Neutralization of Phosphogypsum for Use in Base Lining System of Phosphogypsum Dumping Yards

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ABSTRACT: Phosphogypsum is generated as a by-product during the manufacturing of phosphoric acid by wet process. Annually, the worldwide projected value of phosphogypsum generation is 100-280 metric tons. Due to its acidic nature, radioactivity, high fluorine content, presence of trace elements and huge volume, direct dumping of phosphogypsum on the ground results in subsoil and groundwater contamination. Hence, it is essential to dump phosphogypsum properly in engineered landfills. To overcome these issues in India, the Central Pollution Control Board (CPCB) has suggested a composite liner system for the safe disposal of phosphogypsum on the ground. The lower part of the suggested liner system comprises of placement of HDPE geomembrane over a layer of compacted clay or compacted amended soil layer or a mixture of native soil with bentonite and in the upper part of the composite liner system, a layer of mechanically compacted and neutralized phosphogypsum is placed above the drainage layer. Hence, the present work is intended to neutralize phosphogypsum with lime, fly ash, and pond ash and to assess the suitability of neutralized phosphogypsum for use in the upper part of the composite liner system of phosphogypsum ponds. The study indicated effective neutralization of phosphogypsum with 1.6% lime and 50% fly ash.

KEYWORDS: Phosphogypsum, Composite Liner System, Neutralization, Lime, Fly ash, and Pond ash.

1. INTRODUCTION

Phosphogypsum is a waste by-product of a chemical reaction wherein phosphate rock is digested by sulphuric acid in phosphate plants and phosphate-based fertilizer industries for producing phosphoric acid. Approximately, 4-5 tons of phosphogypsum are generated for producing one ton of phosphoric acid (Dvorkin *et al.,* 2018; Tayibi *et al.,* 2009; Islam *et al.,* 2017). It is estimated that nearly 6.5 – 11 million tons of this waste by-product is produced yearly in India (Tulasi and Satyanarayana Reddy, 2022; Suresh Palla *et al.,* 2022; CPCB Guidelines, 2014).

Based on the methods used in producing phosphoric acid, the phosphogypsum is either produced in slurry or powdered form. The acidic nature, radioactivity, high fluorine content, and presence of trace elements and heavy metals such as Cd, Cr, Pb, etc. are the major issues faced while handling this high-volume solid waste by-product (Rutherford *et al.,* 1995; Gennari *et al.,* 2011; Saadaoui *et al.,* 2017; Arocena *et al.,* 1995). The absence of rules and regulations for disposing of phosphogypsum in the earlier days has resulted in stockpiling of large amounts of phosphogypsum directly on the ground in many parts of the world. Some countries like Morocco, Tunisia, South Africa, and Mexico released the by-product into the water bodies without any treatment, which affected the quality of both water and aquatic life, while in countries such as The United States of America, harmful waste is backfilled into mines. With increased awareness regarding subsoil and groundwater contamination, many countries evolved agencies like the United States Environmental Protection Agency (USEPA) and categorized phosphogypsum waste into the hazardous category and restricted the dumping of waste exceeding certain limits without treatment.

In India, CPCB (2014) has formulated the norms and conditions for dumping phosphogypsum by suggesting a single composite liner system with proper drainage (CPCB Guidelines, 2014). Figure 1 shows the single composite liner system suggested by CPCB.

