

**Guidelines for
Management and Handling of Phosphogypsum
Generated from Phosphoric Acid Plants
(Final Draft)**



CENTRAL POLLUTION CONTROL BOARD
(Ministry of Environment & Forests)
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June 19, 2012

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Abbreviations

AERB	-	Atomic Energy Regulatory Board
BOD	-	Biochemical Oxygen Demand
CETP	-	Common Effluent Treatment Plant
COD	-	Chemical Oxygen Demand
CPCB	-	Central Pollution Control Board
EMP	-	Environment Management Plan
E (P) Act	-	Environment (Protection) Act, 1986
ETP	-	Effluent Treatment Plant
F	-	Fluoride
FDEP	-	Florida Department of Environmental Protection
GW	-	Ground Water
GWT	-	Ground Water Table
HDPE	-	High Density Polyethylene
IRC	-	Indian Road Congress
Kg	-	Kilogram
Km	-	Kilometre
MoEF	-	Ministry of Environment & Forests
NAAQS	-	National Ambient Air Quality Standards,
NHAI	-	National Highway Authority of India
PCC	-	Pollution Control Committee
PG	-	Phosphogypsum
SLF	-	Secured Landfill
SPCB	-	State Pollution Control Board
SPM	-	Suspended Particulate Matter
TPA	-	Tonnes per annum
TCLP	-	Toxicity Characteristics Leaching Procedure

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1 Introduction

Phosphate, in the form P_2O_5 is a nutrient for plants and a building bloc in food production. Agriculture sector uses large amount of chemical fertilizers to replenish and supplement the nutrients that growing plants take up from the soil. Modern intensive agriculture boosts natural phosphate levels in the soil through the addition of the phosphate Fertilizers.

Rock phosphate is the naturally occurring source for P_2O_5 . The phosphogypsum is generated from the phosphoric acid plants. If the phosphogypsum is disposed in open yards or disposal in phosphogypsum stack yards, it may pose threat to the environment. Handling and management of phosphogypsum is a major problem in phosphoric acid plants because of the large volumes and large area required and the potential for release of dust, fluoride and heavy metals in seepage.

Phosphogypsum generated from phosphoric acid plants is presently stacked and some quantity of the same is sold to the other industries for beneficial use especially as raw material in cement manufacturing as substitute for mineral gypsum as well as for alkali soil amendments or re-conditioning. The handling of phosphogypsum through trucks or railways involves loading, unloading and temporary storage at yards/depots is likely to cause environmental impacts especially during rainy season. In order to have minimal impacts on environment, there is a need for evolving the guidelines for safe handling, utilization and disposal of phosphogypsum.

The Hazardous Waste (Management, Handling & Transboundary Movement) Rules, 2008 notified under the Environment (Protection) Act, 1986 excluded phosphogypsum from hazardous waste category under Schedule-I, and stipulate that the management of phosphogypsum from phosphoric acid fertilizer plants will be carried out in accordance with the guidelines of Central Pollution Control Board (CPCB).

In view of the above, this guideline has been prepared to address the over all aspects of phosphogypsum handling storage and disposal including its utilization. The report covers present scenario with regard to the generation of phosphogypsum from fertilizer units, existing management and handling practices followed by the phosphoric acid plants in the Country as well as the practices being followed in other parts of the World. The report also deals with the guidelines to be followed for safe handling and storage of phosphogypsum within the phosphoric acid plants, safe disposal of phosphogypsum through stacking and end use of phosphogypsum for beneficial use that may be encouraged in order to solve the problem associated with the disposal of phosphogypsum.

Issues relating to the radioactivity present in the phosphogypsum are not covered in detail under these guidelines as such issues fall under the purview of the Atomic Energy Regulatory Board. However, the guidelines issued by the Atomic Energy Regulatory Board (AERB) i.e. 'Use of Phosphogypsum in Building & Construction Materials & in Agriculture (AERB Directive No. 01/09) need to be adopted (**Annexure –I**).

2 Phosphoric acid manufacturing process, production scenario in phosphoric acid plants

Phosphorus content present in the form of calcium phosphate in the phosphate rock cannot be taken up by the plants directly. Hence, the water soluble form of phosphorous is derived from rock phosphate by converting the calcium phosphate to phosphoric acid.

The rock phosphate required for production of phosphoric acid in the country is mainly through imports. The chemical composition of the Indian rock phosphate as well as imported phosphate rock, production of rock phosphate in India are given in **Table 1, 2 and 3** respectively.

2.1 Manufacturing process of phosphoric Acid

Production figures for phosphoric acid are expressed in terms of P₂O₅ content. For example, 100 Tonnes per day P₂O₅ corresponds to 333 Tonnes per day of phosphoric acid of 30 per cent concentration (P₂O₅). There are two basic methods for commercial production of phosphoric acid namely the wet process and the furnace process. In India, wet process is mostly used for the production of phosphoric acid for making phosphatic Fertilizer. Phosphoric acid manufacturing details are given in the following sections.

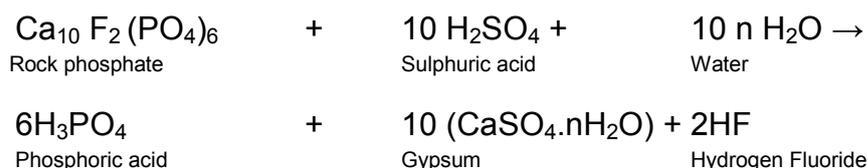
2.1.1 Thermal furnace phosphoric acid

In this process, phosphate nodules or lump phosphate material, silica pebble and coke are mixed and fed to an electric furnace. The material is fused in the furnace and phosphate is reduced to release phosphorus vapour and carbon monoxide gas from the furnace. This elemental phosphorus produced is converted to P₂O₅ which is dissolved in water to form phosphoric acid. This process can use low grade rock phosphate and produce pure phosphoric acid. However, this process is used in small plants for manufacturing chemical grade phosphoric acid in India. This method is not used in Fertilizer grade production due to high power requirement resulting in high cost of production.

2.1.2 Wet process phosphoric acid

Production of phosphoric acid by this process is as follows:

- (i) Acidulation of finely ground rock phosphate with sulphuric acid to form phosphoric acid and gypsum.



Where n = 0, ½ or 2 depending on the hydrate from in which the calcium sulphate is crystallised.

- (ii) Separation of gypsum from the acid by filtration.
(iii) Washing of gypsum to remove adhering phosphoric acid.
(iv) Concentration of the acid by evaporation to the desired concentration.

Washing of gypsum is employed to recover as much phosphoric acid as possible without excessive dilution of the acid. Dilute acid is recycled to the first stage filter cake washing. The acid from the filter is concentrated through indirect heating by steam in a vacuum evaporator. By-product phosphogypsum is disposed off in dry or slurry form.

There are two distinct processes for manufacture of phosphoric acid, namely, the di-hydrate process and the hemihydrate process. Combination of di-hydrate and hemi-hydrate processes is also used for production of phosphoric acid to achieve higher degree of P_2O_5 recovery.

(a) **Dihydrate process (DH):**

This involves reaction between ground rock phosphate and sulphuric acid below $80^\circ C$, in either a single or multi tank reactor configuration. Product acid of 26-32 per cent concentration (as P_2O_5) is filtered from the gypsum crystals. The filter cake is subjected to counter current washing with water on the filter and dilute acid so obtained is returned to the reactor. The phosphoric acid from the filter is normally evaporated to about 40 per cent in a single stage. If 50-54 per cent P_2O_5 acid is required, further evaporation is necessary. The concentration of acid consumes high energy. Further during concentration, around 70-80 per cent of fluorine present in the acid is released which is recovered as hydrofluosilicic acid (H_2SiF_6). Hydrofluosilicic acid may be used to make cryolite, AlF_3 or other fluorine compounds. A flow sheet for the manufacture of phosphoric acid is given in **Fig. 1**.

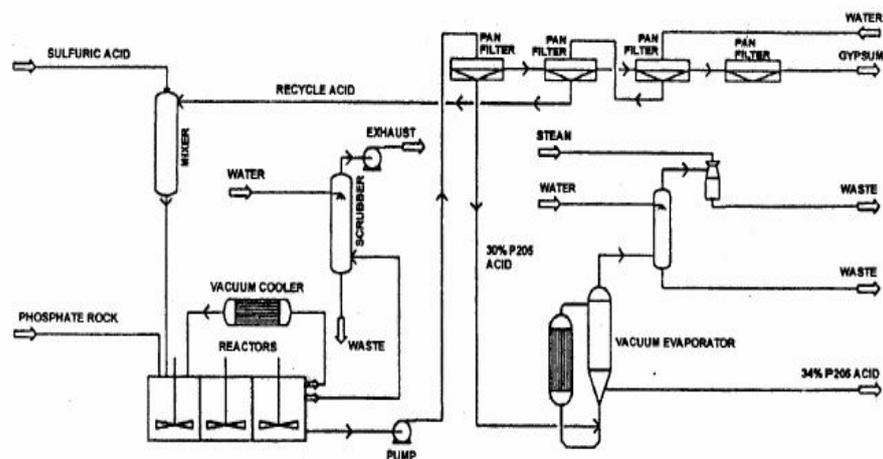


FIG. 1. Manufacture of Phosphoric Acid

The major advantages of the single-stage di-hydrate process are related to flexibility and reliability factors. In the di-hydrate process,

more moisture is permissible in the phosphate feed, and there is more tolerance to the use of weak sulphuric acid, since the overall water balance in the system is not so critical. The di-hydrate process also has greater flexibility with respect to rock phosphate quality but, it may simply be due to the fact that, the di-hydrate process to-date being the most popular process, more operating experience has been accumulated with diverse rock types than for other processes. In the di-hydrate route, the operating temperatures are low and the start-up and shutdown are easy and require the lowest operational skills. The P_2O_5 recovery efficiency is 94-96 percent. Most of the plants in the county have adopted di-hydrate process.

Di-hydrate process remains the most predominant because of its low capital cost, low operating temperatures and flexibility of operation. Technologies evolved in manufacturing phosphoric acid have been striving to achieve rapidly filterable gypsum crystals, lower P_2O_5 losses and product acid of higher concentration. The di-hydrate process suffers from relatively low P_2O_5 recovery and low strength of acid.

Newer processes claimed to overcome these limitations of the di-hydrate processes are Hemi-hydrate–di-hydrate (HDH) (double filtration stage) and di-hydrate–hemi hydrate (DHH) and three stage re-crystallisation.

