citric acid. This review paper presents details of the increase in strength parameters and permeability of PG when combined with other wastes materials used in different geotechnical fields.

KEY WORDS: Phosphogypsum; Geotechnical applications; By-products; Strength parameters.

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RESUMEN: *Revisión sobre el empleo de fosfoyeso junto con otros aditivos en geotecnología.* El calentamiento global genera varios efectos adversos y fallas hidromecánicas en el suelo. Al mismo tiempo, el rápido desarrollo industrial ha producido varios subproductos a gran escala. La reutilización de residuos industriales en diferentes campos de la ingeniería sin comprometer las características técnicas es propicia desde el punto de vista ingenieril, ambiental, ecológico y económico. El fosfoyeso (PG) se puede utilizar como material alternativo de ingeniería civil ya que es rico en sulfato de calcio, aunque contiene algunas moléculas radiactivas. Los investigadores continúan evaluando la utilización de PG mezclándolo con otros materiales tradicionales, para convertirlos en materiales alternativos cuando los minerales radiactivos se encuentran dentro de los límites permisibles. Sin embargo, el efecto de contaminación se puede reducir mediante el tratamiento con ácido cítrico. Este artículo de revisión presenta detalles del aumento en los parámetros de resistencia y permeabilidad del PG cuando se combina con otros materiales de desecho utilizados en diferentes campos geotécnicos.

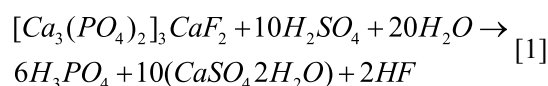
PALABRAS CLAVE: Fosfoyeso; Aplicaciones geotécnicas; Subproductos; Parámetros de resistencia.

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1. INTRODUCTION

Soil, a material in civil engineering, is used as a load-carrying or supporting material, construction material in road bases, embankments, earth dams, clay liners etc., as a result of which there is a constant depletion of this natural resource. Contrarily, due to global warming, soil as a geotechnical material experiences different short- and long-term threats like strength reduction, drying, soil desiccation cracking, shrinkage, microbial oxidation of soil organic matter, fluctuation of the groundwater table, land and exterior erosion, and highly dynamic pore pressure changes (1, 2). Hence, geo-engineering researchers are working hard to overcome this adverse situation. The simultaneously rapid growth of industry produces a large volume of industrial wastes like fly ash (FA), red mud (RM), copper slag (CS), paper pulp, ground granulated blast furnace slag (GGBS), phosphogypsum (PG), rice husk (RH) and so on, which are generally either stored as stockpile or directly deposited into oceans globally. The accumulation of these wastes demands a large land area and causes environmental hazards such as soil and groundwater (GW) contamination and air pollution. Therefore, alternative uses of these wastes for different engineering purposes can solve the aforementioned concerns as well taking another step forward towards sustainable development. The productivity of the food industry is increased by the use of fertiliser to help meet the increasing demand from global population growth. Consequently, there have been hikes in the scale of the fertiliser industry and hence the amount of PG. PG, chemically identified as hydrated calcium sulphate ($\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$), is a by-product waste, 90% of which is produced by the fertiliser industry worldwide from phosphate rock digested by sulphuric acid by wet process (3-5). The amount of PG generated is estimated to be 280 MT per year globally, while India produces 6 million tonnes. However, only 15% of these were utilised due to the presence of phosphorus (P_2O_5), fluoride (F) and other organic substances and the rest was subsequently either landfilled or deposited into the ocean (6-10). Despite the economic benefit of the wet process, it has a demerit in generating as much as 4 to 5 tonnes of PG per tonne production of phosphate fertiliser and other phosphorus compounds (6, 11, 12). PG contains heavy metals and radioactive elements, namely uranium (^{238}U), radium (^{226}Ra), and thorium. Of these, ^{226}Ra produces radon gas which has a short half-life of 3.8 days and its intense radiation capacity causes significant damage to internal organs, so it is classified as TENORM (Technologically Enhanced Naturally Occurring Radioactive Material) (11, 13). The effluent of phosphorus, fluoride, cadmium, total suspended solids, other toxic elements and radionuclides from PG affect human health, for example causing liver dysfunction and lung disease,

and also affect both soil and groundwater (14, 15). The presence of phosphoric acid, sulphuric acid and hydrofluoric acid within the porous structure in residual form prevents its application without proper guidelines on a large scale (16, 17). The first utilisation of PG was started in the USA in road construction and since that time it has been used as a binder, filler and other construction material. It has a good filling or binding property as its basic component is CaSO_4 (18), which helps to form ettringite. The general chemical reaction for the production of PG obtained at a temperature of 70–80 °C as proved by (19, 20) is shown in Equation [1]:



The strength modification, utilization of optimum percentage of PG for different purposes along with proper justification is summarised in this review paper. The summarised results are presented in tabular and graphical form so as to help the new researchers and user to use Phosphogypsum along with other additives as alternative construction materials. This paper also emphasises the use of optimum percentage of PG for different geotechnical fields to start with so as to save time for the experimental work.

