Hazardous Waste Management Series: HAZWAMS/......2014-2015

## Guidelines for Management, Handling, Utilisation and Disposal of Phosphogypsum Generated from Phosphoric Acid Plants





CENTRAL POLLUTION CONTROL BOARD
(Ministry of Environment, Forests & Climate Change)
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DELHI -110 032
Website: www.cpcb.nic.in
October, 2014

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#### **FOREWORD**

The Hazardous Waste (Management, Handling & Transboundary Movement) Rules, 2008 (HWM Rules, 2008) notified under the Environment (Protection) Act, 1986 has excluded phosphogypsum generated from 'Phosphoric Acid Plants' from the list of hazardous wastes under Schedule-I of the said rules. The said Rules categorizes phosphogypsum as 'High Volume Low Effect Waste' and stipulates that the management of phosphogypsum shall be carried out in accordance with the guidelines of Central Pollution Control Board (CPCB).

There are 11 phosphoric acid plants generating about 6.5 million tonnes per annum of phosphogypsum. About 4.5 - 5 Tonnes (dry basis) of phosphogypsum is generated per Tonne of phosphoric acid (as P2O5) recovered from phosphate rock. Phosphogypsum is presently stacked within the phosphoric acid fertiliser plants and some quantity is sold for use in cement as well as plaster board etc. However, improper handling of phosphogypsum is likely to cause environmental impacts due to low pH, fluoride and phosphates present in the phosphogypsum.

In order to ensure safe management of phosphogypsum, CPCB in consultation with the concerned stakeholders, has prepared these guidelines envisaging present scenario of phosphogypsum generation, existing management and handling practices as well as safe handling, transportation, intermediate storage, stacking and with emphasize on its utilisation. Considering the technological developments, these guidelines need to be reviewed or relooked at least once in five years for updating the developments with respect to the possible beneficial utilisation of phosphogypsum over course of time.

The contributions by way of providing inputs for preparing these guidelines by the various organizations especially Atomic Energy Regulatory Board (AERB), State Pollution Control Boards (SPCBs) of Gujarat & Orissa, The Fertilisers Association of India (FAI), Cement Manufacturers Association (CMA), Technical Review Committee (TRC) of Ministry of Environment, Forests and Climate Change and CPCBs Technical Expert Committee (TEC) as well as the officials of CPCB who were involved directly or indirectly is gratefully acknowledged. The in house efforts of Shri J. Chandra Babu, Scientist 'D' and Shri B.Vinod Babu, Scientist 'D' & I/c HWM Division in preparing these guidelines is appreciated. These guidelines have been finalized under the supervision of Dr.A.B.Akolkar, Member Secretary, CPCB whose contribution is also highly appreciated.

These mandatory guidelines should be useful to all the concerned stakeholders and it is expected that all the phosphoric acid plants, phosphogypsum utilisers and other stakeholders would take part in ensuring voluntary compliance to these guidelines as well as the Rules notified under the Environment (Protection) Act, 1986.

(Susheel Kumar) Chairman

October 17, 2014



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#### **Abbreviations**

AERB - Atomic Energy Regulatory Board

ASTM - American Society for Testing Materials

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

FDEP - Florida Department of Environmental Protection

GW - Ground Water

GWT - Ground Water Table

HDPE
 IBM
 Indian Bureau of Mines
 IRC
 Indian Road Congress

Kg - Kilogram Km - Kilometre

MoEF & CC - Ministry of Environment, Forests & Climate Change

NAAQM - National Ambient Air Quality Monitoring NAAQS - National Ambient Air Quality Standards

NABL - National Accreditation Board for Testing and

**Calibration Laboratories** 

NHAI - National Highway Authority of India

PCC - Pollution Control Committee in Union Territory

PG - Phosphogypsum SLF - Secured Landfill

SPCB - State Pollution Control Board in State

SPM - Suspended Particulate Matter

TPA - Tonnes per annum

TCLP - Toxicity Characteristics Leaching Procedure

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#### 1 Introduction

Phosphorus in the form of Phosphate (expressed as  $P_2O_{5}$ ) is a nutrient for plants and a building bloc in food production. Agriculture sector uses large amount of chemical fertilisers 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 addition of the phosphate fertilisers.

Rock phosphate is the naturally occurring source for  $P_2O_5$ . The phosphogypsum essentially 'calcium sulphate' is generated as a waste from the phosphoric acid plants by the reaction of rock phosphate with sulphuric acid. If the phosphogypsum is disposed in open 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 volume if generated and large area required as well as the potential for release of dust, fluoride and heavy metals.

Phosphogypsum generated from phosphoric acid plants is presently stacked and some quantity is sold to the other industries for beneficial use especially as in cement manufacturing as raw material substitute for mineral gypsum, plaster board manufacturing as well as for alkali soil amendments or re-conditioning. Handling of phosphogypsum by trucks or railways involves loading, unloading and temporary storage at yards are likely to cause environmental impacts especially during rainy season if proper measures are not taken. In order to have minimal impacts on environment, there is a need for evolving the guidelines for safe handling including transportation, storage, utilisation 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 stipulates that the management of phosphogypsum from phosphoric acid fertiliser plants shall 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 overall aspects of phosphogypsum handling, storage and disposal including its utilisation. The document covers present scenario with regard to the generation of phosphogypsum from fertiliser units, existing management and handling practices followed by the phosphoric acid plants in the Country. The document also deals with the guidelines to be followed for safe handling, transportation, storage of phosphogypsum within the phosphoric acid plants, safe disposal of

phosphogypsum through stacking, end use of phosphogypsum for beneficial use that may be encouraged in order to solve the problems associated with the disposal of phosphogypsum.

Issues relating to the radioactivity present in the phosphogypsum are not covered in detail under these guidelines as same fall under the purview of the Atomic Energy Regulatory Board (AERB). However, the AERB guidelines i.e. 'Use of Phosphogypsum in Building & Construction Materials & in Agriculture (AERB Directive No. 01/09) may be strictly followed (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 phosphorus is derived from rock phosphate by converting the calcium phosphate to phosphoric acid or to Single Super Phosphate (SSP). In the production of SSP, calcium sulphate (gypsum) remains with the product. The rock phosphate required for production of phosphoric acid in the country is mainly obtained through imports. The chemical composition of the Indian rock phosphate as well as imported phosphate rock and 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  $P_2O_5$  content. For example, 100 Tonnes per day  $P_2O_5$  corresponds to 333 Tonnes per day of phosphoric acid of 30 percent concentration as  $P_2O_5$ . 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 production of phosphoric acid for making phosphatic fertiliser. 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  $P_2O_5$  which is dissolved in water to form phosphoric acid. This process can use low grade rock phosphate and produce pure phosphoric acid. However, in India, this process is used in small plants for manufacturing

chemical grade phosphoric acid. This method is not used in fertiliser grade production due to high power requirement resulting in high cost of production.

#### 2.1.2 Wet process phosphoric acid

The production of phosphoric acid by this process is as follows:

Acidulation of finely ground rock phosphate with sulphuric acid to form phosphoric acid and gypsum. The chemical reaction is detailed below:

Ca<sub>10</sub> F<sub>2</sub> (PO<sub>4</sub>)<sub>6</sub> + 10 H<sub>2</sub>SO<sub>4</sub> + 10 n H<sub>2</sub>O 
$$\rightarrow$$
 Rock phosphate Sulphuric acid Water

6H<sub>3</sub>PO<sub>4</sub> + 10 (CaSO<sub>4</sub>.nH<sub>2</sub>O) + 2HF
Phosphoric acid Gypsum Hydrogen Fluoride

Where n = 0,  $\frac{1}{2}$  or 2 depending on the hydrate form in which the calcium sulphate is crystallised.

- Separation of gypsum from the acid by filtration.
- Washing of gypsum to remove adhering phosphoric acid.
- 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 hemi-hydrate 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) Di-hydrate 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 % concentration (as  $P_2O_5$ ) is filtered from the di-hydrate gypsum (CaSO<sub>4</sub>.2H<sub>2</sub>O) 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 % in a single stage. If 50-54 %  $P_2O_5$ 

acid is required, further evaporation is necessary. The concentration of acid consumes high energy. During concentration, around 70-80 % of fluorine present in the acid is released which is recovered as fluorosilicic acid ( $H_2SiF_6$ ). Fluorosilicic acid may be used to make cryolite,  $AIF_3$  or other fluorine compounds. A flow sheet for the manufacture of phosphoric acid is given in **Figure 1**.