(b) Hemi-hydrate process (HH):

This involves the reaction between rock phosphate and sulphuric acid above 80°C . Selective operating conditions are maintained to crystallize calcium sulphate hemi-hydrate, rather than the di-hydrate form. The single stage hemi-hydrate process generates a reaction slurry which, when filtered, produces directly a phosphoric acid product of 40-52 % P_2O_5 concentration with considerable savings in energy requirements. After washing the filter cake to remove further P_2O_5 , dilute acid is returned to the reaction stage. However, P_2O_5 recovery efficiency is lower than di-hydrate process at 90-94 per cent. The unrecovered P_2O_5 is retained in phosphogypsum hemihydrate and hence its disposal or use could be a problem. The process is easy to operate and can use coarse rock. The advantages of this process are lower capital cost, high purity and concentration than di-hydrate process and usage of much coarser rock. Some of the disadvantages of this process are: hemi-hydrate slurry are difficult to filter since the crystals are smaller and less well formed compared to the di-hydrate, higher P_2O_5 losses, corrosion of pipes and equipment due to operation at higher temperature and higher acid concentration etc.

(c) Hemi-hydrate–di-hydrate with Intermediate filtration (HDH):

The first reaction takes place under hemi-hydrate conditions, followed by filtration to obtain purer product acid of 40-52 per cent P_2O_5 . As usual, dilute acid from washing the cake returns to the primary reactor. The hemi-hydrate filter cake is then repulped at a lower temperature in dilute sulphuric acid and held for sufficient time for the hemi-hydrate to re-crystallize to the di-hydrate form. Any occluded rock phosphate particles exposed in the process dissolve in the additional sulphuric acid. This process produces a

purier form of phosphogypsum and filtrate solutions, which are used to wash and repulp the hemi-hydrate filter cake. Thus, a high concentration purier product acid of about 45 per cent P_2O_5 is obtained. This may need no further evaporation before use, at a much higher P_2O_5 recovery efficiency, typically above 98 per cent than is possible in a single stage process.

(d) Di-hydrate–hemi-hydrate:

The acid reaction is carried out under di-hydrate conditions followed by recrystallisation of calcium sulphate hence first filtration is less important. Slightly more concentrated acid (32-37 per cent P_2O_5) than the single stage di-hydrate process is produced. This unwashed di-hydrate filter cake is repulped and converted to hemi-hydrate to release further P_2O_5 , and the resultant slurry is filtered once more to obtain a hemi-hydrate that is less residual level of P_2O_5 and hence can be used directly in the manufacture of plaster, plastic board or as a cement retarder. In this process, the recovery efficiency of P_2O_5 is around 98 per cent.

(e) Three Stage Re-crystallisation:

It is possible to change the form of the calcium sulphate twice during the process. In this way, the maximum of P_2O_5 trapped in the crystal structure of the calcium sulphate is released and P_2O_5 recoveries in excess of 99 per cent are claimed. The best known system of this type is the hemi-di-hemi-hydrate process. The initial reaction is carried out in the hemi-hydrate mode, and the product acid is separated at 40-45 per cent P_2O_5 or more. The filter cake is then re-slurried and converted to di-hydrate to release P_2O_5 and then converted back to hemi-hydrate once more, usually without filtration at the di-hydrate stage. The process, therefore, appears to combine the best of all possibilities, high strength acid, very high P_2O_5 recovery, and production of potentially much more useful pure hemi-hydrate filter cake, but at the price of increased capital equipment and complex manufacturing stages in processes .

A typical phosphate rock conveying system, washing of phosphogypsum cake prior to the disposal is given in **Fig.2 and Fig. 3** respectively.



FIG. 2. Phosphate rock silo & conveyance system



FIG. 3. Washing of phosphogypsum cake prior to the disposal

2.2 Phosphoric acid production scenario in India

In India, there are **11** no. of phosphoric acid manufacturing units located in 07 States namely Andhra Pradesh, Gujarat, Kerala, Maharashtra, Orissa, Tamil Nadu and West Bengal. The total production of phosphoric acid is about 1.2 Million Tonnes during the year 2009-2010. The phosphoric acid production and the consumption scenario in the Country, is given in **Table 4**.

3 Generation of Phosphogypsum

Phosphogypsum is generated from filtration process in phosphoric acid plants where insoluble gypsum (and other material) are separated from the product i.e. phosphoric acid as efficiently as possible. Depending on the source of rock phosphate about 4.5 -5 Tonnes (dry basis) of phosphogypsum (by-product phosphogypsum) is generated per ton of phosphoric acid (as P_2O_5) recovered.

The quality & quantum of phosphogypsum generation depends upon the quality of the phosphate rock, process route used to produce phosphoric acid, calcium sulphate generated either in di-hydrate ($CaSO_4 \cdot 2H_2O$) or the hemi-hydrate ($CaSO_4 \cdot 1/2 H_2O$) form. Phosphogypsum generation in the Country is about 11 Million Tonnes per annum (based on the assumption that 5 Tonnes of phosphogypsum generated per ton of phosphoric acid production). The industry-wise production of phosphoric acid scenario in the country as per the information provided is compiled and given in **Table 5**.

4 Characteristics of phosphogypsum

Phosphogypsum is a gray coloured, damp, fine grained powder, silt or silty-sand material with a maximum size ranges between 0.5 mm (No. 40 sieve) and 1.0 mm (No. 20 sieve) and the majority of the particles (50-75 %) are finer than 0.075 mm (No. 200 sieve). The specific gravity of phosphogypsum ranges from 2.3 to 2.6. The maximum dry bulk density is likely to range from 1470 to 1670 kg/m^3 (92 to 104 lb/ft^3), based on Standard Proctor Compaction. The gypsum cake, after filtration, usually

has free moisture content between 25 and 30%. Hemihydrate, in the presence of free water will rapidly convert to dihydrate and in the process, if left undisturbed will set into a relatively hard cemented mass and does not cause dust problem unless disturbed.

Phosphogypsum consists of primarily of calcium sulphate dihydrate with small amounts of silica, usually as quartz and unreacted phosphate rock, radioactive material (like radium, uranium), heavy metals namely arsenic, cadmium, chromium, mercury and fluoride. The concentration of the metals depends on the composition of the phosphate rock. The following are the main concerns with respect to management of phosphogypsum;

- i) High fluoride concentration (in the range of 0.5 -1.5 %) may leach fluoride and contaminate the groundwater, if not stored and handled properly;
- ii) Presence of radio-nuclide radium -226 which upon decay may emits harmful alpha particles;
- iii) May contain heavy metals (Cd, Cr, Pb etc) that may enter into the food chain through potable water and agriculture products.

Permeability of phosphogypsum depends on stabilization. Permeability in unstabilized phosphogypsum has been found to range from 1.3×10^{-4} cm/sec down to 2.1×10^{-5} cm/sec for stabilized phosphogypsum. Typical chemical characteristics of the phosphogypsum is given in **Table 6**.

5 Management and handling of phosphogypsum

Phosphogypsum retains 18-35 % moisture depending upon type of filtration and handling facilities installed for necessary disposal. In most cases, washed filter cake is received into hopper and mixed with process or return or make-up water to make slurry so that it can be pumped to the phosphogypsum disposal stack. In some cases, phosphogypsum is removed from filter as dry cake and transported to the disposal area by conveyor belt or any other means of solids handling system. However, this method is not widely practiced as slurry handling is simpler and less expensive.

Majority of the phosphoric acid plants in the Country are based on wet process (di-hydrate) for production of phosphoric acid. Certain degree of differences can be seen in the process or technology adopted which influences the characteristics and type of handling of phosphogypsum within the plant. The first of handling of phosphogypsum is first done by the industry itself wherein it is required to shift the washed phosphogypsum to the phosphogypsum stack / intermediate storage /direct disposal for utilisation / loading point for sale or disposal.

5.1 Handling of Phosphogypsum - within phosphoric acid plants

In dry stacking, the filtered cake of phosphogypsum is transported to the disposal area by trucks or belt conveyor where dozers with or without a mechanical stacker and movable lateral conveyors are used to spread the phosphogypsum evenly. The top surface of the stack is continuously distributed evenly using the bull dozer equipment. Except in very high rainfall locations, where the surface of the stack never gets a chance to dry out, dust generated by construction equipment is a problem which can be controlled by limiting the operational area of phosphogypsum

handling and keeping the surfaces damp by spraying water or recycling wastewater as needed.

In wet stacking, phosphogypsum slurry from an agitated surge tank is conveyed by gravity or pumped to the phosphogypsum stack through a rubber-lined steel or HDPE pipeline. Additional phosphogypsum pipelines are required, for both pumping and return line. In this method, the phosphogypsum slurry (5 – 30%) settles out on the top portion of the stack with slurry flow distribution through peripheral rim ditches. The decanted water flows down by gravity to the surge tank or holding pond from where it is pumped back for reuse in phosphoric Acid plant. Internal dike walls are built up from the dewatered phosphogypsum to give a steadily elevating pond. Phosphogypsum stacks up to a height of 20m are in operation in the country. This water cannot be discharged as such as it contains significant quantities of fluorine and phosphates as P_2O_5 . The outer dikes are generally earthen dikes designed to prevent the escape of contaminated water into nearby streams.

A stabilized phosphogypsum stack may not cause any dust problem however, dust emission can be seen during the excavation, shaping, movement of vehicles as well as maintenance of the access roads, this can be readily kept in damp condition to control particulate emissions.

Slurry pumping for transporting phosphogypsum offers significant operating, economic and environmental advantages over dry stacking even though it requires more make-up water, which might upset water balance, especially for lower capacity plants.

The pictures given at **Fig. 4, 5 and 6** show the operations in transportation of phosphogypsum by 'belt conveyor' and by vehicles to the Stack area respectively. The **Fig. 7, 8 & 9** shows handling of phosphogypsum in slurry form at phosphogypsum dikes.



FIG. 4. Conveyance of phosphogypsum to the Stack Area through 'Belt Conveyor'



FIG. 5 & 6. Truck loaded with phosphogypsum in Phosphoric Acid plant and unloading in phosphogypsum stack area (Dry stacking)



FIG. 7. Phosphogypsum stacking



FIG. 8. Pumping of phosphogypsum to the 'Ridge Dyke' in the form of slurry to the phosphogypsum stack



FIG. 9. Cooling water collection in 'surge pond' over the phosphogypsum stack

Waste Water Treatment, existing phosphoric acid plants in the country have installed Effluent Treatment Plants (ETPs) in order to treat excess process water which may require disposal especially during monsoon. The excess water is generally treated by neutralisation with lime followed

by clarification so as to meet the discharge norms for pH, phosphates, fluoride, sulphate, prior to disposal.

5.2. Utilization of Phosphogypsum – Existing practice

Presently, most of the phosphoric acid plants are disposing the phosphogypsum within the plant premises in stack (s). Depending on the demand, the phosphoric acid units sell the phosphogypsum for different applications which include (i) for use as soil conditioning (for alkaline soil) or as fertilizer in agriculture (ii) in cement manufacturing to control the settling time of cement (as a retardant) and (iii) small quantity is used in the production of plaster, plaster boards, gypsum fiber boards, and gypsum blocks.

Above utilization requires handling and transportation of phosphogypsum by means of railways [Fig. (11)] and or trucks. The utilization of phosphogypsum depends on the degree of impurities such as fluoride, phosphoric acid and radio-activity which depends on type of raw material used, process adopted or pre-treatment given to phosphogypsum.