2. CHARACTERISTICS OF PHOSPHOGYPSUM

The application of PG can be made easier in a large part of the civil engineering field by analysing its characteristics. Therefore its physical, chemical and other characteristics are compiled for further use. The properties of PG are not only limited to the phosphorus ore but also determined by the method adopted for the extraction of phosphoric acid, the industrial operation efficiency, disposal method, age, location, the height of the landfill storage and the number of water molecules in PG crystals, namely calcium sulphate generated either in anhydrite (CaSO_4), di-hydrate ($\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$) or hemi-hydrate ($\text{CaSO}_4 \cdot 1/2\text{H}_2\text{O}$) (13, 21–23). PG feels like a slightly moist powdery material, having silt size particles with very low or no plasticity as an amalgam of gypsum (>90%) and fluorosilicate (24, 25). The existence of orthophosphoric acid, in which the heavy metals and fluorine are in a soluble state, promotes leaching (26). Leaching of these hazardous elements from a PG stack is one of the prime concerns for groundwater contamination (27–29). Ultimately these dissolved elements are transferred to living bodies via the groundwater (30). The orthophosphoric acid and calcium sulphate (CaSO_4) cause the pH value to lie between 2 and 3, which indicates the acidic behaviour of PG (24, 26). The lower pH value of PG makes it resistive in reac-

tion with soil grains and Ca ions, whereas the addition of cement decreases the acidity, hence encapsulating the impurities present in the PG (24). The pH value determines the solubility of the material and means that it is highly soluble in salt water (31). Distinguishing between gypsum and phosphogypsum is done by microscopic analysis, as both have the same chemical formula. Scanning electron microscopy (SEM) reveals that PG has a more crystalline and distinct structure than gypsum, the crystals of which are hexagonal and rhombic in shape (32). The performance of radioactive elements such as ²²⁶Ra, ²¹⁰Pb, ²¹⁰Po, ²³⁸U and ²³⁴U depends upon the parent phosphate rocks (33, 34). Different researchers have referred to different radioactive nuclides as most hazardous; for example, Rutherford (1994) reported ²²⁶Ra, whereas Pérez-López (2007) indicated the ²³⁴U of parent rock is associated with non-mobile fraction whereas PG contains high Uranium concentration bounded to the bio-available fraction (34, 35). The application of PG was banned in the USA in 1990 and the EU discontinued its use in 1992 (36). Due to all these problems, the Environmental Protection Agency (EPA) restricted the use of PG to up to 370 Bq per kg concentration of ²²⁶Ra in agricultural soil and the European Atomic Energy Community (EURATOM) set the limit of 500 Bq/kg (37-40). Despite these contaminants, it cannot be classified as toxic waste because it is not corrosive and the average total elemental concentra-

tions of elements categorised as toxic (Ba, As, Cr, Cd, Hg, Pb, Se and Ag) by the Environmental Protection Agency (EPA) are lower than the allowable toxic elemental criteria for toxic hazardous waste (35). The main constituents of PG and the impurities need to be known for application and in view of environmental concerns. Therefore, the chemical compositions obtained through X-ray fluorescence (XRF) testing are summarised in Table 1, based on different sources. The experimental results proved that the electrical conductivity of PG is greater than soil, with values from 20 to 5 dSm⁻¹ (very saline) and <5 dSm⁻¹ (slightly saline) respectively, which confirms rich nutrients (41). The surface area obtained from Moroccan PG is 0.64 m²/g (42). The mineralogical and morphological characteristics can be obtained by X-ray diffraction and scanning electron microscopy (SEM) spectrophotometry tests. The crystalline morphology characteristics found in SEM analysis of unprocessed PG appear as platelets oriented in a parallelepiped shape, with lengths ranging from a few to 400 micrometres (µm) and a thickness of fewer than 10 µm. The higher value of the aspect ratio becomes a favourable criterion for quick crushing under different stresses (42).

