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Hazardous Waste Disposal Studies taken up by GSFC for Safe Disposal

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Gujarat State Fertilizer & Chemical Ltd fabrique des engrais et s'est diversifiée dans la Pétrochimie, les plastiques industriels et les gaz industriels. Les principales matières premières utilisées pour ces produits sont le gaz naturel, LSHS, naphta, benzène, soufre, et phosphate brut. Les produits chimiques tels que carbonate de potassium, soude caustique, acide chlorhydrique, catalyseurs, résines etc sont également nécessaires dans la fabrication d'engrais et de produits pétrochimiques .Les polluants générés peuvent être classés ainsi : (i)polluants de l'air comme le dioxyde de soufre, les oxydes d'azote, le dioxyde de carbone, les hydrocarbures, des matières en particules, et l'ammoniac et (ii) les polluants de l'eau comme les solides dissous, les solides en suspension, l'azote ammoniacal et l'azote total, les phosphates ,les fluorures, l'huile grasse et la matière organique (BOD/COD° et (iii) les déchets solides tels que le gypse, la chaux, la boue soufrée, la boue d'arsenic, les batteries, le catalyseur épuisé, les déchets d'effluents traités biologiquement, les déchets de cantine, les sacs plastiques usagés, etc. GSFC a conscience de ces polluants et leurs effets possibles sur l'écologie du voisinage et des mesures appropriées sont prises pour sauvegarder l'environnement. Les mesures prises pour la maîtrise des déchets solides chez GSFC sont présentées dans cet exposé.

Les questions relatives à l'environnement et aux changements climatiques deviennent de plus en plus significatives au niveau national et international. Avec une industrialisation et une urbanisation croissantes, les problèmes de pollution augmentent en Inde. Les progrès industriels ne peuvent exister aux dépens de la santé et du bonheur des hommes. La conscience en Inde des questions liées à la pollution s'affirme. La vibrante démocratie indienne, l'activisme judiciaire, les protestations de la communauté et des NGO ont tous commencé à mordiller les industriels. Il est donc dans l'intérêt de l'industrie de jouer un rôle prééminent dans le traitement de l'environnement. On a identifié au total 12 516 unités dans le pays qui génèrent des déchets à risque dont 2 984 dans l'Etat de Gujarat Le total des rejets à risque généré dans le pays atteint 8 377 271 tonnes par an dont 430 030 générées au Gujarat. Sur 116 incinérateurs mis en marche dans le pays, 30 l'ont été au Gujarat (les faits font l'objet de l'annexe-VI). GFSC pense fortement qu'avec des mesures dynamiques le développement économique et la protection de l'environnement peuvent aller la main dans la main. Dans cet exposé on a essayé d'expliquer brièvement différentes étapes franchies par GSFC pour combattre les problèmes de pollution et, dans certains cas, de recycler les déchets comme sous-produits à valeur ajoutée.

INTRODUCTION

Gujarat State Fertilizer & Chemical Ltd is manufacturing fertilizers and it has diversified into petrochemicals, industrial plastics and industrial gases. The major raw materials used for these

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products are natural gas, LSHS, naphtha, benzene, sulphur and rock phosphate. The chemicals such as potassium carbonate, caustic soda, hydrochloric acid, catalysts, resins, etc. are also required during the manufacture of fertilizers and petrochemicals. The pollutants that are generated can be classified as follows: (i) air pollutants such as sulphur dioxide, oxides of nitrogen, carbon dioxide, hydrocarbon, particulate matter and ammonia and (ii) water pollutants such as dissolved solids, suspended solids, ammonical nitrogen and total nitrogen, phosphate, fluoride, oil grease and organic matter (BOD/COD) and (iii) solid wastes such as gypsum, chalk, sulphur sludge, arsenic sludge, used batteries, spent catalyst, biologically processed effluent waste, canteen waste, plastic bag wastes, etc. GSFC is conscious of these pollutants and its possible effects on the ecology of the surrounding areas and suitable measures are taken to safeguard the environment. Steps taken on solid waste management at GSFC are presented in this paper.