Two phosphoric acid plants are in the process of commissioning plaster board manufacturing units as an integral part of the phosphoric acid plants [Fig. (12)]. Two phosphoric acid plants already constructed model low cost houses using plaster boards/panels [Fig. (13) & (14)] manufactured from phosphogypsum.

The industry-wise present practices of phosphogypsum waste disposal are given in Table 7. One of the plant is manufacturing a by-product i.e NPK Granulated Fertilizer Mixture.



FIG.11. Phosphogypsum lying at rail yards for transportation to the end users



FIG. 12. Plant & Machinery for plaster board/panel manufacturing using phosphogypsum



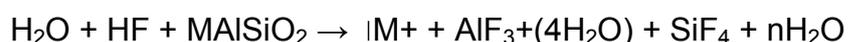
FIG. 13 & 14. Phosphogypsum Board/panel and the house made of phosphogypsum panels

6 Environmental impacts associated with phosphogypsum dumping yards

Phosphogypsum (fresh & untreated) is acidic in nature due to residual phosphoric acid, sulphuric acid and hydrofluoric acid within the porous structure. The acidic nature of fresh phosphogypsum may keep trace elements dissolved from the phosphate rock in a potentially mobile state (i.e leachable form) and the impurities include fluorides, sulphates, residual acids, organics, trace metals as well as naturally occurring radionuclides.

The environmental concerns associated with phosphogypsum stacks include fluoride uptake, ground and surface water pollution if located nearby. Main vectors for their transport into the environment are wind and water erosion, infiltration, leaching into surface and ground water and airborne emissions of gaseous and radioactive elements. Fine particles of phosphogypsum can be picked up and transported by wind and vehicular traffic on stacks into adjacent areas. Dust particles containing fluoride is a concern for operational and non operational stacks. Elevated levels of fluoride have been found in soil/vegetation adjacent to the stacks.

Disposal of phosphogypsum on land may pose seepage problems beneath the repositories or the process water holding ponds if not lined or controlled properly. Fluoride contaminant present in phosphogypsum may attack silicate minerals and dissolve them, according to the following equation:



where:

MAiSiO₂ represents an aluminosilicate mineral
M represents Ca, Mg, Na, K, and Fe

Some of the SiF₄ may hydrolyse to form H₂SiF₆ (fluorosilicic acid) within the phosphogypsum leachate. The presence of H₂SiF₆ may result in dissolution of clay soils at the bottom of phosphogypsum repositories, which may allow accelerated movement of contaminants into the groundwater in course of time if phosphogypsum is not contained properly.

Water erosion of phosphogypsum stacks may create solution cavities and instabilities in constructed berms and dykes, lead to surface runoff of phosphogypsum, erosion around piping systems and gully erosion. Slopes may become more susceptible to failure and erosion with heavy rain fall.

Typical trend analysis of the characteristics of the groundwater in and around the Phosphoric acid plants is given in **Table 8 & Table 9**. As a part of preparation of these guideline, Central Pollution Control Board (CPCB) conducted visit to some of the phosphoric acid plants and phosphogypsum samples were collected and the analysis results of the samples are given in **Table 10**.

7 International practices of phosphogypsum management & handling

Phosphogypsum contains three types of impurities that are considered to be potentially harmful such as residual acidity, fluorine compounds, trace elements including radioactivity. International practices of phosphogypsum management and handling aspects are given in the subsequent paras.

7.1. U.S.Practices

Several of the phosphoric acid plants in Florida use mined-out phosphate rock land for phosphogypsum disposal. For sea coast locations, phosphoric acid plants are permitted to discharge phosphogypsum into the ocean for disposal. In such cases, solids content of the wastewater is usually below 5%, low enough for quick dispersion and dissolution in the ocean water. Only very limited uses have been found for by-product phosphogypsum in the United States.

Combined phosphogypsum disposal and pond water cooling is the most common practice in handling phosphoric acid plant waste streams; however, the use of a separate pond to handle most of the cooling load with clean water is not unusual. The separate ponds system has the disadvantage of higher initial cost but offers the potential advantage of greater flexibility and may provide better land utilization.

A few plants have used cooling towers (of acid-resistant material) rather than a cooling pond. Also, closed-cycle lime treatment of process water, followed by clarification and cooling of the clarified water in a conventional cooling tower, has been used successfully. However, lime requirements by this process are quite high, up to 300 lb/ton of P₂O₅ produced.

7.1.1 Florida State and local management requirements for phosphogypsum stack systems

In 1993, the Florida Department of Environmental Protection (FDEP) promulgated new management requirements for phosphogypsum stack systems. These standards (Section 17-673.100-900, Florida Administrative Code) include requirements for permitting, design, operation, monitoring, and other activities, such as closure, and financial assurance. For the construction and operation of a new phosphogypsum stack system, a permit issued by FDEP is required. In addition, the Florida Department of Community Affairs, regional planning agencies (e.g., the Tampa Bay Regional Planning Council and the Central Florida Regional Planning Council) and local government have the authority to require a development of regional impact (DRI) review for new phosphogypsum stack systems to analyse potential environmental and socioeconomic impacts and to propose mitigation measures.

7.1.2 Design requirements for new phosphogypsum stacks as per Florida State regulations

As per the design requirements applicable to new phosphogypsum stack systems (according to F.A.C. 17-673), the basic performance standard for a phosphogypsum stack is to not violate ground water and surface water quality standards and criteria specified for the system. The Florida regulations stipulate requirements of the system: liner, leachate control system, and liquid containment and conveyance systems. The regulations allow for two types of liner designs. The synthetic component

of the liner is a 60-mil or thicker geo-membrane liner with a maximum water vapor transmission rate of 0.24 grams per square meter per day. This liner can either be placed: (1) above a layer of compacted soil at least 18 inches thick, with a maximum hydraulic conductivity of 1×10^{-7} cm/sec, or (2) below a layer of mechanically compacted phosphogypsum at least 24 inches thick, with a maximum hydraulic conductivity of 1×10^{-4} cm/sec.

7.2 European practices of phosphogypsum disposal

In Europe the practice of phosphogypsum disposal is somewhat different from that in America mainly because there is less open space in industrialized areas and because the geographical location of the phosphoric acid plants follows a different pattern. The data surveyed on 18 major phosphoric acid plants with a total annual capacity of over 1 million metric Tonnes of P_2O_5 shows that the plants operate a dihydrate process, most of them using traveling-pan filters (belt or rotary). Three plants dump the material on their own land and 2 plants use excavated areas, e.g., old lignite mines, for the purpose. Only 1 plant, located in inland Germany, uses a settling pond and reuses the water drained from the pond, as is the practice in Florida. The various methods utilized are discussed below, with emphasis on specific problems associated with each method.

7.2.1 Disposal into sea and rivers

After removal from the filter, the phosphogypsum is slurried with about a tenfold quantity of seawater. The slurry is subsequently pumped into the sea through plastic pipelines with diameters of at least 6 inches. When the plant is located very close to the coast, concentration and flow rate of the slurry is kept at levels such that plugging of the lines is prevented. A solids percentage of about 10% and a pumping rate of at least 6 ft/sec are generally used.

When a plant is located at a river or estuary, too far from the coast to use a pipeline, another intermediate stage may be used. The rivers into which phosphogypsum is directly discarded are usually tidal ones which entrain and dissolve the material effectively. Phosphogypsum disposal into smaller inland rivers is not allowed at all.

7.2.2 Disposal into pits and quarries

When plants are located inland in industrial areas, or close to sand or lignite pits, mines, or quarries, the waste phosphogypsum is dumped into the excavated areas or unused parts of mines. This is especially true in Germany, particularly in the Ruhr area.

7.2.3 Disposal on land

Two methods are used to dump the waste phosphogypsum on land (land which, incidentally, is usually the property of the company producing the phosphogypsum). When the disposal area is close enough to the phosphoric acid plant, the material, as it comes off the filter, is transported by conveyor belts. When the area is too far from the plant for conveyor belts to be practicable, the phosphogypsum is slurried with water and pumped to the dumping area through pipelines or ditches. Either the disposal area may consist of a settling pond, with the water recirculated to the plant or removed to a river, or the slurry may be dumped and the water allowed soaking into the soil.

In some countries, especially France, phosphogypsum is used agriculturally as a structure-improving agent for the soil. The quantities used are negligible, as compared to the amount of waste phosphogypsum available. In special cases very considerable quantities of waste phosphogypsum from phosphoric acid plants are used to reclaim land after flooding of the sea. In this case, the phosphogypsum is used as an ion-exchange agent to remove adsorbed sodium ions from the soil. Sodium ions in the soil have a very bad influence, resulting in reduced permeability and various other adverse effects. After the great flood in 1953, large amounts of waste phosphogypsum from phosphoric acid plants were used in England, France, and the Netherlands.

7.3 By-product utilization: As raw material for plaster and cement

Phosphogypsum is also used in countries like Japan, Germany as raw material for plaster board manufacturing as well as cement, details are given in subsequent paras.

7.3.1 Japanese practice as raw material

- (a) Plaster and Gypsum Board manufacturing: There were 16 companies (21 factories) manufacturing gypsum board in Japan in 1966, and 6 companies (6 factories) producing gypsum plaster. Over 90% of the phosphogypsum used for these products was phosphogypsum from phosphoric acid manufacture; little or no natural gypsum is used for these products. There were 15 companies (16 factories) manufacturing plaster of paris for industrial uses, but most of them were small. Much of the gypsum for plaster of paris is natural gypsum. A very large increase has taken place in production of these materials since 1959.
- (b) For Cement manufacturing: The Onoda Cement Company, Tokyo, Japan has succeeded in complete practical utilization of phosphogypsum, by first calcining it to hemihydrate and soluble anhydrite and then neutralizing this with lime water to convert the impurities to insoluble, inactive calcium salts.

7.3.2 European practices of utilisation of phosphogypsum as raw material

Germany is the only European country utilizing its resources of by-product gypsum to any extent; but due to the presence of adequate natural supplies of gypsum, considerable quantities of gypsum from the wet-process phosphoric acid manufacture are simply dumped. However, in view of the continually increasing costs of mining natural gypsum and the availability of more and more by-product phosphogypsum each year, it seems reasonable that in the future by-product phosphogypsum will start to replace natural gypsum as a raw material for building products. The growing awareness of the problems of water pollution and the expense involved in dumping phosphogypsum will also compel the more efficient utilization of a by-product which occurs in large and expanding quantities. By-product gypsum will therefore play a much more important part in the industrial economics of Europe in the future than it has ever done in the past.

Except for building products, there is little use of by-product gypsum. The production of ammonium sulfate by the double decomposition reaction between ammonium carbonate and by-product gypsum is now used only

to a limited extent in Europe. At various times small quantities of ammonium sulfate have been produced from by-product gypsum in Europe, and ICI in the United Kingdom used the process for a short time.

8 Guidelines for storage, management, handling and disposal of phosphogypsum

Following guidelines are applicable to the phosphogypsum stacks which are in operation, or closed or proposed to be closed, or proposed for lateral expansion as well as for new phosphogypsum stacks including expansion in phosphoric acid production. These guidelines are also applicable for handling of phosphogypsum waste at yards, and phosphogypsum stacks.