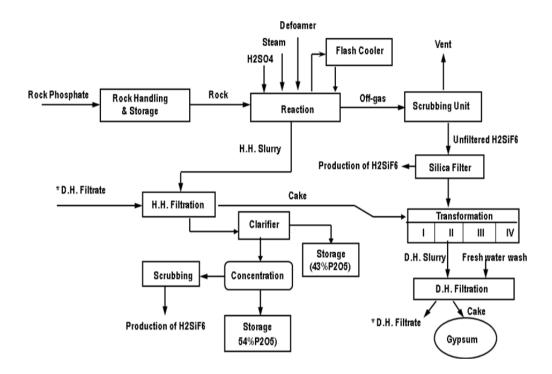


Figure 1: Manufacture Process of Phosphoric Acid

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. In the di-hydrate route, the operating temperatures are low and the start-up and shutdown are easy and require lowest operational skills. The  $P_2O_5$  recovery efficiency is 95-96%.

Most of the phosphoric acid plants in the county have adopted di-hydrate process and 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 gives low strength of acid. Newer processes claimed to overcome these limitations of the di-hydrate processes are

- (i) Hemi-hydrate-di-hydrate (HDH) (double filtration stage) and
- (ii) Di-hydrate-hemi hydrate (DHH) (three stage re-crystallisation).

## (b) Hemi-hydrate process (HH):

This process involves the reaction between rock phosphate and sulphuric acid above 80°C. Selective operating conditions are maintained to crystalize calcium sulphate hemi-hydrate, rather than the di-hydrate form (CaSO<sub>4</sub>.1/2H<sub>2</sub>O) . The single stage hemi-hydrate process generates a reaction slurry which, when filtered, produces directly a phosphoric acid product of 40-42 % P<sub>2</sub>O<sub>5</sub> concentration with considerable savings in energy requirement. After washing the filter cake to remove further P<sub>2</sub>O<sub>5</sub>, dilute acid is returned to the reaction stage. However, P<sub>2</sub>O<sub>5</sub> recovery efficiency is lower than di-hydrate process at 93-94 %. The unrecovered P<sub>2</sub>O<sub>5</sub> is retained in phosphogypsum hemi-hydrate 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 (i) lower capital cost, (ii) high purity and concentration than di-hydrate process and (iii) usage of much coarser rock. Some of the disadvantages of this process are (i) hemi-hydrate slurry is difficult to filter since the crystals are smaller and less well formed compared to the di-hydrate, (ii) higher P<sub>2</sub>O<sub>5</sub> losses, (iii) 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):

In this process, the first reaction takes place under hemi-hydrate conditions, followed by filtration to obtain purer product acid of 40-42 %  $P_2O_5$ . 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 is dissolved in the additional sulphuric acid. This process produces a purer form of phosphogypsum and filtrate solutions, which are used to wash and repulp the hemi-hydrate filter cake. Thus, a high concentration purer product acid of about 45 %  $P_2O_5$  is obtained. This may need no further evaporation before use, much higher  $P_2O_5$  recovery and efficiency above 98 % is possible.

## (d) Di-hydrate-hemi-hydrate:

The acid reaction is carried out under di-hydrate conditions followed by recystallisation of calcium sulphate hence first filtration is less important. Slightly more concentrated acid (32-37 %  $P_2O_5$ ) 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 of paris board or as a cement retarder. In this process, the recovery efficiency of  $P_2O_5$  is around 98 %.

## (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<sub>2</sub>O<sub>5</sub> trapped in the crystal structure of the calcium sulphate is released and P2O5 recovery in excess of 99 % is 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 % P<sub>2</sub>O<sub>5</sub> or more. The filter cake is then re-slurried and converted to di-hydrate to release P<sub>2</sub>O<sub>5</sub> 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 P2O5 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 phsophogypsum cake prior to the disposal is given in Figure 2 and Figure 3 respectively.



Figure 2: Phosphate rock silo & conveyance system





Figure 3: Washing of phosphogypsum prior to the storage or disposal

## 2.2 Phosphoric acid production scenario in India

In India, there are 11 number 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 1.4 Million Tonnes during the year 2012-2013. The phosphoric acid production and phosphogypsum generated 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 insolubles are separated from the product i.e. phosphoric acid as efficiently as possible. Depending on the source of rock phosphate, about 4.5 to 5 Tonnes (dry basis) of phosphogypsum is generated per Tonne of phosphoric acid (as  $P_2O_5$ ) recovered.

The quality & quantum of phosphogypsum generation depends on the quality of the phosphate rock, process route used to produce phosphoric acid, calcium sulphate generated either in di-hydrate (CaSO<sub>4</sub>.2H<sub>2</sub>O) or the hemi-hydrate (CaSO<sub>4</sub>.1/ $_2$  H<sub>2</sub>O) form. Phosphogypsum generation in the country is about 6.5 Million Tonnes per annum. The industry-wise production of phosphoric acid and estimated phosphogypsum scenario in the country as per the information provided by the phosphatic fertiliser units 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 range between 0.5 mm (No. 40 mesh sieve) and 1.0 mm (20 mesh sieve) and majority of the particles (50-75 %) are finer than 0.075 mm (200 mesh 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/m³ (92 to 104 lb/ft³), based on Standard Proctor Compaction. The gypsum cake, after filtration, usually has free moisture content between 18 to 35%. Hemi-hydrate, in the presence of free water will rapidly convert to di-hydrate 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 primarily of calcium sulphate dihydrate with small amounts of silica, usually as quartz and unreacted phosphate rock, traces of radioactive material (like radium, uranium), traces of heavy metals namely arsenic, cadmium, chromium, lead and fluoride. The concentration of the metals depends on the composition of the phosphate rock. Following are the main concerns with respect to management of phosphogypsum;

- i) High fluoride concentration (in the range of 0.5 -1.5 %) which may leach and contaminate the groundwater, if not stored and handled properly;
- ii) May contain heavy metals (Cd, Cr, Pb etc.,) that may enter into the food chain through potable water and agriculture products;
- iii) Presence of radio-nuclide radium-226 which upon decay may emit harmful alpha particles; and
- iv) Acidic run-off from phosphogypsum due to presence of residual phosphoric acid may cause fish mortality in receiving water bodies such as ponds/lakes (due to low pH).

Permeability of phosphogypsum depends on degree of stabilization. Based on the literature, typical permeability in unstablised phosphogypsum to the stabilised phosphogypsum range from  $1.3 \times 10^{-4}$  cm/sec down to  $2.1 \times 10^{-5}$  cm/sec. The analysis of phosphogypsum generated in some of the phosphoric acid plants is given in Table 6.

## 5 Management and handling of phosphogypsum

Phosphogypsum retains 18-35 % of moisture depending upon the type and degree of filtration and handling facilities installed for further 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 may be seen in the process or technology adopted which influences the characteristics and type of handling of phosphogypsum within the plant. The handling of phosphogypsum is first done by the industry itself wherein washed phosphogypsum is shifted to the phosphogypsum stack / intermediate storage /direct disposal for utilisation / loading point for sale or disposal.

#### 5.1 Handling of phosphogypsum in phosphoric acid plants

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. Handling of phosphogypsum is detailed below:

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. Phosphogypsum dry stacks which are in operation in the country are having a height of 30 to 60 m. 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 pipeline is required for pumping back of decanted water. In this method, the phosphogypsum

slurry 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. This water cannot be discharged as such as it may contain low pH, fluorine and phosphate as  $P_2O_5$ . The outer dikes are generally earthen dikes designed to prevent the escape of contaminated water into nearby streams. Phosphogypsum dry stacks which are in operation in the country are designed for having height of 60 to 80 m. A stabilized phosphogypsum stack may not cause any dust problem, however, dust emission can be seen during the excavation, shaping and movement of vehicles as well as maintenance of the access roads. As far as possible, this may be readily kept in damp condition to control particulate emissions.