Issues relating to environment and climate change are becoming increasingly significant at national and international levels. With increasing industrialization and urbanization pollution problems are increasing in India. Industrial progress cannot be at the cost of healthy and happy human life. The awareness in India on pollution related issues is growing. The vibrant Indian democracy, judicial activism, community and NGO protests have all begun to bite the industrialists. Hence, it is in the industry's own interest to take a proactive role in environmental management. A total of 12516 units are identified in the country generating hazardous wastes and out of which 2984 units are in Gujarat State. Total hazardous waste generated in the country is 8,377,271 MT/Yr of which 430,030 MT/Yr is generated in Gujarat. Out of the total 116 incinerators in operation throughout the nation, 30 are in Gujarat State. (Facts are enclosed as Annexure-VI). GSFC strongly believe that with proactive measures, both economic development and environmental conservation can go hand in hand. In this paper, an attempt is made to briefly explain different steps taken by GSFC to combat the pollution problems and in few cases to recycle the waste as value added byproducts.

Solid Waste Management at GSFC:

During production of fertilizers and industrial products five main types of solid wastes viz., chalk, phosphogypsum, sulphur muck, arsenic sludge and biologically processed effluent wastes are generated. For ecofriendly management of these wastes, the following measures have been taken.

1. PHOSPHOGYPSUM

Phosphogypsum (PG) is generated in phosphoric acid plant wherein rock phosphate and sulphuric acid are used as raw materials. Impervious lined area for transit storage of gypsum is provided at the cost of Rs 8million (USD 180,000). The gypsum content is about 96.24 % on dry basis. Typical analysis enclosed as Anneuxure -I .It is acidic in nature and contains traces of heavy metals which are below the acceptable limits recommended by the Hazardous Waste Amendment Rules 2000.

Gypsum is a source of S and Ca to the crops and it is also an amendment to sodic soil. Usefulness of PG as soil amendment has been internationally (Richcigl, 1995), nationally (Tandon, 1995) and regionally (Kalyana Sundaram et al, 1996) well documented. Generally crops require 20 to 40 Kg S/ha or 108 to 216 Kg/ha of gypsum. As an amendment to sodic soil, its amount depends upon the Exchangeable Sodium Percentage (ESP) of the soil but it is generally in the order of 2 to 4 tonnes or more per ha. The acidic nature of PG can be an added advantage in bringing down the pH of the sodic soils. Gujarat has about 1.2 million ha. of salt affected soils. The Department of Agriculture, Gujarat State, recommends GSFC's PG as soil amendment to sodic soils. The Govt. of Gujarat has appointed GSFC as nodal agency for distribution of PG

Heavy metals like Cr, Cu, Cd, Pb, Fe, Mn, Zn and Ni present in PG are in trace levels as per EIA study of NEERI in August 1998. As per the report, there is no migration of contaminants to the ground water. Heavy metals present in PG are insoluble and hence do not leach out to the ground water source.

PG was analyzed for radionuclides by gamma spectrometry by BARC - Bombay. It contains only natural radionuclides and the limits are not applicable to them.

1.1 Use of PG in Agriculture :

GSFC awarded a research project to GAU (Gujarat Agricultural University) for assessing the suitability of PG for agricultural use. They have submitted their interim report from field experiments carried out for one year. These field experiments were conducted at three different locations viz. Anand (Sandy loam alluvial soil), Junagadh (calcareous black soil) and Navsari (heavy black soil) with varying type of soils. This was necessary because heavy metal accumulation varies with different crop species and soils (Patel et al., 1998). In rabi (winter) season of 1998-99, wheat was grown at Anand and Junagadh whereas summer groundnut was sown at Navsari. In the next kharif (rainy) season pearl millet (bajra) was grown at Anand and groundnut was cultivated at Junagadh. The experimental treatments are such that a comparison of PG can be made with calcium sulphate (CS) and mineral gypsum (MG) at two sulphur levels viz., 20 and 40 Kg S/ha and their direct, residual and cumulative effects can be brought out in the course of three years.

In first crop of wheat at Anand (Annexure -I ; Table-1) indicated that the growth of the crop and yield due to PG was comparable with that of CS and MG. The second crop of pearl millet (without any treatment) was grown on the residual effect of S treatments given in the kharif season. Increase in the yields due to PG, CS and MG at 40 Kg S/ha level could be observed (Annexure-I ; Table-2). These data indirectly suggest that PG had no such adverse effect on physical, chemical or biological properties of soil that can have adverse effect on soil productivity. On the other hand, a beneficial effect was seen on the second crop. Similar beneficial effect was also obtained on wheat crop at Junagadh and summer groundnut at Navsari. The concentrations of available metallic micronutrients (Fe, Cu, Mn, Zn) and available heavy metals (Ni, Cd, Pb, Co and Cr) in soil (Annexure-I; Table 1 and 3) were not significantly influenced by the treatments indicating that PG application did not increase the micronutrients or the heavy metals in soil to any toxic level.

