



# Sustainable Management of the Phosphogypsum Waste with Green and Innovative Approaches

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## Phosphogypsum: Its Role and Importance in the Phosphoric Acid Industry

Phosphogypsum (PG: CaSO<sub>4</sub>·2H<sub>2</sub>O) is a bulk industrial solid waste of "wet process" phosphoric acid production



### Phosphogypsum annual production in several countries



Country	production (million tons/year)	Reference (Awad et al 2024)			
China	22.0–75.0	Yang et al. 2016; Sun et al. 2022			
USA	30.0–50.0	Wędrychowicz et al. 2019; Liang et al. 2017			
Morocco	14.0-15.0	Ennaciri et al. <u>2020a</u>			
Russia	14.0	Lutskiy et al. <u>2018</u>			
Tunisia	10.0-12.0	Garbaya et al. <u>2021</u> ; Samet et al. <u>2019</u> ; Lassaad and Kammoun <u>2021</u> ; Zmemla et al. <u>2022</u>			
India	5.0–12.0	Naresha et al. <u>2016</u> ; Filho et al. <u>2023</u> ; Havanagi et al. <u>2018</u> ; Karim et al. <u>2021</u> ; Palla et al. <u>2022</u>			
South Korea	11.0	Rychkov et al. <u>2018</u>			
Ukraine	10.0	Thakur et al. <u>2023</u>			
Brazil	5.6-10.0	Thakur et al. <u>2023;</u> Andrade Neto et al. <u>2021</u> ; Nisti et al. <u>2014</u>			
The Netherlands	4.0	Bituh et al. <u>2021</u>			
Spain	3.0	Pérez-López et al. <u>2010</u>			
Turkey	3.0	Değirmenci 2008; Türkel and Aksin 2012			
Jordan	3.0	Al-Hwaiti et al. <u>2005</u>			
Poland	1.5–2.5	Wędrychowicz et al. 2019; Folek et al. 2011			
Vietnam	1.2	Ngo et al. <u>2022</u>			
Algeria	1.0	Chaalal et al. <u>2020</u>			

### Phosphogypsum: Its Potential Detrimental Role in Environment and Agriculture

Direct and recurring use of PG as fertilizer can reduce soil fertility

- I. Heavy Metal Accumulation:
- II. Soil pH Imbalance:
- III. Nutrient Imbalance:
- IV. Soil Microbial dysbiosis

Environmental and Soil health deterioration

- I. Radioactivity:
- II. Heavy Metals:
- III. Eutrophication:
- IV. Air Emissions:
- V. Soil Microbial dysbiosis

#### Huge financial cost:

- I. Storage and Handling (\$5 to \$10 per ton)
- II. Environmental Monitoring (\$1 to \$2 per ton)
- III. Remediation and Disposal (\$20 to \$30 per ton)

### Phosphogypsum management approaches



- Chemical Approaches
- ✓ Neutralization
- ✓ Sulfur Recovery
- ✓ Phosphorus Recovery
- ✓ Rare Earth Elements (REEs) Extraction
- ✓ Carbonation
- ✓ Roasting
- ✓ Microwave Heating
- ✓ Recrystallization

- Mechanical Approaches
- ✓ Stacking
- ✓Grinding
- ✓ Compaction
- ✓ Pelletization



I. The potential for soil and water contamination, if not managed properly.II. Toxic secondary by-product.

(2016 stack failure in Florida led to a sinkhole that released over 200 million gallons of contaminated water into the Floridan Aquifer)

- **Costly:** Many of these methods are expensive and may not be economically feasible for all regions or industries (approx. <u>\$20 to \$50 per ton of PG</u>).
- **Safety:** Handling and processing PG can pose health and safety risks to workers, especially when dealing with hazardous chemicals or fine particles.
- **Time:** Some of these process are slow and time taking process (Weeks to years)