In the presence of a hydraulic binder, the chemical composition aids in understanding the response between PG and other constituents. It can be predicted from the table that the abundant calcium ion in PG can form a gel of calcium aluminate hydrate or calcium-silicate when

TABLE 1. Chemical composition of PG.

Country	Industry	Reference	Chemical composition									
			CaO	SiO ₂	Al ₂ O ₃	Fe ₂ O ₃	MgO	SO ₃	Na ₂ O	K ₂ O	CaCO ₃	P ₂ O ₅
Tunisia	Unknown sources	(43)	34.6	2.45	0.17	0.23	0.14	-	0.32	0.05	44.1	0.71
India	Coromandel International Limited	(44)	35.728	16.957	0.649	35.728	0.661	-	0.106	0.042	-	10.701
Morocco	Phosphoric acid production plant	(42)	31.16	1.03	0.85	0.012	-	44.01	0.21	0.001	-	0.96
Poland	GZNF “Fosfory”		26	25.5	-	-	-	-	53.3	-	-	-
South Africa	Phosphoric acid manufacturing plant	(45)	44	1.37	0.23	0.121		51	-	-	-	1.28
China	Mianzu of Sichuan	(46)	30.85	4.65	4.20		0.24	31.85	0.34	-	-	3.22
Latvia	Fertiliser production plant (AB Lifosa, Lithuania)	(47)	37.6	4.8	0.26	0.1	0.8	54	-	-	-	1.7
Unknown sources	Unknown sources	(48)	38.14	0.86	0.19	0.21	-	48.12	0.17	0.01	-	0.69
Poland	Recycling Plant Eko Harpoon sp. z o.o.	(18)	69.5 as CaSO ₄	1.7		2.51	-	-	0.89	0.5	-	2.9

mixed with other material that is rich in silica and alumina, to reduce the water sensitivity and subsequently increase the mechanical properties. The chemical composition of PG includes radioactive elements, traces of heavy metals such as As, Cr, Cd, Hg, Pb, fluoride, zinc, antimony, and copper (49), along with some other chemical elements that can be used for the production of bricks, blocks, tiles, and artificial stone.

3. TREATMENT OF PG

Landfilling of PG waste releases dust as well as leachate of hazardous elements, fluoride and heavy metals, which causes air, soil and groundwater pollution (50, 51). The presence of natural radioactive nuclides and impurities, namely phosphate and fluoride, reduces the strength and extends the setting time, causing a high level of pentafluoroaluminate (ALF^{-5}) to disturb the gypsum development, thus limiting its use as a construction material to as low as 15% globally (52, 53, 12). Researchers all over the world have been treating the waste to make it safe for disposal and increase the potential for its massive application without environmental concerns. Manjit *et al.* (1993) washed PG using aqueous hydroxide solution (5–20%) then dried it at 42 °C to minimise the amount of P_2O_5 , F, and all the contaminants were abridged (54). Aly and Mohammed (1999) recovered fluorine and lanthanides by using nitric acid (HNO_3) (55). A wet sieving and hydro-cyclone method followed by heat drying was adopted by Manjit (1996), who identified the reduction of impurities and increment of pH and SO_3 values (56). The extraction of radionuclides of more than 60% and rare earth elements by organic extractors in kerosene diluent with a liquid to solid ratio of 1:1 at 55 °C was examined by El-Didamony *et al.* (57). The exchange or membrane technique was adopted, combined with recrystallisation by Koopman and Witkamp, who showed that more than 90% of the heavy metals and lanthanides were removed (58). Mashifana *et al.* (2018) used 0.5M citric acid with a 40% solid load concentration based on the studies of (59–62) and observed remarkable results in removing radionuclides, P_2O_5 and F by up to 92.8%, 34.7% and 18.87% respectively (22, 63). Al-Jabbari *et al.* washed PG with water and passed it through a 100 mm sieve, then calcined it by hydrated lime at various temperatures, and reported this as the lowest cost method of treatment. The modified PG was free of pollutants, with both setting and strength properties improved (64).

4. APPLICATION OF PHOSPHOGYPSUM IN CONSTRUCTION

Chemical tests have confirmed that PG is highly acidic and contains radionuclide elements. However, the Atomic Energy Regulation Board of India in

2009 decreed in its directive (number 01/09) that the sale of PG for construction purposes does not require its approval, provided the activity concentration of ^{226}Ra is less than 1.0 Bq/g (65). Campos *et al.* examined the radon exhalation of PG-manufactured bricks and plates and found it to be the same as ordinary construction materials, and therefore suggested a safe practice without any prior handling (66).