1.2 Reuse of waste PG in cement industry:

Reuse of PG in cement industry is being explored. For cement manufacturers, use of PG is more economical as compared to natural gypsum because of higher cost of natural gypsum and lower purity level (75%). It is added as retarding agent at the rate 4% ISI specs for gypsum for cement industry indicates $CaSO_4$:80~85%, MgO : 3% and chloride (as NaCl) max. 0.5%.

In view of these facts, it seems probable that PG can be categorized as non-hazardous under the new amendment of Hazardous Waste Rules, 2000.

2 SULPHUR MUCK

Sulphur muck (SM) is generated during the manufacture of sulphuric acid. It contains 28.8% S and is acidic (pH 6.6). For storage of sulphur muck a suitable interim storage facility as per recommendation of NPC / GPCB having covered area with impervious lining at the bottom is provided at the cost of Rs 1.6 million.

The SM is being evaluated for its suitability as a source of S for the crops in the GAU research project mentioned earlier. The treatments having SM to supply 20 and 40 Kg S/ha (70 and 140 Kg/ha of SM) are included in the same experiments described under PG. The performance of SM was found similar to that of PG in increasing the crop yields when applied @ 40 Kg S/ha without increasing the available metallic micronutrients and the heavy metals in soil (Annexure -I ;Tables 1, 2 and 3). Department of Agriculture, Govt. of Gujarat has permitted GSFC to mix SM to the tune of 1% with gypsum for agricultural use. Encouraged by GAU report, the possibilities for using SM as a source of S including its supplement in organic fertilizer are being explored.

3 BIOPROCESSED EFFLUENT WASTE:

For treatment of wastewater generated from Caprolactam-I and II plants, two BOD reduction plants are installed using Activated Sludge process. It consists of NH3 Stripping, Denitrification , Modern design Bio-tower and Aeration tank for providing necessary oxygen to bio-mass for reduction of BOD. Biological sludge generated during the treatment is purged out and dried.

This sludge is stored as per recommendation of NPC/GPCB in a suitable area, which is impervious lined with a shed at the cost of Rs 8 lacs (800,000 rupees, circa USD 18,000). The sludge analysis (Annexure-II) indicates that the concentration of heavy metals present in the waste is less than that specified in class A and B of Schedule 2 of Amendment Rules, 2000.

The GAU project includes studies on the bioprocessed waste (EW) as well. In a separate experiment, EW is compared with farm-yard manure (OM) at two levels 5 and 10 t/ha on organic carbon basis, other experimental details remain same as that of PG and SM study. There was no significant influence of either EW or OM on the first crop of wheat (Annexure – II, Table 4) but both EW and OM at 10 t/ha basis increased the yield of subsequent pearlmillet crop (Annexure -II ; Table-5). The available metallic micronutrients (Fe, Mn, Cu, Zn) and the available heavy metals (Cd, Ni, Pb, Co, Cr) were not significantly influenced by

EW or OM (Annexure -II ; Table-4 and 6) indicating EW can possibly be a good source of organic amendment as FYM for agricultural lands. Results from Junagadh centre (Annexure -II ; Table-7) showed that just like organic matter such as FYM, EW also increased available N, P, K and S and also organic carbon content in soil.

GSFC has obtained membership of NECL for disposal of biologically processed waste at the land fill facility. Necessary permission from GPCB for the same has been obtained.

In the year 1997, GSFC had assigned NPC to carry out Solid Waste Management & Environmental Impact Assessment Study within the complex at the cost of Rs 540,000.