### **Green and Sustainable management approaches (Available)**



# Problem with the current biotechnological Phosphogypsum management approaches



# Solution: Indigenous Microorganisms (IMO) based Technology

to evaluate the feasibility of the biostimulation based aerobic biotransformation of PG using the indigenous microorganism





### **Summary of the work**







### Plan of work: Microcosm

	Microcosom Designation	pH with NaHCO <sub>3</sub>	Acetate as carbon and electron acceptor	NaNO <sub>3</sub> as N sources	K <sub>2</sub> HPO <sub>4</sub> as phosphate sources	Tween 80 as surfactant	
	К						1. K: Killed control
	U						2. U: Un-amendment
	pН						3. pH: pH Neutralization
	С						4. N: Nitrogen
Microcosm setup Experiment	N						<ol> <li>C: Carbon</li> <li>P: Phosphate</li> <li>S: Surfactant amendment</li> <li>pH+C: pH with Carbon</li> </ol>
Ļ	Р						
Physiochemical parameter analysis of PG and PG amended soil samples	S						
	pHC						9. pH+N: pH with Nitrogen
<b>↓</b>	pHN						10.pH+P: pH with Phosphate
Anion and other mineralogical analysis PG and PG amended soil samples	pHP						11.pH+S: pH with Surfactant
	pHS						13 C+P: Carbon and Phosphate
•	CN						14.C+S: Carbon and Surfactant
Community Level Microbial profiling of PG and PG amended soil samples	СР						<ul> <li>15.N+P: Nitrogen and Phosphate</li> <li>16.N+S: Nitrogen and Surfactant</li> <li>17.P+S: Phosphate and Surfactant</li> <li>18.C+N+P: Carbon, Nitrogen and Phosphate</li> </ul>
	CS						
	NP						
	NS						
	PS						19.C+N+P+S: Carbon, Nitrogen,
	pHNPS						Phosphate and Surfactant

### **Result: pH neutralization**



Among all the microcosm sets pH of carbon amended samples (C, pH + C, C + N, C + P, C + S, CNP and CNPS) was significantly higher (p < 0.001) than the control sets during 180 day of incubation.



Revival of pH from 3.9 to 7.1; close to fertile soil

Effect of pH of 22 different nutrient amendments on PG contaminated soil samples of 180 days

# **Result: Sulphate and Phosphate reduction**



Sulfate and phosphate concentration was significantly reduced (p < 0.001) in the CNPS microcosm set compared to PG contaminated soil in 180 days.

- >95% reduction in sulphate concentration.
- > 96% reduction in phosphate concentration.

C + N + P + S: Carbon, Nitrogen, Phosphate and Surfactant amendment



(A) Sulfate reduction profile, (B) Phosphate reduction profile, in microcosms over 180 days incubation period.



Fluoride and chloride concentration revealed an overall reduction in all the amended samples with respect to PG contaminated soil, although their values varied significantly among the treatments

- 40% reduction in chloride concentration
- 68% reduction in fluoride concentration



Anion distribution plot of nutrient amendment treated samples over 180 days incubation period.



### **Result: Microbial physiological profile**

The substrate utilization response of C and S amended population (individually or in combination) was significantly enhanced in compare to control.

 AMR response of indigenous microorganisms enhanced by 75%



Community level physiological profile of nutrient amendment treated samples over 180 days incubation period.



Our (IMO) technology successfully recover the contaminated soil close to fertile soil by neutralizing soil pH (pH: 3.9 to 7.1), reducing anions, sulphate and phosphate concentration and by promoting the metabolic activity (75% enhancement in average metabolic rate) of the indigenous microorganisms.



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Impact of elevated phosphogypsum on soil fertility and its aerobic biotransformation through indigenous microorganisms (*IMO's*) based technology

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### **Microbial Induced Calcium Carbonate Precipitation (MICP)**



#### **SDG and MICP**











PhosAgro/ UNESCO/ IUPAC Partnership in Green Chemistry for Life



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