8.1. General guidelines for location, construction, operation and maintenance of phosphogypsum stack (for both dry and wet stacks)

General guidelines w.r.to the location, construction, operation and maintenance of phosphogypsum stacks are given in subsequent paras:

8.1.1 Requirement of approvals for new phosphoric acid plants

- (i) Phosphoric acid plants proposing to construct new or additional phosphogypsum stack (s) shall obtain Consents under Water (Prevention and Control of Pollution), Act, 1974 & Air (Prevention and Control of Pollution), Act, 1981 from the concerned State Pollution Control Board (SPCB) or Pollution Control Committee (PCC) prior to the construction and shall also submit the details along with the Consent application, such as (a) ownership of the land, (b) details of temporary storage area, (c) design drawings of the proposed phosphogypsum stack, (d) details of handling, (e) construction schedule, (f) operational practices and monitoring protocols schedules, (g) maintenance and remedial plans or any other relevant information.
- (ii) The phosphogypsum stack system, henceforth, shall not be constructed, operated, expanded, modified or closed without prior approval/ intimation to the SPCB/PCC.
- (iii) SPCB/PCC shall make periodic visits to ensure that the construction of the phosphogypsum stacks is as per the approved designs.

8.1.2 Site selection and location criteria for new phosphogypsum stack (for both dry and wet stacks)

- (i) Phosphogypsum stack may be located within the existing industry premises or it may be located at isolated locations preferably 1 KM away from any notified habitat area human habitation at suitable location as approved by the SPCB/PCC and shall be provided with proper approach roads for safe transportation of phosphogypsum.
- (ii) *The phosphogypsum stacks of new plants shall not be located on the 100-year flood plain where it will restrict the flow.*
- (iii) *Phosphogypsum stacks of new plants should be located atleast at a distance of 500 meters away from any natural or artificial water bodies and whereas the existing Phosphoric Acid plants having*

phosphogypsum stack system should take adequate measures such that the runoff from the phosphogypsum storage yard should not be allowed to go into the surface water or any natural or artificial water bodies.

8.2 Design parameters of the new phosphogypsum stack (both dry and wet stacks)

- (i) All the new Phosphogypsum stack including the lateral expansion of the existing phosphogypsum stack (s) shall be designed, constructed, operated and maintained at least for a period of 05 years.
- (ii) As far as possible, the phosphogypsum stack should be constructed above the ground level and over the natural clayey strata (also blended with bentonite) to eliminate any seepage.
- (iii) The side slopes of the stacks shall be maintained suitably keeping the safe stability of the stack.

Requirements of the composite liners and its specification (for both dry and wet stacks) are as follows:

- (iv) Any new phosphogypsum stack should have impervious liner system possessing adequate physical, chemical and mechanical properties to prevent failure due to physical contact with phosphogypsum or process wastewater or leachate, local climatic conditions, hydrostatic uplift pressure and the stresses which may arise due to stacking of phosphogypsum waste.
- (v) Phosphogypsum stack base liner shall have a single composite liner comprising of a HDPE geo-membrane minimum thickness of 1.5 mm over a compacted clay or compacted amended soil layer of thickness 60 cm or mixture of native soil with bentonite and having a coefficient of permeability of 10^{-7} cm per second (10^{-9} m/sec) or less. Further, a layer of mechanically compacted phosphogypsum at least 30 cm thick, placed above the drainage, with a maximum coefficient of permeability of 1×10^{-4} cm per second (10^{-6} m /sec) serving as the second part of the required composite liner system.
- (vi) Emphasis on protection of the geomembrane during placement and compaction of the phosphogypsum, and on prompt placement of phosphogypsum on the geomembrane shall be taken care of to avoid failure of the geomembrane while operating the phosphogypsum stack.
- (vii) All the joints of the geomembrane liner prior to commencement of the phosphogypsum stacking shall be tested for leakages if any and measures should be taken for proper welding of such joints.

Leachate collection, process wastewater, surface runoff collection and surge pond should have the following provision.

- (viii) The under-drain system comprising of lateral drains of 15 cm. diameter, perforated, corrugated HDPE pipe shall be laid in a bed of non-reactive silica fine gravel, placed approximately at 30 m interval. The lateral drains which, in turn are surrounded by an

envelope of clean silica sand that acts as a filter for the phosphogypsum. A 20 cm thick blanket of sand is also provided beneath the perimeter piping system and diverted to surge pond, from where it is returned to the process plant for re-use and excess flow to the holding pond.

- (ix) A peripheral ditch or garland dyke (with passage at suitable intervals) shall be constructed surrounding the phosphogypsum stack so as to retain and collect runoff as well as collection of lateral seepage at the toe of the outer dyke or embankment.
- (x) Excess wastewater in the recirculation system between the phosphoric acid plants and the phosphogypsum stack shall be routed to Effluent Treatment Plant (ETP) for further treatment to comply with the liquid effluent discharge norms stipulated under the Environment (Protection) Act, 1986 prior to disposal.

Suggested liner system for Phosphogypsum Stack is given in **Fig.15** and a typical cross section of a phosphogypsum stack is given in **Fig. 16**.

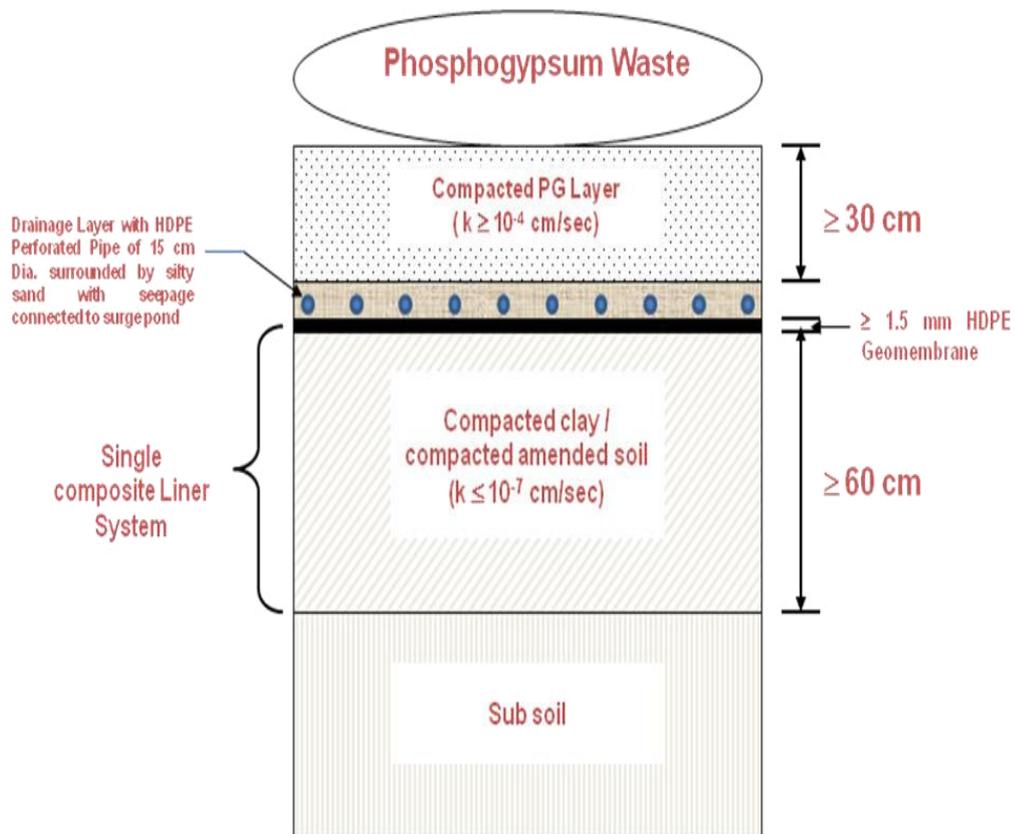


Fig. 15. Suggested Liner System for the Phosphogypsum Stack

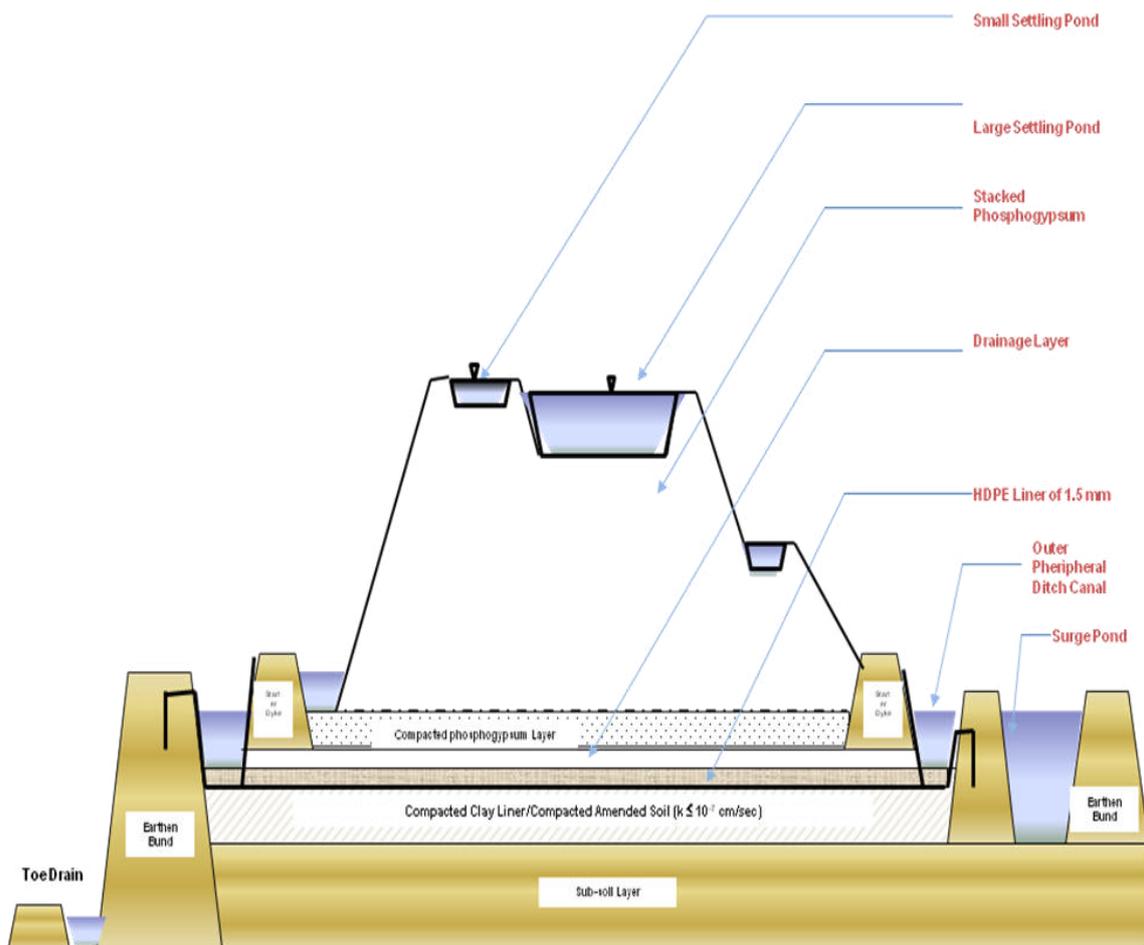


Fig.16. Typical Cross Section of a Phosphogypsum Stack

Note: All the existing phosphoric acid plants presently storing the phosphogypsum in open yards and not meeting these guidelines shall be permitted to store in such stack till the new phosphogypsum stack meeting these guidelines are developed within a period of three years since enforcement of these guidelines. During this period, all such phosphoric acid plants periodically monitor the surface and ground water resources around the phosphogypsum stack (s) as per the monitoring protocol suggested under these guidelines, through a laboratory recognized under the Environment (Protection) Act, 1986 or any NABL Accredited Laboratory for assessment of the contamination if any and such assessment reports be submitted to Central Pollution Control Board through the respective SPCB/PCC. In case, adverse environmental impacts are observed, then such phosphoric acid plant is required to submit remediation plan which may also include existing phosphogypsum waste utilization plan seeking approval of Central Pollution Control Board.