4 CHALK

Chalk is generated during manufacture of ammonium sulphate fertilizer from phosphogypsum. It is alkaline in nature having pH 7-8.Chalk as $CaCO_3$ is 68~73%. Typical analysis is enclosed as Annexure-III. As per the earlier Hazardous Waste (Management & Handling) Rules 1989, the waste category was based on the quantity but now the new amendment considers hazardous waste based on concentration i.e. qualitatively rather than quantitatively. As per the earlier rules, chalk was falling under hazardous waste category No 16, as total alkalinity was exceeding 200 Kg per annum due to large quantity. The chalk contains 50~70 mg/L of alkalinity. Now the quantitative consideration has been replaced by qualitative classification based on concentration and characteristics as per the new Amendment. Hence, under new amendment of Hazardous Waste Rules 2000, chalk does not fall under hazardous category. At present there is no generation of fresh chalk as we have discontinued operation of Ammonium Sulphate-I plant. Approx. 4 million MT of chalk is stored in 140,000 M2 area and encapsulated in the complex as per Environment Impact Assessment (EIA) Study. Stored chalk is compacted leveled and covered with 250 mm thick layer of earth, impervious HDPE liner is covered on the earth and further a 1000 mm thick layer of earth is laid over the HDPE liner. Subsequently, plantation and vegetation is carried out on and around the entire storage area with the help of treated domestic sewage of GSFC in place of utilizing fresh water. Encapsulation was carried out based on recommendation of NPC, M.S. University and other consultant. Capital cost incurred for encapsulation is Rs 45.5 million and recurring cost for plantation and green belt development is Rs 27 lacs/Yr. The cost of civil maintenance of the encapsulated chalk heap is Rs 25 lacs/yr.

4.2 Studies taken up by GSFC for safe disposal of chalk.

(a) GSFC's R&D dept has taken up the project for manufacture of 10,000 bricks/day demonstration plant consuming 15 MT/day chalk within GSFC. The cost of chalk bricks approximately would work out to be Rs. 1.6 to 1.7 / brick. This includes raw-material cost, utility, labour, sales tax, octroi, finished product transportation but does not include fixed cost & overheads. The chalk bricks are superior to clay-made bricks because of its perfect shape, higher crushing strength, less absorption of moisture and less of plastering requirement.

(b) Use of chalk as neutralizing agent or manufacture of cement / sagol has also been taken up on experimental scale.

5. ARSENIC BEARING WASTE FROM AMMONIA PLANTS

In Ammonia-I and II plants, GV system is installed for removal of CO2 and purification of synthesis gas for the manufacture of Ammonia. Arsenic waste originates from Vitrocoke process for CO_2 removal.Arsenic bearing effluent from this section is judiciously segregated and collected in pits and finally evaporated to concentrate to form a thick sludge. After drying, it is packed in polyethylene bags and stored in thick metallic vessels duly gunited as per the guidelines of GPCB. Typical Analysis of stored Arsenic Sludge is enclosed as Annexure - IV.

5.1 Studies taken up by GSFC for safe disposal of arsenic waste from Ammonia plants.

(a) Chemical Treatment:

GSFC has taken up R&D work as per recommendation of NPC to convert the soluble arsenic waste into insoluble form.

(1) Arsenic sludge is suspended in water (arsenic sludge water ratio 1:4) in a stirred reactor and reaction with 30% hydrogen peroxide is carried out at room temperature for 2 hours.

(2) A clear solution of ferric chloride is added to the above reaction mixture and pH is adjusted to 2.5 by addition of sufficient caustic lye. Reaction is continued at room temperature for a further 3 hours and then at reflux temperature (95-100 deg.C) for another 3 hrs.

(3) The reaction mixture is cooled and removed for settling for 15 hrs. Supernatent is removed and sludge is filtered and dried.

The waste water contains less than 1 ppm arsenic which is as per recommendation by NPC. However, further experiments have been undertaken to recycle this waste water so that practically no waste water is generated during the process. This waste water will be used for making solution of ferric chloride to be used in the process.

The arsenic sludge after this experiment becomes unleachable. This sludge was kept in equilibrium with water for 7 days with one hour agitation every day. The water does not show any increase in arsenic content and continuously remains below 1 ppm. The capital cost of plant works out to be Rs 130 lacs for 1 MT/day treatment of sludge. The process diagram for the said experiment is enclosed (Annexure IV ; Diagram-I).

This process poses problem of filtration and drying. Hence alternate solutions are explored.