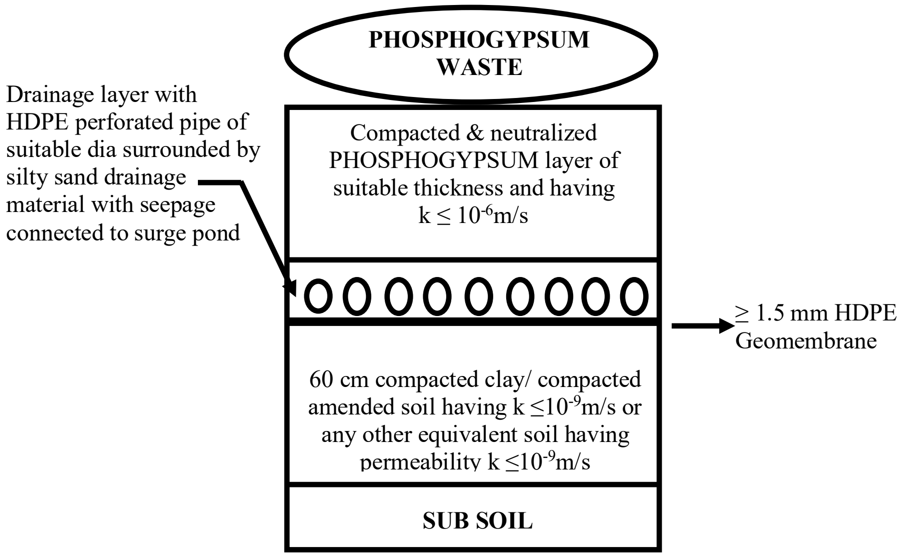

Figure 1 Base lining system for phosphogypsum stack suggested by CPCB

Currently, phosphogypsum is being neutralized with lime in the proportion of 2-12% for rendering it suitable for various applications such as application in supersulphated cement, cement production, road construction, etc. (Dvorkin *et al.,* 2018; Liu *et al.,* 2020; Sarra Meskini *et al.,* 2021; Shen *et al.,* 2007; José *et al.,* 2021; Jiahui Men *et al.,* 2022; Dutta and Kumar, 2016).

In the present study, an attempt is made to explore the possibility of using fly ash and pond ash to neutralize the phosphogypsum to reduce the cost of the neutralized phosphogypsum layer in the composite liner system. The neutralized phosphogypsum samples in the study are tested for permeability as CPCB specifies a permeability of less than 10^{-4} cm/s for use in a single composite liner system.

2. MATERIALS

2.1 Phosphogypsum

Phosphogypsum is a powdered, grey-colored, silty sand-sized waste by-product from the fertilizer industry. Phosphogypsum used in the present study is procured from Coromandel International Pvt Ltd, Visakhapatnam, Andhra Pradesh, India. The laboratory tests are conducted to evaluate the engineering properties of phosphogypsum. The compaction characteristics are determined using IS Heavy Compaction test as per IS 2720 Part 8, 1983 (IS 2720: Part 8, 1983). A direct shear test is conducted to calculate the shear parameters both in OMC-MDD and Saturated states (IS 2720 Part 13, 1986). The coefficient of permeability of the phosphogypsum is found from the variable head permeability test (IS 2720 Part 17, 1986). The California Bearing Ratio of phosphogypsum in OMC – MDD compacted state is determined after 96 hours of soaking (IS 40 2720 Part 16, 1987). The properties of phosphogypsum are presented in Table 1.

Table 1 Properties of phosphogypsum

Property	Value
pH	2.47
Specific Gravity	2.59
Grain size distribution Gravel (%) Sand (%) Fines (%) Clay fraction (%)	 0 5 95 7.6
Compaction Characteristics (i) Optimum moisture content (%) (ii) Maximum unit weight (g/cc)	 22.8 1.44
Shear Parameters (OMC&MDD condition) (i) Cohesion (kN/m^2) (ii) Angle of internal friction	 0 34°
Shear Parameters (Saturated condition) (i) Cohesion (kN/m^2) (ii) Angle of internal friction	 0 26°
Coefficient of permeability (m/s)	1.36×10^{-6}
Soaked CBR (%)	2.2

2.2 Lime

Commercially available lime is used in the study. The lime is found to have a pH of 12.1. The chemical constituents of lime given by the manufacturer are presented in Table 2.