The **Figure 4, 5, 6 and 7** show the operations in transportation of phosphogypsum by 'belt conveyor' and by vehicles to the stack area respectively. The **Figure 8, 9 & 10** show handling of phosphogypsum in slurry form at phosphogypsum dikes.



Figure 4 & 5: Conveyance of phosphogypsum to the stack area by 'Belt Conveyor'





Figure 6 & 7: Phosphogypsum loading to truck in phosphoric acid plant and unloading in phosphogypsum stack area (Dry stacking)



Figure 8: Phosphogypsum stacking



Figure 9: Pumping of phosphogypsum in the form of slurry to the 'Ridge Dike' of the phosphogypsum stack



Figure 10: Decanted water collection in 'surge pond' over the phosphogypsum stack

**5.1.1 Wastewater 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 and as stipulated under the Environment (Protection) Act, 1986.

#### 5.2. Utilisation 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 plants sell the phosphogypsum for different applications which include (i) for use as soil conditioning (for alkaline soil) or as fertiliser in agriculture (ii) in cement manufacturing to control the setting 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. Utilisation requires handling and transportation of phosphogypsum by means of railways [Figure 11] or by road (mainly in trucks/tractors). The utilisation 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.

As per Indian Minerals Year Book 2012 published by Indian Bureau of Mines (IBM), Ministry of Mines, Government of India, about 8.12 Million Tonnes of gypsum in all forms was reported to be consumed in organised sector in 2011-12. In addition, a substantial quantity of mineral gypsum as well as phosphogypsum was used in agricultural sector for conditioning of alkaline soil. During the year 2010-11, phosphogypsum was reported to be consumed for manufacture of cement and meagre consumption was in ceramic and fertilizer industries. During the year 2011-2012, about 3.35 Million Tonnes of phosphogypsum were consumed by the cement industries, 600 Tonnes of phosphogypsum used by the ceramic industries and 1 Tonne as fertiliser.

Two phosphoric acid plants have commissioned two plaster board manufacturing units (at Kochi & Trombay) as an integral part of the phosphoric acid plants [Figure 12]. Two phosphoric acid plants have constructed model low cost houses using plaster boards/panels [Figure 13 & 14]. The product has also received 'in principle' approval from Building Material Technology Promotion Council (BMTPC) under the Ministry of Housing and Urban Poverty Alleviation. One plant (Odisha) is manufacturing a by-product i.e. NPK Granulated Fertiliser Mixture. The industry-wise present practices of phosphogypsum disposal are given in **Table 7**.



Figure 11: Phosphogypsum lying at rail yards for transportation to the end users



Figure 12: Plant and machinery used for plaster board/ panel manufacturing using phosphogypsum





Figure 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 the 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 may be picked up and transported by the prevailing 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 or vegetation adjacent to the phosphogypsum 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, which can be seen by the following equation:

 $\label{eq:H2O+HF+MAlSiO2} H_2O + HF + MAlSiO_2 \rightarrow \square \ M+ + AlF_3 + SiF_4 + nH_2O$  Where.

MAlSiO<sub>2</sub> represents an aluminosilicate mineral M represents Ca, Mg, Na, K, and Fe

Some of the  $SiF_4$  may hydrolyse to form  $H_2SiF_6$  (fluorosilicic acid) within the phosphogypsum leachate. The presence of  $H_2SiF_6$  may result in dissolution of clayey soils at the bottom of phosphogypsum repositories, which may allow accelerated movement of contaminants into the groundwater in due course of time if phosphogypsum is not contained properly.

Water erosion of phosphogypsum stacks may create solution cavities and instabilities in constructed berms and dikes, leading to surface runoff of phosphogypsum, erosion around piping systems and gully erosion. Slopes of phosphogypsum stacks may become more susceptible to failure and erosion with heavy rain fall. The run-off from phosphogypsum may result acidic condition in receiving water ponds such a water and ponds may cause fish mortality.

Typical trend analysis of the characteristics of the groundwater in and around the Phosphoric acid plant is given in **Table 8 & Table 9.** Prior to preparation of these guidelines, Central Pollution Control Board (CPCB) conducted visit to 07 no. of phosphoric acid plants and phosphogypsum samples were collected and the analysis results of the samples are given in **Table 10.** 

## 7 Guidelines for transportation, storage, management, handling, utilisation and disposal of phosphogypsum

## 7.1 Applicability of the guidelines:

These guidelines are applicable

- (a) To the existing generators of phosphogypsum or phosphoric acid plants; any construction of new phosphogypsum stack; Operation or closure or proposed for closure of phosphogypsum stack (s); lateral expansion of the existing phosphogypsum stack (s); and any expansion in the phosphoric acid production.
- (b) For Transportation, temporary storage (intermediate storage, and at rail yard loading points) and handling of phosphogypsum at yards and/or phosphogypsum stacks.
- (c) Utilisation of the phosphogypsum such as cement industry, road construction activity, plaster board manufacturing industry and for soil conditioning in agriculture.

## 7.2 Approvals required, site selection, location criteria, construction, operation and maintenance of phosphogypsum stack (for both dry and wet stacks)

General guidelines with respect to the approvals required, site selection, location criteria, construction, operation and maintenance of the phosphogypsum stacks are given in subsequent paras.

## 7.2.1 Requirement of approvals for new phosphogypsum stacks including expansion of old stacks

- (i) Phosphoric acid plants proposing to construct new or additional phosphogypsum stack (s) shall obtain necessary amendment in 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) as well as shall obtain necessary approvals as required prior to the construction.
- (ii) The phosphogypsum stack system, henceforth, shall not be constructed, operated, expanded, modified or closed without prior approval from the State Regulatory Authorities i.e SPCB/PCC as the case may be.

- (iii) The Phosphoric acid manufacturing unit shall submit the following details along with the Consent application such as
  - (a) the details with regard to the ownership of the land where phosphogypsum stack is proposed to be constructed in accordance with these guidelines;
  - (b) details of temporary storage area for storage of phosphogypsum if any;
  - (c) design drawings of the proposed phosphogypsum stack;
  - (d) details of transportation (within the phosphoric acid plant as well as to any end user of phosphogypsum);
  - (e) construction and completion schedule;
  - (f) operational, maintenance and monitoring protocols;
  - (g) remedial plans including disaster management plan; and
  - (h) any other relevant information.

SPCB/PCC shall make periodic visits to ensure that the construction, operation, maintenance of the phosphogypsum stack is as per the approved designs.

## 7.2.2 Site selection and location criteria for the phosphogypsum stack (for both dry and wet stacks)

- (i) As far as possible, new phosphogypsum stack (s) may be located within the existing industry premises. In case, if the stack is required to be located outside the industry premises, it may be located at a suitable location preferably I KM away from any notified habitat area or at suitable location as approved by the SPCB/PCC.
- (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 such as rivers, ponds or lakes.
- (iv) Existing phosphoric acid plant having phosphogypsum stack system close to any natural or artificial water bodies or not meeting the 500 m distance criteria, such phosphoric plants should take adequate measures such that the runoff from the phosphogypsum storage yard should not be allowed to discharge into the surface water or any natural or artificial water bodies if any, located nearby.