8.3 Operation and monitoring of phosphogypsum stacks:

Following guidelines are suggested w.r.to the surface and ground water monitoring requirement and periodic inspections.

8.3.1 Surface and ground water monitoring provision

Monitoring of the groundwater quality and the water accumulated adjacent to the phosphogypsum stack during the monsoon shall be carried out at the regular intervals and is required to be taken up in accordance with the monitoring protocol suggested under Section 9 of these guidelines.

8.3.2 Periodic inspections

During the operational phase and post-closure maintenance period (atleast for 05 years) of the stack (both wet & dry), following measures are suggested:

- (i) The phosphogypsum stack shall be inspected at least once in a quarter as a part of the maintenance and contingency plan and suitable remedial measures shall be taken to have no impact on the environment.
- (ii) Suitable measures shall be taken to avoid fugitive emissions due to wind erosion of phosphogypsum from the phosphogypsum stack.

8.4 Record maintenance and precautionary measures

The Phosphogypsum should be guarded round the clock. Provision shall be made for security room, vehicle weighing platform, vehicle tyre washing at the exit. Daily records of quantity of phosphogypsum received in the stack, and the quantity lifted for utilization shall be maintained. Further, following provision should be provided:

- (i) Proper housekeeping at the material storage areas, loading & dispatch areas, service facilities, etc., shall be practiced.
- (ii) Motorable road shall be constructed on outer most dyke of the phosphogypsum yard.
- (iii) There should be a peripheral garland road all around the phosphogypsum stack for inspection and monitoring purposes. This road shall be within 50 m from the outer dyke of the phosphogypsum stack.

8.5 Guidelines for intermediate storage for temporary storage of phosphogypsum within the phosphoric acid plants or any other beneficial use

Intermediate storage and handling of phosphogypsum is required within the phosphoric acid plant for the purpose of lifting and transportation of waste to the phosphogypsum stack or for utilization by the outside agencies. Following guidelines are applicable:

- (i) Phosphogypsum shall be handled under a covered shed of adequate size (for storage of phosphogypsum and the floor should

be of impervious nature surrounded by the proper drainage system for collection of floor washings. Under no circumstance, phosphogypsum shall be stored outside the designated shed.

- (ii) Intermediate storage area shall be provided with a provision of vehicle weighing platform, vehicle washing bay (for washing wheels of the vehicle while leaving the temporary storage area), security room, and a provision of recording system to record entry of vehicle and lifting of phosphogypsum quantities.
- (ii) Floor wash water, wastewater generated from vehicle washing bay and run-off contaminated with phosphogypsum shall be collected properly and routed to Effluent Treatment Plant (ETP) or Common Effluent Treatment Plant (CETP) for treatment and to ensure complying with the effluent discharge norms stipulated under the Environment (Protection) Act, 1986.
- (iii) Measures should be taken for proper collection of spillages from the filter area to the temporary storage area or along the conveyor belts.
- (iv) While transportation of phosphogypsum from the temporary storage area by trucks / tippers / wagons through public roads, the vehicles shall be properly covered (with tarpaulin sheets)
- (v) In case of any spillage of phosphogypsum on public roads while transporting, it is the sole responsibility of the transporter for clearing such spillage immediately.

Note: Above guidelines are also applicable to the Units utilizing the phosphogypsum where there is a necessity for intermediate/temporary storage of phosphogypsum, prior to its use is required.

8.6 Closure of the existing phosphogypsum stacks or abandoned phosphogypsum stacks

When the storage capacity of a phosphogypsum stack is exhausted or no longer receiving phosphogypsum and when the owner or operator does not, deposit any quantity of phosphogypsum or not wishing to dispose of the phosphogypsum in phosphogypsum stack yard, seepage out of the stack and rainfall runoff from the slopes need to be contained on-site and/or treated before discharge, then a phosphogypsum stack considered as inactive and requires closure. Closure plans for phosphogypsum stack system shall include the following:

- (i) Phosphogypsum stack where rainwater collection provision is made over the top of the stack, there is a need to transfer ponded process water from the top of the stack to process water storage ponds.
- (ii) To construct a new buried "toe drain" on all the sides of the stack to collect leachate.
- (iii) To grade side slope roads into drainage channels sloped to flow to stormwater retention ponds; cover the grade channels with clayey sands and establish grass, and

- (iv) To construct a surface water management system to collect rainfall and to control runoff from retention ponds. Place a cover of topsoil and grass on all areas of side slopes that are bare or have insufficient grass cover.

Note: *In case, the phosphoric acid plants does not prefer for permanent closure of the existing phosphogypsum stack, in such a case, such phosphoric acid plant is required to submit a proposal for the existing phosphogypsum waste utilisation plan through concerned SPCB/PCC with their views to the Central Pollution Control Board for further approval.*

8.7 Guidelines for storage, handling and loading of phosphogypsum at railway yard by the Phosphoric Acid Plants

This guideline is applicable in case the railways are used as a mode of transportation of phosphogypsum and intermediate storage of phosphogypsum is required in railway yard:

- (i) Covered intermediate storage of adequate size shall be provided with impervious flooring and proper drainage system for collection of floor washings. Under no circumstance, phosphogypsum shall be stored outside the designated shed in rail yards before transportation.
- (ii) Floor wash water, and run-off contaminated with fluoride and phosphates shall be collected properly and routed to effluent treatment plant (ETP) or Common Effluent Treatment Plant (CETP) for treatment and to ensure complying with the effluent discharge norms stipulated under the Environment (Protection) Act, 1986.
- (iii) Measures should be taken for maintaining proper house keeping and collection of spillages within the rail yard which may arise during unloading of waste from trucks or loading of phosphogypsum into rail rakes.

9 Guidelines for beneficial use of phosphogypsum

As far as possible, the phosphoric acid plants should put efforts to utilize the generated phosphogypsum for beneficial purposes such as (i) plaster board manufacturing, in cement manufacturing as substitute for natural gypsum, recovery of by-products such as ammonium sulphate, sulphuric acid, reclamation of the alkali soils. For utilization of the phosphogypsum, following guidelines are required to be followed:

- (i) All the gypsum board manufacturing industry shall utilize phosphogypsum waste (*Specifications: low radioactivity, low in organic matter and sodium content*) as raw material for manufacture of plaster, gypsum boards, putty, plaques etc. after reduction in impurities to the level as given in Indian Standards I.S: 12679.
- (ii) All the phosphoric acid plants may explore possibilities of recycling of the phosphogypsum in plaster/gypsum board manufacturing through their own establishment as an integral part of the phosphoric acid plant or any other small scale unit.

- (iii) As far as possible, Cement manufacturing unit (s) shall use the phosphogypsum (*Specifications: less than 0.05% co-crystallized and soluble P₂O₅ less than 0.05% soluble F*) in place of the natural gypsum as a regulator for setting time of cement, at the rate of 4 to 5% in its composition. Phosphogypsum used for manufacture of cement retarder, plaster and plaster or gypsum boards, shall necessary conform to the specifications, as given below:

S.No.	Parameter	Suggested limit (in %)
1	Insoluble P ₂ O ₅	0.50 to 0.60
2	Insoluble Fluoride	0.40 to 0.60
3	Soluble P ₂ O ₅	0.02 to 0.10
4	Soluble Fluoride	0.00 to 0.02
5	Moisture	Less than 10.0

Note: All parameters are in % age except otherwise mentioned

- (iv) Any entrepreneur who wishes to manufacture ammonium sulphate from the phosphogypsum waste may approach the concerned State Pollution Control Board (SPCB) / Pollution Control Committee (PCC) for obtaining consents as required for establishment of such recycling industry. *Merseberg reaction:*



- (v) Any entrepreneur wishes to recover or manufacture of sulphuric acid from the phosphogypsum waste may approach the concerned State Pollution Control Board (SPCB) / Pollution Control Committee (PCC) for obtaining consents as required for establishment of such recycling industry. *Müller-Kühne process reaction:*



- (vi) The phosphogypsum may be used to reclaim alkali soils and saline –alkali soils with high sodium ion concentration. The calcium ions in phosphogypsum replace the sodium ions, which may be leached down during the course of irrigation. Fertilizer (Control) Order has also approved the use of phosphogypsum as Fertilizer in view of its nutrient values, therefore, Fertilizer industry may maximize the use of phosphogypsum as 'Fertilizer'. Phosphogypsum is also a major soil amendment for reclamation of alkali soils. For this purpose the Indian Standard specifications for By-product Gypsum as stipulated under IS: 10170-1982 need to be followed. In case of use of phosphogypsum as Fertilizer, it shall meet the following specifications:

Name of the Parameter	Testing Method	Recommended Limit (not exceeding)
Fluoride	TCLP	200 mg/l
Cadmium	TCLP	1 mg/l
Lead	TCLP	5 mg/l
Arsenic	TCLP	5 mg/l
Mercury	TCLP	0.2 mg/l
Moisture	Free moisture As per IS 10170-1982	15 %

10 Monitoring protocol for assessment of environmental impacts in and around the phosphogypsum stacking yard

Monitoring of emissions plays an important part in environmental management. It can be beneficial in some instances to perform continuous monitoring. This can lead to rapid detection and recognition of irregular conditions and can give the operating staff the possibility to correct and restore the optimum standard operating conditions as quickly as possible. Emission monitoring by regular spot checking in other cases will suffice to survey the status and performance of equipment and to record the emission level.