Table 2 Chemical composition of lime

Constituent	(%)
Cao	83.4
MgO	0.4
Fe_2O_3	1.4
Al_2O_3	1.2
SiO_2	1.9
SO_3	0.4
Na_2O	2.8
CO_2	3.2
$CaCO_3$	7

2.3 Fly Ash

Fly ash used in the study is procured from National Thermal Power Corporation (NTPC), Visakhapatnam, Andhra Pradesh. The pH of the fly ash is found to be 7.9. The fly ash is categorized as class – F. The chemical composition of fly ash obtained from NTPC is presented in Table 3 and the engineering properties of Fly Ash determined in the laboratory are presented in Table 4.

Table 3 Chemical composition of fly ash

Constituent	(%)
$SiO_2+Al_2O_3+Fe_2O_3$	93.78
SiO_3	60.16
Reactive silica	34.46
MgO	0.79
Na_2O	0.90
SO_3	0.16
Cl	0.006
Loss of ignition	0.47

Table 4 Engineering properties of fly ash

Property	Value
Specific Gravity	2.1
Grain Size Analysis Gravel (%) Sand (%) Fines (%)	 0 18 82
Plasticity Characteristics (i) Liquid Limit (%) (ii) Plastic Limit (%)	 NP NP
Compaction Characteristics (i) Optimum moisture content (%) (ii) Maximum unit weight (g/cc)	 18.5 1.39
Shear Parameters (OMC&MDD condition) (i) Cohesion (kN/m^2) (ii) Angle of internal friction	 0 29
Shear Parameters (Saturated condition) (i) Cohesion (kN/m^2) (ii) Angle of internal friction	 0 26
Permeability(m/s)	2.72×10^{-7}

2.4 Pond Ash

Pond Ash is procured from NTPC. The pH of the pond ash is 8.53. The chemical composition and the engineering properties of pond ash determined in the laboratory are presented in Table 5 and Table 6 respectively.

Table 5 Chemical composition of pond ash

Constituent	(%)
SiO_2	69
Al_2O_3	22
Fe_2O_3	5
CaO	0.16
K_2O	< 1
TiO_2	< 1

Table 6 Engineering properties of pond ash

Property	Value
Specific Gravity	2.1
Grain Size Analysis	
Gravel (%)	0
Sand (%)	83
Fines (%)	17
Plasticity Characteristics	
(i) Liquid Limit (%)	NP
(ii) Plastic Limit (%)	NP
Compaction Characteristics	
(i) Optimum moisture content (%)	15
(ii) Maximum dry unit weight (g/cc)	1.23
Shear Parameters (OMC&MDD condition)	
(i) Cohesion (kN/m^2)	0
(ii) Angle of internal friction	33^0
Shear Parameters (Saturated condition)	
(i) Cohesion (kN/m^2)	0
(ii) Angle of internal friction	29^0
Permeability(m/s)	2.19×10^{-7}

3. NEUTRALIZATION OF PHOSPHOGYPSUM

Phosphogypsum is neutralized to use in the upper part of the liner system above the drainage layer, as suggested by CPCB. To minimize the usage of lime which further reduces the cost of neutralization, alkaline industrial wastes such as fly ash and pond ash are used along with lime. Neutralizing phosphogypsum involved mixing 10 g (phosphogypsum + neutralizing material) of the sample in 100 ml of distilled water. The sample is thoroughly mixed and left undisturbed for 24 hours. The pH of the supernatant is measured after 24 hours using a pH meter.

3.1 Neutralization of Phosphogypsum with Lime

Lime is added to phosphogypsum in proportions ranging from 0.5% to 3% (by weight, in the intervals of 0.5%) to study the increase in pH of phosphogypsum. The pH values of lime-treated phosphogypsum are presented in Table 7.

Table 7 pH of phosphogypsum with the addition of lime

Lime (%)	pH value
0.5	2.8
1	3.6
1.5	5.2
2	5.6
2.5	6.1
3	7.2

From Table 7, the optimum percentage of lime for neutralizing phosphogypsum is found to be 3%. 3% lime treated phosphogypsum is further tested for permeability in the compacted state to assess its suitability for use in the upper part of the composite liner system. The Compaction and Permeability characteristics of phosphor-gypsum treated with 3% lime determined in the laboratory are presented in Table 8.