## 7.3 Design requirements of the new phosphogypsum stack (both dry and wet stacks)

- (i) All the new Phosphogypsum stacks including the lateral expansion of the existing phosphogypsum stack (s) shall be designed at least for a period of 05 years.
- As far as possible, the phosphogypsum stack should be (ii) constructed above the ground level and over the natural clavev strata (also blended with bentonite) to eliminate any seepage. preparing or levelling the bottom layer of the phosphogypsum stack, in case of absence of sufficient quantity of native local soil/clay, completely stabilised or phosphogypsum may be used henceforth with the prior approval from CPCB. For this purpose, a proposal is required to be submitted through concerned SPCB/PCC with their views and recommendations to the Central Pollution Control Board (CPCB) seeking further approval.
- (iii) The side slopes of the stacks shall be maintained suitably from the stability point of the stack.
- (v) 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.
- (vi) Phosphogypsum stack base liner shall have a single composite liner comprising of a HDPE geo-membrane of 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 or any other material of sufficient thickness and having or conforming to the coefficient of permeability of 10 -7 cm per second (10 -9 m/sec) or less. Further, a layer of mechanically compacted & neutralized phosphogypsum of suitable thickness may be placed above the drainage layer, 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.
- (vii) Emphasis on protection of the geomembrane during placement and compaction of the phosphogypsum, and on prompt placement of phosphogypsum on the geomembrane shall be

- given to avoid failure of the geomembrane while operating the phosphogypsum stack.
- (viii) All the joints of the geomembrane liner prior to commencement of the phosphogypsum stacking shall be tested for leakages if any (as per ASTM D 6392/ASTM D 5820/ASTM D 5641 or any ASTM standard protocol as applicable) and measures should be taken for proper welding of such joints, if required.

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

- (ix) The under-drain system comprising of perimeter piping system, lateral drains of suitable diameter, perforated and corrugated HDPE pipe shall be laid in a bed of non-reactive gravel, placed approximately at suitable interval. The collected leachate should be diverted to surge pond, from where it is returned to the process plant for re-use and excess flow if any be pumped to the effluent treatment plant, if required.
- (x) A HDPE lined peripheral ditch or garland dike (with passage at suitable intervals) need to 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 dike or embankment.
- (xi) Excess wastewater in the recirculation system between the phosphoric acid plant and the phosphogypsum stack shall be routed to Effluent Treatment Plant (ETP), if required for further treatment to comply with the liquid effluent discharge norms stipulated under the Environment (Protection) Act, 1986 prior to final discharge or disposal.

A typical phosphogypsum stack showing the design details is given in **Figure 15 to 16.** 

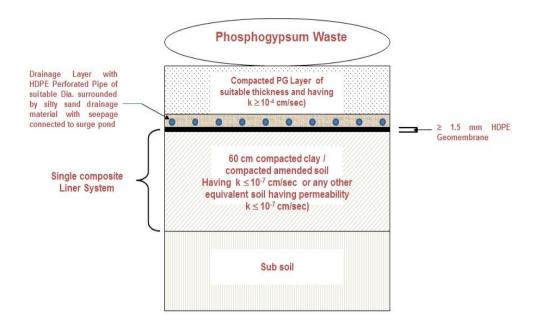
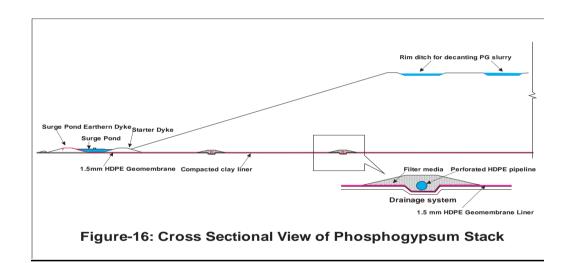


Figure 15. Suggested Liner System for the Phosphogypsum Stack



Note: All the existing phosphoric acid plants presently following the practice of stacking the phosphogypsum may continue the same operation for a period of five years from enforcement of these guidelines. During this period, all such phosphoric acid plants should 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 recognised under the Environment (Protection) Act, 1986 or any NABL Accredited Laboratory for assessment of the contamination if any and such assessment reports be submitted once in a year to the Central Pollution Control Board through the respective SPCB/PCC with remarks if any. In case,

adverse environmental impacts are observed, then such phosphoric acid plant is required to submit remediation plan which may also include existing phosphogypsum utilisation plan seeking approval of Central Pollution Control Board (CPCB).

# 7.4 Guidelines for transportation of phosphogypsum from source of generation to the temporary storage within the industry premises or railway yard or storage yard or place of designated utilisation

- (i) The vehicles used for collection and transportation of phosphogypsum from the source of generation to the temporary storage yard or phosphogypsum stack (s) or destination for utilisation, does not require authorization under the Hazardous Waste (Management, Handling and Transboundary Movement) Rules 2008 from the concerned State Pollution Control Board (SPCB) or Pollution Control Committee (PCC).
- (ii) The Transportation vehicles registered under the Motor Vehicle Act, 1988 only be used for collection and transportation of phosphogypsum from the source of generation to the temporary storage yard/phosphogypsum stacks or destination for utilisation as raw material
- (iii) 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).
- (iv) 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.
- (v) From the safety point of view, the occupier (generator of phosphogypsum) ensures that the transporter carries requisite documents having details such as
  - (a) source of generation of phosphogypsum;
  - (b) complete address of the generator;
  - (c) quantity of phosphogypsum transported;
  - (d) vehicle registration number;
  - (e) destination with complete address;
  - (f) date of departure of transportation vehicle from the source of generation;
  - (g) expected date of arrival to the destination;

- (h) route chart and
- (i) any other relevant documents as required for transportation.
- (vi) 'NOC' from the respective SPCB/PCC for interstate transportation of phosphogypsum is not required under the Hazardous Waste (M, H & TM) Rules, 2008 as amended.

## 7.5 Guidelines for intermediate storage or 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 phosphogypsum to the phosphogypsum stack or for utilisation by the outside agencies. Following guidelines are applicable:

- (i) Phosphogypsum shall be stored under a covered shed of adequate size and the floor should be of impervious nature surrounded by the proper drainage system for collection of floor washings. Alternatively, storage in open can be permitted provided only if adequate arrangements are made for minimisation of run-off, collection and treatment of run-off.
- (ii) Records to be maintained at the intermediate or temporary storage area: A provision of recording system to record entry of vehicle and lifting of phosphogypsum quantities and other details as per the Table given below are maintained:

S. No	Date	Time		Vehicle /Train Nu	Number mber		rmediate	Phosphogypsum or temporary les
		Arrival time	Departure Time	Arrived	Departed	Unloaded or Stored	Lifted	Net Accumulated Quantity of PG

(iii) 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) and security room.

- (iv) In phosphogypsum storage and handling area, adequate arrangements (like water spray) are provided to arrest fugitive dust emissions.
- (v) 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 so as to comply with the effluent discharge norms stipulated under the Environment (Protection) Act, 1986.
- (vi) Measures should be taken for proper collection of spillages from the filter area to the temporary storage area or along the conveyor belts or at the temporary or intermediate storage areas.
- (vii) The occupier of phosphogypsum is required to maintain records with regard to the phosphogypsum generated, accumulated quantity of phosphogypsum stored in phosphogypsum stacks or temporary storage yard, date-wise quantity of phosphogypsum sold or auctioned to the end users and their complete addresses and same should be provided as and when required by the regulatory authorities.

Note: Above guidelines are also applicable to the Units (including cement manufacturing industry) utilising the phosphogypsum where there is a necessity for intermediate/temporary storage of phosphogypsum, prior to its utilisation.

## 7.6 Closure of the existing phosphogypsum stacks or abandoned phosphogypsum stacks and the maintenace.

In case existing phosphogypsum stack is proposed for closure, in such a case, seepage out of the stack and rainfall runoff from the slopes need to be contained on-site and routed to the storm water retention ponds or treated before discharge. Closure of the existing phosphogypsum stack is required,

- (a) when the storage capacity of a phosphogypsum stack is exhausted or no longer receiving phosphogypsum; (or)
- (b) the occupier/owner/operator does not deposit or dispose off any quantity of phosphogypsum; (or)
- (c) the occupier/owner/operator is no longer wishing to dispose off the phosphogypsum in phosphogypsum stack yard; (or)

(d) in case, the existing phosphogypsum stack may be posing threat to the human health and the environment.

Closure plans for phosphogypsum stack system shall also include the following:

- (i) Phosphogypsum stack where rainwater collection provision is made over the top of the stack, there should be a suitable provision to transfer decanted water from top of the stack to process water storage ponds (HDPE lined).
- (ii) To construct a suitable "toe drain" on all the sides of the stack to collect leachate.
- (iii) The side slopes and top of the phosphogypsum stack is required to be covered with native soil or clayey sands of suitable thickness and also covered with coir matting and grass of suitable variety.
- (iv) To grade side slope roads into drainage channels suitably so as to ensure smooth flow of collected surface run off to the storm water retention ponds.
- (v) To construct a surface water management system to collect rainfall and to control runoff from stack as well as retention ponds.
- (vi) In case of any spillage of phosphogypsum at the time of closure of the existing phosphogypsum stack, concerned phosphoric acid plant is required to take suitable measures for clearing such spillages.
- (vii) Wherever possible, green belt around the closed phosphogypsum shoule be developed.