10.1 Ambient air quality monitoring

- (i) **Number of monitoring stations:** Air quality monitoring stations at upwind, downwind and at three stations at 120° angle around the phosphogypsum stack (or within the industry boundary) is necessary. Location of the air quality monitoring stations should be as approved by the State Pollution Control Board (SPCB)/ Pollution Control Committee (PCC).
- (ii) **Parameters to be monitored and frequency of ambient air quality monitoring:** Parameters stipulated under the Consent under Air (Prevention and Control of Pollution) Act, 1981 should be monitored to know the status of ambient air quality in and around the phosphogypsum stack (s) or within the industry premises to take preventive measures if required. *In any case, Ambient Air Quality around the phosphogypsum stack (s) should be monitored for the parameters such as 'Particulate Matter, F and SO₂' as per NAAQS criteria (minimum of 104 measurements in a year taken twice a week, 24 hourly).*

10.2 Ground water monitoring

It is recommended to monitor ground water characteristics at least **once in a quarter** around the phosphogypsum stacks.

- (i) **Parameters to be analysed:** It is recommended that ground water samples should be analysed for pH, P and F on quarterly basis and other parameters like EC, SS, BOD, COD, heavy metals (such as As, Cd, Cr, Hg, Ni, Pb and Zn), Fe, Cl, NO₃, SO₄, TKN, Total Alkalinity and Total Hardness shall be analysed (or) for the parameters as per the Consent conditions issued by the SPCB/PCC.
- (ii) **Sampling locations:** It is recommended that the ground water samples should be collected at least up to a radial distance of 1 KM from the phosphogypsum stack. If no open wells or tube wells are available within a radial distance of 1 KM, action need to be taken to provide at least **four monitoring wells (piezometric)** around the phosphogypsum stack i.e. one on up gradient of the ground water flow and other three on the down gradient side of the ground water flow at least up to 'shallow water bore well'. Depending upon the situation, if required, the monitoring wells till second aquifer should also be extended in consultation with the SPCB/PCC. The directions of the ground water flow have to be established in consultation with the State Ground Water Board or any other approved authority. The ground water flow direction is

required to be ascertained periodically and reported at least **once in three years** so as to know any changes in the ground water flow directions due to any changes in the local conditions such as draw down of ground water.

10.3 Surface water monitoring: Monitoring of surface water (nullah/ river, impoundments) at upstream and downstream, surge ponds, retention ponds, toe drains and holding ponds located in adjoining area is necessary at least **twice in a year** (i.e. pre-monsoon and post-monsoon). It is recommended that the surface water samples should be analysed for pH, EC, Turbidity (NTU), SS, TDS, BOD, COD, heavy metals (such as As, Cd, Cr, Hg, Ni, Pb and Zn), Fe, P, F, Cl, NO₃, SO₄, TKN, Total Alkalinity and Total hardness. Also, monitoring of surface water is required to be conducted 'once in a week' for specific parameters such as pH, P, F, SS and NH₄-N' ,

10.4 Soil samples monitoring

- (i) **Parameters to be analysed:** It is recommended that the soil samples should be analysed for pH, EC, heavy metals (such as As, Cd, Cr, Hg, Ni, Pb and Zn), P, F.
- (ii) **Sampling location & frequency of sampling:** At least one number of composite soil sample is required to be collected upto a depth of 0.50 m beneath the soil surface for every grid size of 250 X 250 m upto a radius of 500 m from the extreme end of the phosphogypsum stack. It is recommended that the soil samples should be collected and analysed for the suggested parameters at least twice in a year i.e. pre-monsoon and post-monsoon.

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Table 1: Chemical composition of the Indian rock phosphate (Weight %)

Constituent	RSMML, Rajasthan			Madhya Pradesh			West Bengal
	HG	MG	Chips	Jhanbua	Hirapur	Krishna Phoschem	
P ₂ O ₅	33-34	31.54	31.5	24	27-29	30.2	19.5
CaO	47-51	46.84	47.17	42-48	42-52	45-46	24.9
SiO ₂	4-7	-	9.84	14-18	5-8	15-16	15.7
F	2.8-3.1	-	3.8	2.5-3	3-3.5	2.5-3	-
R ₂ O ₃	1-2	2.5	2-11	3.3-6	2-11	2-2.5	25.8
MgO	1-2.5	0.64	0.49	0.5-0.75	0.1-1.0	0.5-0.75	1.9
Organic Matter	-	-	-	0.4	-	-	-
Cl (ppm)	100	-	-	0.1	0.05	-	-
CO ₂	-	-	-	1-1.6	0.3-1	1.5-2.0	-
SO ₃	Traces	-	-	0.40	0.03	-	-
TiO ₂	-	-	-	-	-	-	1.5-2.0
MnO	-	-	-	-	-	-	2-2.5
Na ₂ O + K ₂ O	-	-	-	-	-	-	-
LOI	5.6	7.12	4.02	-	0.1	-	10.7

Source: Fertilizer Association of India.

Table 2: Typical chemical composition of the imported rock phosphate (Weight %)

Constituent	Algeria	Jordan	Moroccan	Egyptian
P ₂ O ₅	29.89	31.50	36.79	28.51
CaO	49.71	51.13	53.05	46.35
SO ₃	3.09	1.10	0.87	1.12
CO ₂	4.54	4.20	1.85	4.92
Al ₂ O ₃	0.35	0.44	0.27	0.76
Fe ₂ O ₃	0.40	0.38	0.10	1.69
SiO ₂ (T)	1.34	7.47	3.42	7.01
SiO ₂ (A)	1.21	5.10	1.37	4.385
F	3.95	3.94	4.00	3.2
SiO ₂ (A)/F	0.31	1.29	0.34	1.37
O.C	0.08	0.09	0.02	0.116
MgO	-	-	-	-
Na ₂ O	-	-	0.25	-
LOI	9.28	8.60	2.19	10.3
Organic Matter (gm/ml)	1.6490	1.4964	1.4	1.6
Cl (ppm)	503	912.00	661	581

Source: Tata Chemicals Limited

Table 3. Production of rock phosphate in India ('000 tonnes)

Year	PPCL ¹	RSMM ²	MPSMC ³		WBMDTC ⁴	Total
	Mussoorie#	Jhamarkotra	Meghnagar (Jhabua)	Hirapur (Sagar)	Purulia#	
2000-01	0.09	732.0*(72.0)#	42.9	23.7	7.8	806.5
2001-02	Nil	866.0*(76.0)#	49.9	26.2	8.8	950.9
2002-03	Nil	1157.7*(60.1)#	47.3	26.9	7.8	1239.7
2003-04	Nil	1181.9*(26.0)#	45.6	13.8	7.9	1249.2
2004-05	Nil	1249.5*(37.6)#	64.9	35.8	9.3	1359.5
2005-06	Nil	1302.0*(59.0)#	137.8	112.6	8.3	1560.7
2006-07	Nil	1312.0*(45.0)#	96.2	96.5	6.0	1510.7
2007-08	Nil	1355.9*(83.0)#	63.4	82.9	4.5	1506.7
2008-09	Nil	1229.8*(100.9)#	132.7	117.8	4.2	1484.5
2009-10	Nil	1378.0 (80) #	127.1	77.8	4.1	1587.0

Source: Fertilizer Association of India.

= For direct application * = Includes quantity manufactured for direct application

1. Pyrites, Phosphates and Chemicals Ltd., Dehradun (Uttaranchal)
2. Rajasthan State Mines and Minerals Ltd., Udaipur (Rajasthan)
3. Madhya Pradesh State Mining Corporation Ltd., Bhopal (M.P.)
4. West Bengal Mineral Development and Trading Corporation Ltd., Kolkata, W.B

Table 4. Production of phosphoric acid and its consumption scenario in the Fertilizer industry ('000 tonnes P₂O₅)

Year	Production	Phosphogypsum**
2000-01	1042.4	4690.8
2001-02	1134.7	5106.15
2002-03	1085.6	4885.2
2003-04	990.1	4455.45
2004-05	1242.5	5591.25
2005-06	1067.8	4805.1
2006-07	1331.8	5993.1
2007-08 (P)	1206.5	5429.25
2008-09 (P)	1201.7	5407.65
2009-2010	1160	

Source: Fertilizer Association of India.

- * = Out of indigenous production
 ** = Estimated quantity of phosphogypsum generated (Apprx. 4.5 tonnes of phosphogypsum/ton of phosphoric acid produced)

Note: Phosphoric acid is expressed as 100% P₂O₅

(P) = Provisional;

Table 5 : Details of phosphoric acid plants and the phosphoric acid production scenario in the Country

S.No.	Name of the Industry	Raw material consumption		Phosphate rock imported from	Production capacity of phosphoric acid
		Phosphate rock (MT/MT of P ₂ O ₅)	Sulphuric acid (MT/MT of P ₂ O ₅)		
1.	TCL, Haldia, WB	3.67	3.13	Algeria, Egypt , Jordan, Morroco	5280 MT per month
2.	PPL, Orissa.	3.43	2.94	Morroco, Jordan & Egypt	900 MT/day
3.	GSFC, Fertilizer Nagar, Gujarat	3.45 – 3.51	2.75 – 2.9	Indigenous - Udaipur, Jordan	165 MT/day
4.	Hindalco Industries Ltd. (HIL) P.O. Dahej, Gujarat	3 – 3.5	2 – 3	JPMC, Jordon & Togo, Africa	1,80,000 MT/annum
5.	Indian Farmers Fertilizer Co-Operative Ltd.(IFFCO) Musadia, Orissa	3.7	2.8	Jordan, Morocco, China, Egypt, Algeria, Vietnam, Israel, Syria and Peru	2650 MT/day
6.	Sterlite Industries (I) Ltd., (SIL) , Tuticorin, TN	3.42	2.85	Jordan, Egypt, Togo, Nauru, Algeria	800 TPD
7.	Coromandel International Limited (CIL), Vishakhapatnam, AP	3.0 – 3.5	2.2 – 2.5	Togo, China, Israel, Algeria	Not provided
8.	Coromandel International Limited (CIL) , Ennore, TN	3.55	-	Israel, Jordan	150 TPD
9.	Southern Petrochemical Industries Corporation Ltd. (SPIC), Tuticorin, TN	3.78	-	Jordan and Egypt	125000 MTPA
10.	Fertilizers and Chemicals Travancore Ltd., (FACT) Ambalmedu, Kerala	3.4	3.13	Morocco and Jordan	360 TPD
11.	Rashtriya Chemicals And Fertilizers Ltd., (RCFL) Chembur, Mumbai	3.2	2.9	Jordon, Togo and Algeria	3100 MT per month

Source: Details as provided by the concerned phosphoric acid manufacturing Units

Table 6. Chemical composition of phosphogypsum in India (weight %) – dihydrate process (dry basis)

Parameter	Composition in %
H ₂ O _{cryst}	18.0
SO ₂	43.6
CaO	32.0
MgO	0.40
Al ₂ O ₃ + Fe ₂ O ₃	1.82
SiO _{2 ins.} In HCl	1.64
Na ₂ O	0.36
P ₂ O _{5 total}	1.03
F _{total}	0.76
Organic matter	0.26