4.1. For geotechnical purposes

Due to the lack of Si and Al content, the formation of aluminosilicate and/ or calcium silicate hydrate gel, which are prime factors for strength and durability, is not possible, which is why PG cannot be used alone as a binding or stabilising agent. In this section, the latent deviations in terms of physico-chemical and mechanical characteristics of soil will be discussed when modified with PG together with other additives. James and Pandian (2016) modified black cotton soil into an enduring engineering soil with the help of PG and lime. The experimental results showed that soil with lime (7%) and PG (2%) effectively reduced the swelling–shrinkage and plasticity behaviour, as shown in Figure 1a and 1b respectively (44). Sivapullaiah and Jha (2014) predicted the reduction in the liquid limit after the addition of lime to fly ash stabilised soil, which may be due to the replacement of sodium ions with calcium ions, reduction in the diffused double layer, and increase in the electrolyte concentration of the pore fluid. The addition of PG, which can act as a source of calcium ions, may have similar effects on the soil. The resulting elevated unconfined compressive strength (UCS) value may be due to the acceleration of the pozzolanic reaction (67). The same pozzolanic reaction was observed by Kumar and Dutta (2017) by treating bentonite soil with 8% lime and 8% PG and 1% sisal fibres, which raised the UCS by 631.46% as compared to raw bentonite soil at 28 days of curing.

The formation of cementing gel and the adhesion of bentonite particles with sisal fibres were affected if the quantity of stabilisers applied was beyond the above-mentioned limit, and the development of lumps lessened the UCS. The trend of the results was verified through the unconfined undrained (UU) triaxial test, which found an identical trend of strength variation. The excess sulphate in PG may be the reason for resistance to the creation of pozzolanic compounds and the subsequent diminution of cohesion. The SEM (EDAS) test revealed that PG content above 8% was caused by a low Si/Al ratio, which resulted in strength reduction (68). Shilva *et al.* (2019) treated laterite soil with hemihydrate phosphogypsum (PGH) and a small quantity of cement; furthermore, they observed the durability and mechanical characteristics to emphasise the suitability for asphalt pavement layers. They observed that

although 7 days of immersion in water reduced the UCS value by 54% in a PG rich sample, the same sample showed an increment in UCS by 603% after 12 wet–dry cycles (69). Though Ho et al. (2017) concluded that the lower the water content, the higher the strength obtained, they found that hydration, carbonation and the late pozzolanic reaction which took place during the wet cycles lead to a decrease in the water content and subsequently increase the resilient modulus. However, the formation of ettringite due to the presence of cement leads to the development of microcracks and pores, which accelerates the uncontrolled leaching (70). Babu et al. (2019) studied the effectiveness of PG and crumb waste rubber (CRW) to stabilise BC soil for use as subgrade material. The improvement of the compressive strength of the soil by using PG is shown in Figure 2.

It was stated that the strength improvement occurred because of the pozzolanic reaction, binder development and discrete reinforcing effect, with an optimum quantity of 6% PG and 2% CRW (71). Based on the above conclusions and experimental results, research has been carried out on using PG in civil engineering materials. Sihag (2019) used PG to stabilise black cotton soil with the addition of lime and FA and found it to be suitable for the non-bituminous layers of a flexible pavement based on the geotechnical characteristics and involvement of PG. The results showed that the soaked California Bearing Ratio (CBR) value increased by 432.25% and the UCS value reached up to 5.1 MPa for the treated soil, whereas it was only 1.5 MPa for untreated soil. The use of only 1% PG along with other agents increased the strength characteristics and made it suitable for the purpose (72). Folek et al. (2011) used stockpiled PG and FA with a binder for constructing a parking lot and checked the serviceability after one and a half years, confirming that both the geotechnical and physio-chemical parameters were satisfactory, following laboratory testing at the time of construction. They suggested that these composites can be used for sub-base without a binder below the frost penetration zone for light traffic (26). An appreciable number of studies have been conducted using PG along with other wastes or conventional materials for stabilising BC or weak soils to make them suitable to apply in different geotechnical fields, mainly sub-grade, sub-base and construction material (12–13, 42, 43, 45, 46, 63, 73–79). The compressive strength of soil with the addition of varying percentages of PG with different curing periods is shown in Figure 3.

The test results of various studies are summarised in Tables 2 and 3 based on the mechanical characteristics. Different studies used different types of additives, which exhibited changes in the results. Therefore, it is easy to understand the effects of the additives by identifying the changes in the properties of soil with different modifiers along with PG.