(b) **Immobilization**: NEERI has conducted experiments for stabilization and immobilization of arsenic waste. Arsenic sludge which originates from Vitrocoke process is treated with various combinations of binder to waste ratio using cement, lime and fly ash. The metal concentration in the leachate of S/S waste was significantly lower than that in raw waste and the concentrations were below the regulatory level. This treated arsenic waste will be in the form of bricks which will finally be disposed of at land fill site. Arsenic content of water extract comes to 1.3 mg/L as per TCLP after 7 days curing. After 28 days curing, it will further reduce. Since Arsenic Standard in drinking water is 0.05 mg/L, a leachate concentration upto 5.0 mg/L is acceptable as per USEPA - TCLP criteria. Total cost estimated for Arsenic fixation and brick manufacturing along with disposal is Rs 1 crore (10,000,000 Rs).

(c) Possibilities for use of arsenic sludge as insecticide and pesticide are also under consideration. But there is no positive response from the pesticide manufacturers.

(d) Studies related to phyto remediation are also being explored. Here arsenic will be taken up by the plant without leaching out to underground water source and converted to CO2 and water. However, this calls for extensive experimentation by experts on the land to ensure that no arsenic migrates to the underground water source.

At present there is no generation of fresh arsenic sludge due to stoppage of old Ammonia plants and commissioning of new 1350 MTPD Ammonia plant, which uses non-toxic MDEA CO_2 removal process.

6. CANTEEN WASTE :

For effective disposal and conversion of bio-degradable waste to an Eco-friendly chemical fertilizer, GSFC is looking into the possibilities for use of vermiculture for disposal of its canteen waste, garden waste, and ETP waste. Experiments are carried out by the Agriculture Department and results are encouraging. This is a positive , low cost technology with in-built social , environmental and hygiene components and falls under zero budget and is ISO 14000 certified. The objective is to produce food of optimum quality and quantity, using technologies like Earthworm technology which seek to co-exist with the natural systems as well help in disposal of waste.

EXPENDITURE ON POLLUTION ABATEMENT MEASURES:

GSFC has made an investment of Rs. 282.14 million on various schemes controlling and minimizing liquid effluent, Rs. 140.8 million on air pollution measures and Rs. 56.5 million have been spent for management of various solid wastes. Additionally a sum of Rs. 50 million is planned to be invested for further upgrading the measures for pollution abatement. The operating cost of Effluent treatment facilities at GSFC is around Rs. 46 million/ year. GSFC on an average spends 2.97 % of its turnover on pollution abatement measures.

IMPACT ASSESSMENT STUDIES

(i) Soil Analysis for heavy metals in nearby villages compared to remote areas:

GSFC had carried out soil analysis for heavy metals in nearby villages compared to remote areas like Pavi-Jetpur, Savli, Waghodia etc. and results are attached as (Annexure-V; Pg 1,2). From the analysis , it can be seen that heavy metal contents i.e. Ni, Cr, Fe, Zn, etc. is comparable in soils in nearby villages and that of remote places**.**

(ii) Analysis of Vegetables from surrounding area and remote areas:

Analysis of vegetables collected from nearby villages surrounding GSFC for heavy metals is attached as (Annexure-V; Pg 3) and those collected from remote area is attached as (Annexure-V; Pg 4). From the analysis it can be seen that the heavy metal content is lower than the permissible limits given by IS-7968 and prevention of Food Adulteration Rules.

(iii) Analysis of Underground Water sources from surrounding areas:

GSFC had analysed underground water sources of nearby villages using Public Health Engineering. Laboratory, Baroda. The results are enclosed as (Annexure-V; Pg 5,6,7,8). It can be seen that quality of water is fit for potable use.

CONCLUSION

In a recent publication (Rechcigl 1995), Mullins and Mitchell reviewed extensively the work done at USA on the sewage and industrial sludges as soil amendments. Out of the 74 studies, only 5 showed adverse effect which were predictable based on the properties of the sludge and high rates of application. In the half of the remaining studies, distinct positive effects were noticed. The authors were of the opinion that widespread public concern about their potential negative effects on crops is largely unsupported by research. They concluded that these sludges may be safely and effectively applied at rates based upon the analysis of the product. Similar picture is largely emerging from the experiences of the GSFC. Not only the environmental pollution can be effectively controlled, but some of the sludges can be recycled as an environmentally safe and value added soil amendment or other useful products.

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