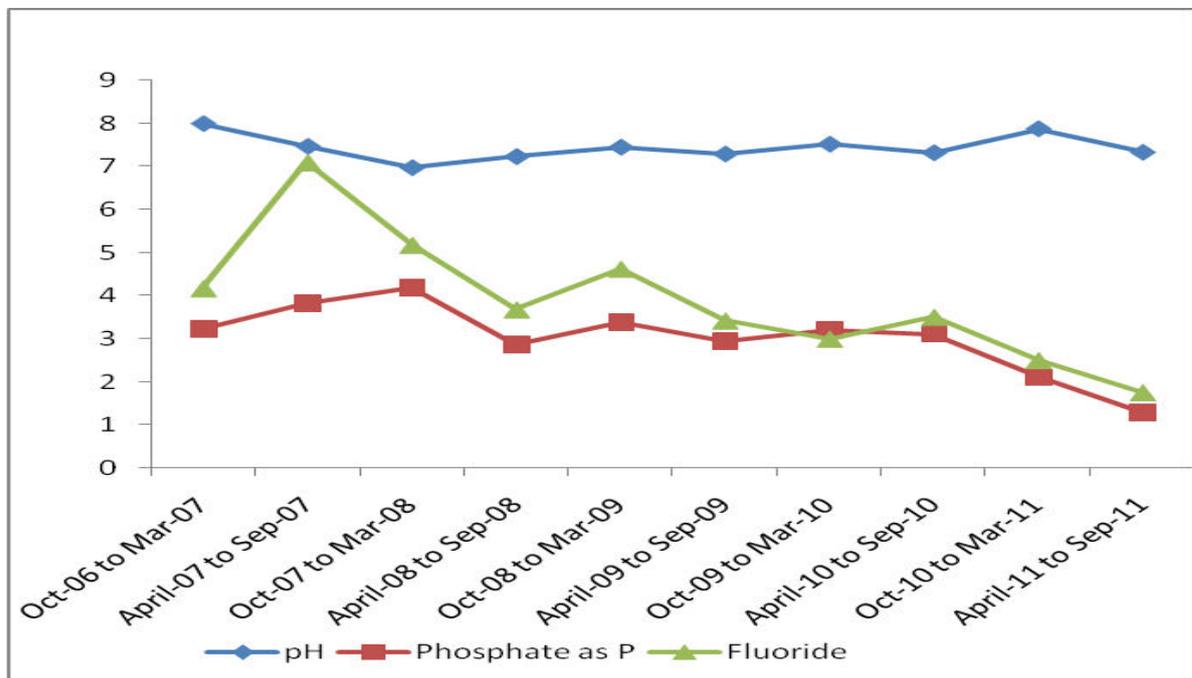
Table 7. Industry-wise phosphogypsum disposal practices in phosphoric acid plants

S. No.	Name of Industry	Phosphogypsum Waste Generation		Phosphogypsum Waste Management Practices		
		Quantity (MT) from 2006 – 2011	Phosphogypsum Generation Rate (MT/MT of P ₂ O ₅)	Dry Disposal	Wet Disposal	Intermediate Storage
1.	TATA chemicals Ltd. Haldia, WB	478591.52	4.5	Dry Phosphogypsum is directly delivered to the gypsum storage area for curing and further sale. In last ten years 19.13 Lac MT of phosphogypsum is reported to be disposed off	Only at the time of start up and shut down of the plant, phosphogypsum slurry has been sent to the gypsum pond for settling and further sales after drying.	There is no intermediate storage facility
2.	Paradeep Phosphates Limited, Paradeep, Orissa.	6229900	5		From Phosphoric Acid Plant phosphogypsum is transported as slurry containing 10-15% through HDPE pipelines to gypsum stack. Phosphogypsum is excavated and transported to railway storage site. Till date 3125735 MT has been sold to SPCB registered end users like M/s Odisha Cement Ltd.; M/s Orrisa Agro Industries corporation etc.	One Intermediate storage shed of area 700 x 15 m with 25000 MT capacity has been provided.
3.	Gujarat State Fertilizer & Chemicals Limited Vadodara, Gujarat.	2043233.4	5.5 – 5.9	-	Phosphogypsum in slurry form is sent to the 'phosgypsum pond' through pipelines which is located within the plant and then phosphogypsum is dispatched in loose/bagged form to farmers on continuous basis. Surplus quantity is repulped and sent to the pond. Capacity of yard is 2000 MT	There is no intermediate storage facility
4.	Hindalco Industries Ltd. Bharuch, Gujarat	2215198	5	Phosphogypsum waste Transportation from plant to the storage yard directly through conveyor belt. Till now 3905808 MT of Phosphogypsum has been disposed off.	-	There is no intermediate storage facility
5.	Indian Farmers Fertilizer Co-Operative Ltd. Musadia.	from 2005 – 2011 : 10922885	4.5 – 5		Wet Phosphogypsum is being sent to the Phosphogypsum pond area through HDPE pipeline. There are 2 nos. of gypsum ponds of 200 acres and 85 acres area respectively. Phosphogypsum is being sold to SPCB authorized end users/transporters from the closed phosphogypsum stack.	There is no intermediate storage facility

6.	Sterlite Industries (I) Ltd., SIPCOT Industrial Complex, Tuticorin	4171306	4.7	Through conveyor system, phosphogypsum is getting transferred and stored in lined phosphogypsum pond. There are 07 conveyors and through tippers the phosphogypsum is shifted to the designated location.		There is no intermediate storage facility
7.	Coromandel International Limited, Vishakhapatnam, AP	3349334	4 – 4.5	Dry phosphogypsum is directly disposed to the HDPE lined gypsum handling area before its final disposal	-	-
8.	Coromandel International Limited, Ennore, Chennai	1576933	5.83	Transported through conveyor belts, toppers and trucks stored in impervious layer pond.		There is no intermediate storage facility
9.	Southern Petrochemical Industries Corporation Ltd. Tuticorin, TN	83200 MTPA	5		Wet disposal is being followed by the unit. Phosphogypsum is first collected in the tank and slurry was pumped to the disposal pond.	There is no intermediate storage facility
10.	Fertilizers and Chemicals Travancore Ltd., Ambalmedu Kerala	1316319	6	Phosphogypsum produced in the plant is conveyed to Phosphogypsum pond and the earmarked area for phosphogypsum disposal, through tippers/trucks.		There is no intermediate storage facility
11.	Rashtriya Chemicals And Fertilizers Ltd., Chembur, Mumbai	561819	5.1		Wet disposal of phosphogypsum is being conducted by the industry through pipeline	There is no intermediate storage facility

Table 8. Typical Groundwater Monitoring Data for Phosphogypsum Pond under Operation

Near old Phosphogypsum pond			
Year	pH	Phosphate as P in mg/l	Fluoride as F in mg/l
Oct-06 to Mar-07	8	3.22	4.17
April-07 to Sep-07	7.47	3.82	7.1
Oct-07 to Mar-08	6.97	4.18	5.18
April-08 to Sep-08	7.23	2.86	3.68
Oct-08 to Mar-09	7.45	3.37	4.62
April-09 to Sep-09	7.29	2.93	3.42
Oct-09 to Mar-10	7.52	3.2	3
April-10 to Sep-10	7.32	3.1	3.5
Oct-10 to Mar-11	7.88	2.1	2.5
April-11 to Sep-11	7.33	1.28	1.75

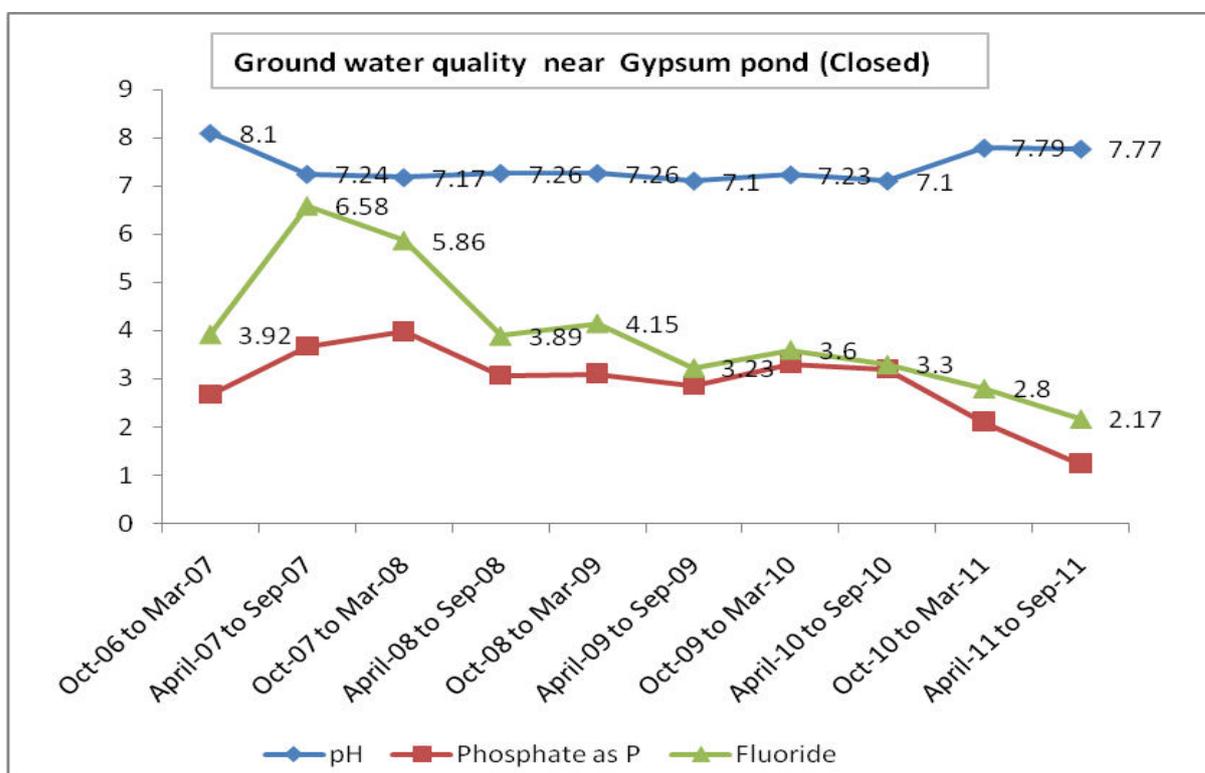


Location of the Unit: IFFCO, Paradeep

Source: Fertiliser Association of India

Table 9. Groundwater Monitoring Data for Phosphogypsum Pond –Closed

Near new Phosphogypsum Pond			
Year	pH	Phosphate as P in mg/l	Fluoride as F in mg/l
Oct-06 to Mar-07	8.1	2.67	3.92
April-07 to Sep-07	7.24	3.67	6.58
Oct-07 to Mar-08	7.17	3.98	5.86
April-08 to Sep-08	7.26	3.07	3.89
Oct-08 to Mar-09	7.26	3.1	4.15
April-09 to Sep-09	7.1	2.85	3.23
Oct-09 to Mar-10	7.23	3.3	3.6
April-10 to Sep-10	7.1	3.2	3.3
Oct-10 to Mar-11	7.79	2.1	2.8
April-11 to Sep-11	7.77	1.23	2.17