Note: In case, the phosphophoric acid plant 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 utilisation plan through concerned SPCB/PCC with their views to the Central Pollution Control Board seeking further approval.

## 7.7 Guidelines for storage, handling and loading/unloading 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 shed of adequate length along the railing rake side should be provided with impervious flooring for intermediate storage or loading of phosphogypsum to railing racks. The height and super structure of the shed shall be such that free movement of loading equipment is ensured.

Alternatively, storage in open can be permitted provided adequate arrangements are made for minimization of run-off and its collection and treatment.

- (ii) Floor wash water, and run-off contaminated with fluoride and phosphates shall be collected and routed to effluent treatment plant (ETP) for treatment and to ensure compliance 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 railway yard which may arise during unloading of phosphogypsum from trucks or loading of phosphogypsum into rail rakes.
- **(iv)** Intermediate storage area at the railway yard shall be provided with a security /restricted entry.
- **(v)** Record to be maintained at the railway yard: a provision of recording system to record entry of vehicle and lifting of phosphogypsum quantities and other details as per the Table given below need to be maintained:

S. N	. Dat	e No. of Rakes	,	Гіте	Details	Total Quantity of Phosphogypsum lifted	
			Arrival	Departure	Consignment Departed to	in Tonnes	

## 7.8 Monitoring requirement of phosphogypsum stacks of phosphoric acid plants

Following guidelines are suggested with respect to the surface and ground water monitoring requirement and periodic inspections of the phosphogypsum stacks.

#### 7.8.1 Surface and ground water monitoring provision

Monitoring of the groundwater quality and the water surface bodies adjacent to the phosphogypsum stack shall be carried out in accordance with the monitoring protocol suggested under **Section 9** of these guidelines.

#### 7.8.2 Periodic inspections and maintenance of phosphogypsum stacks

During the operational phase and post-closure maintenance period (at least for 05 years) of the stack, following measures need to be adopted:

- (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 need to be taken to avoid fugitive emissions due to wind erosion of phosphogypsum from the phosphogypsum stack.
- (iii) A record should be maintained with regard to the observations made, remedial measures suggested during the periodic inspections and remedial measures taken, as per the Table suggested below.

S. No	Date and Inspection Date	Time of Time	Observations made during the inspection	Remedial measures suggested	Remedial Actions Taken	Compliance Verified	
						Ву	Signature with date

#### 7.9 Precautionary measures

The Phosphogypsum should be guarded round the clock. Provision shall be made for security room, vehicle weighing platform, vehicle tyre washing near exit gate. Further, following provision should be provided:

- (i) Proper housekeeping at the material storage areas, loading & dispatch areas, service facilities, etc..
- (ii) Suitable road shall be constructed on outer most dike 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 dike of the phosphogypsum stack.

Daily records of quantity of phosphogypsum generated, phosphogypsum received at the phosphogypsum stacks, and the quantity lifted for utilisation shall be maintained. Further, following provision should be provided:

(i) Every generator of phosphogypsum should maintain records, vehicle used for dumping or lifting of phosphogypsum in accordance with the Table given below:

S. No	Date	Vehicle Number	ŗ	Гime	Details		Total Quantity of Phosphogypsum lifted
			Arrival	Departure	Arrived from	Departed to	in Tonnes

<sup>\* -</sup> pl. write complete address of the contact person

## 8 Guidelines for utilisation of phosphogypsum

As far as possible, the phosphoric acid plants should put efforts to send phosphogypsum for beneficial use such as plaster board manufacturing, cement manufacturing as substitute for natural gypsum, recovery of by-products such as ammonium sulphate, sulphuric acid, reclamation of alkali / saline-alkali soils or controlled use as fertiliser, road making.

Utilisation of the phosphogypsum can be achieved as per the guidelines given below:

## (i) Utilisation by installing captive plaster/gypsum board manufacturing unit:

All the phosphoric acid plants may explore possibilities of recycling of the phosphogypsum by installing captive plaster/gypsum board manufacturing unit as an integral part of the phosphoric acid plant by sending to any other plaster/gypsum board manufacturing unit located nearby.

## (ii) Utilisation by plaster, blocks or gypsum board manufacturing industry:

Plaster, Blocks or Gypsum Boards manufacturing industry shall utilize phosphogypsum as raw material for manufacture of plaster, putty blocks or gypsum boards after reduction in impurities to the specifications as given in Indian Standards IS: 12679-1989, Reaffirmed 2010 (Requirement of By-product Gypsum for Use in Plaster, Blocks and Gypsum Boards).

## (iii) Utilisation by cement manufacturing units:

As on March 31, 2014 the installed capacity of cement industry is about 360 Million Tonnes and is producing about 255 Million Tonnes. About 4 to 5 % of natural gypsum is used in cement production i.e. about 10 Million Tonnes. If the natural gypsum is replaced by phosphogypsum generated from phosphoric acid plants, whole phsophogypsum generated can be consumed by the cement industry alone in the country.

As far as possible, cement manufacturing unit (s) shall use the phosphogypsum in place of the natural gypsum as a regulator for setting time of cement, at the rate of 4 to 5% in its composition.

## (iv) Manufacture ammonium sulphate:

Any entrepreneur who wishes to manufacture ammonium sulphate from the phosphogypsum as per the following reaction may approach the concerned SPCB / PCC for obtaining Consent as required for establishment of such recycling industry.

$$CaSO_4 + (NH_4)_2 CO_3 -----> CaCO_3 + (NH_4)_2 SO_4$$

## (v) Recover or manufacture sulphuric acid:

Any entrepreneur who wishes to recover or manufacture sulphuric acid from the phosphogypsum may approach the concerned State Pollution Control Board (SPCB) / Pollution Control Committee (PCC) for obtaining Consents as required for establishment of such recycling industry.

## (vi) Reclamation of alkali soils and saline –alkali soils and use as fertiliser in agriculture:

Phosphogypsum may be used to reclaim alkali soils and saline – alkali soils with high sodium ion concentration. Fertiliser industry may maximise the use of phosphogypsum as 'Fertiliser'. For this purpose the Indian Standard Specifications for By-product Gypsum as stipulated under IS: 10170-1982, need to be followed. For conditioning alkaline soil , as a manure in agriculture mainly for correcting black alkali soil, BIS specifications for low-grade gypsum for agriculture use should be followed (i.e., IS:6046-1982 (First Revision; reaffirmed 2008).

## (vii) Road making:

Neutralised, stabilised or suitably treated phosphogypsum (i.e., blending with suitable stabilising material, binding material and bentonite) and free from water leachable contaminants like fluoride, cadmium, lead, arsenic and mercury content (as per the limits suggested below) and having coefficient of permeability not more than 10-7 cm /sec shall be permitted for construction of highways and access roads except in residential areas, in consultation with the Central Road Research Institute (CRRI) as well as the respective SPCB or PCC. Suggested specification of *phosphogypsum for use as sub-base/Sub-grade for road making:* 

Name of the	Recommended Water Leachable Limit			
Parameter	(not to exceed as per water leach test )			
Fluoride	< 50 mg/l			
Cadmium	< 2 mg/l			
Lead	< 2 mg/l			
Arsenic	< 1 mg/l			
Mercury	< 0.1 mg/l			
Moisture	< 15 %			

**Note:** Any utilisation of phosphogypsum other than the above, the proponent is required to submit the proposal along with relevant details to CPCB through the respective **SPCB/PCC** with their assessment and recommendation to examine the same further by CPCB for permitting the same.

## 9 Monitoring protocol for assessment of environmental impacts in and around the phosphogypsum stack

Monitoring of emissions plays an important part in environmental impact assessment. This can lead to rapid detection and recognition of adverse conditions and can give the operating staff an opportunity to take corrective measures and enable to restore the optimum standard operating conditions as quickly as possible.