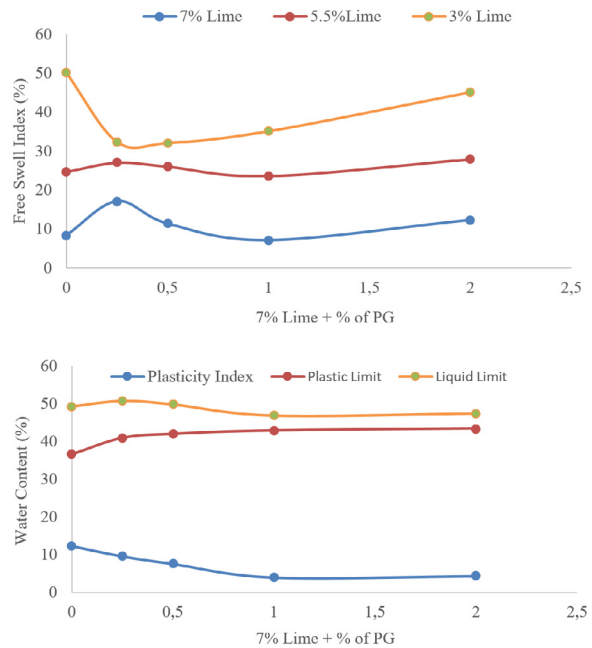


FIGURE 1. a) Free swelling of lime-stabilised soil admixed with PG (reproduced from (44)); b) Effect of PG on the plasticity of 7% lime-stabilised soil (reproduced from (44)).

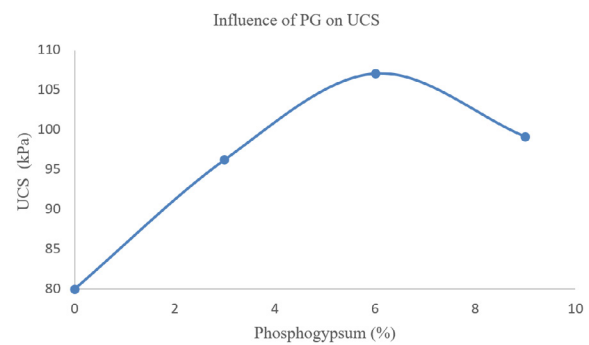


FIGURE 2. Variation of UCS of soil along with change in percentage of PG (reproduced from (71)).

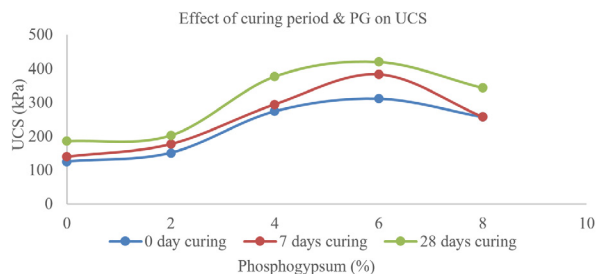


FIGURE 3. Variation of UCS of soil with variation of PG content at different curing periods (reproduced from (79)).

The swelling of expansive soil is the foremost concern as it causes damage to structures. The plasticity index is an indirect indicator of the swelling

TABLE 2. Comparative index properties of soil.

Composition	Reference	Liquid limit	Plastic limit	Plasticity index
Black cotton soil (BC)	(75)	54	19	35
BC + 4% lime + 8% PG		35	25	10
Clay and PG	(79)	49.4	22.9	26.5
		41.3	20	21.3
Black cotton soil	(45)	94.9	74.5	20.4
BC + Treated PG		65.26	50.05	15.21
Expansive soil (ES)	(44)	68	27	41
ES + 7% lime + 1% PG		46.75	43.22	3.55

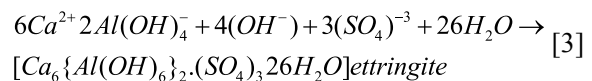
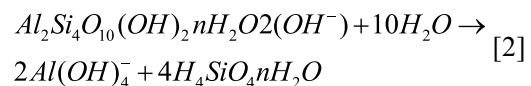
TABLE 3. Maximum strength parameters of untreated and treated soil.