Location of the Unit: IFFCO, Paradeep

Source: Fertiliser Association of India

Table 10. TCLP Values of the heavy metals in phosphogypsum waste

S. No.	Name of the Industry	TCLP values in mg/kg										
		Moisture in %	Chloride (Cl)	Calcium (Ca)	Magnesium (Mg)	Cadmium (Cd)	Chromium (Cr)	Copper (Cu)	Iron (Fe)	Nickel (Ni)	Lead (pb)	Zinc Zn
1	GSFC, Vadodara.	17.65	24	952	29	0.03	NT	NT	NT	NT	0.19	0.33
2	RCF, Chembur	19.07	44	992	73	0.05	NT	NT	NT	NT	0.17	0.33
3	CIL, Ennore	18.99	20	856	24	0.14	NT	NT	NT	NT	NT	0.48
4	Sterlite Industries (I) Ltd., Tuticorin	2.66	24	1144	29	0.05	NT	0.12	0.55	0.11	0.1	0.35
5	SPIC, Tuticorin	18.74	20	640	360	0.26	NT	NT	0.13	NT	NT	0.15
6	IFFCO, Paradeep	-	-	-	-	0.03	NT	NT	0.17	NT	NT	0.09
		-	-	-	-	0.05	NT	NT	0.1	NT	NT	0.12
		-	-	-	-	0.06	NT	0.09	0.14	NT	0.15	0.18
7	Paradeep Phosphates Paradeep,	-	-	-	-	0.03	NT	0.05	0.23	NT	0.1	0.08
		-	-	-	-	0.04	NT	NT	0.14	NT	0.14	0.13



परमाणु
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Atomic
Energy
Regulatory
Board



No. CH/AERB/IPSD/78/2009/

March 20, 2009

AERB Directive No. 01/09

[under Rule 5 of the Atomic Energy (Radiation Protection) Rules, 2004]

Subject: Use of Phosphogypsum in Building & Construction Materials & in Agriculture

Rock phosphates imported in India by the fertilizer plants for production of phosphoric acid contain small concentrations of radioactive nuclides, viz., Uranium-238 and Radium-226. Phosphogypsum produced as byproduct during wet processing of imported rock phosphates contains activity concentration of U-238 typically in the range 0.1-0.2 Bq/g and Ra-226 typically in the range 0.5-1.3 Bq/g.

The subject of processing of imported rock phosphates and the use of phosphogypsum so produced in commercial applications like Building and Construction Materials and in Agriculture has been examined in the Atomic Energy Regulatory Board (AERB) from the radiological safety considerations and the following directives are issued.

1. Analysis of Rock Phosphate and Phosphogypsum

All rock phosphate processing industries shall carry out analysis to determine U-238 and Ra-226 content in each imported consignment of rock phosphate as well as in the phosphogypsum produced from its processing and shall report the results to AERB on quarterly basis. This



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data will be reviewed in AERB for a period of about two years for deciding on the frequency of such analysis in future.

2. Sale of Phosphogypsum by Fertilizer Plants

AERB approval is not required for selling phosphogypsum for its use in building and construction materials provided the activity concentration of Ra-226 in it is less than or equal to 1 Bq/g. [If Ra-226 concentration in phosphogypsum is more than 1Bq/g, it is to be mixed with other ingredients such that the Ra-226 activity concentration in bulk material is less than or equal to 1.0 Bq/g.]

3. Manufacturing and Use of Phosphogypsum Panels and Blocks

AERB approval is not required for manufacturing and use of phosphogypsum panels or blocks provided they have Ra-226 activity less than 40 kBq/square metre area of any surface of the panels/blocks.

4. Use in Agriculture

There is no restriction for use of phosphogypsum in agricultural applications from the radiological safety considerations.



(S. K. Sharma)
Chairman
Atomic Energy Regulatory Board
Competent Authority

CHEMICAL SYMBOLS

The following chemical symbols used where appropriate in the text.

C	Carbon
Ca	Calcium
CaCO ₃	Calcium Carbide
Cd	Cadmium
CO	Carbon Monoxide
CO ₂	Carbon Dioxide
F	Fluorine
F ⁻	Fluoride
H (H ₂)	Hydrogen
H ₂ O	Water
H ₂ S	Hydrogen Sulphide
H ₂ SiF ₆	Hydrofluorosilicic Acid (Hexafluorosilicic Acid)
H ₂ SO ₄	Sulphuric Acid
H ₃ PO ₄	Phosphoric Acid
HNO ₃	Nitric Acid
K	Potassium
KCl	Potassium Chloride (Muriate of Potash) ("Potash")
K ₂ O	Potassium Oxide
N (N ₂)	Nitrogen
N ₂ O	Dinitrogen Monoxide (Nitrous Oxide)
NH ₃	Ammonia
NH ₄ -N	Ammonical Nitrogen
NH ₄ NO ₃	Ammonium Nitrate
NO	Nitrogen Monoxide (Nitric Oxide or Nitrogen Oxide)
NO ₂	Nitrogen Dioxide
NO ₃ -N	Nitric Nitrogen
NO _x	Oxides of Nitrogen (Excluding Nitrous Oxide)
O (O ₂)	Oxygen
P	Phosphorus
P ₂ O ₅	Phosphorus Pentoxide
S	Sulphur
SO ₂	Sulphur Dioxide
SO ₃	Sulphur Trioxide

GENERAL INFORMATION ON PHOSPHORIC ACID

1. Identification

Chemical name	: Orthophosphoric acid
Commonly used synonyms	: Phosphoric acid, 40-60%
	: Merchant grade acid
C.A.S. Registry number	: 7664-38-2
EINECS Number	: 231-633-2
EINECS Name	: Orthophosphoric acid
Molecular formula	: H ₃ PO ₄

2. Hazards to Man and the Environment

To man

- Phosphoric acid is corrosive to all parts of the body.
- Contact with the skin can cause redness and burns.
- Splashes in the eyes cause irritation and burns.
- Acid mists may cause throat and lung irritation.

To the environment

- Phosphoric acid is harmful to aquatic life.

3. Physical and Chemical Properties

Appearance	: Brownish/greenish viscous liquid.
Odour	: Slight acid odour.
pH (no dilution)	: < 1
Freezing point	: -17.5°C (75%)
Boiling point	: 133°C (75%)
Auto-ignition temperature	: Not applicable
Vapour pressure	: 267Pa at 20°C
Solubility in water	: Miscible in all proportions.
Density	: 1.58 gm/cm ³ at 15.5° C (75%)

Glossary of Terms

- (1) **"Aquifer"** means a geologic formation, group of formations, or part of a formation capable of yielding a significant amount of groundwater to wells, springs or surface water.
- (2) **Auxiliary holding pond (AHP)** – a lined storage pond, typically used to hold untreated process water.
- (3) **Berm** – A shelf that breaks the continuity of the slope of an embankment in order to arrest the velocity of storm water flowing down the face and/or to enhance the stability of the embankment.
- (4) **"Closing"** means the time at which a phosphogypsum stack system ceases to accept wastes, and includes those actions taken by the owner or operator of the facility to prepare the system for any necessary monitoring and maintenance after closing.
- (5) **"Closure"** means the cessation of operation of a phosphogypsum stack system and the act of securing such a system so that it will pose no significant threat to human health or the environment. This includes closing, long-term monitoring, maintenance and financial responsibility.
- (6) **Cooling/surge pond** – impounded areas within the phosphogypsum stack system, excluding settling compartments atop the phosphogypsum stack, that provide cooling capacity, surge capacity, or any combination thereof, for the phosphoric acid process water recirculation system including phosphogypsum stack transport, runoff, and leachate water from the process watershed
- (7) **Dike** – A barrier to the flow of phosphogypsum and process water which is constructed of naturally occurring soil (earthen dike) or of phosphogypsum and which is a component of a phosphogypsum stack system.
- (8) **Drain** – A material more pervious than the surrounding fill which allows seepage water to drain freely while preventing piping or internal erosion of the fill material
- (9) **Earthen dike** – A barrier to the flow of phosphogypsum and process water which is constructed of naturally occurring soil and which is a component of a phosphogypsum stack system used only when necessary to avoid an unpermitted surface water discharge resulting from dike overtopping or failure. An earthen dike is typically located outside the footprint of a phosphogypsum stack system.
- (10) **"Final cover"** means the materials used to cover the top and sides of a phosphogypsum stack upon closure.

- (11) "**Geomembrane**" means a low-permeability synthetic membrane used as an integral part of a system designed to limit the movement of contaminants within the system.
- (12) "**Gypsum dike**" means the outermost dike constructed within the perimeter formed by a starter dike for the purpose of raising a phosphogypsum stack and impounding phosphogypsum and/or process water. This term specifically excludes any dike inboard of a rim ditch, any partitions separating stack compartments, or any temporary windrows placed on the gypsum dike.
- (13) "**100-year floodplain**" means the lowland and relatively flat areas adjoining inland and coastal waters, including flood-prone areas of offshore islands that are inundated by the 100-year flood.
- (14) "**Leachate**" means liquid that has passed through or emerged from phosphogypsum.
- (15) "**Liner**" means a continuous layer of low permeability natural or synthetic materials which controls the downward and lateral escape of waste constituents or leachate from a phosphogypsum stack system.
- (16) "**Phosphogypsum**" means calcium sulphate which is a byproduct produced by the reaction of sulfuric acid with phosphate rock to produce phosphoric acid.
- (17) "**Phosphogypsum stack**" means any defined geographic area associated with a phosphoric acid production facility in which phosphogypsum is disposed of or stored safely.
- (18) "**Phosphogypsum stack system**" means the phosphogypsum stack (or pile, or landfill), together with all pumps, piping, ditches, drainage conveyances, water control structures, collection pools, cooling ponds, surge ponds and any other collection or conveyance system associated with the transport of phosphogypsum from the phosphoric acid plant to the phosphogypsum stack and its management at the stack, and the process wastewater return to the phosphoric acid production or other process. This definition specifically includes toe drain systems and ditches and other leachate collection systems, but does not include conveyances within the confines of the fertilizer production plant or existing areas used in emergency circumstances caused by rainfall events of high volume or duration for the temporary storage of process wastewater to avoid discharges to surface waters of the state, which process wastewater shall be removed from the temporary storage area as expeditiously as possible.
- (19) "**Process wastewater**" means any water which is generated during manufacturing or processing, comes into direct contact with or results from the production or use of any raw material, intermediate product,

finished product, by-product, or waste product, along with any leachate or runoff from the phosphogypsum stack system.

- (20) **Railway siding** - A railway siding is a place/ area which is used to receive, temporarily store and load / unload phosphogypsum in rakes before dispatch.
- (21) **"Shallow water bore well"** means any potable water bore well which pumps water from an unconfined water table aquifer.
- (22) **"Toe drain"** is a wedge-shaped drain supporting the downstream toe of the dam

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