#### 9.1 Ambient air quality monitoring

- (i) **Number of monitoring stations:** Air quality monitoring stations at 3 prominent (upwind, downwind) locations at 120° (within the industry boundary) covering the phosphogypsum stack yard at regular intervals is necessary. Location of the ambient air quality monitoring stations should be as per the State Pollution Control Board (SPCB)/ Pollution Control Committee (PCC).
- quality monitoring: Source emission parameters stipulated in the Consent issued 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). In any case, Ambient Air Quality around the phosphogypsum stack (s) should be monitored for the parameters such as 'Particulate Matter (i.e Particulate Matter size less than 10 μm i.e PM 10 and Particulate Matter size less than 2.5 μm i.e. PM 2.5) and SO<sub>2</sub> ' as per National Ambient Air Quality Monitoring (NAAQM) criteria. For heavy metals (Pb and As) monitoring frequency is once in a year.

#### 9.2 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 suggested that ground water samples should be analysed for pH, P and F on *quarterly basis* 

and other parameters like EC, SS, heavy metals (such as As, Cd, Cr, Hg, Ni, Pb and Zn), F, NO<sub>3</sub>, SO<sub>4</sub>, PO<sub>4</sub>, Total Alkalinity (excluded in coastal region) and Total Hardness shall be analysed for the parameters as per the Consent conditions issued by the SPCB/PCC.

- (ii) **Sampling locations:** It is suggested that the atleast 3 ground water samples should be collected up to a radial distance of 1 KM from the phosphogypsum stack in down gradient of prevailing groundwater flow. If no open wells or tube wells are available within a radial distance of 1 KM, it is required to drill new test wells. 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 aguifer should also be extended in consultation with the SPCB/PCC. The direction 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.
- 9.3 **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 suggested that the surface water samples should be analysed for pH, EC, SS, TDS, heavy metals (such as As, Cd, Cr, Ni, Pb and Zn), P O<sub>4</sub>, F, SO<sub>4</sub>, Total Alkalinity and Total hardness.

## 9.4 Soil samples monitoring

- (i) **Parameters to be analysed:** It is suggested that the soil samples should be analysed for pH, EC, heavy metals (such as As, Cd, Cr, Ni, Pb and Zn) and leachable concentration of PO<sub>4</sub> and Fluoride.
- (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 edge of the phosphogypsum stack. It is recommended that the soil samples should be collected and analysed for the above

parameters *at least twice in a year* (i.e. pre-monsoon and post-monsoon).

# 9.5 Testing of Radioactivity in Groundwater around the phosphogypsum stacks:

Radioactivity present in ground water around the phosphogypsum stacks should be got analysed once in a year through AERB by the concerned Phosphoric Acid Plant and analysis results is required to be submitted to the concerned SPCB/PCC as well as CPCB and for taking further action if necessary .

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

Constituent	RSMML, Rajasthan Madhya Pradesh				West Bengal		
	High Grade	Medium Grade	Chips	Jhanbua	Hirapur	Krishna Phoschem	
$P_2O_5$	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 <sub>2</sub>	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 <sub>2</sub> O <sub>3</sub>	1-2	2.5	2-11	3.3-6	2-11	2-2.5	25.8
Mg0	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 <sub>2</sub>	-	-	-	1-1.6	0.3-1	1.5-2.0	-
SO <sub>3</sub>	Traces	-	-	0.40	0.03	-	-
TiO <sub>2</sub>	-	-	-	-	-	-	1.5-2.0
MnO	-	-	-	-	-	-	2-2.5
Na <sub>2</sub> O + K <sub>2</sub> O	-	-	-	-	-	-	-
LOI	5.6	7.12	4.02	-	0.1	-	10.7

Table 2: Typical chemical composition of imported rock phosphate (Weight % - dry basis)

Country	Jordon	Morocco	Senegal	Togo	Nauru	Egypt	Algeria	Syria	Tunisia
Constituent									
P <sub>2</sub> O <sub>5</sub>	32.09	32.85	36.40	35.25- 36.16	38.0	28.0- 29.0	31.45	28.0- 29.0	34.00
CaO	48.30	50.84	50.15	50.5	53.1	46.0- 48.0	50.15	48.0- 50.0	51.00
SiO <sub>2</sub>	7.29	1.94	3.00	5.0-7.0	0.51	6.3-7.1	2.80	5.0-8.0	2.00
F	3.54	4.00	3.50	3.9-4.2	2.6-3.9	3.1-3.6	3.75	2.0-3.5	-
$R_2O_3$	0.91	0.64	0.95	2.48	0.65- 1.72	2.1-2.6	0.75	0.25- 0.35*	-
Mg0	0.31	0.30	ı	0.21	0.17- 0.51	0.30- 0.50	0.80	0.4-1.2	0.20
Organic Carbon	0.18	0.30	0.13	0.04	0.37	0.08- 0.30	-	0.4-0.6	-
Cl (ppm)	136-300	100-200	120	400	-	-	300	-	-
CO <sub>2</sub> (as CaCO <sub>3</sub> )	-	4.94	-	1.65	2.54	3.4-5.8	6.00	5.0-8.0	-
<b>SO</b> <sub>3</sub>	-	-	-	-	-	-	-	-	-
LOI	-	-	-	1.5 (max)	-	7.07	-	-	-
Na <sub>2</sub> O	0.25-0.4	0.70	0.09	0.1-0.3	-	-	0.70	-	-
K <sub>2</sub> O	0.03-0.06	0.69	0.01	0.02- 0.06	-	•	0.1	-	-
Country	Israel	Vietnam	Vietnam	China	Florida	African	Braziliar	Ru	ssia
Constituent		HG	LG			Pharla- borwa		Kola	Kovdor
P <sub>2</sub> O <sub>5</sub>	31.5	33.19	27.13	35.11- 36.25	34.3	36.8	34.52	38.9	37.0
Ca0	-	32.30	37.36	49.41- 50.62	49.8	52.1	50.42	50.5	52.5
SiO <sub>2</sub>	1.5-2.5	12.0	8.75	3.64- 3.88	3.7	2.6	3.45	1.1	2.0
F	3.0-3.4	2.50	2.20	3.4- 3.49	3.9	2.2	3.71	3.3	8.0
R <sub>2</sub> O <sub>3</sub>	0.22-0.60	3.94	3.95	1.4- 1.89	2.2	0.5	1.8	0.7	0.3
Mg0	0.3-0.9	2.0	,	-0.7- 1.13	0.3	1.1	1.65	0.1	2.1
Organic Carbon	0.13	-	-	0.37- 0.43	0.2	0.1	0.33	0.1	0.2
Cl (ppm)	-	-	-	-	-	-	-	-	-
CO <sub>2</sub> (as CaCO <sub>3</sub> )	6.2	0.8	-	1.98- 2.51	3.1	3.5	4.21	0.2	-
<b>SO</b> <sub>3</sub>	-	-	-	-	-	0.2	0.8	0.1	-
LOI	-	-	-	2.61- 3.34	-	•	-	-	-
Na <sub>2</sub> O	-	-	1	0.35- 0.37	0.5	0.1	•	-0.4	-
K <sub>2</sub> O	-	-	ı	0.11- 0.19	0.1	0.1	-	0.5	-

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

Year	PPCL1	RSMM <sup>2</sup>	MPSM	C3	WBMDTC <sup>4</sup>	Total
	Mussoorie	Jhamarkotra	Meghnagar	Hirapur	Purulia#	
	#		(Jhabua)	(Sagar)		
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)#	62.8	81.8	4.5	1505.0
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
2010-11	Nil	1791.0*(74.9) #	60.1	68.3	1.5	1920.9
2011-12	Nil	1669.0*(33.6) #	110.2	129.7	1.2	1910.2
2012-13	Nil	904.8*(4.8) #	133.0	115.0	0.5	1154.2

# = 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 Estimated Phosphogypsum Generation Scenario in the Fertilizer Industry ('000 Tonnes)