Composition (reference)	Test conducted	Results	
		Untreated	Treated
BC soil + lime 4% + PG 4% (75)	Shear	0.98 kg/cm ²	0.164 kg/cm ²
Soil + PG 6% (76)	UCS (28 days curing)	122 kPa	336 kPa
Soil + PG 6% + CRW 2.5% (71)	Soaked & unsoaked California Bearing Ratio	1.7 & 3.3	8.5 & 10.3
	UCS (28 days curing)	80 kPa	180 kPa
100% PG (16)	TRIAXIAL – UU TEST saturated PG & partially saturated PG	-	765 kPa 185 kPa & 42°
	CBR	-	260
	UCS (0 days curing)	-	4.97 MPa
	Compression index	0.25	0.158
PG: soil material (SM) = 40:60 (42)	Soaked CBR	9	19
	Modified Proctor compaction γ_d & OMC	14.8 kN/m ³ & 17% respectively	16.5 kN/m ³ & 15% respectively
	Shear parameters C and ϕ	2 kPa and 35° respectively	7 kPa 31° respectively
Mashfana (45) soil with 30% raw PG stabiliser RPG (PG 50% FA 30% 20% lime)	UCS (7 days curing)	0.15 MPa	0.82 MPa
Mashfana (45) Soil with 50% TPG (50% PG 10% FA 10% lime 30% BOF slag)			1.65 MPa
Bian et al. (81) cement 100 kg/m ³ PG 20 kg/m ³ SOIL.	UCS (28 days curing)	65 kPa	470 kPa
Satyaveni et al. (82) Marine Soil: 20% baggage ash: 6% PG	OMC & MDD	29.5 & 1.36 g/cc respectively	27.9 & 1.46 g/cc respectively
	UCS	72 kPa	119 kPa
	Soaked CBR	1.4	6.5
Harrou et al. (83) bentonite clay: 8% lime: 8% PG: 8% steel slag	UCS (28 days curing)	0.23 MPa	1.057 MPa
Yu et al. (84) dredge sludge: 15% lime: 7.5% PG	UCS (28 days curing)	-	1966.10 kPa
	UCS (90 days curing)	-	3028.5 kPa
Dhanasekar et al. (85)	OMC & MDD respectively	26 & 1.51 g/cc	1.84 g/cc
	Unsoaked & soaked CBR		5.89 & 4.1 respectively

potential of expansive soil (80). The data tabulated in Table 2 reveals that PG can be used as a good modifier as it lessens the value of the plasticity index which refers to medium-to-low swelling potential.

It has been observed that the addition of PG flattened the compaction curve, which implied low water sensitivity of the composites, hence increasing the strength parameters. The strength increment of treated soil was caused by the formation of calcium silicate hydrate, calcium aluminate hydrate gel and ettringite when the soil stabilised chemically in a high alkali environment (86). The pozzolanic and hydration reaction absorbed a large quantity of water, so the moisture content of the soil decreased as a consequence, solving the key problem of highly plastic clay or water-sensitive clay when treated by cement/ lime, FA and PG, but the strength increased up to a certain limit of additives, then decreased. This may be caused by the unreacted lime, which acts as filler material and also increases the pH value, subsequently reducing the shear strength (45, 87, 88). The presence of gypsum in PG activates the pozzolanic reaction in the presence of a hydraulic binder that contains high-level hydroxyl (OH⁻) ions also released from lime or cement at the time of hydration at a higher pH value. As this reaction is a slow process, a longer curing period helps to generate more strength. The integrated particles are formed due to sorption, cementation and cation exchange between the PG and other additive materials (71, 89, 90). The consumption of hydroxyl (OH⁻) ions produces ettringite, due to which the overall pH of the composite decreased with the increase of PG content. But the lowest value of pH ended at 10.9 after 28 days of curing, which is itself a good alkaline environment for the future pozzolanic reaction (91, 92). High temperature during the curing period accelerates the early hydration and pozzolanic reaction as well as the intensity of the endotherms of ettringite, which helps to obtain a high strength value (22). The stabilisation and curing of PG transform it from an acidic to alkaline composite because of the hydroxide component that decreased the plasticity and increased the sustained pozzolanic reaction, which helps to achieve long-term strength (93). With the increase in curing time, the PG content reduced the moisture content because the reaction between PG and calcium aluminate hydrate demanded a large amount of water (94). Xue et al. (2019) studied the ability of PG to reduce the alkalinity of waste material like RM and to make it suitable for agricultural purposes and other comprehensive use. They found that an optimum quantity of 2% PG with a liquid/solid ratio of 2 mL/g at 30 °C for a reaction time of 12 h reduced the pH of RM from 12 to 8.1 and transformed the loose granular structure of RM into a large aggregate structure (95). The lower pH value restricted its use alone, although at the same time this property makes