Table 8 Compaction and Permeability characteristics of phosphogypsum neutralized with 3% lime

Property	Value
Compaction characteristics	
(i) Optimum moisture content (%)	23.6
(ii) Maximum dry unit weight(g/cc)	1.33
Permeability(m/s)	1.49×10^{-6}

As the phosphogypsum neutralized with 3% lime does not satisfy the permeability requirement specified by CPCB ($k \leq 10^{-6}$ m/s), it cannot be used in the upper part of the composite liner system.

3.2 Neutralization of Phosphogypsum with Pond Ash

Phosphogypsum is mixed with different proportions of pond ash ranging from 10% to 50% by weight. The pH values of the samples prepared by mixing phosphogypsum with the required amount of pond ash are presented in Table 9.

Table 9 pH of phosphogypsum with the addition of pond ash

Pond Ash (%)	pH value
10	2.63
20	2.67
30	2.72
40	2.79
50	2.86

From Table 9, it can be noted that there is no significant change in the pH of phosphogypsum even with adding up to 50% of pond ash. Therefore, using only pond ash is not ideal for neutralizing phosphogypsum.

3.2.1 Neutralization of Phosphogypsum with Pond Ash and Lime

The pH of lime-treated phosphogypsum with the addition of various proportions of pond ash ranging from 10% to 50% is determined using a pH meter. The amount of lime added to the phosphogypsum also varied from 0.5% to 2.5%. Table 10 summarizes the pH values of phosphogypsum with the addition of varying proportions of pond ash and lime.

Table 10 pH of phosphogypsum with different proportions of pond ash and lime

Pond ash (%)	Lime Content (%)				
	0.5	1	1.5	2	2.5
10	2.78	4.22	4.86	5.37	6.41
20	3.21	4.72	5.26	5.54	6.47
30	4.41	4.92	5.48	5.94	6.56
40	4.65	5.28	5.74	6.38	6.92
50	4.94	5.68	6.24	6.52	7.01

From Table 10, it is found that the optimum amount of pond ash and lime is 50% and 2.5%, respectively. The phosphogypsum treated with pond ash and lime is tested further to check the permeability in the compacted state as suggested by CPCB. The Compaction and permeability characteristics of phosphogypsum neutralized with pond ash and lime are presented in Table 11.

Table 11 Compaction and Permeability characteristics of phosphogypsum neutralized with 50% pond ash and 2.5% lime

Property	Value
Compaction characteristics	
(i) Optimum moisture content (%)	26
(ii) Maximum dry unit weight(g/cc)	1.26
Permeability(m/s)	$6.17 x 10^{-5}$

From Table 11, it can be noted that the phosphogypsum neutralized with 50% pond ash and 2.5% lime does not satisfy the permeability requirement ($k \leq 10^{-6}$ m/s) of CPCB. Hence, phosphogypsum neutralized with pond ash and lime is not suitable for use in the upper part of the composite liner system suggested by CPCB.

3.3 Neutralization of Phosphogypsum with Fly Ash

Proportions of fly ash varying from 10% to 50% (by weight) is added to phosphogypsum to study the improvement in pH value and to assess the neutralization potential of fly ash. Variation in pH values of phosphogypsum with the addition of different proportions of fly ash are presented in Table 12.

Table 12 pH of phosphogypsum with the addition of fly ash

Fly ash (%)	pH value
10	3.2
20	4.2
30	4.4
40	4.5
50	4.8

From the Table 12, even with the addition of 50% fly ash, the pH value did not reach 7. Also, further increase in fly ash increases permeability value. Hence, neutralization of phosphogypsum with the addition of fly ash alone is not a viable option.