Year	Phosphoric Acid	Estimated
	Production *	Phosphogypsum Generation
		**
2000-01	1042.4	4690.80
2001-02	1134.7	5106.15
2002-03	1085.6	4885.20
2003-04	990.1	4455.45
2004-05	1242.5	5591.25
2005-06	1067.8	4805.10
2006-07	1331.8	5993.10
2007-08 (P)	1206.5	5429.25
2008-09 (P)	1201.7	5407.65
2009-10 (P)	1160.0	5220.00
2010-11 (P)	1544.6	6950.70
2011-12(P)	1740.4	7831.80
2012-13(P)	1394.7	6276.15

\* = Out of indigenous production

\*\* = Estimated quantity of phosphogypsum generated

(Apprx. 4.5 tonnes of phosphogypsum/ton of phosphoric acid produced)

(P) = Provisional;

Note: Phosphoric acid is expressed as 100% P<sub>2</sub>O<sub>5</sub>

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

S.No.	Name of the	Raw material	consumption	Phosphate rock	Production
	Industry	Phosphate rock (MT/MT of P <sub>2</sub> O <sub>5</sub> )	Sulphuric acid (MT/MT of P <sub>2</sub> O <sub>5</sub> )	imported from	capacity of phosphoric acid
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	17,500 MT per month
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 MT/day
7.	Coromandel International Limited (CIL), Vishakhapatnam, AP	3.2 - 4.24	2.59 - 3.6	Togo, China, Israel, Algeria	700 MT/day
8.	Coromandel International Limited (CIL) , Ennore, TN	3.55	3.25	Israel, Jordan	150 MT/day
9.	Greenstar Fertilizers Limited (Formerly Known as Southern Petrochemical Industries Corporation Ltd SPIC)), Tuticorin, TN	3.2-3.45	-	Jordan and Egypt	10420 MT per month
10.	Fertilizers and Chemicals Travancore Ltd., (FACT) Ambalmedu, Kerala	3.4	3.13	Morocco and Jordan	360 MT/day
11.	Rashtriya Chemicals And Fertilizers Ltd., (RCFL) Chembur, Mumbai	3.2	2.9	Jordon, Togo and Algeria	3100 MT per month

MT: Metric Tonnes

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

Table 6. Analysis of Phosphogypsum generated in some of the Phosphoric Acid Plants in India

S.No.	Name of the	Type of	Characteristics ( in %)						
	Industry	Process	Insoluble P <sub>2</sub> O <sub>5</sub>	Insoluble F	Soluble P <sub>2</sub> O <sub>5</sub>	Soluble F	Moisture		
1.	TCL, Haldia, WB	DH	0.50	0.25	0.30	0.60	15		
2.	PPL, Orissa.	DH	0.75	-	0.30	0.80	20		
3.	GSFC, Fertilizer Nagar, Gujarat	DH	0.80 to 0.85	0.20-0.50	0.5-1.0	-	20-24		
4.	Hindalco Industries Ltd. (HIL) P.O. Dahej, Gujarat	DH	0.50-1.60	0.45-0.65	0.05-0.60	0.03-0.06	18-22		
5.	Indian Farmers Fertilizer Co-Operative Ltd.(IFFCO) Musadia, Orissa	DH	0.70-0.90	0.20-0.50	0.04-0.10	0.04-0.06	6-12		
6.	Rashtriya Chemicals And Fertilizers Ltd., (RCFL) Chembur, Mumbai	HDH	0.20-1.20	0.06-0.20	0.05-0.60	0.02-0.16	15-20		
	Range		0.2-1.6	0.06-0.65	0.04-1.0	0.02-0.16	6 -24		

DH - Dihydrate HDH - Hemi-Dihydrate

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

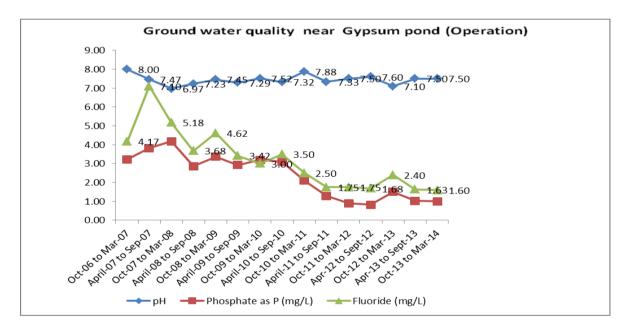
S.	Name of	Phosphogy	rpsum (PG)	Phosphogypsum Management Practices					
No.	Industry	Gener	ation						
		Net Quantity	Rate of PG Generation	Dry Disposal	Wet Disposal	Intermediate Storage			
		from	(MT/MT of			Storage			
		2006 -2011	$P_2O_5$						
(1)	(2)	(MT)	(4)	(5)	(6)	(7)			
(1) 1.	(2)	(3) 478591.52	4.5	(5) Dry Phosphogypsum is	(6) Only at the time of	(7) There is no			
	Chemicals	170071102	1.0	directly delivered to the	start up and shut	intermediate			
	Ltd. Haldia, WB			gypsum storage area for curing and further sale.	down of the plant, phosphogypsum	storage facility			
				In last ten years 19.13	slurry has been				
				Lac MT of phosphogypsum is	sent to the gypsum pond for settling				
				reported to be disposed	and further sales				
				off. About 1.23 Lakh Tonnes sold to cement	after drying.				
				plant during 2011-2012					
2.	Paradeep	6229900	5	During the year 2011-	From Phosphoric	One Intermediate			
	Phosphates Limited,			2012, about 5.09 Lac Tonnes of	Acid Plant phosphogypsum is	storage shed of area 700 x 15 m			
	Paradeep,			Phosphogypsum sold to	transported as	with 25000 MT			
	Orissa.			cement plant and other use.	slurry containing 10-15% through	capacity has been provided.			
				usei	HDPE pipelines to	provided.			
					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				
3.	Gujarat	2043233.4	5.5 - 5.9	During 2011-2012, 6106	corporation etc. Phosphogypsum in	There is no			
3.	State	2043233.4	3.3 - 3.9	tonnes of	slurry form is sent	There is no intermediate			
	Fertilizer &			Phosphogypsum sold to	to the	storage facility			
	Chemicals Limited			cement plant.	'phosgypsum pond' through				
	Vadodara,				pipelines which is				
	Gujarat.				located within the				
					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				
4.	Hindalco	2215198	5	Phosphogypsum	-	There is no			
	Industries Ltd.			Transportation from plant to the storage yard		intermediate storage facility			
	Bharuch,			directly through					
	Gujarat			conveyor belt. Till now 3905808 MT of					
				Phosphogypsum has					
				been disposed off.					
				During the year 2011					
				During the year 2011- 2012, about 5.7 Lac					

5.	Indian Farmers Fertilizer Co- Operative Ltd. Musadia.	from 2005 - 2011 : 10922885	4.5 - 5	During the year 2011- 2012, about 3.11 Lac Tonnes of Phosphogypsum sold to the Cement Plants	Wet Phopshogypsum 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 Internationa l Limited, Vishakhapat nam, AP	3349334	4 - 4.5	Dry phosphogypsum is directly disposed to the HDPE lined gypsum handling area before its final disposal		
8.	Coromandel Internationa l 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.	Greenstar Fertilizers Limited (Formerly Known as Southern Petrochemic al Industries Corporation LtdSPIC), 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	During 2011-2012, 1.06 Lac MT of PG used in house gypsum board manufacturing.	Wet disposal of phosphogypsum is being conducted by the industry through pipeline	There is no intermediate storage facility

**Note: MT-Metric Tonnes** 

Table 8. Typical Groundwater Monitoring Data near Old Phosphogypsum Pond

	Near Old Phosphogypsum Pond										
Year	рН	Phosphate as P (in mg/L)	Fluoride (in mg/L)								
Oct-06 to Mar-07	8.00	3.22	4.17								
April-07 to Sep-07	7.47	3.82	7.10								
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	3.20	3.00								
April-10 to Sep-10	7.32	3.10	3.50								
Oct-10 to Mar-11	7.88	2.10	2.50								
April-11 to Sep-11	7.33	1.28	1.75								
Oct-11 to Mar-12	7.50	0.90	1.75								
Apr-12 to Sept-12	7.60	0.82	1.68								
Oct-12 to Mar-13	7.10	1.50	2.40								
Apr-13 to Sept-13	7.50	1.03	1.63								
Oct-13 to Mar-14	7.50	1.00	1.60								