it suitable for reducing the alkalinity of a material to enable its use in essential purposes. Wang et al. (2019) studied the effects of earthquake action based on liquefaction and deformation affecting the groundwater on a PG tailings pond by using FLAC^{3D}. The study revealed that the tailings slipped along the shear strain zone because liquefaction of saturated tailings during dynamic loading led to overtopping failure (96). Rong et al. (2020) used hemihydrate PG for mine filling because of its cementitious properties, conducting laboratory tests verified by industrial experiments on the goaf filling; it decreased the surface subsidence and strengthened the stability of the surrounding rocks, which may enable the extraction of more resources. They also observed that the underground construction could proceed faster due to the rapid consolidation rate (97). Gaidajis et al. (2017) conducted laboratory experiments to find the potential of PG in quarry and mine fillings. The test results showed that PG can be compacted easily and exhibits the desired strength and compressibility values. It was suggested that the leachability of heavy metals was within permissible limits, thus making it suitable for the above-mentioned purposes (16). However, AFt (ettringite), while being one of the major sources of strength, also has swelling potential; hence, it was suggested to apply a moderate quantity of PG to control the swelling of stabilised soil (98, 99). The subsequent reactions between the PG and the hydrated products of stabilised soil for the formation of ettringite are shown in Equation [2] and Equation [3] (89, 90):



4.2. Binder

Phosphorus pentoxide, fluoride, radionuclides and other organic substances in PG have restricted its application as a retarder in concrete technology (72). Bumanis et al. (2018) converted the dihydrate PG to hemihydrate PG (PGH) at elevated temperatures (100–80 °C) and observed the binding features as an alternative to gypsum. The binder composite made from PG with slacked lime and plasticisers had a long initial setting time, reduced the water–PG ratio from 0.8 to 0.43 and had a high compressive strength of 29 MPa for a 14 days hardened sample (47). Because of the lower AFt content formation compared to lime+gypsum by-product, Huo et al. (2021) advised using slag–cement with gypsum by-product to resist expansion (100). Xiao et al. (2019)

solidified oily sludge by treating ordinary Portland cement (OPC), FA, and silica fume (SF) as binders with PG as a stabiliser. An optimum combination of binders (OPC: FA: SF = 1: 0.7: 0.8) with PG produced AFt which improved the compressive strength, water stability performance, freeze–thaw resistance and volumetric stability (46, 101, 102). The fusions reduce the leachate of heavy metals by refining pores with compact microstructure. The test results confirmed that the final composite can be used for Grade II Highway Sub-base according to the Specification for Construction Technology of Highway Pavement Base. When PG was partially replaced with cement as binding material, the early strength increased. The desired early strength not only reduced the cost of stocking but also enabled its use in the field of application. Fractional replacement of cement also reduced the cost (90).

5. XRD ANALYSIS

Mineralogical changes of raw materials after treatment help to understand the structure and strength of the new composite. These changes depend decisively upon the raw materials, their proportions, curing period and their ambience. The mineralogy of PG is crystalline in form and hence has strength potentiality. When PG is mixed with cementitious materials, the formation of portlandite and ettringite indicates good strength (78). When clay-rich soil is modified with either treated or raw PG together with other additives, the new form of minerals is different in both cases. Among the three strength compounds of C-S-H, C-A-H and ettringite, the formation intensity of ettringite was greater, which contributed to the early strength development with the addition of PG. Meanwhile, the C-A-H compound was reduced, whereas the C-S-H gel remained unchanged. The ettringite formed bridged the solid particles due to its needle-like structure, and hence improved the strength as well as the density by compressing the pore space of the soil with high water content (86, 91, 103). Mashifana *et al.* (2019) reported the XRD analysis of raw PG, RPG20 (lime, FA, 10% BOF and 20% raw PG), treated PG and TPG20 (lime, FA, 10% BOF and 20% treated PG), as shown in Figure 4 to Figure 6 respectively. In both of these composites, kieserite is the common predominant mineral that has a significant role in high strength (63). Mashifana *et al.* (2018) tested expansive soil, rich in montmorillonite $8(KAl_4(SiAl)O_{10}(OH)_4)$, bentonite $(Ca_{0.06}Na_{0.21}K_{0.27})(Al_{11.64})$, kaolinite $(Al_2(Si_2O_5)(OH)_4)$, and quartz (SiO_2) . When this soil was modified with PG, new hydration products formed; namely calcium magnesium silicide $(CaMgSi)$, sillimanite $(Al_2(SiO_4)O)$, kaolinite $(Al_2(Si_2O_5)(OH)_4)$, feldspar $(Al_2Si_2O_8)$, and trikalsilite $((KNa)AlSiO_4)$. Treated PG helped to dissolve siliceous and aluminous