3.3.1 Neutralization of Phosphogypsum with Fly Ash and Lime

The study is extended to neutralize the phosphogypsum by adding fly ash and lime. Lime mixed phosphogypsum is mixed with varying proportions of fly ash to study the increase in pH values. The amount of lime added to phosphogypsum varies from 0.5% to 2% by weight. The values of pH of lime treated phosphogypsum with addition of fly ash are presented in Table 13.

Table 13 pH of phosphogypsum with different proportions of Fly ash and lime

Fly ash (%)	Lime Content (%)			
	0.5	1	1.5	2
10	3.16	4.52	5.61	6.88
20	4.18	5.79	5.82	6.9
30	4.38	5.88	6.14	7.22
40	4.46	6.32	6.43	7.7
50	4.78	6.41	6.58	7.72

From Table 13, it can be stated that for a given percentage of lime, as the percentage of fly ash increases, the pH also increases. Also, for a given percentage of fly ash, the pH value of the sample increased with the increase in the percentage of lime. A plot is made to fix the amount of lime and utilize the fly ash to the maximum extent possible as presented in Figure 2.

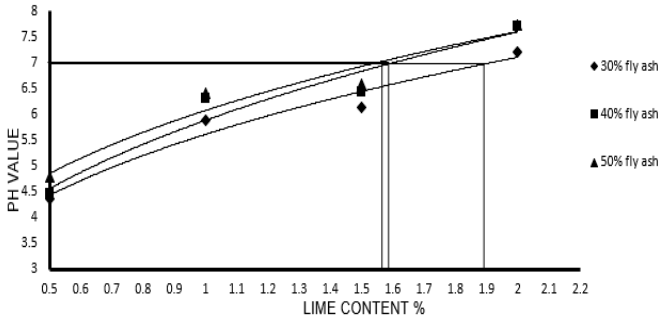

Figure 2 Neutralization of phosphogypsum with different proportions of Lime and Fly ash

From Figure 2, it is found that the optimum amounts of fly ash and lime for neutralizing phosphogypsum are 50% and 1.6% respectively. The permeability of neutralized phosphogypsum in compacted state is determined to assess its suitability for use in upper part of the composite liner system. The Compaction and Permeability characteristics of phosphogypsum neutralized with fly ash and lime are presented in Table 14.

Table 14 Compaction and Permeability characteristics of phosphogypsum neutralized with 50% Fly ash and 1.6% lime

Property	Value
Compaction characteristics	
(i) Optimum moisture content (%)	23
(ii) Maximum unit weight (g/cc)	1.32
Permeability(m/s)	$3.99 x 10^{-7}$

From Table 14, it can be seen that phosphogypsum neutralized with 50% fly ash and 1.6% lime has permeability less than 10^{-6} m/s. Hence, it can be used in the upper part of the composite liner system.

4. CONCLUSIONS

Based on the extensive laboratory studies conducted on Phosphogypsum and lime treated phosphogypsum mixed with fly ash and pond ash, the following conclusions are drawn.

1. Phosphogypsum neutralized by 3% lime has a permeability of $1.49 x 10^{-6}$ m/s which does not satisfy the permeability condition specified by CPCB ($k \leq 10^{-6}$ m/s). Hence, it cannot be used in the upper part of the base lining system.
2. There is no significant change in the pH of the phosphogypsum with the addition of pond ash up to 50%.
3. Phosphogypsum treated with 50% pond ash and 2.5% lime has a permeability of $6.17 x 10^{-5}$ m/s. Hence, phosphogypsum blended with pond ash and lime cannot be used in the liner system.
4. Neutralization of phosphogypsum did not happen even with the addition of fly ash in greater proportions (up to 50%).
5. Phosphogypsum neutralized with 50% fly ash and 1.6% lime has a permeability of $3.99 x 10^{-7}$ m/s and satisfies the permeability requirement specified by CPCB. Hence, it can be used in the upper part of the composite liner system.

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