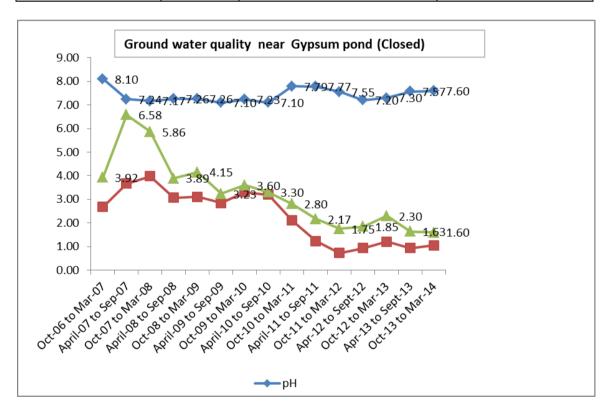


Location of the Unit: IFFCO, Paradeep

Source: Fertliser Association of India

Table 9. Groundwater Monitoring Data near New Phosphogypsum Pond

	Near New Phosphogypsum Pond									
Year	pН	Phosphate as P (mg/L)	Fluoride (mg/L)							
Oct-06 to Mar-07	8.10	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	3.10	4.15							
April-09 to Sep-09	7.10	2.85	3.23							
Oct-09 to Mar-10	7.23	3.30	3.60							
April-10 to Sep-10	7.10	3.20	3.30							
Oct-10 to Mar-11	7.79	2.10	2.80							
April-11 to Sep-11	7.77	1.23	2.17							
Oct-11 to Mar-12	7.55	0.73	1.75							
Apr-12 to Sept-12	7.20	0.93	1.85							
Oct-12 to Mar-13	7.30	1.20	2.30							
Apr-13 to Sept-13	7.57	0.93	1.63							
Oct-13 to Mar-14	7.60	1.05	1.60							



Location of the Unit: IFFCO, Paradeep

Source: Fertliser Association of India

Table 10. TCLP Values of heavy metals present in phosphogypsum generated in some of the Phosphoric Fertiliser Units in India

S.	Name of the					TCLP values	in mg/kg					
No.	Industry	Moisture in %	Chloride (Cl)	Calcium (Ca)	Magnesium (Mg)	Cadmium (Cd)	Chromium (Cr)	Copper (Cu)	Iron (Fe <sup>.</sup> )	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	Greenstar Fertilizers Ltd., (Formerly known as SPIC), Tuticorin	18.74	20	640	360	0.26	NT	NT	0.13	NT	NT	0.15
6	IFFCO,	-	-	-	-	0.03	NT	NT	0.17	NT	NT	0.09
	Paradeep	-	-	-	-	0.05	NT	NT	0.1	NT	NT	0.12
		-	-	-	-	0.06	NT	0.09	0.14	NT	0.15	0.18
7	Paradeep	-	-	-	-	0.03	NT	0.05	0.23	NT	0.1	0.08
	Phosphates Paradeep,	-	•	-	-	0.04	NT	NT	0.14	NT	0.14	0.13

NT - Not Traced



**प**रमाणु **ऊ**र्जा **नि**यामक **प**रिषद







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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#### परमाणु ऊर्जा नियामक परिषद ATOMIC ENERGY REGULATORY BOARD

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

## International practices of phosphogypsum management and handling

The World reserves of natural gypsum are large and adequate to meet the demand. The total reported production of gypsum in 2011 was about 141.3 Million Tonnes as against 138.3 Million Tonnes in 2010. China was the largest producer accounting for 26 %, followed by Iran, Iraq & Thailand (8 % each), USA (7 %), Mexico & Spain (5 % each), Brazil (3 %) and Australia, Canada, Egypt, France, India & Russia (2 % each)

Phosphogypsum generated from phosphoric acid plants contains three types of impurities that are considered to be potentially harmful such as residual acidity, fluorine compounds, trace elements including radioactivity.

Based on the literature, the International practices of phosphogypsum management and handling are given in the subsequent paras.

## 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 utilisation.

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/tonne of  $P_2O_5$  produced.

## 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.

## 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: (a) above a layer of compacted soil at least 18 inches thick, with a maximum hydraulic conductivity of  $1x10^{-7}$  cm/sec, or (b) below a layer of mechanically compacted phosphogypsum at least 24 inches thick, with a maximum hydraulic conductivity of  $1x10^{-4}$  cm/sec.

## 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 industrialised 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  $P_2 0_5$  shows that the plants operate a di-hydrate 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.

## 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.

## 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.

## 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 France, phosphogypsum is used in agriculture as a structureimproving agent for the soil. The quantities used are negligible, as compared to the amount of phosphogypsum available. In special cases very considerable quantities of 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.

## 3) By-product utilisation: 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.

## 3.1) Japan: utilisation of phosphogypsum as raw material

- Plaster and Gypsum Board manufacturing: There were 16 (a) 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 manufacture; little or no natural gypsum is used for these products. There were 15 companies (16)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 utilisation 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.

## 3.2) European: utilisation of phosphogypsum as raw material

Germany is the only European country utilising its resources of by-product gypsum to large extent; but due to the presence of adequate natural supplies of gypsum, considerable quantities of gypsum from the wet-process phosphoric acid plants 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 utilisation 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.

#### **Annexure -III**

#### **CHEMICAL SYMBOLS**

The following chemical symbols used where appropriate in the text.

As Arsenic

BOD Bio-chemical Oxygen Demand

C Carbon Ca Calcium

CaCO<sub>3</sub> Calcium Carbide

Cd Cadmium

CO Carbon Monoxide

COD Chemical Oxygen Demand

CO<sub>2</sub> Carbon Dioxide

Cl Chloride Cr Chromium

EC Electrical Conductivity

 $\begin{array}{lll} F & & Fluoride \\ Fe & & Iron \\ H \ (H_2) & & Hydrogen \\ Hg & & Mercury \\ H_2O & & Water \end{array}$ 

H<sub>2</sub>S Hydrogen Sulphide

H<sub>2</sub>SiF<sub>6</sub> Fluorosilicic Acid (Hexafluorosilicic Acid)

H<sub>2</sub>SO<sub>4</sub> Sulphuric Acid H<sub>3</sub>PO<sub>4</sub> Phosphoric Acid HNO<sub>3</sub> Nitric Acid K Potassium

KCl Potassium Chloride (Muriate of Potash) ("Potash")

K<sub>2</sub>O Potassium Oxide

N (N<sub>2</sub>) Nitrogen Ni Nickel

N<sub>2</sub>O Dinitrogen Monoxide (Nitrous Oxide)

NH<sub>3</sub> Ammonia

NH<sub>4</sub>-N Ammonical Nitrogen NH<sub>4</sub>NO<sub>3</sub> Ammonium Nitrate

NO Nitrogen Monoxide (Nitric Oxide or Nitrogen Oxide)

NO<sub>2</sub> Nitrogen Dioxide NO<sub>3</sub>-N Nitric Nitrogen

NOx Oxides of Nitrogen (Excluding Nitrous Oxide)

 $O(O_2)$  Oxygen  $PO_4$  Phosphate  $O(O_2)$  Phosphat

P<sub>2</sub>O<sub>5</sub> Phosphorus Pentoxide

S Sulphur

SS Suspended Solids
SO<sub>2</sub> Sulphur Dioxide
SO<sub>3</sub> Sulphur Trioxide

Zn Zinc

#### 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<sub>3</sub>PO<sub>4</sub>

## 2. Hazards to the human and the Environment

#### To the human:

- Phosphoric acid is corrosive to all parts of the body.
- Contact with the skin can cause redness and burns.
- Splashes in the eves 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 : 267 Pa at 20°C

Solubility in water : Miscible in all proportions.

Density : 1.58 gm/cm³ 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 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 gypsum dike

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