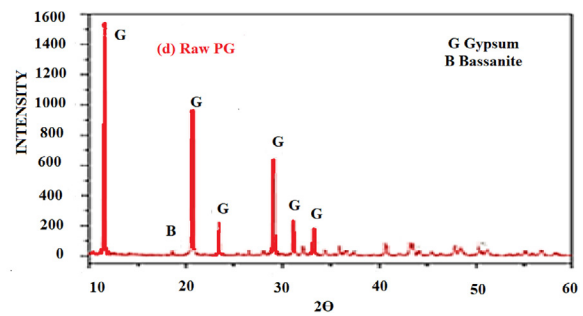


FIGURE 4. XRD analysis of raw PG (reproduced from 73).

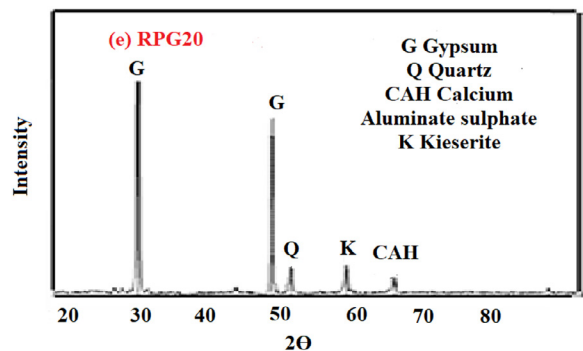


FIGURE 5. XRD analysis of RPG 20 (reproduced from 73).

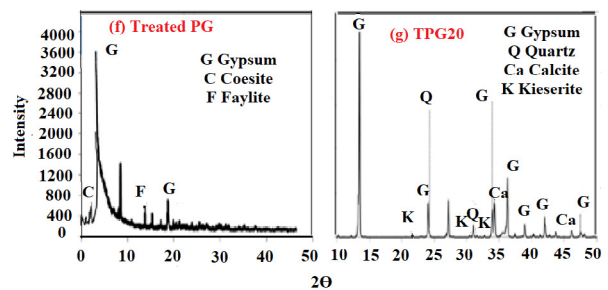


FIGURE 6. XRD analysis of treated PG and TPG 20 (reproduced from 73).

compounds from the soil lattice. These ions reacted with the calcium ions in the pore water to form calcium silicate hydrate and calcium aluminate hydrate, which coated the soil particles. Subsequently, crystallisation bonded them, hence the strength was significantly improved (45, 104).

6. CONCLUSIONS.

The reuse of locally available waste materials on a large scale in various practical fields is a sign of progress towards achieving sustainable development. The fertiliser industry by-product waste phosphogypsum is acidic and contains

trace materials and radioactive nuclides like ^{226}Ra . Therefore, it needs to be either purified or used in different engineering fields with proper guidelines to avoid effects on human health and the environment. Many research studies have been conducted on the use of PG in different fields of civil engineering, like construction material, road base material, and binder and soil stabilisation. All these studies showed that the success of the application of PG largely depends upon the grain sizes, relative consistency, compressibility, and the chemical and mineralogical composition of the material to be treated. The leachate problem and radioactivity problems can be solved to a reasonable extent by treating them with a mild acid. But it can also be concluded that it cannot be used alone due to its acidic behaviour, so it needs to be stabilised with other materials like FA, GGBS, rubber tyre and lime, cement etc. There is another by-product waste, RM obtained from the aluminium industry as an alkaline bauxite residue, and these can neutralise each other because of their opposite characteristics. Future investigations could usefully be attempted by researchers to stabilise the PG with RM and make the mixture suitable for different geotechnical purposes like backfilling of mechanically stabilised earth (MSE) walls, paver blocks, MSE walls, clay liners etc. However, the leaching property of the combined material should still be tested before using it as a construction material due to continuing environmental concerns.

AUTHOR CONTRIBUTIONS:

Conceptualization: G. Debabrata. Data curation: B. Anamika. Formal analysis: B. Anamika. Investigation: B. Anamika. Methodology: B. Anamika. Supervision: G. Debabrata. Writing, original draft: B. Anamika. Writing, review & editing: G. Debabrata.

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